This is to certify that the

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Partition Coefficients of Aroma Compounds between Polyethylene and Aqueous Ethanol and Their Estimation Using UNIFAC and GCFEOS

presented by

Albert Lawrence Baner

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Partition Coefficients of Aroma Compounds between Polyethylene and Aqueous Ethanol and Their Estimation Using UNIFAC and GCFEOS

By

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Volume I

A DISSERTATION

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Department of Food Science and Human Nutrition
and
Department of Agricultural Engineering

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Abstract

Partition Coefficients of Aroma Compounds between Polyethylene and Aqueous Ethanol and Their Estimation Using UNIFAC and GCFEOS

By

Albert Lawrence Baner III

Partition coefficients were measured for n-alkanes (pentane to docosane) and 13 different aroma compounds (isoamylacetate, d-limonene, camphor, linalylacetate, L-menthol, dimethylbenzylcarbinol, citronellol, phenylethylalcohol, diphenylmethane, diphenyloxide, eugenol, τ-undelactone) at dilute concentrations between aqueous ethanol solutions (100%, 66% and 33% for n-alkanes; 100%, 75%, 50%, 35% w/w) and nitrogen at 25°C using a gas stripping column method. Partition coefficients for n-alkanes (octane, nonane, decane, dodecane, tetradecane, hexadecane, octadecane, eicosane, docosane) and the aromas were also measured between low density polyethylene, high density polyethylene and ethanol and aqueous ethanol liquid phases (100%, 75%, 50% and 35% ethanol w/w) at 10°, 25° and 40°C using an equilibrium sorption method.

Within the experimental uncertainty no significant differences were found for polyethylene samples with

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different crystallinities and very little temperature effect was seen for the polymer/liquid partition coefficients. The polymer/liquid partition coefficients were most affected by the chemical nature of the mixture. The liquid/gas and polymer/liquid partition coefficients were estimated using UNIFAC with UNIFAC-FV and using the Group-Contribution Flory Equation-of-State (GCFEOS). UNIFAC and GCFEOS are useful for qualitative estimations. Significant quantitative differences between the experimental data and the estimations were found for the liquid/gas and polymer/liquid partition coefficients of some solutes, in particular middle polarity aroma compounds. A correlation of the size of estimation error with increasing molecular weight was observed for the n-alkanes and phenols. The variances between experimental and estimated values are explained in terms of the methods' group-contribution additivity and solution of groups assumptions and the methods' semi-empirical nature. UNIFAC gave more consistent and on average better quantitative estimations than GCFEOS.

Ded

Dedicated to my Parents for helping me find my way in life.

To
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AKNOWLEDGEMENTS

For her support and understanding

Gisela Baner

For his vital scientific support and inspiration

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that inspired me to start this quest

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Nomenclature

a	activity (dimensionless)
A	food contact surface area of package (cm²)
cal	GC calibration factor (g/mL/au)
c_i	Eq 30 empirical degrees of freedom
c_{i0}	initial concentration (g/mL)
c_P, c_i^P	solute polymer concentration (g/mL)
c_L, c_i^L	solute liquid concentration (g/mL)
d	polymer thickness (cm)
den	density (g/mL)
D	diffusion coefficient (cm²/sec)
erfc	co-error function = 1 - erf
f_i	fugacity (pressure)
f_i°	standard state fugacity (MPa)
GC	gas chromatograph peak area units (au)
G_i^{ex}	partial molar Gibbs free energy
h_m	measured heat of fusion (Eq 34) (KJ/mol)
h_m^c	heat of fusion of polymer crystal (KJ/mol)
H	Henry's law constant (g/mL MPa)
J	flux (g/sec)
K	partition coefficient (dimensionless)
$K_{L/G}$	solute liquid/gas partition coefficient
$K_{P/G}$	solute polymer/gas partition coefficient
$K_{P/L}$	solute polymer/liquid partition coefficient
m	mass (g)
M_i, MW_i	relative molecular mass (g/mol)
M_n	polymer number molecular weight
P	total pressure of system (MPa)
P_i°	pure component vapor pressure (MPa)
r_i'	normalized van der Waals volume per gram (Eq 31)
R	gas law constant
S	solubility coefficient (g/mL MPa)
t	time (sec)
T	temperature (K)

Nomenclature (cont.)

T_M	melt temperature
v	specific volume (mL/g) (Eq 35)
v_a	specific volume (mL/g) (Eq 35)
v_f	free volume (mL/mol)
v_G	flow rate of gas (mL/sec) (Eq 36)
v^*	hard core volume (mL/mol) (Eq 33)
v_i^w	volume of solvent per gram
v_i	reduced volume (dimensionless)
v_M	reduced mixture volume (dimensionless)
V	volume (mL)
$\underline{V}$	molar volume (mL/mol)
$\underline{V}_i^W$	Van der Waals molar volume (mL/mol)
w	weight fraction (dimsionless)
x	length dimension
x_i	liquid mole fraction
x_c	crystalline fraction of polymer (Eq 34)
y_i	gaseous mole fraction
	density (g/mL)
τ_i^C	combinatorial activity coefficient
τ_i^R	residual activity coefficient
τ_i^{fv}	free volume activity coefficient
τ_i	solute activity coefficient (dimensionless)
τ^∞	infinite dilution activity coefficient
Φ	fugacity coefficient (dimensionless)
∞	infinity
θ	molar volume fraction

Subscripts and Superscripts

F	food
G	gas
h	hexane
i	solute

L

0

P

t

v

w

UE

UO

1

2

Acr

Avg

c.v

EOS

HDP

GCF

LDP

LLE

ppm

s.d.

VLE

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Nomenclature (cont.)

L	liquid
0	initial (time = 0)
P	polymer
t	time
v	volume basis
w	weight basis
UE	upper liquid reservoir at t = end (Eq 37)
UO	upper liquid reservoir at t = begin (Eq 37)
1	first gas washing bottle (Eq 36)
2	second gas washing bottle (Eq 36)

Acronyms

Avg	average
c.v.	coefficient of variation
EOS	equation-of-state
HDPE	high density polyethylene
GCFEOS	Group-Contribution Flory Equation-Of-State
LDPE	low density polyethylene
LLE	liquid liquid equilibrium
ppm	part-per-million (μg/mL)
s.d.	standard deviation
VLE	vapor liquid equilibrium
UNIFAC	UNIQUAC Functional-group Activity Coefficients
UNIFAC-FV	UNIFAC with free volume correction

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Introduction

The prediction of partition coefficients between polymers and liquids is important in a number of applied fields. In addition to polymer processing, the predictions are important for protective clothing design (Mansdorf et al., 1988), biomedical uses (Dunn et al., 1986), chromatography (Barton, 1983), chemical separations (Lee et al., 1989) and, of major interest to this study, packaging (Hotchkiss, 1988). Partition coefficients ($K_{P/L}$), defined as the ratio of a solute's concentration in the polymer phase (c_P) to its concentration in the food (or liquid, L) contacting phase (c_L), are important for food package safety and for food quality. The coefficients are used in modeling migration of substances from packaging into food and from food into the package (Reid et al., 1980).

Migrations from the package material into the food can affect the safety and wholesomeness of the food and are subject to governmental rules and regulations which protect public health. There is also concern that sorption of food constituents and components by the packaging material diminishes both food quality and mechanical properties of the package (Hirose et al. 1988). In recent ye

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years, food quality considerations, largely driven by the increased use of polymer laminate structures in flexible aseptic packages, have stimulated a great deal of interest in the sorption or partition of aromas between foods and their polymeric packaging.

There are standardized experimental migration testing methods for measuring migration and sorption in polymer/food systems which cover migration of specific components, global migration (or total migration) and general testing (ASTM 1992, BGA 1992, DIN 1989, EEC 1980, 1982, 1985, USA 1992). There is also a large body of experimental data outlining migration measurement methods (e.g. Till et al. 1982, Figge et al. 1983). Much of the published experimental data suffers because the polymer, food, and solute systems studied are often not the same as the package system of interest. Package designers must oftenb design a package system with very little idea of the types and magnitudes of interactions that may occur between the packed product and its package. This problem is compounded by the great number of polymeric materials and food combinations possible. Even if a polymer is designated for food use or has been used successfully with some products, there is still the possibility that for another product excessive migration or sorption may occur, creating regulatory problems or diminishing product quality.

The estimation of partition coefficients between foods and polymeric packaging is a complex problem. Foods can contain both solid and liquid phases, each containing a variety of macro and micro-constituents with varying polarities and chemical properties. The macro-constituent properties can range from very polar associating hydrogen bonded systems, e.g. water and acids, to very nonpolar systems, e.g. oils and fats. The micro-constituents of foods, such as flavor and aroma constituents, with concentration ranges of approximately 0.001 to 200 ppm (w/v) include every class of chemical compound but mainly unsaturated and oxygenated compounds. Commonly used food packaging polymers can be semi-crystalline (e.g. polyethylene) or oriented (e.g. polypropylene); they may have undergone surface treatment (e.g. fluorination, sulfonization, silicone oxides, metallization and plasma polymerization); they may contain various additives and other constituents (e.g. plasticizers, antioxidants and monomers) and they can have a range of polarities (e.g. non-polar polyethylene, or polar ethylene vinylalcohol).

In recent years, chemical engineers have developed a number of group-contribution activity coefficient estimation models which can be used for estimating

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partition coefficients in polymer and liquid systems. Group-contribution methods allow estimation of activity coefficients from knowledge of the molecular structures of the system's components. Two of the more promising models are the UNIFAC-FV and Group-Contribution Flory Equation-of-State (GCFEOS). These techniques have been shown to give good estimations of activity coefficients (γ) in amorphous polymer and low molecular weight solvent systems. Partition coefficients (K) can be calculated using these estimated activity coefficients. These estimation methods have not been previously applied to the estimation of partition coefficients between polymers and their contacting liquid phases. The models have been seldom applied to estimations of activity coefficients for solutes with molecular weights larger than solvents (i.e. MW > 100).

It is hypothesized that the UNIFAC and GCFEOS activity coefficient estimation methods can be used to estimate polymer/liquid partition coefficients and that these estimations will be more accurate that the activity coefficient estimations for the polymer and liquid phases alone. It is expected that the estimated partition coefficient, which is a ratio of liquid and polymer activity coefficients, will be more accurate because of a canceling of errors between the two activity coefficients. This canceling of errors will be important when the method's empirical interaction parameters contain errors and the ratio should eliminate any errors arising from the combinatorial terms used in the two methods.

The goal of this dissertation is to systematically measure the partitioning of aroma compounds and alkanes between two polyethylenes of different crystallinity (LDPE, HDPE) and aqueous ethanol food simulants (100%, 75%, 50%, 35% ethanol). In addition, the data will be collected at three different temperatures (10°C, 25°C, 40°C) to study the temperature dependence of the partition coefficient. These experimental data will then be compared with the partition coefficient estimations of the UNIFAC-FV and GCFEOS methods. To better evaluate the methods's polymer/gas and liquid/gas partition coefficient estimations, the partitioning of the solutes between the aqueous ethanol mixtures and nitrogen will be measured at 25°C.

Literature Review and Definitions

Review of Literature: Partition Coefficient Data

Table 1 gives an overview of some of the aroma partition studies published in the past 10 years.

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Table 1

Overview of Aroma Food/Package Partition Studies at 20-25°C

Source	parameter	polymer	Liquid	aroma or solute
Baner et al. (1991)	K	11L	G	d-Limonene, n-hexanal ethyl acetate, α-terpineol
Becker et al. (1983)	K	1,2,3,4	M	13 aromas
DeLassus (1985)	S	1,3,4O,13	G	d-Limonene
DeLassus et al. (1988)	S	1,10,13	G	trans-2-hexenal
Farrell (1988)	K	1,1F	WE	d-Limonene
Halek & Meyers (1989)	A	1	WE	terpenes, ethyl butyrate
Harita & Tanaka (1989)	D	1,10	WS	d-Limonene
Ikegami et al. (1987)	D	0,1,2,3,9	WS	n-alcohols, terpenoids,n-aldehydes aliphatic ethyl esters
Ikegami et al. (1988)	D	4,5	WS	ditto
Jabarin & Kollen (1988)	K	5	F	d-limonene
Koszinowski (1986a)	K	1,3,4,5	A,E,H,M	n-alkanes
Koszinowski (1986b)	K	1	E	n-alcohols, phenols
Koszinowski & Piringer (1989)	K	1,3,4,7	E,W,WE,F	13 aromas, n-alkanes
Koszinowski & Piringer (1990)	K	1	M	104 different aromas
Kwapong & Hotchkiss (1987)	K	1,14	WE	d-Limonene, linalool, ethyl butyrate,citral
Letinski & Halek (1992)	A	4	WE	d-Limonene, 1-carvone
Mohney et al. (1988)	S	2,11L	G	d-Limonene
Nielsen et al. (1992)	K	0,1,4,9,15	W	10 aromas
Radovanovic & Thiel (1990)	K	12	W	alcohols
Shimoda et al. (1984)	D	3,5	F	8 terpenoids
Shimoda et al. (1987a)	S	2	G	octane, octanol, octanal,ethyl caproate
Shimoda et al. (1987b)	S	0,1,2,3,16	G	n-alkanes, n-alcohols n-aldehydes aliphatic ethyl esters
Shimoda et al. (1988)	D	1,2,3	WS	aliphatic ethyl esters n-aldehydes, benzoates

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Table 1 (cont.)

Parameter: K = Partition Coefficient, S = Solubility Coefficient, D = distribution ratio, A = % absorption, H = Henry's law constant. MI = migration data.

Polymer: 0 = linear low density polyethylene (LLDPE), 1 = LDPE, 2 = medium density polyethylene (MDPE), 3 = HDPE, 4 = homopolymer polypropylene (HPP), 5 = ethylene-propylene copolymer polypropylene (COPP), 6 = crystalline polypropylene (CPP), 7 = polyvinyl chloride (PVC), 8 = regenerated cellulose, 9 = polyethylene terephthalate (PET), 10 = ethylene vinyl alcohol (EVOH), 11 = polyvinyl alcohol (PVOH), 12 = cellulose acetate, 13 = polyvinylidene chloride (PVDC), 14 = ionomer, 15 = polyamide (nylon), 16 = ethylene vinyl acetate (EVA), 17 = polystyrene, 18 = polyvinyl acetate (PVA),F = fluourinated, O = oriented, L = laminate.

Liquid Phase: A = acetone, E = ethanol, F = food, H = hexane, M = methanol, O = oil, W = water or aqueous mixture, WS = aqueous food simulant, WE = aqueous ethanol mixture, G = gas.

Review of Literature: Migration Data

The migration literature consists of hundreds of references on the transfer of polymer additives and constituents into foods and food simulants. Not all references contain useful data due to ill defined measurement conditions or poorly characterized data. Table 2 lists some important sources of quantitative migration data. In addition migration data is found in the references found listed in Table 3 which contains references containing partition data for polymer constituents and additives.

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Table 2

Important Migration Data Sources

Source	Title
Noorduijk (1971)	Fact Finding Symposium On Packaging Materials
A.D.Little (1985) and Till et al. (1987)	A Study of Indirect Food Additive Migration
MAFF (1987)	Survey of Plasticiser Levels in Food Contact Materials and Foods.
Figge, K. (1988)	Migration Theory and Practical Examples
MAFF (1990)	Plasticisers: Continuing Surveillance

Table 3

Overview of Polymer Constituent and Additive Partition Data

Source	parameter	polymer		Migrant
Jenke et al. (1990)	K	7	**W**	**15 solutes with phthalates**
Kochmann et al. (1985a)	K	15,17	**W,WE,E**	**6 organic solvents, 6 glycol ethers**
Kochmann et al. (1985b)	K	4	**WE,F**	**2,6-di-tert-butyl hydroxytoluene**
Keinhorst & Niebergall (1986a)	K	15,17	**W**	**8 organic solvents**
Keinhorst & Niebergall (1986b)	K	15,17	**Milk**	**benzoic acid, Di-2-ethylhexylphthalate**
Koszinowski (1986b)	K	1	**E**	**n-alcohols, phenols**
Koszinowski and Piringer (1987)	M	8	**F**	**diethylene glycol**
Tzouwara-Karayanni et al. (1987)	K	7	**WS,WE,O**	**vinylchloride**
Sato et al. (1988)	H	7,18	**G**	**15 organic solvents**

see Table 1 for symbol meanings

The Use of Ethanol and Aqueous Ethanol as Food Simulants

Foods have complex compositions and are difficult to work with. It is often necessary to use food simulating solvents for migration testing. Low molecular weight alcohols, in particular ethanol and aqueous solutions of it have been suggested as food simulants (Schwartz, 1988, Piringer, 1990, Baner et al. 1992) for a wide variety of polymers. Ethanol and aqueous ethanol mixtures are particularly good simulants for the migration of substances between polymers (especially polyolefins) and fatty type foods (Schwartz, 1988, Piringer, 1990, Baner et al., 1992). Alcohols do not cause swelling of polyolefins (Becker et al., 1983); flavors and polymer additives are readily soluble in them; and they have clear analytical advantages over oil food simulants (Baner et al., 1992). Ethanol and aqueous ethanol food simulants have been widely used in the partition references listed in Tables 1 and 3 and in the migration references (A.D.Little, 1985 and Till et al., 1987).

Use of Partition Coefficients in Migration Theory

Migration theory describes the migration of low molecular weight components from polymeric packaging materials into contacting food layers. This situation can be described by Eq 2 derived from Fick's second law (Reid et.al., 1980) in Eq 1 for an immobile food contact phase (e.g. solid) with a lar

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large food volume to polymer sheet transfer area. The mass transfer process is controlled by (a) diffusion of the additive in the polymer which is assumed to be a function only of temperature (independent of concentration and time) and (b) the polymer sheet and food phase which are treated as if they were infinitely thick. A scheme of this system is shown in Figure 1.

$$\frac{c_i^P}{t} = D_P \quad \frac{c_i^P}{x^2} \qquad (1)$$

Eq 1 is solved having the initial conditions:

at $t = 0, x \geq 0 \qquad c_i^P = c_{io}^P$ (2)

$x < 0 \qquad c_i^F = 0$ (3)

and has the following boundary conditions at the food-polymer boundary (x=0):

$x = 0 \quad J = D_P \ (c_i^P / x)$ (4)

which is the flux of the component from the polymer, and a local equilibrium partitioning is assumed to occur:

at $x = 0 \quad K_{P/F} = (c_i^P/c_i^F)$ where $K \neq f(c_i^P,c_i^F)$ (5)

The diffusion in the food phase is described by:

$$\frac{c_i^F}{t} = D_F \quad \frac{c_i^F}{x^2} \qquad (6)$$

where the diffusion coefficient is a assumed to be a function only of temperature. In addition when the ratio of food volume to transfer area is very large then the concentration of the component becomes:

$c_i^F = 0$ for any $t, x \to -\infty$ (7)

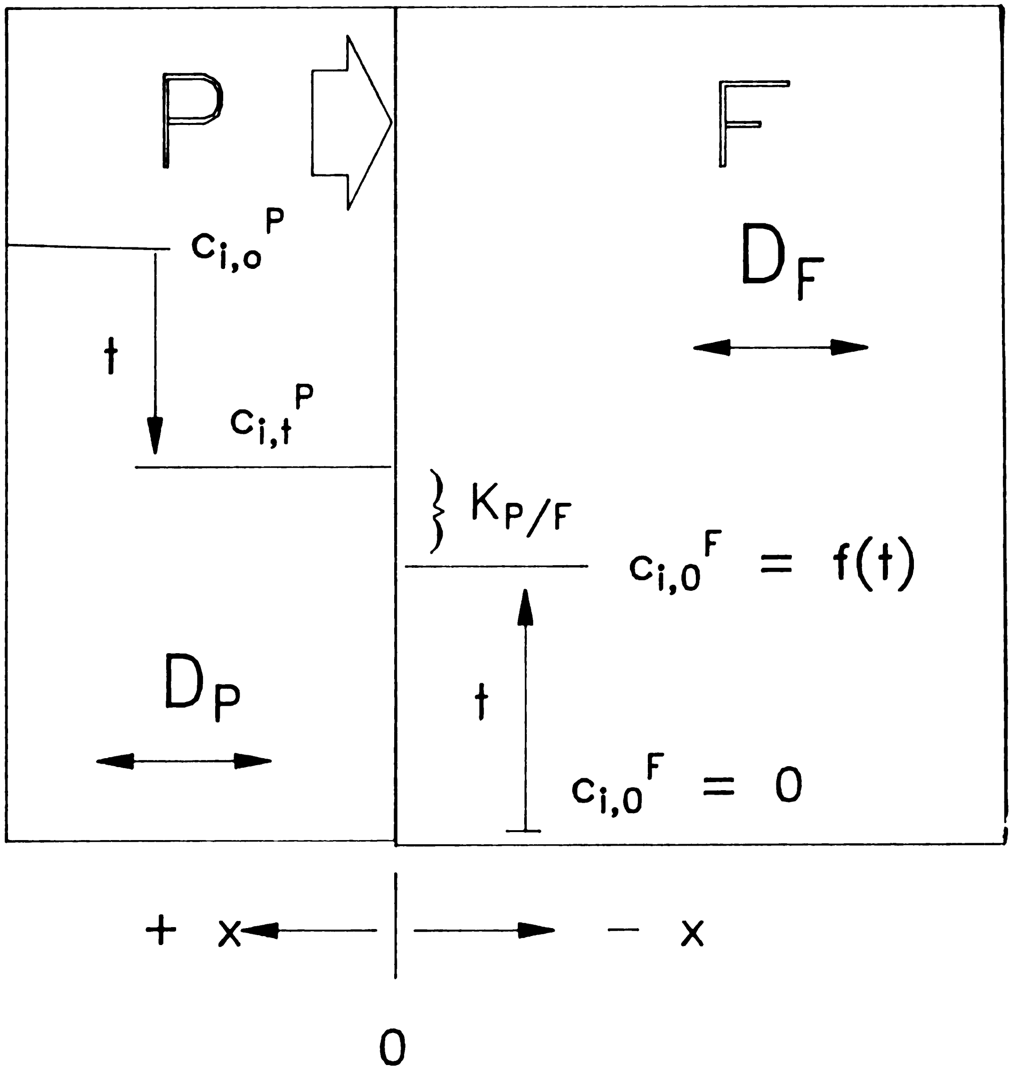

Figure 1. Migration from Polymer Sheet into Solid Food

$$J\ t = m_t/A = 2\ c_{io}^{P}\ (\beta/(1+\beta))\ (D_P\ t\ /\ \pi)^{1/2} \qquad (8)$$

where: $\beta = (1/K_{P/F})\ (D_F/D_P)^{1/2}$

m_t = amount migrated at time t (g)

t = time (sec)

A = food contact surface area of package (cm²)

J = flux (g/sec)

c_i^F = concentration of component in food (g/mL)

c_i^P = concentration of component in polymer (g/mL)

c_{io}^P = original concentration of migrant in polymer (g/mL)

D_P = diffusion coefficient in polymer (cm²/sec)

D_F = diffusion coefficient in food (cm²/sec)

$K_{P/F}$ = Polymer/Food Partition coefficient (dimensionless)

Here the partition coefficient exerts an effect on m_t through the ß term. When there is a small $K_{P/F}$, then $\beta \geq 1$, which leads to increased migration of the component from the polymer to the food. An example of this situation could be a fatty food packaged in a semi-polar plasticized polymer. Conversely with a large $K_{P/F}$, the potential migrant favors the polymer phase so even in the worst case where Dp and Df have similar orders of magnitude, then $\beta \leq 1$, and there is less migration.

The loss of flavors and aromas by foods packaged in a polymeric package system, barring any chemical reactions, is a function of two physical interaction phenomena: the migration of the flavor from the food into the polymer and the permeation of the flavor through the package into the surrounding environment. Eq 12 demonstrates the strong influence of the partition coefficient on the predicted migration of flavors from the food into the polymer. This equation is also a solution of Fick's second law with a finite amount of well mixed food having one or two sided contact with a polymer sheet of known thickness, d in cm (Crank, 1975). A schematic of the system is shown in Figure 2. For two sided contact the polymer thickness is one half d. To derive Eq 12 Fick's law (Eq 1) is solved with the following initial conditions:

$$\text{at } t = 0 \qquad c_i^P = 0 \text{ for } x \geq 0 \qquad (9)$$

$$c_i^F = c_{io}^F \text{ for } x < 0 \qquad (10)$$

and with the boundary condition listed in Eq 5 and

$$\text{at } x = d \text{ for } t > 0 \qquad \alpha \frac{c_i^P}{t} = D_P \frac{c_i^P}{x} \qquad (11)$$

This boundary condition means that the rate at which a component leaves the solution is always equal to that at which it enters the polymer sheet over the surface at x = 0.

$$m_t/m_\infty = (1+\alpha)\ [1-\exp(z)^2\ \mathrm{erfc}(z)] \qquad (12)$$

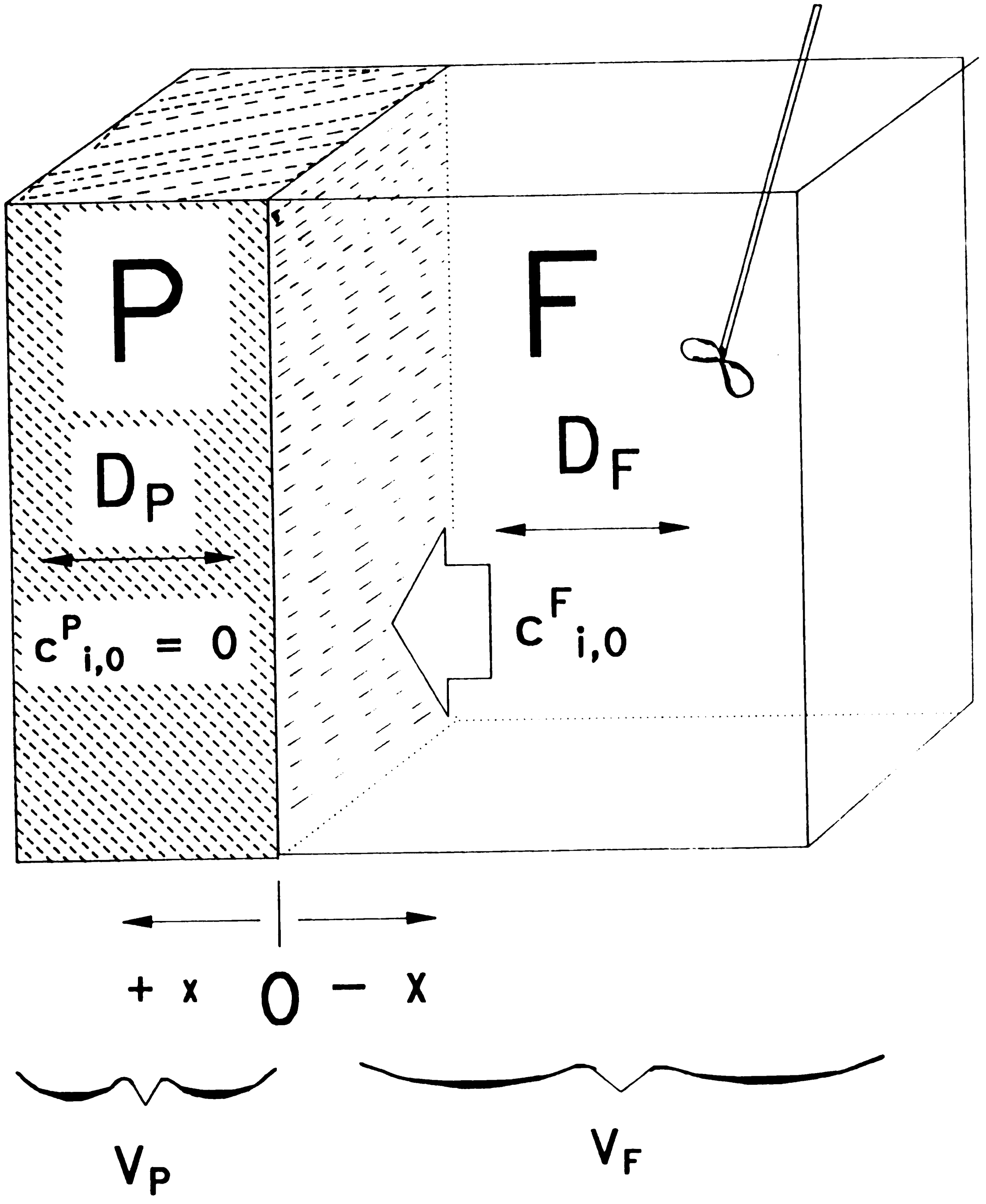

Figure 2. Migration from Finite Liquid Food into Polymer Sheet

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where $\alpha = (V_F/V_P)\ (1/K_{P/F})$

$z = K_{P/F}\ (V_P/V_F)\ (D_P\ t\ /\ d^2)^{1/2}$

m_t/m_∞ = ratio of amount migrated at time t (g) to the total migration at equilibrium (g)

V_F = volume of food phase (mL)

V_P = volume of polymer material (mL)

d = thickness of polymer (cm)

Significant migration of components into the polymer phase from food can occur even when the polymer has a low diffusion coefficient if the food component has a large partition coefficient. A large partition coefficient means the food component thermodynamically favors the polymer phase over the food phase.

Eq 12 can also be used to describe the migration (or desorption) of an evenly distributed component in the polymer into a well mixed food having a finite volume. In this case the movement of the migrant is in the opposite direction and m_t is taken to be the amount of solute leaving the sheet up to time t and m_∞ the corresponding amount after infinite time.

Derivation of Partition Coefficient Equations

Equilibrium in a package system can be defined as the condition where the fugacity (f) of the solute (i) in the gas phase (G) above the polymer (P) and the food or liquid (L) phases are equal:

$$f_i^G = f_i^P = f_i^L \qquad (13)$$

Fugacity has the dimensions of pressure and is a function of temperature, total pressure and composition of the mixture. The fugacity coefficient, Φ_i, accounts for non-idealities in mixtures. Where Eq 14 is for gas mixtures and Eq 15 is for liquid mixtures.

$$f_i^G = \Phi_i^G \, y_i \, P \qquad (14)$$

$$f_i^L = \Phi_i^L \, x_i \, P \qquad (15)$$

Where y_i is the mole fraction in the gas phase, x_i is the mole fraction in the liquid phase and P is system pressure. For condensed phases like polymers (P) and liquids (L), fugacity is often defined as:

$$f_i^P = \gamma_i^P \, x_i^P \, f_i^\circ \qquad (16)$$

$$f_i^L = \gamma_i^L \, x_i^L \, f_i^\circ \qquad (17)$$

Where f_i° is the fugacity of the pure liquid solute and τ is called the activity coefficient which corrects for non-idealities in fluid mixtures. According to Sandler (1989), "The activity coefficient arises because the nature of the interactions between the solute species i and the solvent is different than that between species i molecules so that τ_i accounts for the effect of replacing solute-solute interactions with solute-solvent interactions". The activity (a_i) of a solute is defined as the ratio of the species in the mixture (f_i) to the fugacity in a chosen standard reference state, e.g. f_i°:

$$a_i = f_i \ / \ f_i^\circ \qquad (18)$$

Combining Eq 17 for fugacity in the liquid state with Eq 18 gives:

$$a_i = \tau_i \ / \ x_i \qquad (19)$$

At low to moderate pressures f_i° is often equivalent to the pure component vapor pressure at the system temperature, P_i°. In addition, Φ_i^G under these conditions is often very close to unity.

For a package system at one atmosphere pressure and assuming the gas phase to be ideal, the definition of equilibrium in Eq 13 combined with Eq 14, 16 and 17 gives an expression for equilibrium in terms of mole fractions and activity coefficients of the solute:

$$y_i / P_i^{\circ} = \tau_i^{P} x_i^{P} = \tau_i^{L} x_i^{L} \tag{20}$$

In this case the calculation of equilibrium ratios for vapor-liquid equilibrium (VLE) is dependent on reliable methods for estimation of the τ_i's.

For dilute concentrations (w/v) of solute in the polymer and liquid phases the respective mole fractions can be approximated by the following equations:

$$x_i^{P} \approx c_i^{P} \underline{V}_P / M_i \tag{21}$$

$$x_i^{L} \approx c_i^{L} \underline{V}_L / M_i \tag{22}$$

Where x_i^P is the mole fraction in the polymer phase based on the polymer segmental molecular weight, M_i is the solute molecular weight, $\underline{V}_L$ is the molar volume of the liquid and $\underline{V}_P$ is the molar volume of one polymer segment. At equilibrium the concentration partition coefficient ($K_{P/L}$) (governed by the Nernst distribution law) can be defined as the ratio of the concentration (w/v) of the solute in the polymer (c_i^P) to the concentration (w/v) of the solute in the liquid (c_i^L). Combining Eq 21 and 22 with the polymer-liquid equilibrium condition described by Eq 20 between the polymer and liquid gives:

$$K_{P/L} = c_i^{P}/c_i^{L} = (\tau_i^{L}\ \underline{V}_L) / (\tau_i^{P}\ \underline{V}_P) \qquad (23a)$$

It is important to recognize that $K_{P/L}$ is an equilibrium parameter and although the solute molecules may experience more than one concurrent or sequential mode of sorption in a polymer material, the amount of solute sorbed at equilibrium and its mode of sorption in the polymer is governed largely by the thermodynamics of the polymer-solute interactions (Rogers, 1985).

The polymer/liquid coefficient can also be calculated from the ratio of the polymer/gas and liquid/gas partition coefficeints:

$$K_{P/L} = c_{i,\infty}^{P} / c_{i,\infty}^{L} = K_{P/G} / K_{L/G} \qquad (23b)$$

The partition coefficient describing solute partitioning between air and the polymer is called the solubility coefficient (S) and is defined by:

$$S = c_i^{P} / P_i^{\circ} \qquad (24)$$

Where P_i° is the pure component vapor pressure at the system temperature. At sufficiently low partial vapor pressures c_i^{P}

is proportional to S and P_i°. S is then often referred to as the Henry's law solubility coefficient, H. The dimensions of H varying depending on the dimensions of c_i^P and P_i° used.

Estimating Non-idealities in Mixtures

The activity coefficient provides one way to estimate solution non-idealities and is applicable in condensed phase systems (i.e. polymers, liquids, solids). The activity coefficient is a function of temperature (T), pressure (P) and system composition (x_i) and is defined from the partial molar excess Gibbs free energy (G_i^{ex}) (Sandler, 1989):

$$\gamma_i(T,P,x_i) = \exp\,(G_i^{ex}/RT) \qquad (25)$$

The molar excess Gibbs free energy can be loosely defined as the difference in free energy of an ideal mixture and that of a real (nonideal) mixture. The γ_i of an ideal mixture is one.

Another method for estimating the fugacity of a very dilute species in a liquid mixture is using Henry's law. It is experimentally observed that the fugacity of a very dilute species is linearly proportional to its mole fraction. This proportionality constant which is a function of temperature and pressure is referred to as the Henry's constant and is defined by:

$$f_i^L = x_i H_i \tag{26}$$

A more universal method for estimating fugacities in solution is to use an equation-of-state (EOS). Equations of state describe the properties of a specie in terms of temperature, pressure and volume. In general the present EOS methods are more applicable to the vapor phase (low densities) because nonidealities are not as great as they are in condensed phases (Sandler, 1989). Vapor phase fugacities at low pressures can also be estimated using virial EOS using experimentally determined virial coefficients (Sandler, 1989). Most EOS methods can be used to estimate fugacities of low to moderate density vapors but associating vapors require special corrections (Sandler, 1989). Recently some fairly accurate EOS methods have been developed for polymer solutions (Fredenslund, 1989).

For approximate fugacity calculations in the gas phase, the Lewis-Randall rule can be used:

$$f_i = y_i f_i^{\circ} \tag{27}$$

Estimating Activity Coefficients in Solvents and Polymers

There are several well accepted methods that can be used for estimating partition coefficients. Reid et al. (1987) presents some of the better recognized methods for estimating activity coefficients. Recently, several equation-of-state (EOS) methods, which describe the pressure, volume and temperature relationships of a substance in a mixture, have been developed. Of particular interest are the group-contribution EOS for mixtures with polymers of Ilyas and Doherty (Goydan, 1990), Holten-Anderson et al. (1987), Chen et al. (1990), and Huang and Radosz (1990). Sanchez (1979) has also developed an EOS method for polymers based on the Flory EOS and lattice fluid theories, however, the model requires equation of state parameters which are currently available for only 60 low molecular weight solutes and 10 different polymers. There are numerous examples of correlations developed for estimating partition coefficients: A novel method from Bao et al. (1988) correlates octanol-water partition coefficients to polymer-water coefficients using solubility parameters. The method is limited only to water solvent systems.

From a molecular chemistry viewpoint, Kamlet et al. (1984) have developed a correlation for the Henry's law solubility coefficients using a parameter that is correlated with a substance's critical temperature. Kasai et al. (1988) have also correlated partition coefficients in solvents based on molecular structure. Computer modeling (Jorgensen et al., 1990) is rapidly developing as a means of predicting partition coefficients directly from molecular structure.

However, computer modeling is not yet available for general application and its use is dependent on the availability of mainframe computers and software. Of the methods presented in Reid et al. (1987), many are not applicable because they cannot be applied to polymer systems. Many methods also require experimental data that is not available for many aromas or they are limited to certain classes of substances (e.g. cannot be used for aqueous systems) and cannot be used with the wide variety of chemical substances found in aromas (e.g. parameters are not available for all functional groups of molecules). Group-contribution methods are used to overcome the problems of estimating model parameters by assigning contributions to each of the functional groups making up the polymer, aroma and solvent phases.

Group Contribution Methods

Although there are thousands of chemical compounds of interest the number of functional groups making up these compounds is much smaller. Group contribution methods assume that a physical property of a fluid is the sum of contributions made by the molecule's functional groups. By using this assumption, it is possible to develop correlation techniques for a large number of fluids using a much smaller number of parameters which characterize the contributions of the individual groups (Fredenslund et al. 1975).

Any group-contribution method is necessarily an approximation because the contribution of a given group in one molecule is not necessarily the same as that in another molecule (Fredenslund et al. 1975). The fundamental assumption of a group-contribution method is additivity (in series), i.e. the contribution made by one group is assumed to be independent of that made by another group. This assumption is valid only when the influence of any group in a molecule is not affected by the nature of other groups within that molecule (Fredenslund et al., 1975).

Of the available activity coefficient group-contribution methods only the UNIFAC-FV, Holten-Anderson EOS, Ilyas and Doherty EOS, GC-Flory EOS and regular solution theory methods can be applied to polymer systems.

UNIFAC Method

The UNIFAC is a group-contribution method for the prediction of activity coefficients in non-electrolyte liquid mixtures originally developed by Fredenslund et al (1975). The method combines the solution-of-functional-groups concept with a model for activity coefficients based on an extension of the unified quasi chemical theory of liquid mixtures (UNIQUAC) of Abrams and Prausnitz (1975), hence the name UNIFAC (UNIQUAC Functional-group Activity Coefficients). In the solution-of-functional-groups concept a solution is viewed as a concentration of functional groups rather than the molecules themselves (Fredenslund et al. 1975). This means that the activity coefficients in mixtures are related to the interactions of functional groups. To be able to do this, data reduction using experimentally obtained activity coefficient data has to be carried out to obtain empirical parameters characterizing interactions between pairs of functional groups. The functional group sizes and interaction surface areas are taken from independently obtained pure-component, molecular structure data.

The UNIQUAC equation is based on the statistical thermodynamics of liquid mixtures using Guggenheim's quasi-chemical analysis. The UNIQUAC equation for the activity coefficient (τ) of molecular component i in a multicomponent mixture contains an entropic combinatorial part (τ_i^C) which is essentially due to differences in size and shape of the molecules in the mixture and an enthalpic residual part (τ_i^R) which is essentially due to energy interactions.

$$\ln \tau_i = \ln \tau_i^C + \ln \tau_i^R \qquad (28)$$

The complete calculation method is described by Fredenslund et al. (1975) and Fredenslund et al. (1977). Fredenslund et al. (1977) contains Fortran computer code for UNIFAC calculations and Sandler (1989) has published a Basic version of UNIFAC using the fourth up-date interaction parameters. The most up-to-date and complete listing (the fifth revision) of the necessary group volume, surface area and interaction parameters can be found in Hansen et al. (1991).

The UNIFAC method is useful for predicting vapor-liquid equilibria (VLE) over the temperature range 250 - 425 K. The accuracy of the method claims predictions of infinite dilution activity coefficients with deviations of less than 20% for most cases (Fredenslund et al. 1975). An average error of prediction of 20.5% by UNIFAC for infinite dilution activity coefficients was reported by Thomas and Eckert (1984) who compared UNIFAC's predictions with experimental data for 3357 compounds and an average error of 21% for 77 systems compared by Park and Carr (1987). UNIFAC does not yield quantitative prediction of liquid-liquid equilibrium (LLE). Hence Magnussen et al. (1988) has published a separate set of interaction parameters for LLE.

In addition to up-dates, several modifications to the original UNIFAC method have been proposed since it was published. Fredenslund (1989) published a review of the state of UNIFAC and discussed the limitations of the original UNIFAC method and the several modifications that have been proposed for it. The modifications of Weidlich and Gmehling (1987) and Larsen et al. (1987) encompass modifications to the combinatorial term and to the residual term giving it more temperature dependence for better prediction of temperature effects. The modifications of Weidlich and Gmehling produced about an 11% improvement in VLE predictions over the original UNIFAC model. Fredenslund (1989) sums up the differences between the original UNIFAC and these two modifications as minimal improvement in VLE predictions but notes that large temperature extrapolations are possible with the modified versions. These modified UNIFAC versions have a smaller set of interaction parameters than original UNIFAC thus limiting their usefulness. This version of Weilich and Gmehling has 21 functional group interaction parameters and Larsen et al. has 23 compared to 50 for original UNIFAC. Sets of interaction parameters for infinite dilution solutions have been proposed for UNIFAC, τ^{∞}-UNIFAC, (Bastas et al, 1988) which provide marginal improvement (28% deviation to 20% deviation) over original UNIFAC. Park et al. (1991) have compared τ estimations of original UNIFAC with modified UNIFAC (Weidlich and Gmehling, 1987) and τ^{∞}-UNIFAC for 6 solutes in the n-alkanes, 1-alcohols and alkanenitriles. The average errors of the estimations were 20%, 7.4% and 31% for original, modified and τ^{∞} UNIFAC models confirming previous observations that modified UNIFAC predictions are better than original UNIFAC and that τ^{∞} UNIFAC is not necessarily better than the original model.

UNIFAC Estimation for Polymers

The original version of UNIFAC underestimates experimental solute activity in polymers. It does not take into account differences in free volumes between the mixture components (Oishi and Prausnitz, 1978). Oishi and Praunsnitz (1978) developed a free volume correction for UNIFAC, which is referred to as UNIFAC-FV. They added a free volume (fv) activity contribution term ($\ln \tau_i^{fv}$) to Eq 28 based on an the equation-of-state theory of Flory (1970) (Oishi and Prausnitz, 1978):

$$\ln \tau_i = \ln \tau_i^C + \ln \tau_i^R + \ln \tau_i^{fv} \qquad (29)$$

where:

$$\ln \tau_i^{fv} = 3c_i \ln \left[\frac{(v_i^{1/3} - 1)}{(v_M^{1/3} - 1)}\right] - c_i[(v_i/v_M - 1)(1 - v_i^{-1/3})] \qquad (30)$$

Where v is a reduced volume, i refers to the solute, M refers to the mixture, and $3c_i$ is the number of external degrees of freedom per solute molecule with c_i set equal to 1.1 from earlier empirical observations. The expression for the reduced volume v_i (dimensionless) of the solvent is:

$$v_i = v_i^w/(15.17\ b\ r_1') \qquad (31)$$

Where v_i^w is the volume of the solvent per gram, r_i' is the normalized van der Waals volume per gram for the solute (based on the normalization used in UNIQUAC) and b is a proportionality factor determined empirically with a value of 1.28. Assuming the volume of the liquid mixture is additive, then the reduced volume for a binary mixture, v_M (mL/g), is:

$$v_M = (v_i w_i + v_P w_P) \, / \, (15.17(r_i' w_i + r_P' w_P)) \tag{32}$$

Where P stands for the polymer phase and w is the weight fraction. UNIFAC-FV calculates activities on a weight fraction basis as opposed to a mole fraction basis in original UNIFAC because mole fractions are awkward units due to the molecular weight differences between the polymer and solute. The UNIFAC free volume modification method like the original UNIFAC method were originally optimized for finite as opposed to infinite dilution concentration solutions because very little data exists in the infinite dilution region. This could conceivably affect the empirical b and c_i parameters used in this free volume term. This free volume term has been found to be highly dependent on the values of the pure-component densities used (Fredenslund, 1989).

In order to better understand the importance and significance of the free volume concept the following discussion is taken from Prausnitz et al. (1986):

"In general, pure fluids have different free volumes, i.e. different degrees of thermal expansion. When liquids with different free volumes are mixed, that difference contributes to the excess functions (e.g. excess free energy). Differences in free volume must be taken into account, especially for mixtures of liquids whose molecules differ greatly in size and shape. For example, in a solution of a polymer in a chemically similar solvent of low molecular weight, there is little dissimilarity in intermolecular interactions but the free volume dissimilarity is significant. The low-molecular-weight solvent may be much more dilated than the liquid polymer; the difference in dilation (or free volume) has an important effect on solution properties."

The calculation of free volume (v_f, cm^3/mol) is dependent on the particular definition used (Bondi, 1968). The sense of the definition used here is the difference between the "hard sphere" or "hard core" volume per mole (v^*) and the volume of solute per mole at some temperature T ($v_i(T)$). This difference is essentially the thermal expansion of the molecule.

$$v_f = v_i(T) - v^* \tag{33}$$

Where the hard core volume is the van der Waals volume (cm^3/mole) of the molecule. The hard core values were calculated from experimental data by Bondi (1968) using the covalent bond distances and the so-called van der Waals radii between a molecule and carbon in the condensed state (i.e. liquid or solid).

The literature has given mixed reviews on the ability of UNIFAC-FV to estimate solute activity coefficients in polymer solutions depending on the system to which it is applied. In addition to agreement with experimental data presented in Oishi and Prausnitz (1987), Arai and Iwai (1980) found UNIFAC-FV to give excellent predictions of Henry's constants for aromatic hydrocarbons in polystyrene. Tseng et al. (1986) found UNIFAC-FV was an improvement over the regular solution theory for predictions of solvent-polymer interactions for polybutadiene, polymethyl methacrylate, and polystyrene systems. Belfiore et al. (1988) found serious shortcomings using UNIFAC-FV to characterize the phase behavior of polymer-polymer blends of polystyrene and poly(vinyl methyl ether) and poly(ethylene glycol) and poly(acrylic acid). Belfiore et al. explained the shortcomings of UNIFAC-FV for polymer blends as being due to residual contribution to the activity (τ_i^R). The residual contribution term uses empirical functional group parameters which although appropriate for small molecules are too large for polymer-polymer blends. Their (Belfiore et al.) problems may be due in part to the shortcomings of using VLE UNIFAC interaction parameters to predict solution

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properties closer to liquid-liquid equilibrium. Sorensen et al. (1990) compared experimental infinite dilution activity coefficients of hydrocarbons in poly(ethylene glycol) (MW 4000, 7500, 10000) and concluded that UNIFAC-FV underestimates the experimental results but can predict the data trends.

Iwai et al. (1985) proposed a new expression for the free volume term which has been shown to be quantitative for the solubilites of hydrocarbon vapors in polystyrene, natural rubber, polyisobutylene and in styrene-butadiene copolymers (Iwai et al., 1991). The method proposed by Iwai et al. (1985) requires the heat of vaporization of the solute as an additional parameter. Goydan et al. (1989) used UNIFAC-FV to estimate the solubilities of various polar and non-polar solutes in several amorphous polymer systems and concluded that it was good qualitatively and "fairly accurate" quantitatively. High and Danner (1990) studied the accuracy of UNIFAC-FV in predicting various solvents in polystyrene and concluded that the solvent activities are well predicted. Balaschova et al. (1990) compared UNIFAC-FV with experimental data for monomers in various styrene blend polymers and found it can be used for calculating VLE in these systems.

Doong and Ho (1991) recently proposed a modification to UNIFAC-FV that allows its use to be expanded to semi-

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crystalline polymers. They added an elastic factor to account for the restraining effect of semi-crystalline regions in polyethylene on its polymer chains which they reasoned can make an elastic free energy contribution. The Doong and Ho model has been applied to polyethylene and several different hydrocarbons at finite concentrations. The method requires an empirical factor, which accounts for the fraction of elastically effective chains in the amorphous regions of the polymer. The method of Doong and Ho remains to be proven since the empirical factor used was calculated from the experimental data on which the model was tested. In general UNIFAC-FV of Oishi and Prausnitz (1978) has been shown to have correlating ability but lacks quantitative correctness for some systems. The UNIFAC-FV methods of Iwai et al. (1985) and Doong and Ho (1991) show promise but both need to be tested on polar solutes. With the exception of Doong and Ho, all of the variations of UNIFAC-FV have not been tested on semi-crystalline polymers. This is mainly due to the lack of experimental data.

Fredenslund (1989) has discussed several of the current developments in UNIFAC and commented on possible future improvements. He pointed out that although the modifications of UNIFAC of Weidlich and Gmehling (1987) and Larsen et al (1987) give better activity coefficient estimations than the original UNIFAC, the infinite dilution activity coefficients do not extrapolate well to polyethylene molecular weights

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(compared to the original) and hence the combinatorial term used in these methods should not be used for polymers. One of the interesting comments made by Fredenslund was that it appears that a free volume contribution may be necessary to improve UNIFAC for other solutions in addition to polymers. This is because there are significant differences between the free volumes of different organic solvents and water in addition to those already recognized in polymers. UNIFAC was derived under the assumption that any free volume effects are constant. One of the underlying problems with UNIFAC may be that free volume effects have been incorporated into the fitted interaction parameters. One of the ways to improve UNIFAC in Fredenslund's opinion is to adopt the new expression for the combinatorial activity coefficient expression of Elbro et al. (1988) which has both combinatorial and free volume parts incorporated into it.

Ilyas and Doherty, and Holten-Anderson EOS

Goydan et al. (1989) have reviewed the use of three group contribution techniques: UNIFAC-FV, Ilyas and Doherty EOS and Holten-Anderson EOS, for use in estimating the solubilities of organic compounds in polymers. They observed that, in general, all three methods were in good agreement with the experimental solubility values for a wide variety of solutes in six different polymers. They ranked the Holten-Anderson EOS as the most accurate while the UNIFAC-FV method o

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method of Oishi and Prausnitz (1978) was fairly accurate and was more widely applicable due to the greater number of functional groups available compared to the other two methods. High and Danner (1990) who estimated various solvents activities in polystyrene noted that while both Holten-Anderson and UNIFAC-FV predict solvent activities well the UNIFAC-FV is generally more accurate and should be used when pure densities are available. The Holten-Anderson EOS requires only the structure of the solvent and polymer and can be applied to liquid-liquid systems as well. Summarizing the work of Doherty et al. and High and Danner comparing UNIFAC-FV with the EOS methods of Ilyas and Doherty and that of Holten-Anderson, the selection of UNIFAC-FV for further study is justified. UNIFAC-FV gives activity predictions as good or better than these two methods and it is applicable to a wider class of substances due to the greater number of functional groups available. The availability of the great number of functional groups is an important consideration for calculations involving aroma compounds.

Group-Contribution Flory Equation-of-State

Recently Chen et al. (1990) developed what they call the Group-Contribution Flory Equation-of-State (GCFEOS) method for estimating solvent activity coefficients in mixtures containing polymers. The GCFEOS method is essentially an

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improvement on the Holten-Anderson EOS and gives better overall estimations of infinite dilution solvent activities in 31 polymer-solvent mixtures than either the UNIFAC-FV or Holten-Anderson methods (Chen et al., 1990). The method is also computationaly easier to use than Holten-Anderson and because it is an EOS method only the structures of the solvent and polymer are needed whereas UNIFAC-FV requires the densities of the pure fluids. GCFEOS takes into account the free volume differences of the mixture's constituents thus offering a good prospect for improving predictions over UNIFAC-FV estimations of VLE. One of the disadvantages of GCFEOS is that it currently has only 26 functional groups available compared to 50 for UNIFAC-FV. GCFEOS represents a state-of-the-art group-contribution approach to polymer-solvent VLE and should be further tested and compared with experimental data.

Regular Solution Theory

Solubility parameters, which are central to the regular solution theory originally proposed by Hildebrand and Scatchard (Hildebrand and Scott, 1950, Hildebrand et al., 1970), can be estimated using group-contribution methods developed by several people notably Hansen (Barton, 1983), Hoy (1970, 1985), Fedors (1974a, 1974b) and Van Krevelen (1990). Van Krevelen (1990) and Barton (1983) have reviewed

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the regular solution theory group contribution method as it is applied to activity coefficient estimation in polymers.

The regular solution theory is by far the simplest and oldest of the group contribution activity estimation methods. However, the regular solution theory is not necessarily the most accurate and is applicable in theory only to regular solutions. Barton (1983) wrote that one should not expect that partition coefficients can be predicted in detail by solubility parameters particularly for polar molecules. The theory and usefulness have been reviewed by Van Krevelen (1990), Barton (1983) and Rider (1985). The method has achieved its widest acceptance in the paint and coatings industry where it is used as a means of predicting the tendency of polymers to dissolve in solvents (Rider, 1985). Very few direct applications of the regular solution theory for the prediction of partition coefficients have been found in the literature (Barton, 1983). Most applications require modification of the regular solution theory using empirical terms and there are many more examples of correlations using only solubility parameters (Barton, 1983).

The regular solution theory using different group contribution methods was applied to the estimation of solute partition coefficients between polyolefins and alcohols (Baner and Piringer, 1991). It was observed that the regular

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solution theory using the Hildebrand solubility parameters and the Hansen type solubility parameters could not quantitatively predict these partition coefficients. Although a fundamental correlative relationship between the experimental data and estimations was observed, it was necessary to calculate an empirical term (whose contribution to τ was larger than that of the solubility parameters!) for the regular solution expression in order to obtain a quantitative partition coefficient prediction. The regular solution prediction method of Baner and Piringer is likely to remain restricted to the partition coefficient estimation of solutes between polyolefins and ethanol or methanol alcohols due to the lack of an experimental data base for calculating additional empirical correction factors. These are dependent on the polymer and liquid system. With the availability of predictive methods more universally applicable (such as UNIFAC) or more theoretically correct (GCFEOS) no further development or study of the regular solution theory is warranted.

Materials and Methods

Materials

Polymers:

The following polyethylenes were used for polymer/liquid partition coefficient measurements.

HDPE : Hostalen GF 4760 (Hoechst Folien AG, Weisbaden, Germany), density = .956, thickness = 98.38 ± 10.4 μm. Same polymer sample used by Becker et al. (1983), Koszinowski (1986a, 1986b), Koszinowski and Piringer (1989, 1990).

LDPE : Hostalen LDH 1018, density = 0.918, thickness = 47.5 ± 2.5 μm. Same polymer sample used by Becker et al. (1983), Koszinowski (1986a, 1986b), Koszinowski and Piringer (1989, 1990).

Determination of Additive Content of Polymers

Samples (2-3 mg) of the polymers were analyzed using coupled SFE/SFC (supercritical fluid extraction/supercritical fluid chromatography) using a Carlo Erba SFE 3000. The samples were extracted using supercritical CO_2 at 30 MPa which was then expanded and the extracted material concentrated in a liquid nitrogen cold trap at -10°C. The extraction was stopped and the sample swept onto the column of the SFC. No significant peaks were found signifying the presence of additives in the polymer. The total extractables (likely oligomers) in the polymers were approximately 44 ppm (μg/g) and 32 ppm for LDPE and HDPE.

Solvents:

Hexane (purity>99.0%) and Ethanol (purity >99.8%) from Merck (Darmstadt, Germany). Water: deionized laboratory water.

Test Solutes:

The aqueous ethanol/nitrogen and polyethylene/aqueous ethanol partition coefficients were measured for the following solutes.

Aromas: supplied by Drom Parfümöle KG (Baierbrunn, Germany). n-Alkanes: from Fluka Chemie. Aroma purity determined by GC, n-alkanes purity as purchased. Table 4 lists the molecular weights, densities and structures of the test solutes.

Aroma	Purity	n-Alkane	Purity
d-Limonene	94.2%	Octane	>99%
Diphenylmethane	94.2%	Nonane	>99%
Linalylacetate	91.8%	Decane	>98%
Camphor	94.1%	Dodecane	>98%
Diphenyloxide	99.9%	Tetradecane	>99%
Isoamylacetate	98.0%	Hexadecane	>98%
τ-Undelactone	98.0%	Octadecane	>99%
Eugenol	98.6%	Eicosane	>99%
Citronellol	96.2%	Docosane	>99%
Dimethylbenzylcarbinol	99.6%		
L-Menthol	99.2%		
Phenylethylalcohol	99.7%		
cis-3-hexenol	94.1		

Table 4. Structure, Molecular Weight, and Density of Solutes

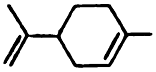
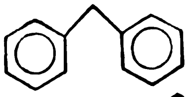
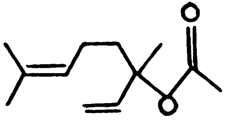
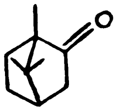
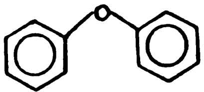
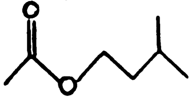
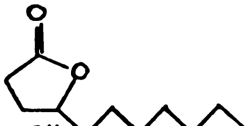
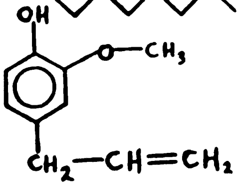
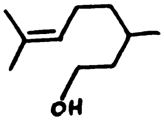
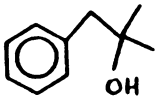
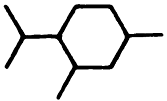
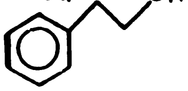
Aroma	$\underline{V}_i^W$	MW	Density	Structure
d-Limonene	88.35	136.24	$.8411^{20}_{4}$	
Diphenylmethane	101.93	168.23	1.0008^{26}_{4}	
Linalylacetate	124.08	196.29	$.895^{20}_{4}$	
Camphor	96.8	152.23	$.9932^{25}$ est.	
Diphenyloxide	96.7	170.21	1.0706^{25}_{4}	
Isoamylacetate	83.47	130.18	$.8656^{24}_{4}$	
τ-Undelactone	117.51	184.28	$.949^{25}_{4}$	
Eugenol	98.98	164.20	1.0664^{20}_{4}	
Citronellol	110.23	156.27	$.855^{20}_{4}$	
Dimethylbenzylcarbinol	94.72	150.22	$.9723^{24}_{4}$	
L-Menthol	106.9	156.27	$.900^{25}$ est.	
Phenylethylalcohol	74.31	122.17	1.01502^{25}_{4}	
cis-3-hexenol	69.26	100.16	$.8453^{22}_{4}$	

Table 4. (cont.)

n-Alkane	$\underline{V}_i^W$	MW	Density	Structure
Pentane	58.03	72.15	$.6213^{25}_{4}$	$CH_3(CH_2)_3CH_3$
Hexane	68.26	86.17	$.6553^{25}_{4}$	$CH_3(CH_2)_4CH_3$
Heptane	78.49	100.20	$.6800^{25}_{4}$	$CH_3(CH_2)_5CH_3$
Octane	88.72	114.22	$.6990^{25}_{4}$	$CH_3(CH_2)_6CH_3$
Nonane	98.95	128.26	$.7144^{25}_{4}$	$CH_3(CH_2)_7CH_3$
Decane	109.18	142.28	$.7259^{25}_{4}$	$CH_3(CH_2)_8CH_3$
Dodecane	129.64	170.41	$.7440^{25}_{4}$	$CH_3(CH_2)_{10}CH_3$
Tetradecane	150.1	198.40	$.7593^{25}_{4}$	$CH_3(CH_2)_{12}CH_3$
Hexadecane	170.56	226.45	$.7699^{25}_{4}$	$CH_3(CH_2)_{14}CH_3$
Octadecane	191.02	254.54	$.7788^{25}$ ext.	$CH_3(CH_2)_{16}CH_3$
Eicosane	211.48	282.56	$.7858^{25}$ ext.	$CH_3(CH_2)_{18}CH_3$
Docosane	231.94	310.61	$.7916^{25}$ ext.	$CH_3(CH_2)_{20}CH_3$

MW = molecular weight Density = obtained from Windholz (1983), Weast (1979), Synowietz (1983).

est. = estimated from molar volume estimation method of Fedors (1974a,b)

ext. = extrapolated from a linear regression of lower molecular weight n-alkane densities.

$\underline{V}_i^W$ = Van der Waals molar volume. Van Krevelen (1990)

Gas:

Nitrogen purity 99.9999% (purity 5.0) from Linde (Munich, Germany).

Methods

Determination of Polymer Crystallinity

The polymer's crystalline fraction was estimated using differential scanning calorimetry (DSC). A Mettler DSC20 with a TC11 TA Processor using a standard gold nickel sensor (dig/k = 2400) was used. The DSC was calibrated with an Indium standard and standard 40μL Al dishes with lids were used. The temperature was scanned from 40°C to 200°C at a rate of 10°C/min. The sample sizes used ranged from 4 to 9 μg and were conditioned prior to testing over silica gel in a desiccator for three weeks at room temperature. The polymer melt temperature was the temperature at the maximum of the endotherm curve. The heat of fusion was calculated using the system's software integration function as the area between the endotherm curve and the scan's baseline. The crystalline fraction (x_c) of the polymer is estimated using Eq 34 (Van Krevelen, 1990).

$$x_c = \Delta h_m / \Delta h^c_m \qquad (34)$$

Where Δh_m is the DSC's measured heat of fusion and Δh^c_m is the heat of fusion of the polymer crystalline fraction. The heat of fusion of polyethylene, Δh^c_m = 8.22 KJ/mol (293.03 J/g), was obtained from Van Krevelen (1990).

The results of the DSC measurements are shown in the Table 5 below along with crystalline fractions calculated using polymer density. The crystalline fraction can be estimated using the polymer density (ρ) and the densities of the amorphous (ρ_a) and crystalline (ρ_c) fractions of the polymer using Eq 35 (Van Krevelen, 1990):

$$x_c = (v_a - v) / (v_a - v_c) = (\rho_c / \rho)(\rho - \rho_a) / (\rho_c - \rho_a)$$
(35)

Where v is the specific volume (cm^3/g) of the polymer.

Table 5. Crystalline Fraction of Polymers Tested

POLYMER	by DSC[a]	by Density[b]	T_M (°C)
LDPE	0.266 ± 0.017	0.473	109.7 ± 0.3
HDPE	0.583 ± 0.006	0.729	133.2 ± 0.7

a) Δh^c_m = 8.22 KJ/mol (Van Krevelen, 1990)

b) ρ_a = 0.855 (g/mL), ρ_c = 1.00 (g/mL) (Van Krevelen, 1990)
ρ = from manufacturer's film specifications.

T_M = melt temperature (the maximum of the enthalpic curve)

The crystalline fractions calculated from density are normally appreciably higher than those from enthalpy measurements (Mandelkern, 1990).

GC Analysis Conditions

The following GC analysis conditions were used to analyze the various test samples needed for partition coefficient measurements.

Aromas: Hewlett Packard (HP) HP5890II capillary GC with HP 7673A automatic sampler. Column: 0.5μm Supelcowax 10 (Supelco, Inc., Bellefonte, PA), 30m x 0.32mm i.d., H_2 carrier gas with 40 cm/sec linear velocity. Temperature Program: 65°C for 6 min. -- 8°C/min ramp -- 230°C for 5 min. 2μL sample injection volume. Split ratio: 10:1 for $K_{P/L}$ hexane extraction samples and 40:1 for $K_{P/L}$ ethanol phase samples.

n-Alkanes: Hewlett Packard HP5890 capillary GC with a HP 7671A automatic sampler. Column: 5.0μm DB-1 (J&W, Folsom, CA) 30 x 0.32mm i.d., H_2 carrier gas with 40 cm/sec linear velocity. Temperature program: 40°C -- 15°C/min ramp -- 240°C for 24 min. 2μL injection volume. Split ratio: 10:1 for $K_{P/L}$ hexane extraction samples and 40:1 for $K_{P/L}$ ethanol phase samples.

The order of elution and retention times (RT = min) of test substances using the above conditions are listed in Table 6.

Table 6. Order of Solute GC Elution and Retention Times

	Ethanol				Hexane
	100%	75%	50%	35%	100%
Aroma			RT		
Isoamylacetate	4.29	4.20	4.13	4.10	4.24
d-Limonene	6.39	6.23	6.09	6.01	6.38
cis-3-hexenol	11.46	11.47	11.49	11.50	11.46
Camphor	14.24	14.23	14.23	14.23	14.25
Linalylacetate	14.93	14.92	14.91	14.91	14.95
Menthol	16.40	16.40	16.40	16.40	16.40
Dimethylbenzylcarbinol	18.34	18.34	18.35	18.35	18.35
Citronellol	18.34	18.34	18.35	18.35	18.35
Phenylethylalcohol	20.69	20.69	20.70	20.70	20.69
Diphenylmethane	22.19	22.19	22.19	22.19	22.21
Diphenyloxide	22.24	22.24	22.24	22.24	22.26
Eugenol	24.14	24.14	24.15	24.15	24.15
γ-undelactone	25.37	25.37	25.38	25.38	25.37
n-Alkane					
Octane	7.29	7.29	7.51	7.81	7.66
Nonane	9.26	9.26	9.33	9.44	9.17
Decane	10.58	10.58	10.60	10.62	10.58
Dodecane	13.14	13.14	13.16	13.17	13.13
Tetradecane	15.78	15.78	15.78	15.83	15.77
Hexadecane	19.63	19.63	19.63	19.70	19.62
Octadecane	25.94	25.94	25.94	26.05	25.91
Eicosane	29.68	29.68	29.70	30.00	29.58
Docosane	36.80	36.80	36.80	36.97	36.75

See preceeding text for analysis conditions.

Liquid/Air Partition Coefficients

Apparatus

Liquid/air partition coefficients were measured using con-current flows of liquid and air (nitrogen) in a thermostated gas stripping column. The column was developed by Piringer and is described in Piringer and Skories (1984). Figure 3 shows a schematic of the column used. The column is a continuous flow method operating under steady-state conditions and uses practically unlimited liquid and gas volumes so that errors from absorption processes are largely eliminated. The column has a 2 L upper reservoir (A), a metering valve for controlling the liquid flow rate (B), a sample valve for removing liquid samples from the upper reservoir (C), and a gas stripping column (D) that allows for long contact times between a thin film of liquid running along a spiral and a con-current flow of nitrogen. The column has an effective spiral length of 62 cm, an inner diameter of 1.5 cm and an outer diameter of 3.0 cm and a total length of 115 cm. At a flow rate of 130 mL/h a drop of water requires 250 s to travel through the column. Underneath the column the liquid passes through a capillary tube and into a collecting reservoir (E). The saturated nitrogen stream is then passed through two gas washing bottles with #2 pore frits in series containing solvent and

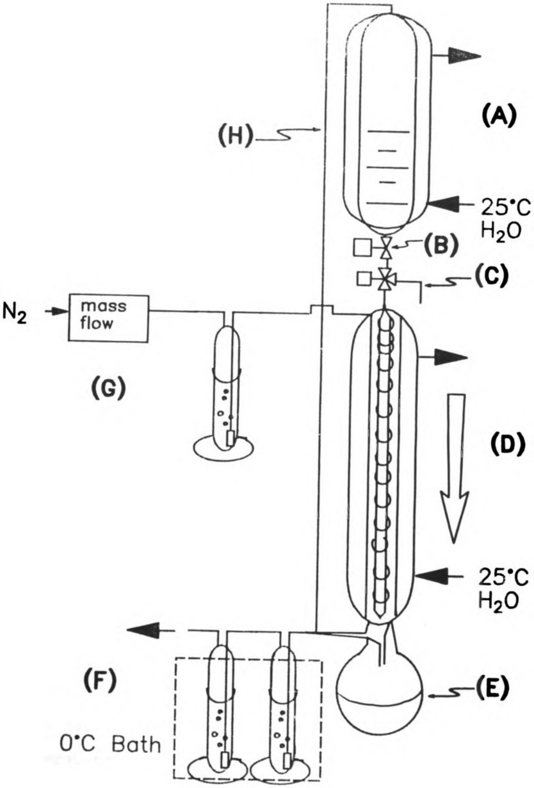


Figure 3. Gas Stripping Column Schematic

held at 0°C in a polyethylene glycol containing water bath (F). The column temperature was held at 25±.5°C using two Lauda RCS6 (Messgeräte-Werk Lauda GmbH, Lauda-Konigshofen, Germany) circulating water baths with R22 remote temperature controllers and Pt 100 thermal resistance temperature sensors for controlling temperature. The actual temperature at the end of the column was measured with a Pt 100 temperature sensor and recorded on a strip chart recorder. The incoming nitrogen stream was conditioned at 25°C by flowing it through a coil in the water bath and the flow rate controlled to within ±1mL/min using a MKS Instruments (Munich, Germany) model 1259C 500mL Mass Flow Controller with a MKS PR-3000 controller which had a precision of ±1%, an accuracy of 0.1% and a reproducibility of 0.2% of scale. The nitrogen stream was saturated with ethanol and water vapor prior to entering the column by passing it through a gas washing bottle with a #2 frit (G) filled with the liquids phase without solutes. The nitrogen flow at the end of the column was remeasured using a soap bubble flow meter. Additional temperature control was provided by heating tapes and strings (Horst Laborgeräte GmbH, Lindefels2-Seidenbuch, Germany) connected to Normag (Otto Fritz GmbH, Hofheim an Taunus, Germany) digital proportional temperature controllers with Pt 100 sensors at the liquid sampling valve (B), the nitrogen conditioner (G), and the gas outlet at the end of the column. To overcome the slight back pressure created by the two gas washing bottles at the end of the column a pressure equalizing tube was connected between the bottom of the column and the top of the reservoir (H).

The $K_{L/G}$ of the aromas were measured using a mixture of all 13 aromas each having an initial average mole fraction of 7.7×10^{-6} corresponding to a total mole fraction of 1×10^{-4} for the aromas in the mixture. The individual aroma mole fractions correspond to a concentration range of 12-24 ppm (µg/mL). The n-alkane $K_{L/G}$ were measured using a mixture of 9 alkanes (pentane to decane, dodecane, tetradecane and hexadecane) having individual mole fractions of 1×10^{-4} for 100% ethanol, $0.031\text{-}4.02\times10^{-5}$ for 66% aqueous ethanol, and $0.07\text{-}19\times10^{-6}$ for 33% aqueous ethanol.

A test run was begun by filling the upper reservoir with a measured volume of liquid mixture and allowing it to equilibrate for 30 minutes. Before each measurement the system was conditioned for one hour using identical conditions to those used during an experiment (e.g. identical solvent traps and flows). At the end of conditioning, the gas and liquid flows were halted temporarily and a sample was taken from the upper reservoir and collection flask (E) and gas washing bottles (F) were changed. The liquid flow was then re-established and the experiment begun with flow of gas through the column. After 12-14 hours (overnight) the experiment was ended by stopping the liquid flow and then the gas flow. The volumes of liquid in the upper reservoir, collection flask and gas washing bottles were measured. Samples were taken from the upper reservoir, the collection flask and the two gas washing bottles and subsequently injected into a GC for quantitation. The liquid/gas partition coefficient, $K_{L/G}$, was calculated with a PC spreadsheet program using Eq 36:

$$K_{L/G} = \frac{GC_L \cdot t \cdot v_G \cdot cal_L}{(GC_1 \cdot V_1 + GC_2 \cdot V_2) \cdot cal_G} \qquad (36)$$

Where GC equals the GC area units for a partitioned substance, V is volume at the end of a run, t is the time, v is the volumetric flow of the gas and cal is the GC calibration factor for the respective phase. The subscripts L, G, 1 and 2 stand for liquid, gas and gas washing bottle 1 and 2 respectively. A mass balance was calculated using Eq 37:

$$\%\ \text{recovery} = 100 \cdot \left(\frac{GC_{UE} \cdot V_{UE} + GC_L \cdot V_L + GC_1 \cdot V_1 + GC_2 \cdot V_2}{GC_{UO} \cdot V_{UO}} \right) \qquad (37)$$

Where the subscript UO stands for the upper reservoir liquid phase concentration of a component at the beginning of a run. The percent mass balance recovery is the mass in the upper reservoir (A) at the end of a measurement plus the mass in the collection reservoir (E) plus the mass in the two gas washing bottles (F) divided by the initial mass input in the upper reservoir (A) times 100.

The liquid/gas partition coefficient can also be calculated using the concentration difference between the upper reservoir and the lower reservoir provided a significant difference in the upper and lower concentrations can be measured.

$$K_{L/G} = \frac{GC_L}{[((GC_{UE} + GC_{UO})/2) - GC_L]\cdot V_L \ / \ t\cdot v_G} \qquad (38)$$

Where GC_{UE} stands for the upper reservoir liquid phase concentration of a component at the end of measurement.

Method Development

The gas stripping column operating parameters were taken from previous work with this column (Piringer and Skories, 1984, Brunner et al., 1990). The optimum operating nitrogen gas flow rate with respect to a mixture of n-alkanes (pentane to dodecane) in ethanol with a liquid flow rate of 1-3 ml/min over 12-15 hours was determined by varying the gas flow rate and measuring the resulting partition

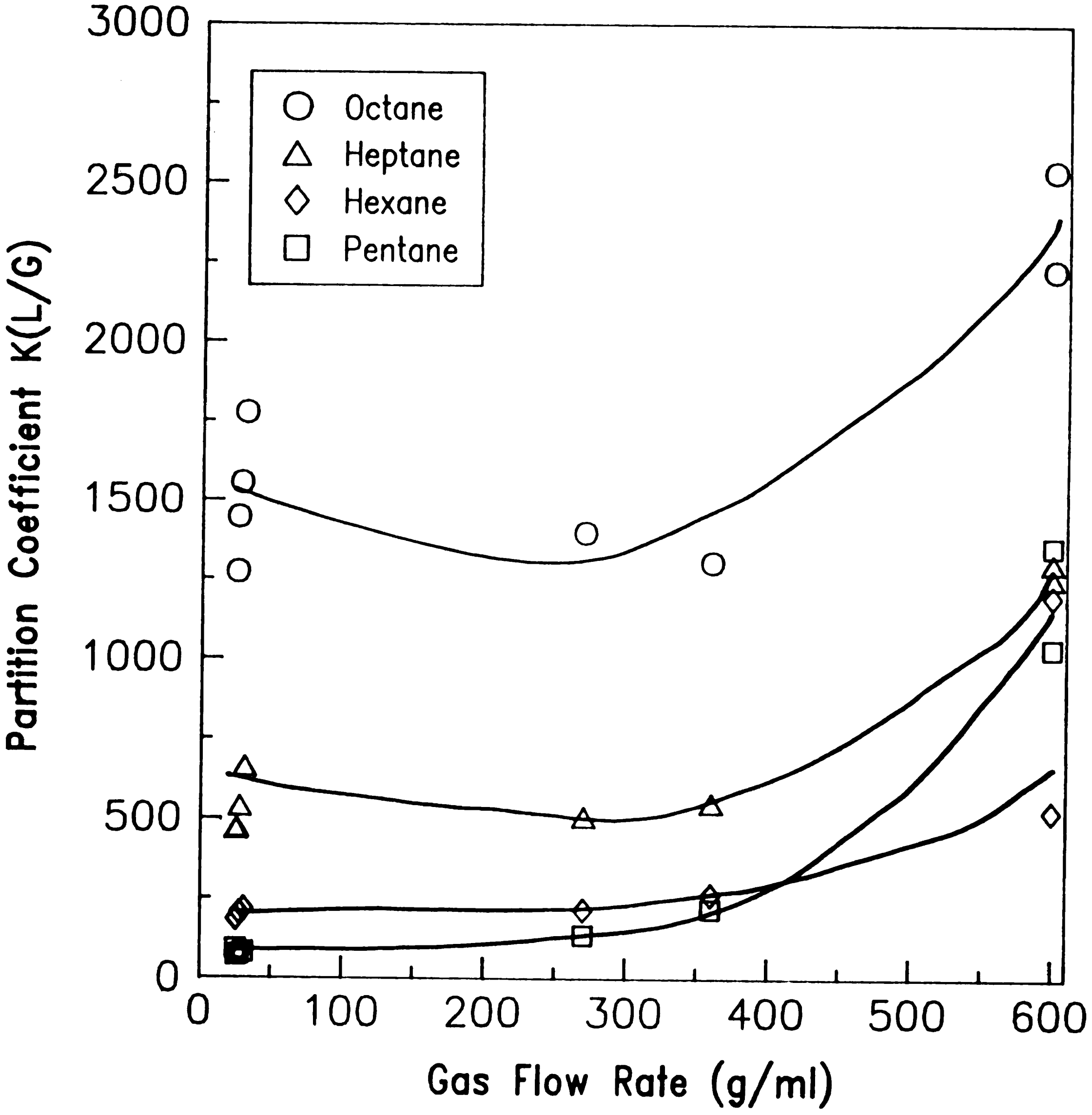


Figure 4. Dependence of $K_{L/G}$ on Gas Flow: Pentane-Octane

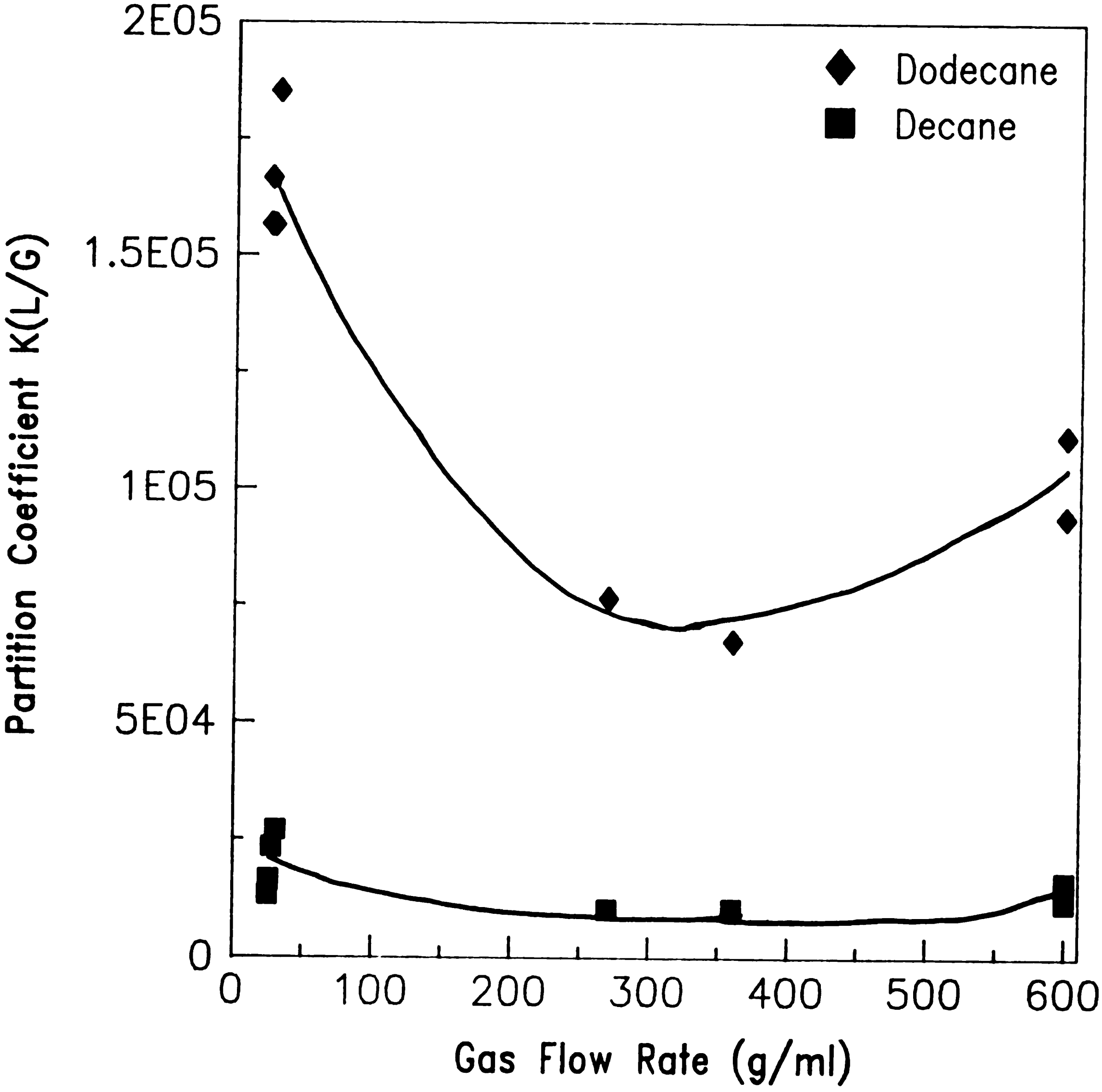


Figure 5. Dependence of $K_{L/G}$ on Gas Flow:
Decane and Dodecane

coefficients. Figures 4 and 5 show partition coefficients calculated using Eq 36 versus gas flow rate produces a minimum at the optimum gas flow rate. At low gas flow rates the error is largest for less volatile alkanes because so little material is collected in the solvent trap over the course of a run. The more volatile substances tend to be swept out of the trap at higher flow rates. There is also an increasing danger that one equilibrium stage is not reached in the column. For these n-alkanes the optimum gas flow rate was in the range of 100 to 300 ml/min.

Partition coefficients calculated using the concentration differences in the liquid phase before and after stripping (Eq 38) gave larger estimates of the partition coefficients and showed much greater variability than those calculated using the solvent traps (Eq 36). The difference method worked best for more volatile alkanes whereas the less volatile alkanes had little concentration change in the liquid phase after stripping that the concentration difference was in the order of the variability of the gas chromatograph measurements themselves and thus could not be accurately measured. The $K_{L/G}$ calculated by concentration difference is best used as a control for comparison with the $K_{L/G}$ calculated from the solvent trap data. If the concentration difference K is smaller than the solvent trap

K then it means that the trap is not retaining all of the substance from the gas phase.

For confirmation, liquid/gas partition coefficients obtained from this gas stripping column method were compared with published data in the literature. Cori and Delogu (1986) reported infinite dilution ($x_i \approx 10^{-4}$) activity coefficients for n-alkanes, pentane to nonane, in 100% ethanol using a gas stripping method similar to Renon et al. (1977). Pierotti et al. (1959) has reported correlations for the log of n-alkane infinite dilution activity coefficients in n-alcohols. Park et al. (1987) reported an infinite dilution activity coefficient for octane in ethanol using a GC method. Liquid/gas partition coefficients ($K_{L/G}$) can be calculated from activity coefficients (τ_i) at room temperatures and atmospheric pressures using Eq 39.

$$K_{L/G} = (R \cdot T) \;/\; (\tau_i \cdot P^{\circ}_i \cdot \underline{V}_L) \qquad (39)$$

Where R is the gas law constant, T is Kelvin, P°_i is the saturated partial pressure of the substance (i) and $\underline{V}_L$ is the liquid molar volume. This equation assumes an ideal gas phase and that Raoult's law can be used due to the low temperatures and pressures and dilute concentrations used. The partition coefficients calculated from these

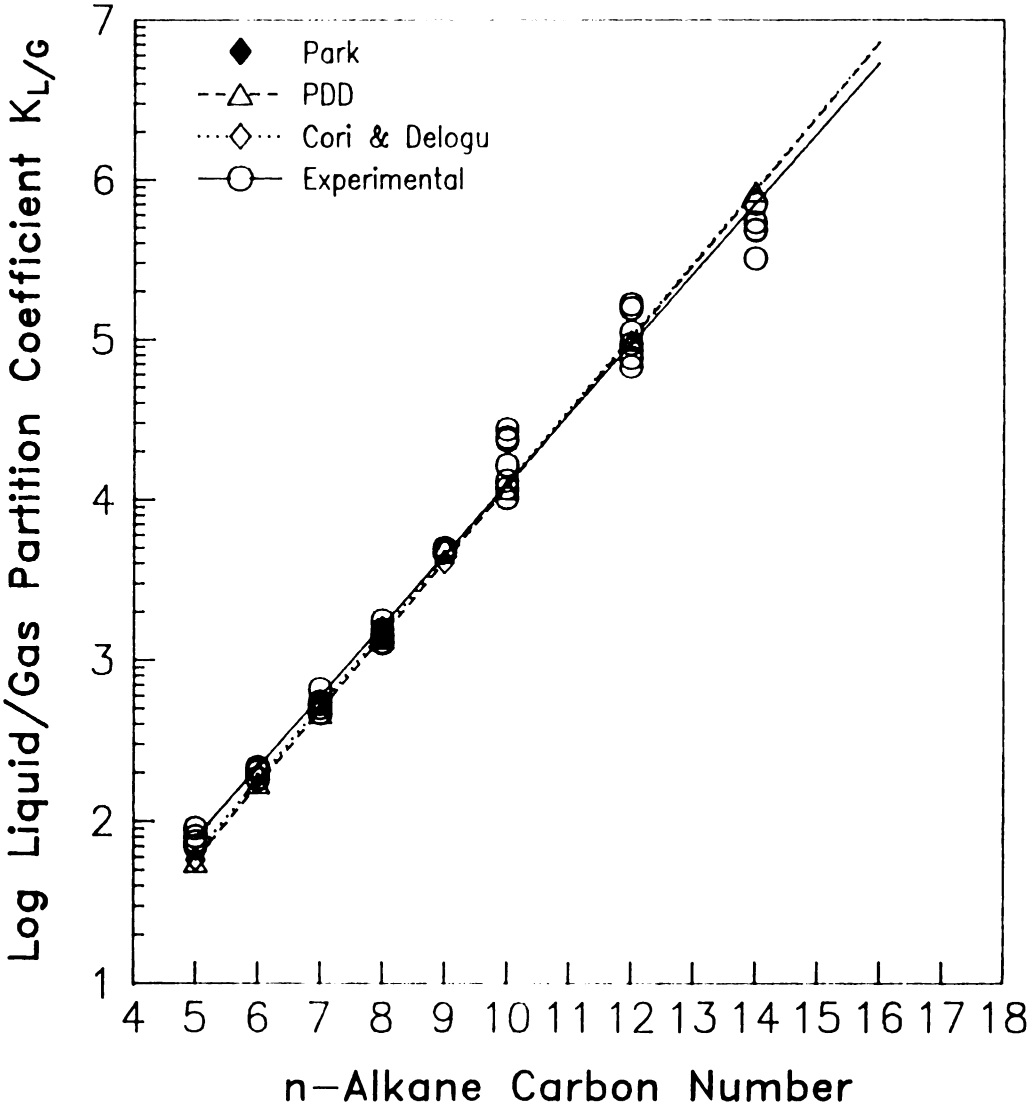


Figure 6. n-Alkanes/100% Ethanol: $K_{L/G}$ Literature versus Experimental

literature sources using the n-alkane saturated partial pressures in Appendix A are plotted in Figure 6 along with the experimental partition coefficients. Linear regression lines were calculated for the experimental and Cori and Delogu data. The regression line for the Cori and Delogu data was very close to the regression line of the correlation data from Pierrotti et al. varying by -2.2% for pentane to -3.9% for hexadecane. The experimental data compared with Cori and Delogu agreed best for decane (-2.2%) but was greater for pentane by 26% and smaller for hexadecane by 25%. These variances are within the uncertainty of these measurements (see Error Analysis).

The effect of solute concentration in the liquid phase was tested by increasing the concentration of the aroma mixture in a 50% aqueous ethanol solution 20 times (from ≈20 ppm to ≈244 ppm). The result was such that within the method's experimental uncertainty no significant difference was seen between the measured partition coefficients. Figure 7 compares the effect of the aroma liquid concentration on $K_{L/G}$.

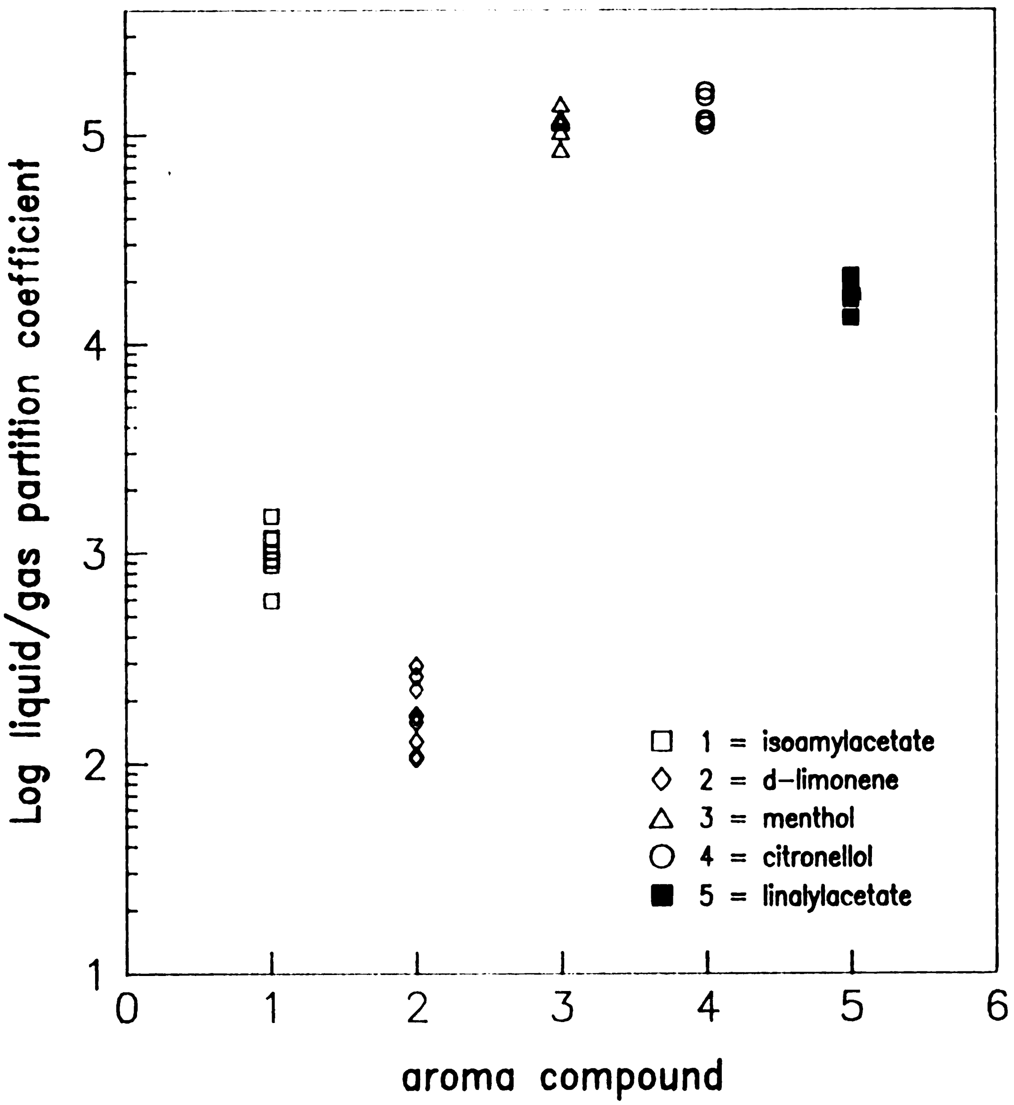


Figure 7. Effect of Aroma Concentration on $K_{L/G}$. 50% Aqueous Ethanol. Aroma concentration range ≈ 20 - 244 ppm (μg/mL).

Polymer/Liquid Partition Coefficients

Apparatus

The method used here follows the ASTM standard D7454-87, Standard Test Method for Two-Sided Liquid Extraction of Plastic Materials Using FDA Migration Cell (ASTM, 1987). The method was originally developed for the USFDA (United States Food and Drug Administration) (Till et al., 1982) and has been applied to a variety of migrant/polymer systems in contact with numerous foods and food simulants. Snyder and Breder (1985) have also used the FDA migration cells to measure styrene migration and Becker et al. (1983) used an adaptation of the FDA cell to measure the sorption of aromas by polymers. A schematic of the vial is shown in Figure 8.

The procedure was as follows: 18 round polymer disks, 24.4 mm diameter with a 3.4 mm hole in the center with a total surface area of 4.59 cm^2, were stamped out of the polymer films (LDPE 50μm, HDPE 100μm) using a punch. The disks were then weighed and threaded onto a stainless steel wire with 2mm high 4mm diameter glass rings (cut from glass tubing) separating the polymer disks. The wires with disks were then placed in 40 mL screw cap vials (28mm diameter, 98 mm high) with teflon coated silicone septa (Alltech,

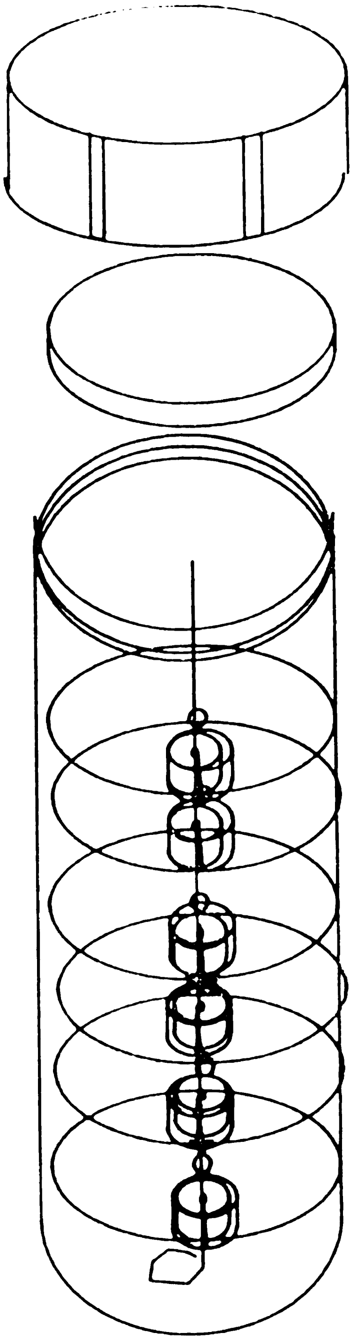


Figure 8. Schematic of $K_{P/L}$ Measurement Vial

Unterhaching, Germany) and 35 mL of the solute containing liquid mixture filling the vial to its shoulder.

The 12 aromas were tested together as mixtures in the ethanol or aqueous ethanol liquid phase with the initial concentrations listed in Table 7.

Table 7. Aroma Initial Concentrations, $K_{P/L}$ Measurements

Flavors	Initial ppm (μg/mL)
Isoamylacetate	73.8-79.5
d-Limonene	67.6-79.7
cis-3-Hexenol	50-57
Camphor	76.3-95.8
Linalylacetate	94.7-108.4
Menthol	81.6-92.8
Dimethylbenzylcarbinol	79-88.5
Phenylethylalcohol	65.6-75.9
Diphenylmethane	93.1-105.1
Diphenyloxide	99.3-108.1
Eugenol	86.1-98.1
τ-Undelactone	95.3-108.2

These concentrations correspond to an approximate total mole fraction of $4.4\text{x}10^{-4}$ and individual aroma mole fractions of $3.7\text{x}10^{-5}$. The higher concentration range was used for the 35% aqueous ethanol mixtures, the lower range for the 100, 75 and 50% mixtures.

The 9 n-alkanes were used in mixtures at varying concentrations depending on the aqueous content of the liquid mixture. This was necessary because the solubility of the higher molecular weight n-alkanes becomes lower the more aqueous the solution becomes. The concentrations used are given in Table 8.

Table 8. n-Alkane Initial Concentrations, $K_{P/L}$ Measurements

n-Alkane Solution:	Initial ppm (μg/mL) 100%	75%	50%	35%
C8	38.5	20	15	5
C9	39.2	20	14.5	5
C10	17.4	19.3	7.8	3.9
C12	22.8	25.3	10.2	5.1
C14	24.2	26.9	10.8	5.4
C16	27.6	30.6	12.3	6.1
C18	31.7	35.2	14.2	7
C20	34.6	38.4	15.4	7.7
C22	37.8	42	16.9	8.4

These concentrations correspond to total molar fractions of $1x10^{-4}$ for the 100% and 75% ethanol solutions, and $1.5x10^{-5}$ and $6.5x10^{-6}$ for the 50% and 35% solutions. For individual n-alkanes these concentrations correspond to mole fractions of $1.1x10^{-5}$ in the 100% and 75% solutions and $1.7x10^{-6}$ and $7.2x10^{-7}$ in the 50% and 35% solutions.

The vials were placed in 10±1°C and 25±1°C controlled atmosphere chambers and in a 40±1°C oven and shaken by hand at three different intervals during their storage. The necessary storage times needed for the sorption process to reach equilibrium were >10 days at 40°C, >20 days at 25°C and >40 days at 10°C. These times were estimated based on previous experience and from equilibrium sorption times reported in the literature. Halek and Meyers (1989) reported aqueous solutions of hydrocarbon terpenes required 25 days and oxygenated terpenes 2 days to reach equilibrium sorption at 20°C. Harita and Tanaka (1989) showed d-limonene sorption from an aqueous solution required 18-20 days to sorb into different polyolefin films at 20°C. Ikegami et al. (1987) reported equilibrium sorption times for aqueous solutions of a variety of aromas into HDPE and PP films were reached in 20 days at 20°C. Using these observations and a kinetic rule of thumb where kinetic processes double with every 10°C increase in temperature, the experimental storage times used should be sufficient to reach equilibrium sorption conditions.

At the end of the storage time, samples of the liquid phase were taken and the remaining liquid phase discarded. The polymer discs were then rinsed two times with aliquots of the liquid phase solvent and the discs blotted dry with a lab tissue and placed in 20 mL crimp cap vials. The sorbed solutes in the polymer were extracted by adding 15 mL of hexane, capping the vials with teflon coated silicone septa and placing them in the 40°C oven for 10 days. The vials were shaken by hand twice during the extraction and after 10 days removed from the oven. Samples of the hexane were taken in 1.0 mL GC autosampler vials and the remaining hexane discarded. The discs were then rinsed with two aliquots of hexane and re-extracted with 15 mL more of hexane for 10 days at 40°C. The concentrations in the liquid and hexane phases was measured by GC and the partition coefficient calculations carried out on a personal computer (PC) spreadsheet program. Eq 40 calculates the polymer/liquid partition coefficient ($K_{P/L}$):

$$K_{P/L} = \frac{c_i^P}{c_i^L} = \frac{[(au_{h1} + au_{h2}) \cdot cal_H \cdot V_h \cdot den_P \;/\; g_P]}{au_L \cdot cal_L} \qquad (40)$$

The numerator in Eq 40 is the concentration of the solute (i) in the polymer determined by the sum of the GC measurements of the two hexane extraction times the calibration factor for the hexane solvent samples times the volume of hexane used times the density of the polymer divided by the total weight of the polymer disks in the vial. The denominator is the GC measurement of the liquid solution times its calibration factor. In Eq 40: au = GC area units, L = liquid, P = polymer, h = hexane, 1 and 2 stand for traps 1 and 2, cal = GC calibration factor (g/mL/au), V = volume (mL), den = density (g/mL), c = concentration (g/mL) and g_P = weight polymer (g).

Testing of $K_{P/L}$ Method

In addition to the method development for $K_{P/L}$ measurements outlined by Becker et al. (1983) the method was tested for concentration effects, surface effects and interaction between aromas in mixtures.

Test for Solute Interactions in Test Mixtures:

Four different aromas, d-limonene, camphor, linalylacetate and citronellol were mixed in 100% ethanol solutions at concentrations corresponding to aroma mole fractions of approximately 2.5×10^{-5} (65±4, 70±4, 84±4, 71±4 ppm (μg/mL) respectively). Mixtures of the four aromas were combined in a completely randomized factorial design and their partition coefficients measured between 100% ethanol and 14 HDPE disks after 25 days equilibrium at 25°C. The disks were then extracted with Hexane and the extractant and liquid solutions analyzed as outlined earlier. An analysis of variance was performed on the results using the STATIT statistics software (Statware, Inc., Kirkland, Washington). The statistical differences between the means at the 95% confidence level are shown in Table 9.

Table 9. $K_{P/L}$ Solute Interaction Test Results

Treatment	Average $K_{P/L}$			
	d-Limonene	Camphor	Linalylacetate	Citronellol
1	-	-	-	-
2	-	-	-	.0117
3	-	-	.0501	-
4	-	-	.0553	.0172
5	-	.0671	-	-
6*	-	.0607	-	.0136
7	-	.0607	.0514	-
8*	-	.0560	.0480	.0135
9	.341	-	-	-
10	.354	-	-	.0131
11	.286	-	.0403	-
12*	.298	.0530	-	-
13	.283	.0495	-	.0227
14*	.285	.0527	.0469	-
15	.482	-	.0711	.0204
16*	.502	.0483	.0829	.0219

* The $K_{P/L}$ for aromas in this treatment are not affected by the presence of the other aromas in the treatment.

The ANOVA tested to see if the $K_{P/L}$ for an aroma depended on the treatment (i.e. how it was combined with other aromas). Treatment numbers followed by (*) have no significant interactions between the aroma $K_{P/L}$ in this treatment and those in the other treatments. All other treatments showed significant differences for the aroma $K_{P/L}$ compared to $K_{P/L}$ in other treatments. Strength-of-association measures (Linton and Gallo, 1975), which describe the difference in the variance between the dependent variable and independent variable, were calculated for the treatments where a significant difference was found. Strength-of-association measures help determine how strong the relationship is between the treatment and the resultant behavior of the $K_{P/L}$. In all cases with significant differences, except for d-Limonene, the strength-of-association measure was less than 4%. For a strength-of-association less than 5%, the relationships may be real but are very weak (Linton and Gallo, 1975). d-Limonene showed a strength-of-association measure of 53% which suggests that there is a somewhat stronger relationship between the $K_{P/L}$ for d-Limonene in combination with other flavors. A strength of association of 53% although large is not an exceptionally strong association (Linton and Gallo) and given the large uncertainty of these measurements (see Error Analysis) it can be assumed for these measurements that there are no strong interaction effects between the partitioning of flavors between HDPE and 100% ethanol in this concentration range. This conclusion is similar to that found by Baner et al. (1991) for polymer/gas partition coefficients measurements between polyethylene laminated structures and a mixture of 4 aromas using headspace GC.

Test for $K_{P/L}$ Method Surface Effects

A test for surface effects in the $K_{P/L}$ measurements was carried out using different numbers of LDPE disks in a 35% aqueous ethanol solution of the 12 aromas at 25°C. The aromas had mole fractions of 7.7×10^{-6} (total mole fraction 1×10^{-4}) corresponding to the concentrations in Table 10.

Table 10. Initial $K_{P/L}$ Surface Effects Test Concentrations

Aroma	**Initial ppm (µg/mL)**
Isoamylacetate	16.98
d-Limonene	17.0
cis-3-Hexenol	12.4
Camphor	18.7
Linalylacetate	23.7
Menthol	20.3
Dimethylbenzylcarbinol	19.8
Phenylethylalcohol	16.2
Diphenylmethane	20.9
Diphenyloxide	19.8
Eugenol	21.7
γ-Undelactone	23.8

The low aroma concentrations and highly polar liquid phase were chosen as a worst case situation for surface effects to occur. Test vials were filled with 3, 7, 14 and 21 polymer disks. The polymer surface area of the 35 mL contacting liquid phase corresponds to ratios of 10, 23.4, 46.7 and 70.1 dm² package surface area to Kg liquid food simulant. A ratio of 6-10 dm²/Kg is considered to be an average package to food ratio by convention (e.g. a 1 liter asceptic package has a ratio ≈ 6.3 dm²/kg). The hexane extraction volumes used were 2,4, 7 and 9 mL for the 3, 7, 14, and 21 disk samples. Five replicates were measured for each number of disks along with control vials. The hexane extract and ethanol phase were analyzed as previously outlined. Following measurement the data was analyzed by ANOVA using STATIT at the 95% confidence level for significant differences. This surface effect test tested the hypothesis: if surface effects are present in the method, the treatments with more surface area to liquid would have higher $K_{P/L}$ values due to absorption on the surface of the polymer. The results are summarized in Table 11.

Table 11. $K_{P/L}$ Surface Effects Test Results

Aroma	No. Disks:	3	7	14	21
Isoamylacetate	$K_{P/L}$:	.755	.664	.596	.620
	s.d.:	.0926	.0674	.0524	.0409
d-Limonene		112.4	109.2	111.4	118.6
		4.91	12.1	9.7	7.82
cis-3-Hexenol		-	-	-	-
Camphor		.865	.817	.790	.769
		.048	.095	.045	.055
Linalylacetate		4.90	4.52	4.75	4.77
		.328	.364	.342	.391
Menthol		.393	.401	.362	.368
		.0312	.0815	.0373	.0416
Dimethylbenzylcarbinol		.436	.417	.383	.376
		.0414	.0511	.0772	.0223
Phenylethylalcohol		.412	.378	.322	.323
		.114	.0323	.0632	.0507
Diphenylmethane		7.1	6.54	6.64	7.05
		.472	.274	.900	.368
Diphenyloxide		18.4	17.2	18.4	19.1
		.987	1.28	1.77	1.21
Eugenol		.234	.186	.165	.114
		.0338	.0383	.0200	.0105
τ-Undelactone		.353	.348	.326	.323
		.0359	.0239	.0355	.0351

$K_{P/L}$ - average of 5 measurements

s.d. - standard deviation

ANOVA results at the 95% level of significance showed there were significant differences for Isoamylacetate between the 3 disk treatment and the 7, 14 and 21 disk treatments and for Eugenol between the 21 disk treatment and the other cases. Both of these significant differences are likely caused by analytical errors. In the case of Eugenol the large difference is caused by a poorly resolved and integrated Eugenol peak in the hexane extract analysis. It can be concluded from this test that there are no significant surface effects for these test conditions. It is then safe to conclude from this test that one will not encounter surface effects in this method for slightly polar to polar substances for other ethanol and aqueous ethanol liquid phases and these polyethylene samples. The test also shows that the hexane extraction step has no measureable surface effects dependent on the volume of hexane or the size of the extraction vials used.

Test for Liquid Phase Concentration Effects

The third test characterizing the $K_{P/L}$ measurement method involves testing for a liquid phase solute concentration dependence. $K_{P/L}$ for even numbered carbon n-alkanes ranging from C10 to C22, were measured at 4 different concentrations ranging from initial liquid phase mole fractions of $1.1x10^{-6}$ to $2.2x10^{-5}$ between 100% ethanol and HDPE at 25°C. The corresponding concentration ranges are listed in Table 12.

Table 12. n-Alkane Concentration Ranges for $K_{P/L}$ Concentration Effects Test

Mole fraction x(i)	Initial ppm (μg/mL) range
control	.064 - .49
1.1E-6	3.5 - 7.6
5.6E-6	17.4 - 37.8
1.1E-5	34.8 - 75.7
2.2E-5	69.7 - 151.4

The HDPE sample contained appreciable amounts of the n-alkanes as oligomer species so a control sample was also measured. The results are shown in Figure 9 where the log of $K_{P/L}$ is plotted versus the n-alkane carbon number at different test concentrations. Also included is a second independent measurement at the mole fraction $x(i)=1.1\times10^{-5}$. The plotted data points are the average values for five observations and the 95% confidence limit error bars are shown. The scatter for the decane alkane is due to analytical problems separating decane from the ethanol peak in some of the GC measurements. Figure 9 shows a statistically significant and systematic increase in $K_{P/L}$ as the concentration of n-alkanes in the liquid phase decreases. The deviations of the three highest concentrations are all within the total uncertainty of the

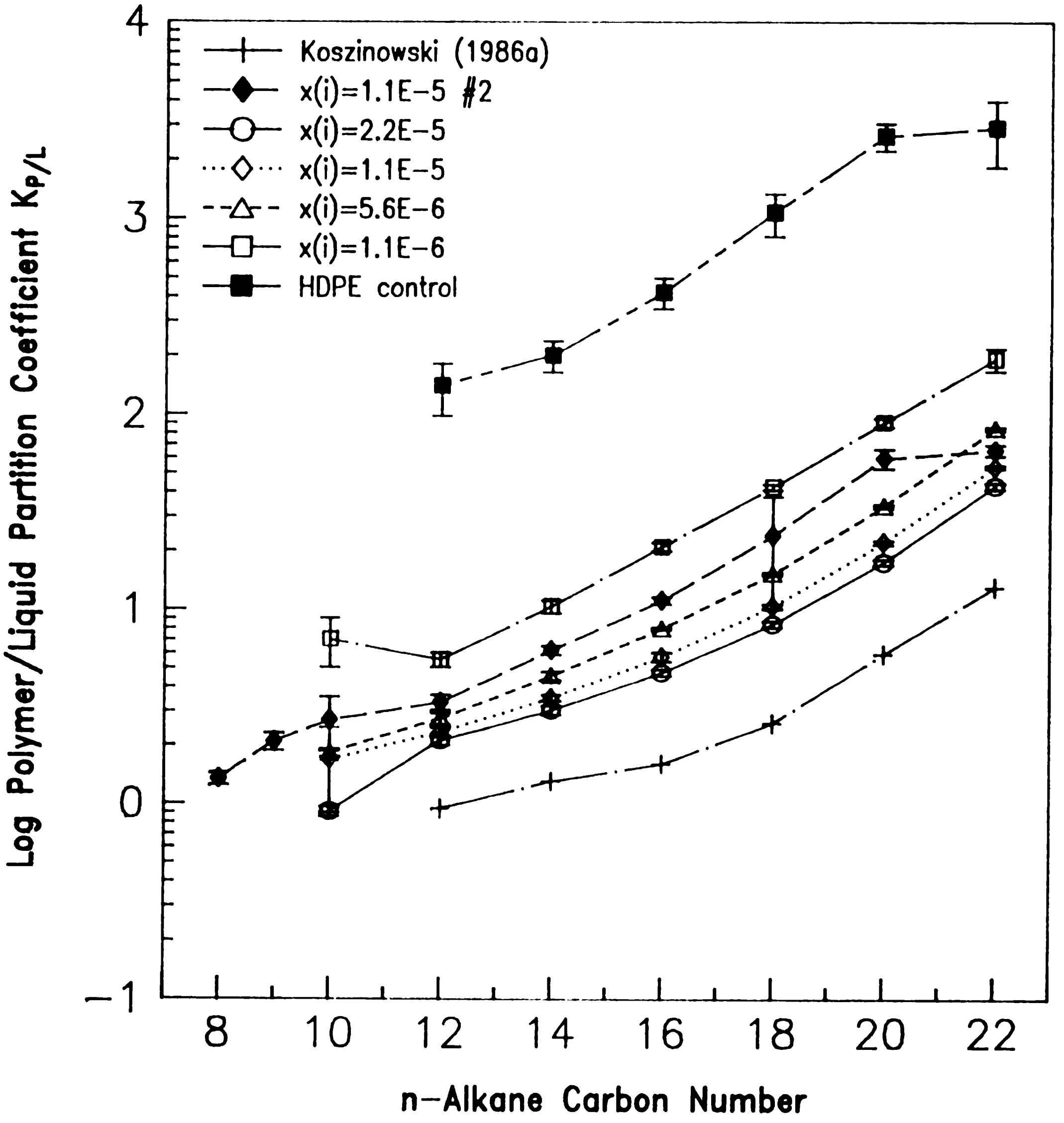


Figure 9. n-Alkanes: Variation of $K_{P/L}$ with Concentration

measurements (see error analysis). The control sample involves a migration mechanism instead of a sorption mechanism before reaching the equilibrium polymer and liquid concentration. The increase in $K_{P/L}$ with carbon number (i.e. molecular weight) is a well-documented phenomenon which comes largely from the decreasing solubility of the higher molecular weight alkanes in ethanol and their increased affinity for the non-polar polyolefin (Koszinowski, 1986).

The n-alkanes were chosen for a test of concentration dependence because the n-alkanes have the largest $K_{P/L}$ and thus partition into the polyolefins giving the highest polymer concentrations for these polymer/liquid systems. If $K_{P/L}$ were concentration dependent then the polymer would become plasticized by the sorbed alkane and the partition coefficient would increase due to increased sorption (see Rogers, 1964). If $K_{P/L}$ were constant then it was expected that as the concentration in the liquid phase increased the concentration in the polymer would increase proportionally leading to a constant $K_{P/L}$. An increase in $K_{P/L}$ as the liquid phase concentration decreases suggests a surface effect with active sites on the polymer that become saturated at higher concentrations or a clustering phenomenon occuring within the polymer. Once the active sites are occupied or once clusters fill the free volume of the polymer then the relative concentration in the polymer phase remains constant. $K_{P/L}$ estimations from permeation and diffusion measurements at 23°C by Koszinowski (1986a) have significantly lower $K_{P/L}$ values than those measured here (see Figure 9). Koszinowski's $K_{P/L}$'s are not directly measured, they were calculated using the relationship: the solubility coefficient is equal to the measured permeation coefficient divided by the measured diffusion coefficient. The $K_{P/L}$'s calculated this way are not directly measured and may not necessarily be subject to surface effects or clustering phenomenon. It is possible that systematic errors occur and incorrect assumptions are made. Measurements of aromas made here compared to measurements by Koszinowski and Piringer (1989) who measured $K_{P/L}$, at concentrations a minimum of two times greater, showed no systematic differences indicating that this concentration phenomenon may be specific to the highly non-polar n-alkanes. It is not known what the concentration behavior in aqueous ethanol solutions would be although similar behavior might be expected.

A concentration dependence appears to exist which may be only significant for n-alkanes. This is most likely due to the higher concentration levels of n-alkanes in the polyethylene because of their large partition coefficients. Until further proof that the measurements in this concentration range are not concentration dependent these n-alkane $K_{P/L}$ measurements are valid only for the concentration ranges at which they were measured.

UNIFAC Calculations

The interactive BASIC language program for personal computers supplied with Sandler (1989) was used as reference program and for single vapor-liquid equilibrium calculations. The combinatorial and interaction parameter files from UNIFAC revision 4 used in Sandler's program were updated with the UNIFAC revision and extension 5 parameters from Hansen et al. (1991). The bulk of the 5th revision parameters do not differ greatly from the 4th revision paramters used in Sandler's program but 6 new molecule groups have been added and 233 interaction pairs have been revised or added to the interaction parameter table. For vapor/polymer equilibrium (VPE) activity coefficient estimations, Sandler's program was rewritten to use the UNIFAC free volume correction (UNIFAC-FV) proposed by Oishi and Prausnitz (1978). The program was rewritten to make calculations on a weight fraction basis and to perform the additional free volume activity contribution calculations. The program was rewritten for UNIFAC-FV using the algorithms in Goydan et al. (1989) for binary polymer-solute systems. The UNIFAC-FV program was tested by comparing the results with the benzene/polyisobutylene example given in the appendix of Oishi and Prausnitz (1978).

After Sandler's program and the free volume modified version were satisfactorily tested, batch versions of the programs were written using sequential input and output files. The batch versions allowed faster calculation, the input data to be rerun and storage of the output data. A hard copy of the output data was obtained after calculation by printing the output file using DOS print commands. A hard copy of the UNIFAC-FV and VLE batch program versions and examples of program input and output files are listed in Appendix F.

The VLE version of UNIFAC requires only molecular structure parameters and mole fractions to be specified at a given temperature. UNIFAC-FV requires the molecular weight and density at the test temperature, in addition to the molecular structure functional groups and the weight fraction instead of mole fraction. The weight fraction w(i) is defined as:

$$w_i = g_i / \Sigma g_i \tag{41}$$

Where g_i is the weight of the ith component. For convenience a subroutine was added to the programs that calculates weight or mole fractions for polymer or liquid binary solutions from experimental polymer/liquid partition coefficients and liquid phase solute concentrations given molecular weights and densities of the mixture's components. For UNIFAC-FV calculations the polymer repeat unit is used as the polymer molecule in the activity calculations.

GCFEOS Calculations

A copy of the POLGCEOS program (March 5, 1991 version) in FORTRAN written by Fei Chen (Chen et al. 1990) for GCFEOS calculations was obtained from the authors. The program and parameters were used as supplied with the program. The version supplied contains parameters for water which were not available in Chen et al. (1990). The program predicts weight basis activity coefficients for polymer solutions and for liquid solutions at a given temperature using only the molecular parameters of the mixture's components and their weight fractions. The program was run on a PC using the WATFOR-77 FORTRAN compiler from WATCOM (Watcom Publications LTD., Waterloo, Ontario, Canada). Appendix F gives an example of the input file needed for POLGCEOS. Polymer segment surface areas and volumes are defined as the polymer monomeric surface areas and volumes multiplied by the number of repeat units (R). R_p for PE (M_n = 30000) would be calculated:

$$R_P = M_n \; 2 \; R_{CH2} \; / \; MW \text{ of monomer} = 30000 \; 2 \; 0.6744 \; / \; 28 = 1443 \qquad (42)$$

Where R_{CH2} is the surface area of the CH_2 group.

Calculations Using Weight Fraction Activity Coefficients

Eq 12 defines partition coefficients in terms of mole fraction activity coefficients. Weight fraction activity coefficients are analogous to mole fraction activity coefficients. Weight fraction activity coefficients $\tau^W{}_i$ are defined as:

$$\tau^W{}_i = a_i \; / \; w_i \qquad (43)$$

so that at equilibrium:

$$f_i = \tau^W{}_i \; w_i \; f_i{}^\circ \qquad (44)$$

Weight fractions in dilute solutions of solutes in polymers and liquids can be approximated by:

$$w_i = g_i \; / \; g_P \qquad (45)$$

$$w_i = g_i \; / \; g_L \qquad (46)$$

$C^P{}_i$ and $C^L{}_i$ are then defined as:

$$C^P{}_i = w_i \ den_P \qquad (47)$$

$$C^L{}_i = w_i \ den_L \qquad (48)$$

Where den_P and den_L are the densities of the polymer and liquid phases. For GCFEOS calculations with both VLE and VPE weight fraction activities the expression for the polymer/liquid partition coefficient is:

$$K_{P/L} = \tau^L{}_i \ den_P \ / \ \tau^P{}_i \ den_L \qquad (49)$$

For UNIFAC calculations where the VLE is on a mole fraction basis and the VPE is on a weight fraction basis the resulting expression for $K_{P/L}$ is:

$$K_{P/L} = \tau^L{}_i \ \underline{V}_L \ den_P \ / \ \tau^P{}_i \ MW_i \qquad (50)$$

The expression for liquid/gas partition coefficients, $K_{L/G}$, in dilute solutions using weight fraction activity coefficients is:

$$K_{L/G} = RT \ den_L \ / \ \tau^L{}_i \ f_i^{\circ} \ MW_i \qquad (51)$$

Polymer/gas partition coefficients, $K_{P/G}$, for dilute solutions in a polymer matrix calculated using weight activity coefficients have the equation:

$$K_{P/G} = RT\ den_P / \tau^P_i\ f_i^\circ\ MW_i \qquad (52)$$

Values for f_i° are estimated using pure component vapor pressures. Appendix A lists the pure component vapor pressures used in these calculations. The vapor pressures for n-alkanes were taken from the literature. Values from the literature were used for aromas when available otherwise they were estimated using Antoine's equation or retention indices if the Antoine equation could not estimate P_i° at 25°C (see Appendix A).

Experimental Results

Liquid/Gas Partition Coefficients

n-Alkanes: Measured Liquid/Gas Partition Coefficients

Table 13 and Figures 10 to 18 summarize the experimental $K_{L/G}$ for n-alkanes in ethanol and aqueous ethanol solutions. A complete listing of the raw data is found in Appendix B. Figure 6 compares the experimental $K_{L/G}$ data with data published in the literature for 100% ethanol at 25°C. No published data were found for n-alkanes in aqueous ethanol mixtures. Although n-alkanes in water were not measured here Pierotti et al. (1959) reported a correlation of $K_{L/G}$ versus n-alkanes carbon number in water. Piringer and Skories (1984) reported a correlation for n-alkanes in water based on the measurements of Drozd et al. (1982). Given only three experimental measurements (100% ethanol, 66% and 33%), aqueous ethanol correlations for $K_{L/G}$ with percentage ethanol are not justifiable. However, there are several recognizable trends and some limitations of the data that should be pointed out. As the ethanol solution becomes more aqueous the $K_{L/G}$ decreases while the scatter of the data increases. The increase in scatter can

Table 13. n-Alkanes: Experimental K(L/G) Data

Ethanol:	100%			66%			33%		
Alkane	Avg. MB% #	s.d.	c.v.	Avg. MB% #	s.d.	c.v.	Avg. MB% #	s.d.	c.v.
C5	78.7	7.6	10	9.52	1.2	13	0.237	0.08	33
	2.5	1.2	49	15.8	5.5	35	56.3	15.6	28
	(4)			(4)			(4)		
C6	199.6	14.2	7	17.4	2.6	15	0.192	0.01	5
	2.8	2.5	89	5.2	4.0	77	60.0	11.9	20
	(5)			(4)			(3)		
C7	531.2	65.8	12	36.0	6.0	17	0.392	0.14	36
	2.8	2.0	71	2.2	1.6	70	46.8	24.3	52
	(6)			(4)			(5)		
C8	1456.7	168.1	12	89+	42.2	21	0.571	0.11	20
	2.6	3.0	116	13.6	13.4	98	47.9	24.2	51
	(6)			(8)			(4)		
C9	4860.0	129.6	3	125+	150.0	13	1.20+	1.85	40
	0.6	0.5	89	20.1	7.1	36	56.4	8.9	16
	(3)			(2)			(4)		
C10	17022.2	6117.7	36	416.8	54.7	13	1.49	-	-
	1.9	1.4	75	2.9	2.6	89	16.6	-	-
	(9)			(5)			(1)		
C12	118228.6	38221	32	1988.3	175.7	9	7.48	3.23	43
	1.6	1.4	89	2.7	1.5	55	28.8	21.1	73
	(7)			(6)			(6)		
C14	506420*	124290	25	7736.4*	2489	32	16.7	5.50	33
	2.2	1.4	63	10.1	12.4	123	30.0	20.3	68
	(5)			(5)			(7)		
C16	1522200*	842400	2E+06	9550*	15300	3800	55.7	19.0	34
	3.5	2.7	4.3	3.2	3.9	2.5	16.9	13.6	81
	(2)@			(2)@			(7)		

Avg. = average value
c.v. = percentage coefficient of variation (s.d./average)
MB% = average absolute % mass balance, deviation from 100%
# = number of observations
s.d. = standard deviation
+ = from difference K(L/G) measurements
* value has high analytical uncertainty
@ = ranges are given in place of s.d. and c.v.
percent ethanol = w/w in aqueous solution

Table 13. n-Alkanes: Experimental K(L/G) Data

Ethanol:	100%			66%			33%		
Alkane	Avg. MB% #	s.d.	c.v.	Avg. MB% #	s.d.	c.v.	Avg. MB% #	s.d.	c.v.
C5	78.7	7.6	10	9.52	1.2	13	0.237	0.08	33
	2.5	1.2	49	15.8	5.5	35	56.3	15.6	28
	(4)			(4)			(4)		
C6	199.6	14.2	7	17.4	2.6	15	0.192	0.01	5
	2.8	2.5	89	5.2	4.0	77	60.0	11.9	20
	(5)			(4)			(3)		
C7	531.2	65.8	12	36.0	6.0	17	0.392	0.14	36
	2.8	2.0	71	2.2	1.6	70	46.8	24.3	52
	(6)			(4)			(5)		
C8	1456.7	168.1	12	89+	42.2	21	0.571	0.11	20
	2.6	3.0	116	13.6	13.4	98	47.9	24.2	51
	(6)			(8)			(4)		
C9	4860.0	129.6	3	125+	150.0	13	1.20+	1.85	40
	0.6	0.5	89	20.1	7.1	36	56.4	8.9	16
	(3)			(2)			(4)		
C10	17022.2	6117.7	36	416.8	54.7	13	1.49	-	-
	1.9	1.4	75	2.9	2.6	89	16.6	-	-
	(9)			(5)			(1)		
C12	118228.6	38221	32	1988.3	175.7	9	7.48	3.23	43
	1.6	1.4	89	2.7	1.5	55	28.8	21.1	73
	(7)			(6)			(6)		
C14	506420*	124290	25	7736.4*	2489	32	16.7	5.50	33
	2.2	1.4	63	10.1	12.4	123	30.0	20.3	68
	(5)			(5)			(7)		
C16	1522200*	842400	2E+06	9550*	15300	3800	55.7	19.0	34
	3.5	2.7	4.3	3.2	3.9	2.5	16.9	13.6	81
	(2)@			(2)@			(7)		

Avg. = average value
c.v. = percentage coefficient of variation (s.d./average)
MB% = average absolute % mass balance, deviation from 100%
# = number of observations
s.d. = standard deviation
+ = from difference K(L/G) measurements
* value has high analytical uncertainty
@ = ranges are given in place of s.d. and c.v.
percent ethanol = w/w in aqueous solution

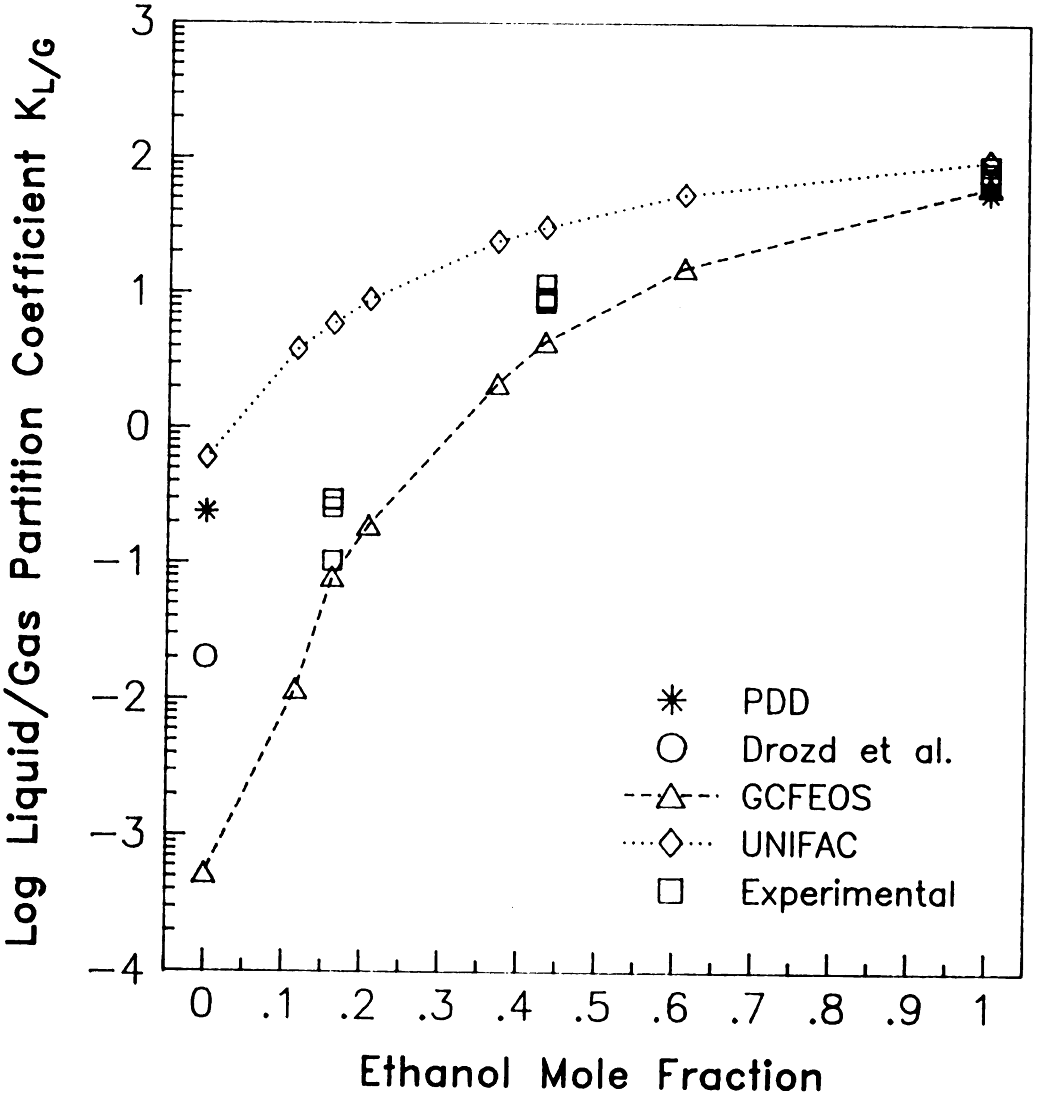


Figure 10. Pentane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

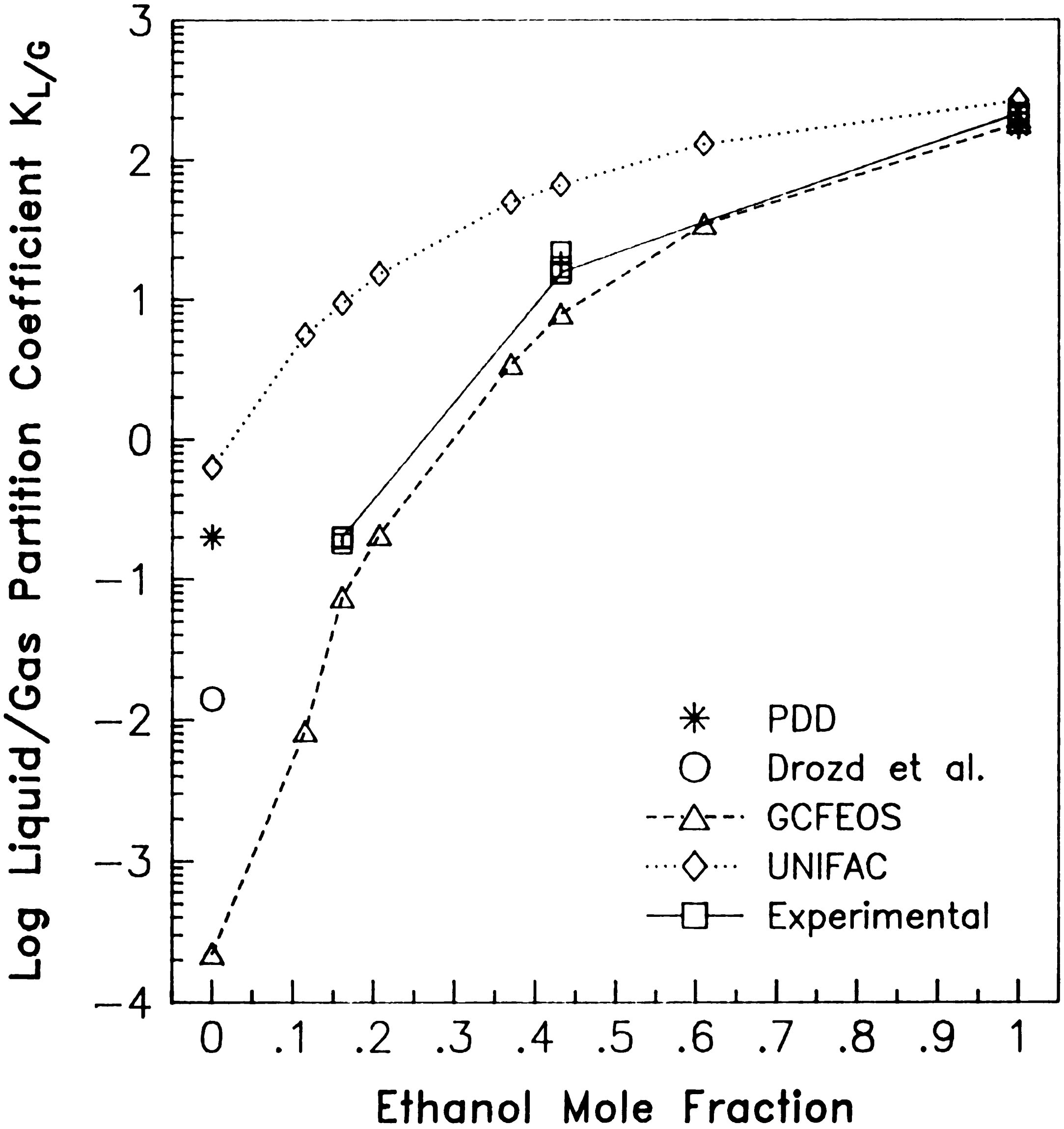


Figure 11. Hexane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

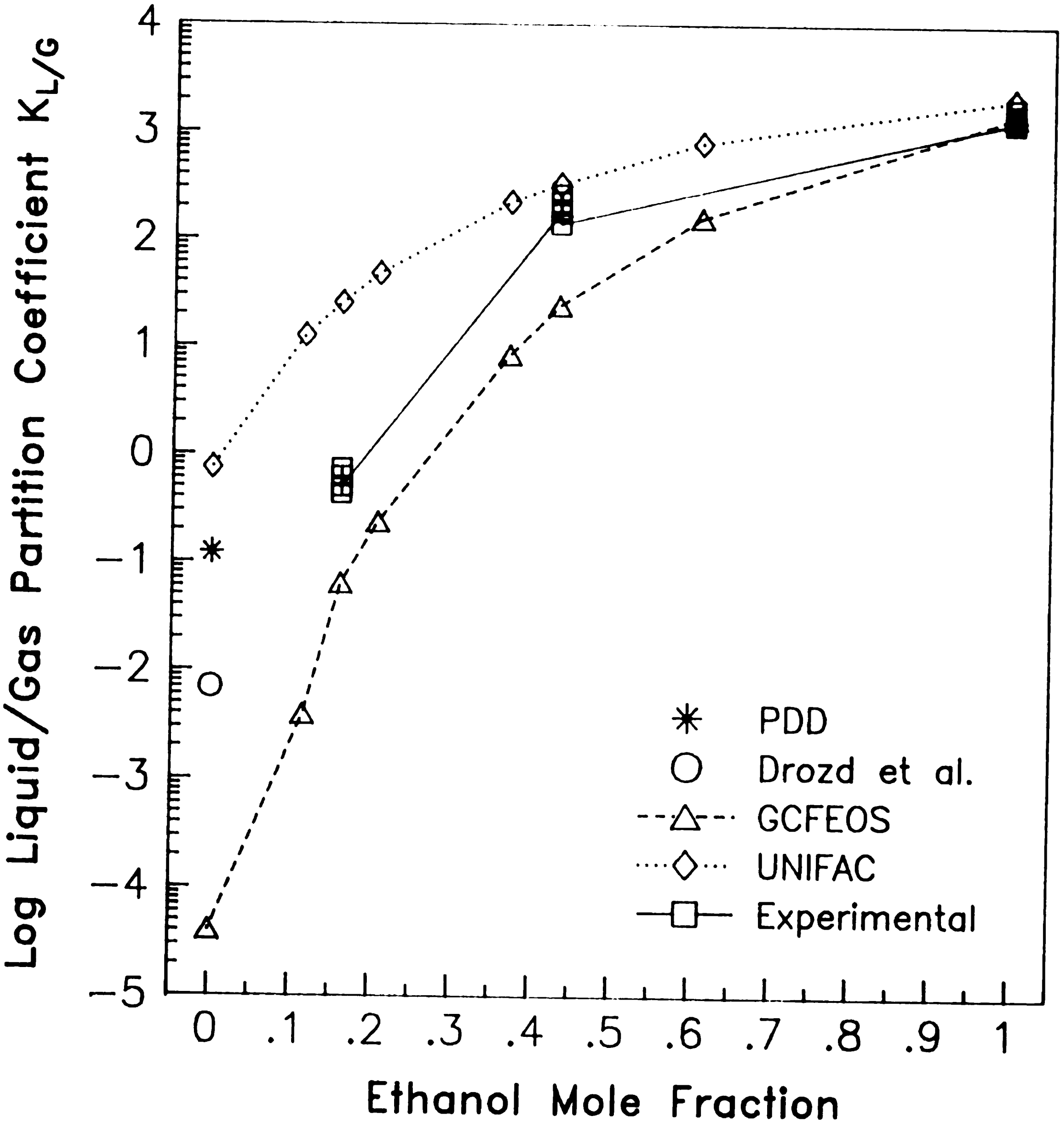


Figure 12. Heptane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

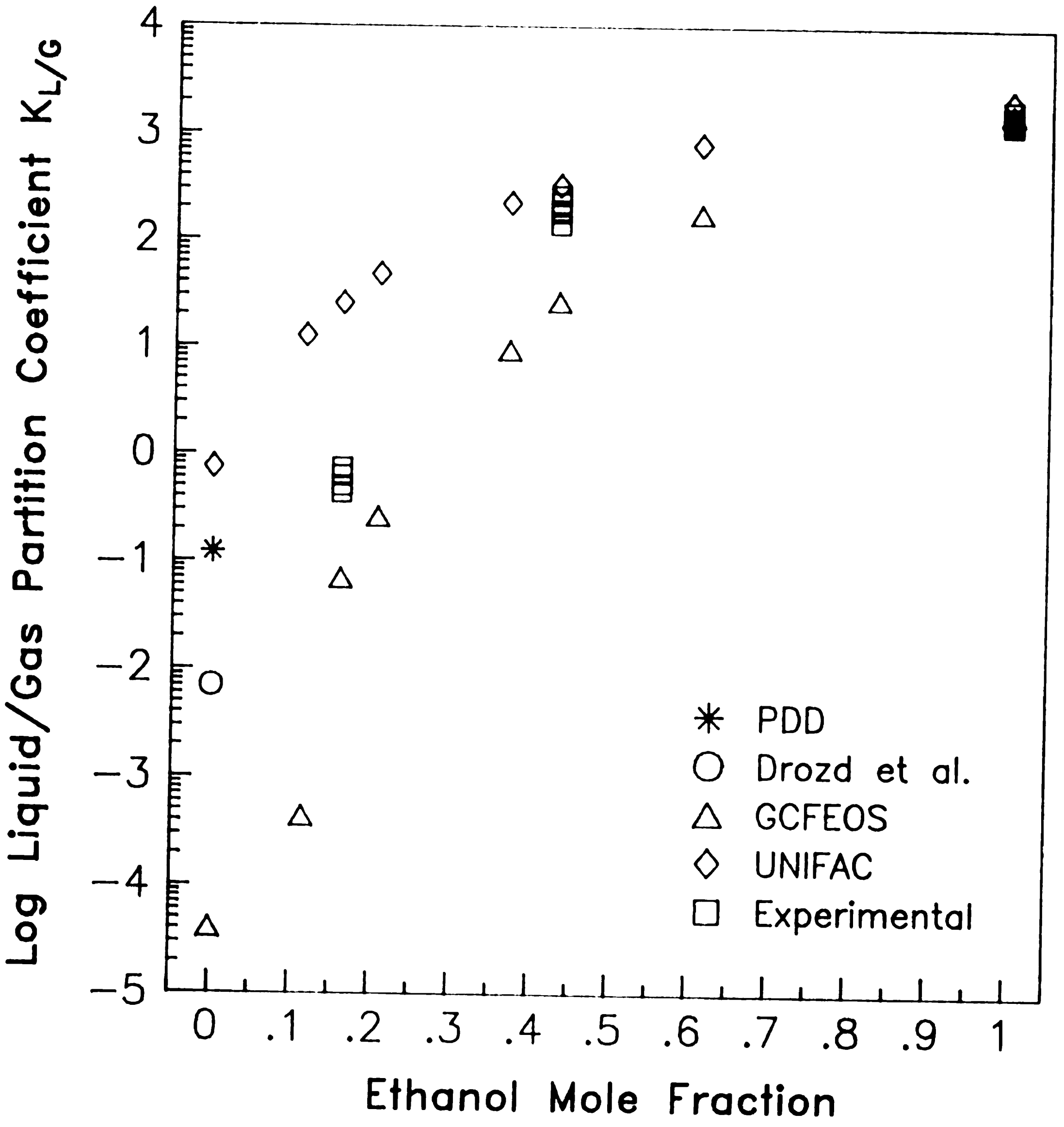


Figure 13. Octane: Experimental $K_{L/G}$ versus UNIFAC and GC-EOS

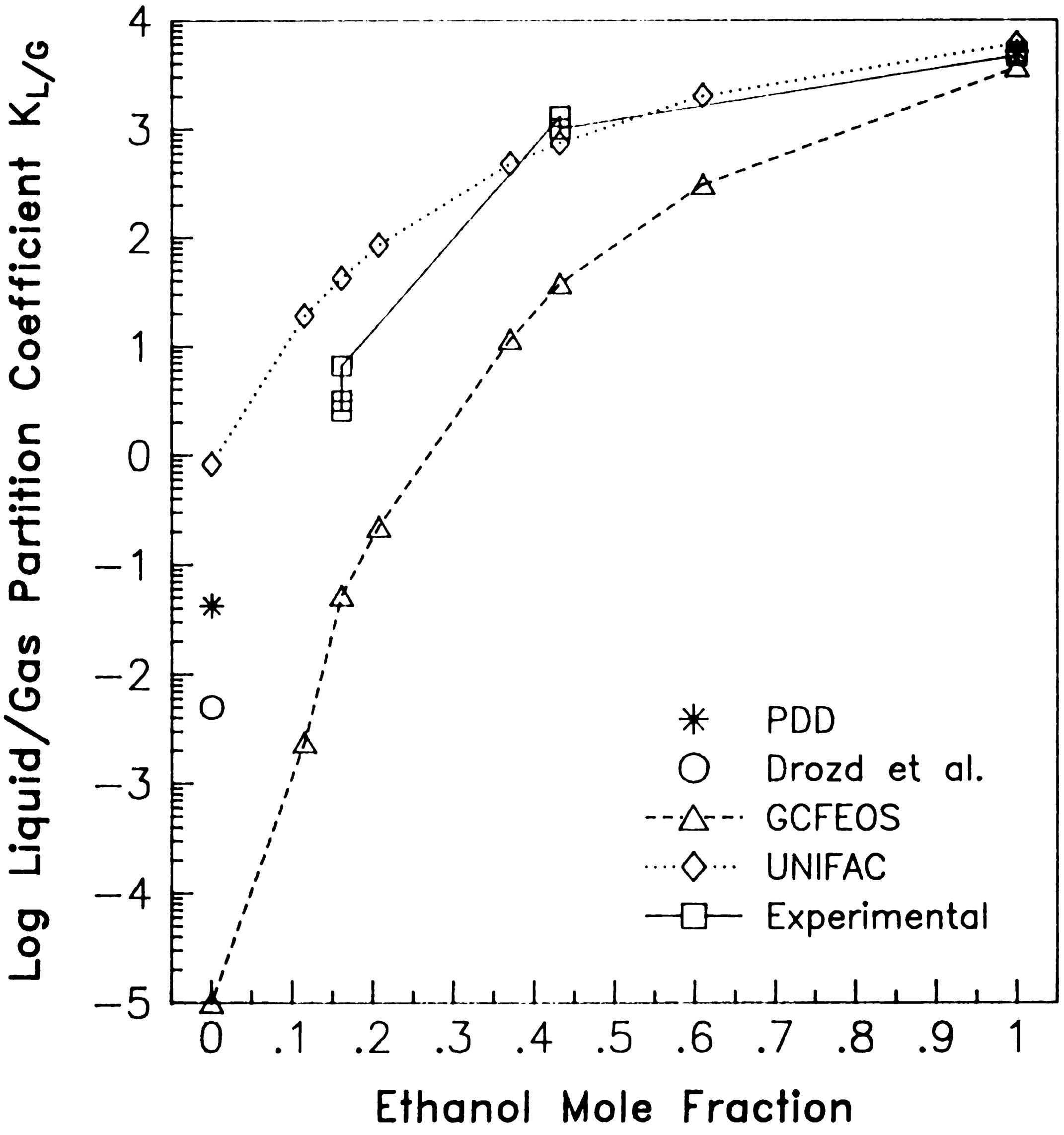


Figure 14. Nonane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

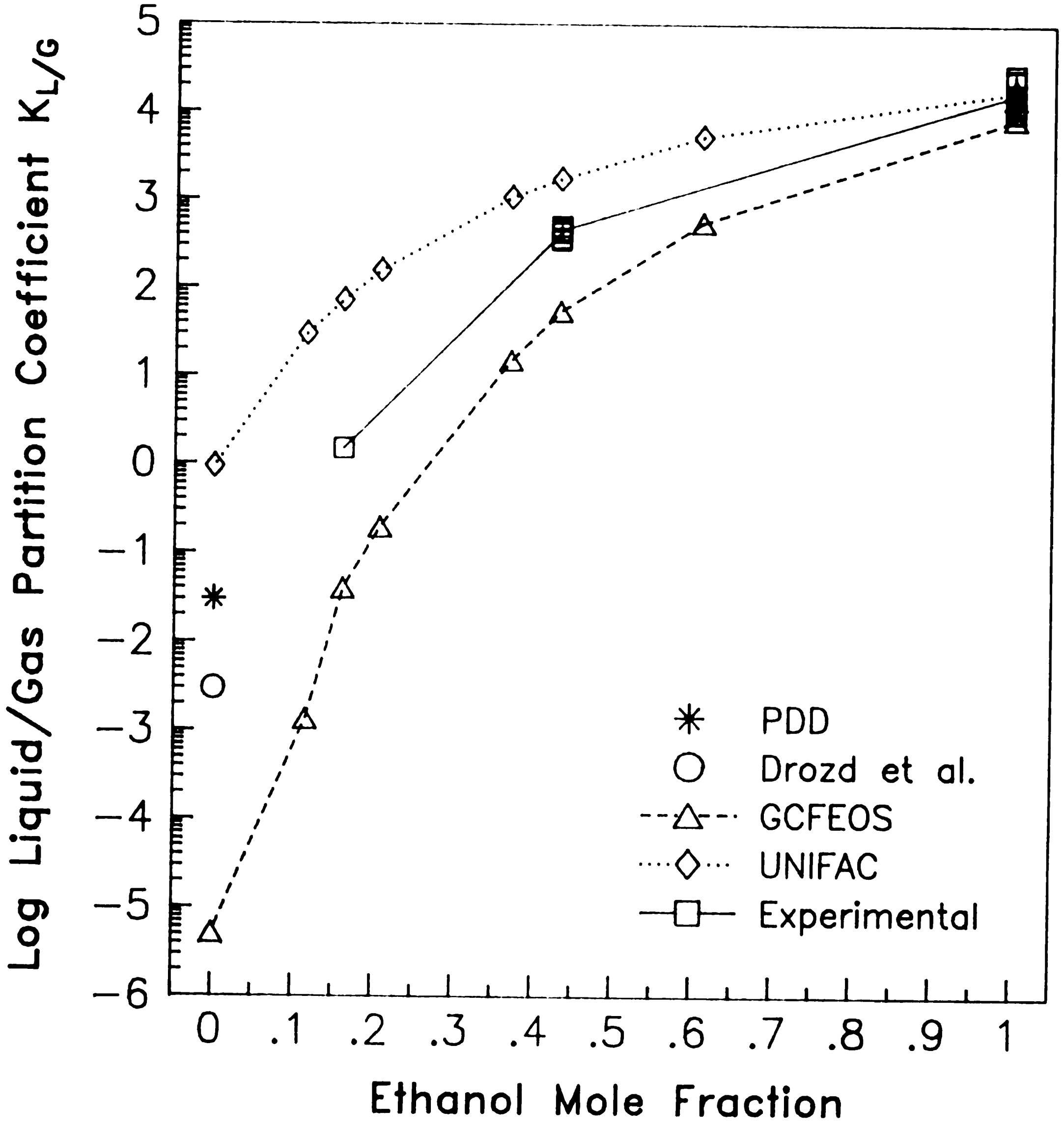


Figure 15. Decane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

Log Liquid/Gas Partition Coefficient $K_{L/G}$

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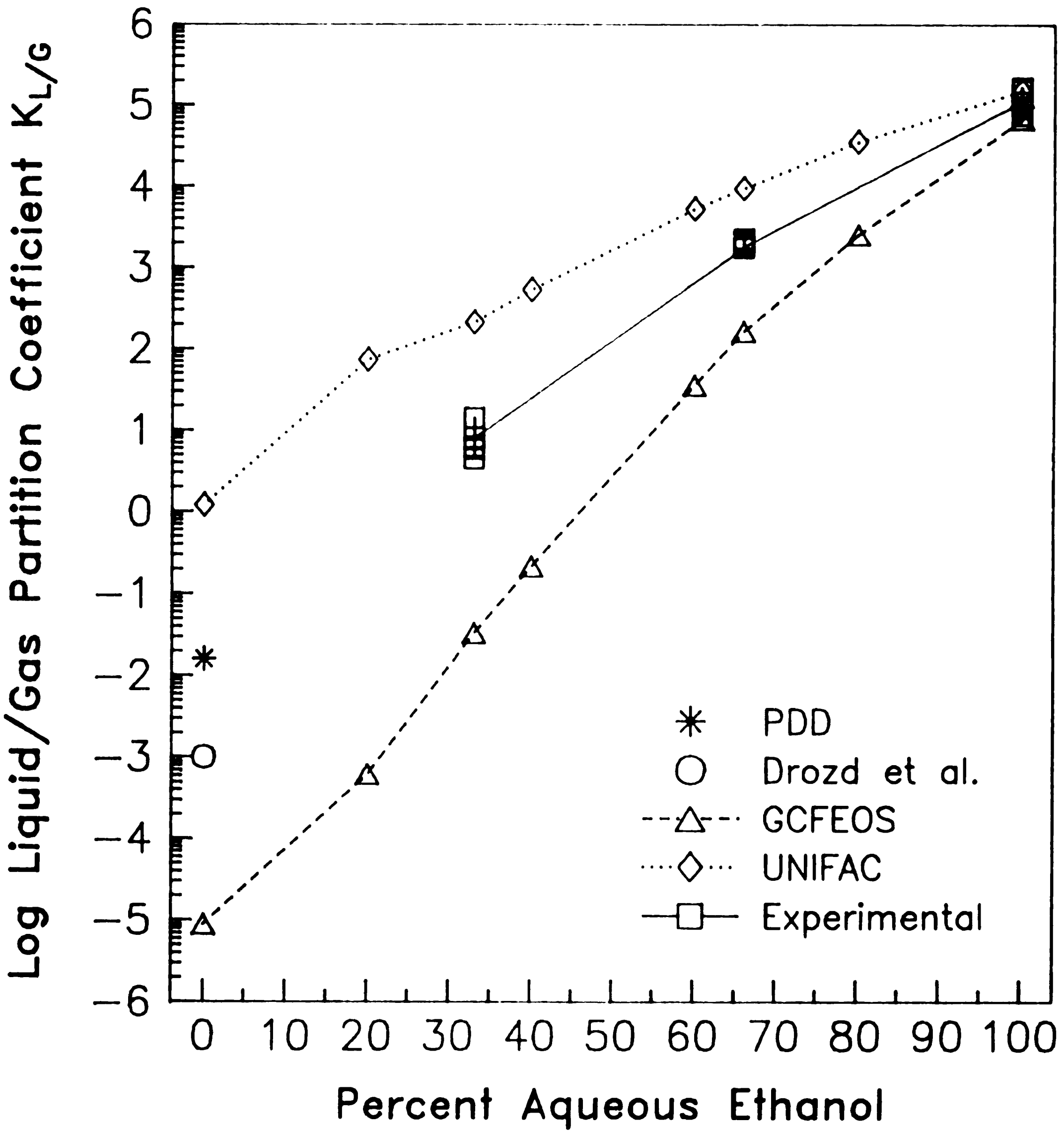

Figure 16. Dodecane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

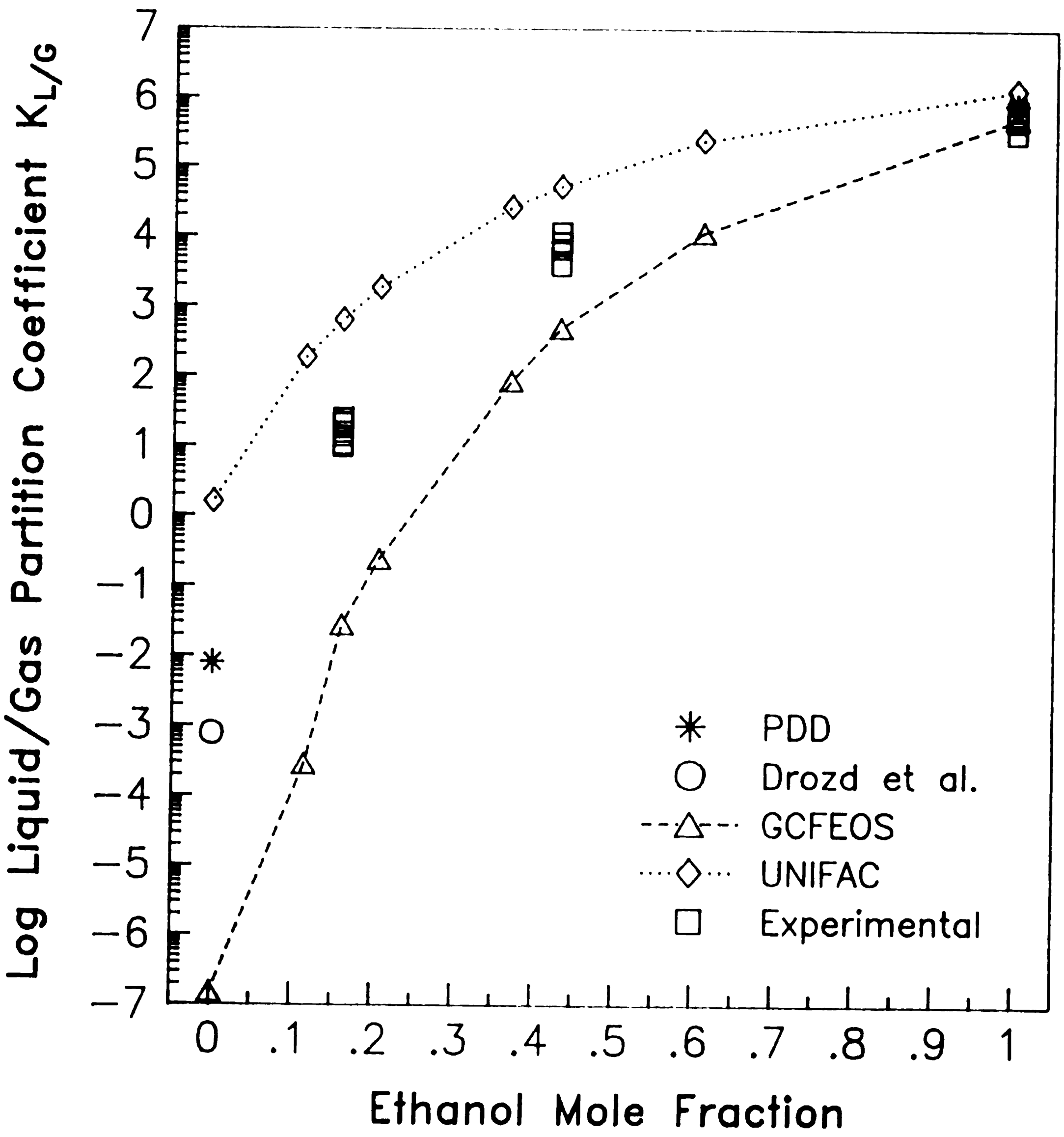

Figure 17. Tetradecane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

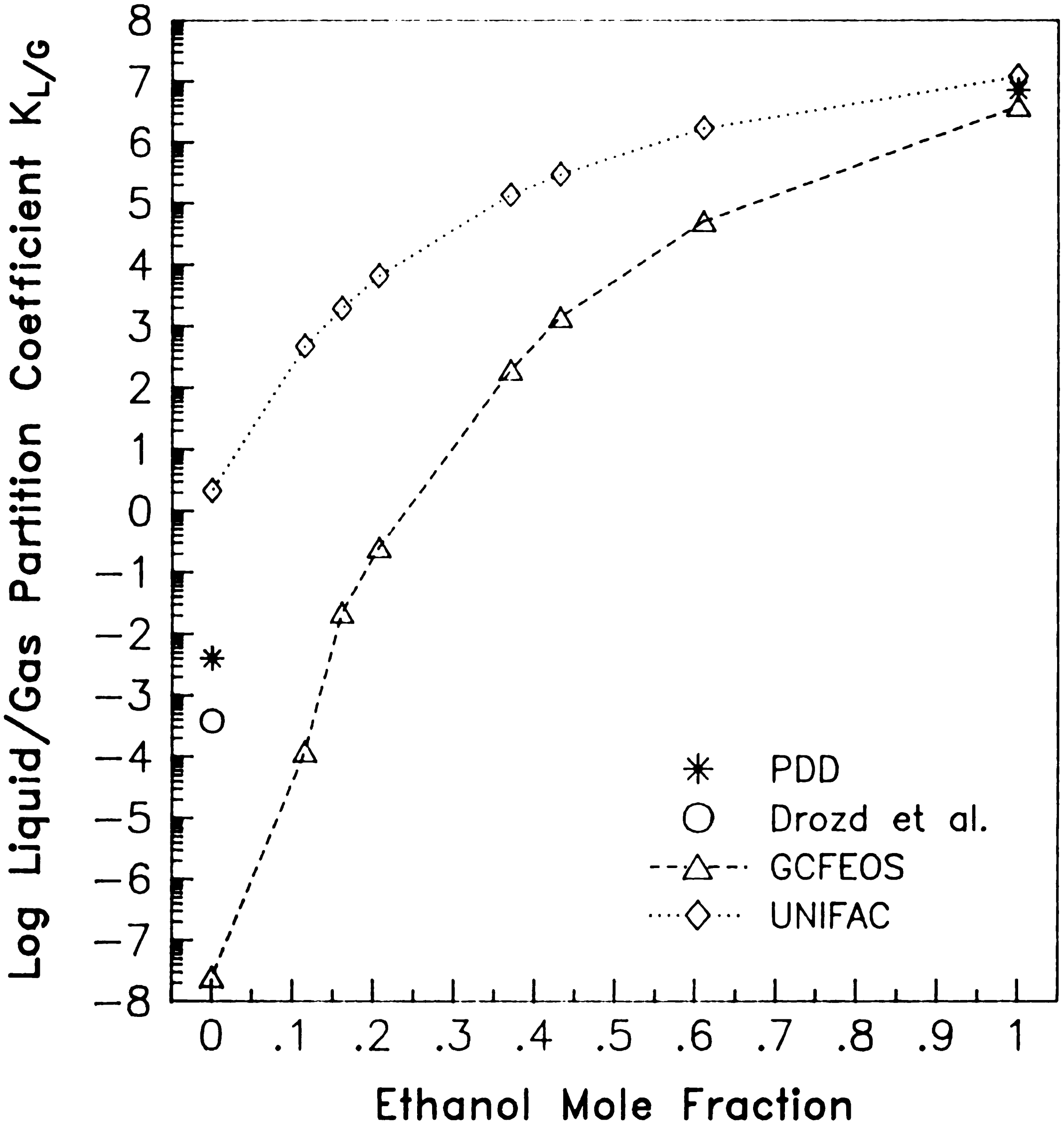

Figure 18. Hexadecane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

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13 Aromas:

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also be seen in the increase in the absolute mass balance as the liquid phase becomes more aqueous. This is largely due to the analytical problems of injecting aqueous solutions in gas chromatographs with split injection. Aqueous solutions containing less than 33% ethanol were not made due to the increasing analytical problems as well as the difficulty of avoiding surface effects in the stripping column for alkanes. The large absolute mass balance percentages found with the aqueous solutions can be attributed to sampling and chromatographic errors in the initial liquid phase concentrations because the difference method calculations agree with the solvent trap K values (see Appendix B). Some difference $K_{L/G}$ values (Eq 38) are included in Table 13 because of GC separation problems between the ethanol and nonane and decane peaks. The peak areas for tetradecane and hexadecane in the 100% and 66% ethanol solutions were near the GC detection limit thus they could contain large systematic errors and should be treated as approximate values.

13 Aromas: Measured Liquid/Gas Partition Coefficients

Table 14 and Figures 19 to 31 summarize the measured partition coefficients results for 13 aroma compounds in ethanol and aqueous ethanol solutions. The raw data can be found in Appendix B. The aromas behaved similarly to the n-alkanes in the way the $K_{L/G}$ decreased and the absolute

Substanc

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d-Limon

Cis-3-H

Camphor

Linaly

Mentho

Citron

Dimeth

Pheny

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(#)
s.d.
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Table 14. Aromas: Experimental K(L/G) Data

Substance	100% Ethanol			75% Ethanol		
	Avg. MB% (#)	s.d.	c.v.	Avg. MB% (#)	s.d.	c.v.
Isoamylacetate	13367	1860	14	5465	613	11
	2.84	2.39	84	6.00	4.82	80
	(6)			(4)		
d-Limonene	15933	2574	16	11257	1047.1	9
	2.76	2.28	83	2.53	0.90	35
	(6)			(3)		
Cis-3-Hexenol	135880	30161	22	95125	15496	16
	3.98	1.80	45	7.25	5.40	74
	(5)			(4)		
Camphor	146750	9782	7	97125	10809	11
	4.61	1.92	42	7.71	5.87	76
	(4)			(4)		
Linalylacetate	317750	45538	14	132425	26299	20
	4.98	2.31	46	7.74	6.35	82
	(4)			(4)		
Menthol	699000	206123	29	669667	81786	12
	4.05	2.32	57	9.15	6.10	67
	(5)			(3)		
Citronellol	331000	-	-	213000	-	-
	2.36	-	-	2.77	-	-
	(2)			(2)		
Dimethylbenzylcarbinol	641000	176287	28	658000	-	-
	4.44	1.85	42	11.60	-	-
	(4)			(2)		
Phenylethylalcohol	671667	4922	1	597000	-	-
	2.23	1.58	71	11.05	-	-
	(3)			(2)		
Diphenylmethane	527000	175313	33	241750	41656	17
	3.79	1.91	50	8.02	5.95	74
	(6)			(4)		
Diphenyloxide	570500	158175	28	236750	36588	15
	4.50	1.89	42	7.62	6.27	82
	(4)			(4)		
* Eugenol	738000	-	-	641333	162145	25
	4.28	-	-	7.88	7.21	91
	(1)			(3)		
* gamma-undelactone	-	-	-	1106000	101183	9
	-	-	-	10.20	7.58	74
				(3)		

* results highly uncertain, large error likely
Avg. = average value
c.v. = percent coefficient of variation (s.d./average)
MB% = average absolute % mass balance, deviation from 100%
(#) = number of observations
s.d. = standard deviation
percent ethanol = w/w aqueous ethanol

Table 14 (cont.)

	50% Ethanol			35% Ethanol		
Substance	Avg. MB% (#)	s.d.	c.v.	Avg. MB% (#)	s.d.	c.v.
Isoamylacetate	1175	220	19	377	21.5	6
	4.87	2.82	58	8.63	3.82	44
	(4)			(3)		
d-Limonene	235.0	45.2	19	34.5	4.0	12
	7.01	3.29	47	5.68	4.47	79
	(4)			(3)		
Cis-3-Hexenol	34525	4409	13	12733	834	7
	1.25	0.84	67	9.98	6.35	64
	(4)			(3)		
Camphor	23450	2802	12	5977	420	7
	10.05	11.52	115	8.15	5.86	72
	(4)			(3)		
Linalylacetate	16975	2756	16	2300	157	7
	11.43	18.70	164	10.19	6.62	65
	(4)			(3)		
Menthol	119000	13058	11	21600	1391	6
	7.77	11.81	152	7.71	7.62	99
	(4)			(4)		
Citronellol	142667	19293	14	72500	20890	29
	3.25	2.57	79	3.94	1.68	43
	(3)			(3)		
Dimethylbenzylcarbinol	265750	60520	23	95400	22208	23
	1.51	0.30	20	6.36	3.53	56
	(4)			(4)		
Phenylethylalcohol	488333	322821	66	203000	73638	36
	4.15	5.41	130	5.12	5.88	115
	(3)			(4)		
Diphenylmethane	27350	3770	14	4155	425	10
	8.81	14.15	161	10.16	9.50	93
	(4)			(4)		
Diphenyloxide	24500	3344	14	3468	377	11
	9.46	14.82	157	6.24	4.82	77
	(4)			(4)		
Eugenol	812750	431148	53	245000	3742	2
	3.61	2.31	64	5.17	2.85	55
	(4)			(3)		
gamma-undelactone	930000	823874	89	310000	62658	20
	11.09	17.16	155	6.02	3.90	65
	(4)			(3)		

Log Liquid/Gas Partition Coefficient $K_{L/G}$

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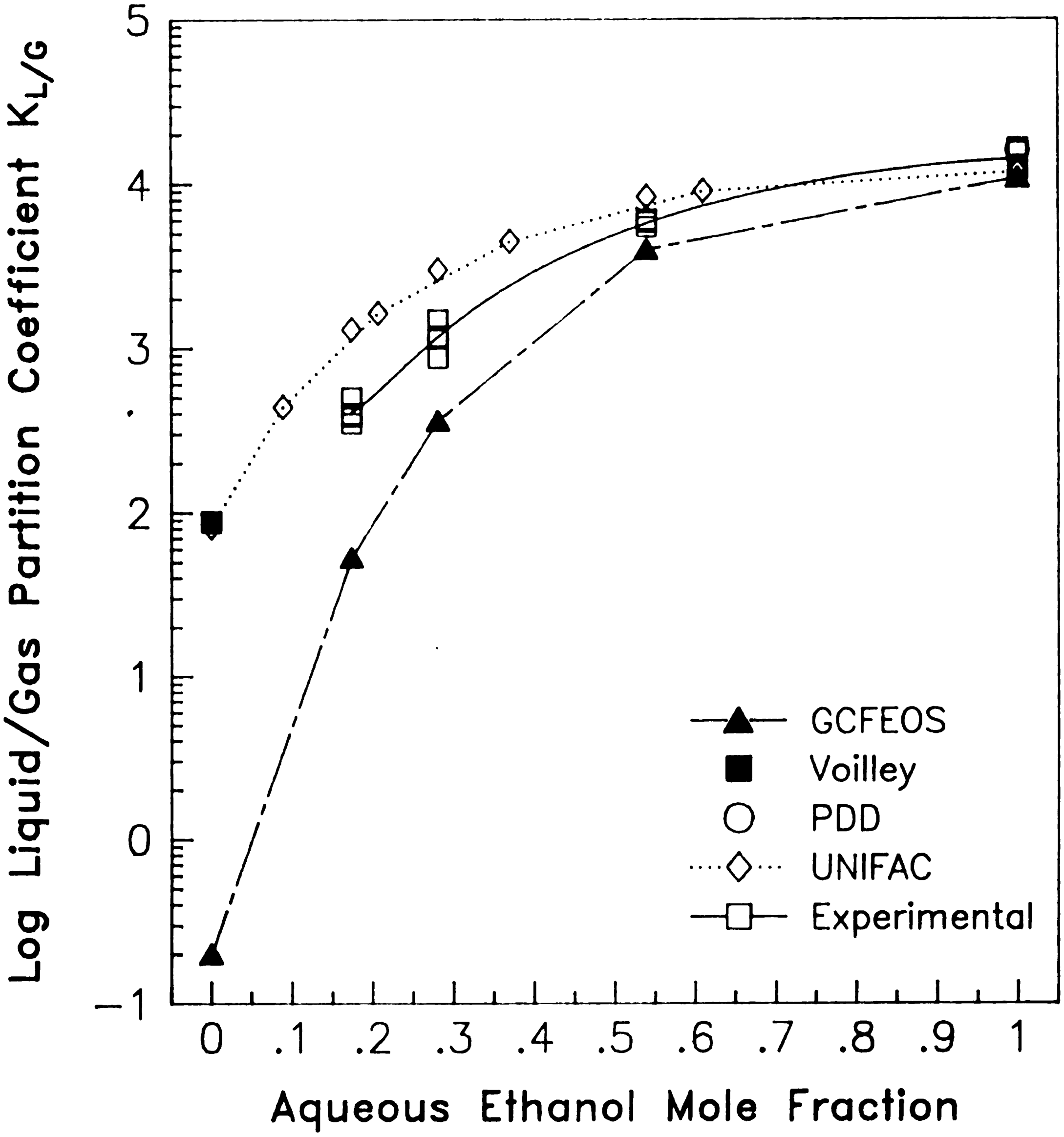

Figure 19. Isoamylacetate: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

Log Liquid/Gas Partition Coefficient $K_{L/G}$

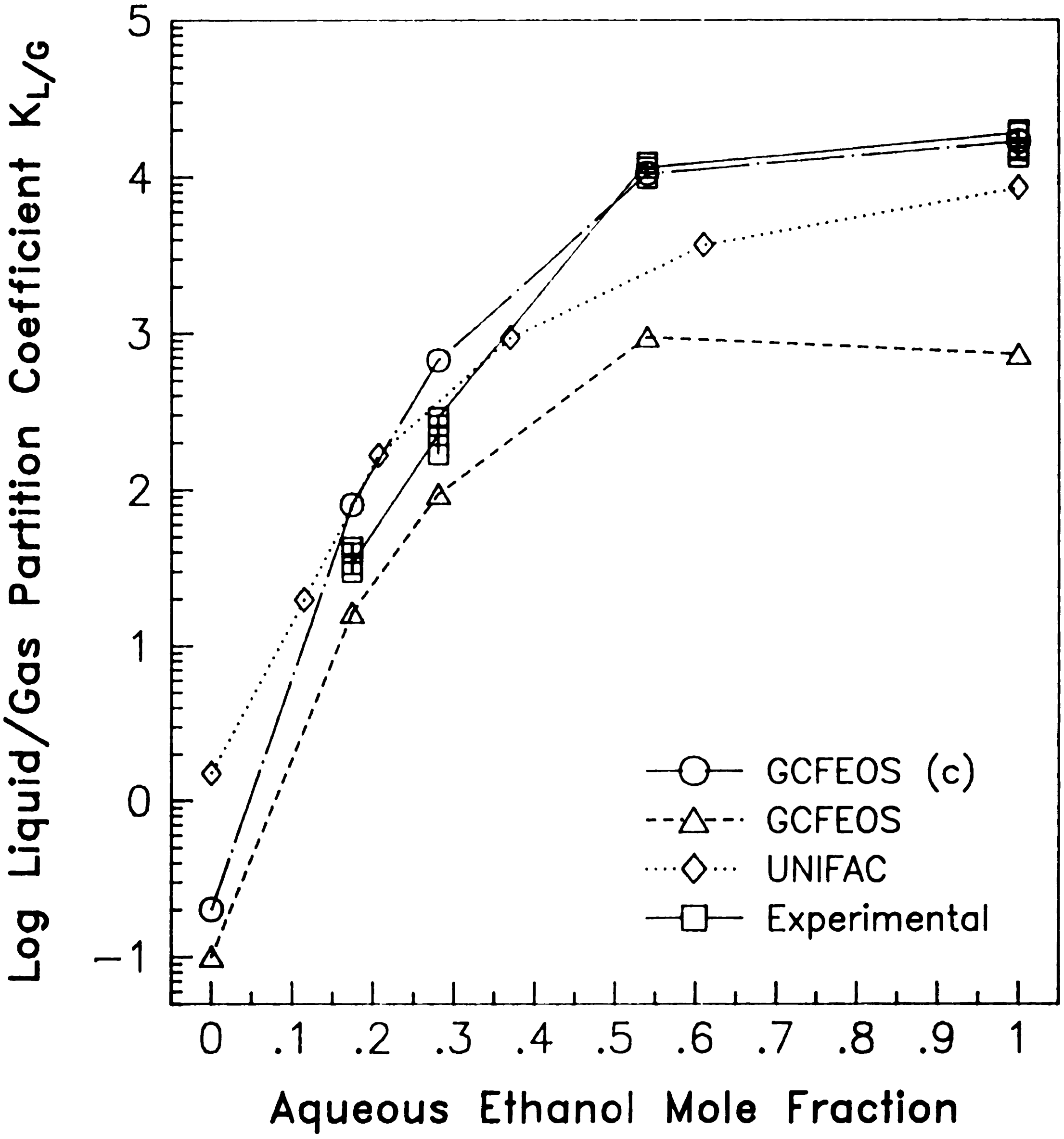

Figure 20. d-Limonene: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

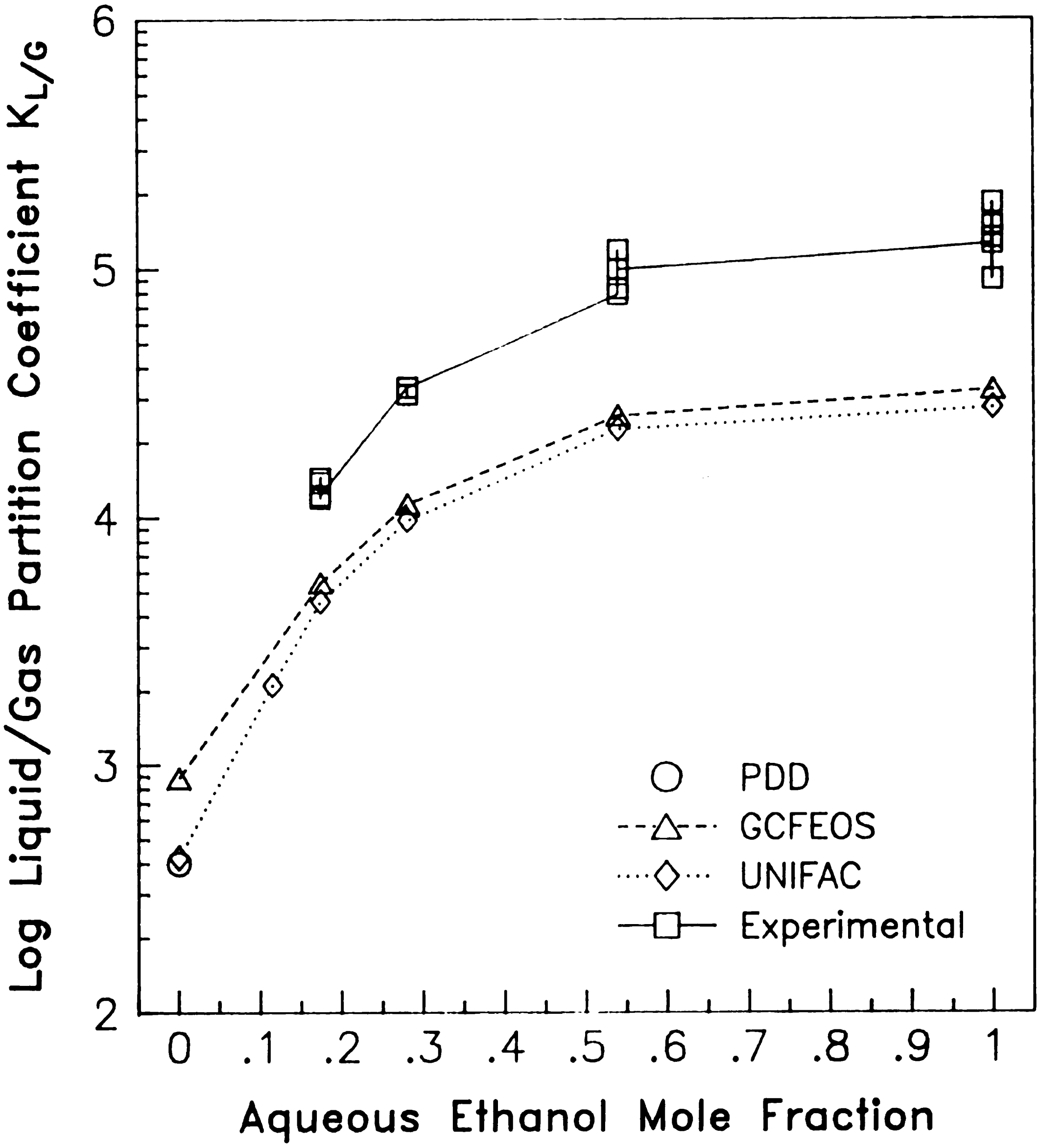

Figure 21. cis-3-Hexenol: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

Log Liquid/Gas Partition Coefficient $K_{L/G}$

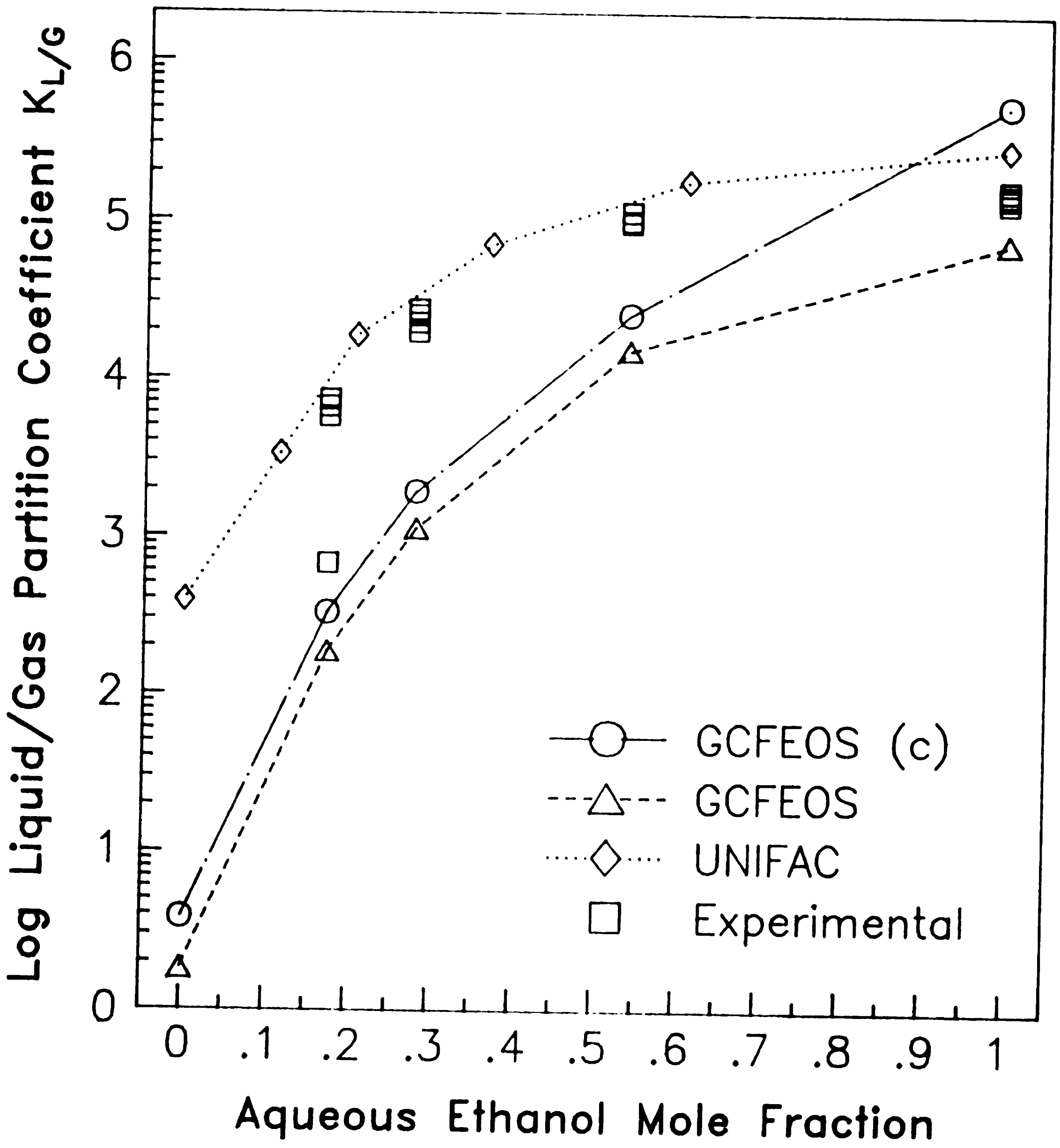

Figure 22. Camphor: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

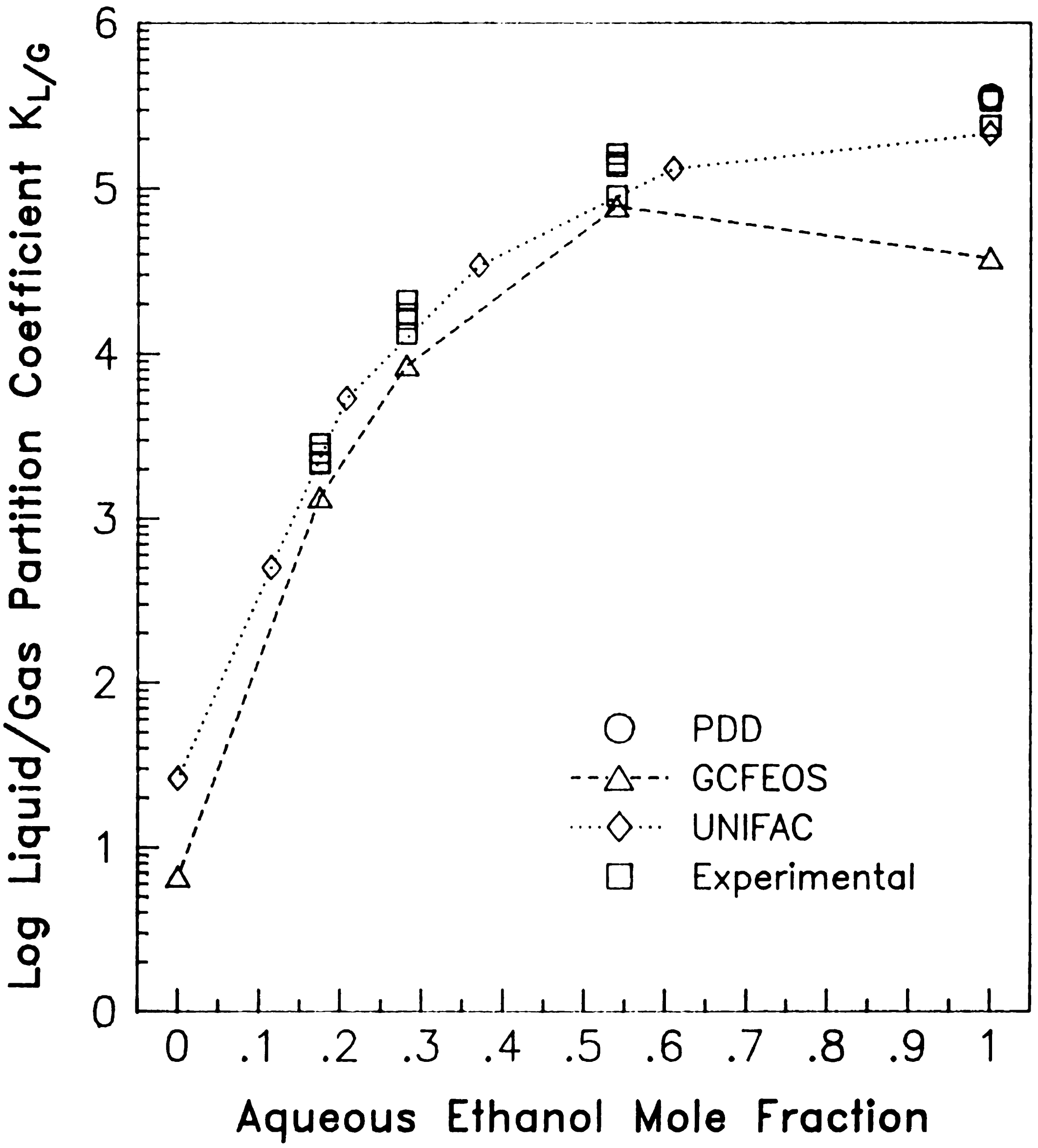

Figure 23. Linalylacetate: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

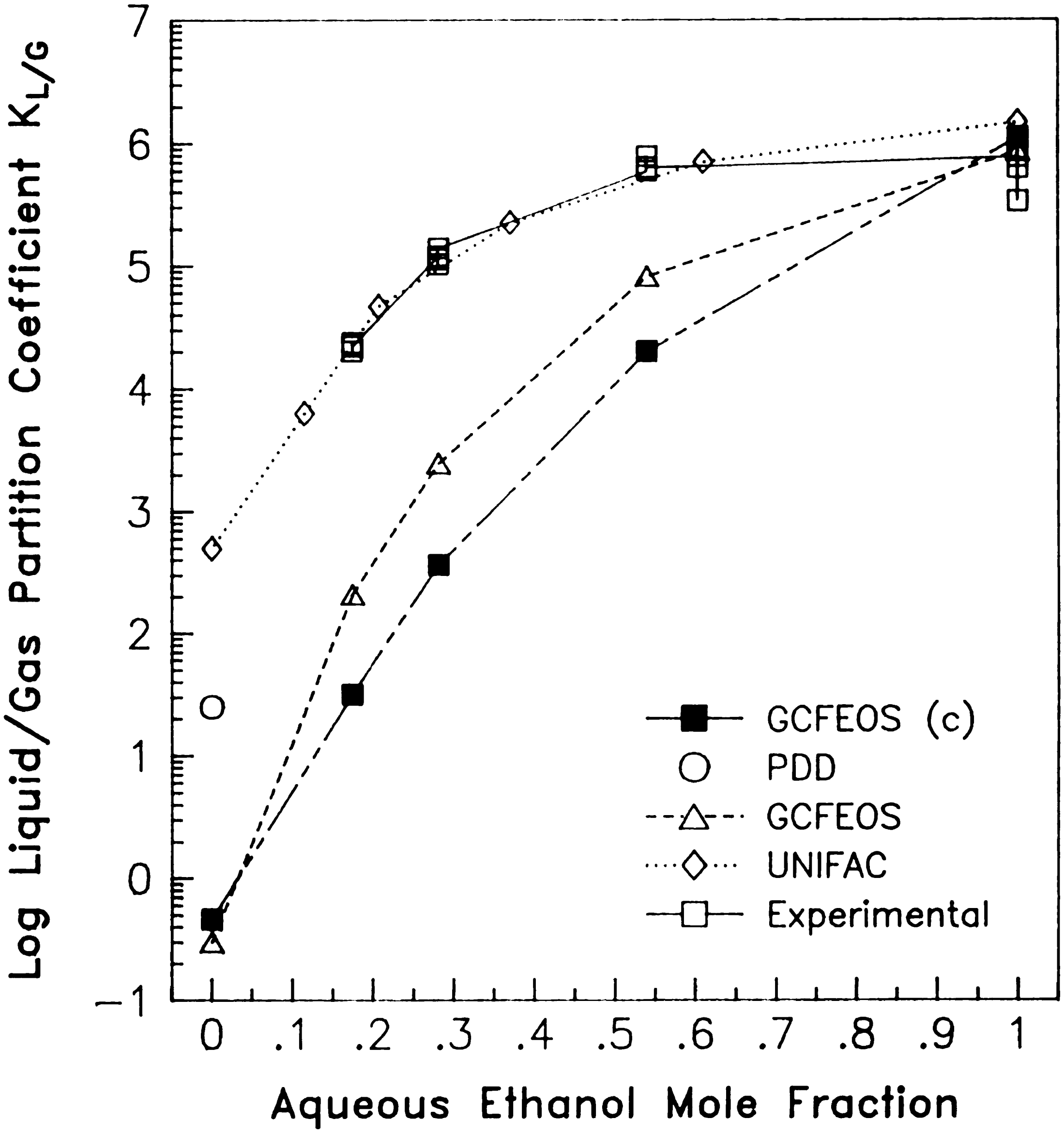

Figure 24. Menthol: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

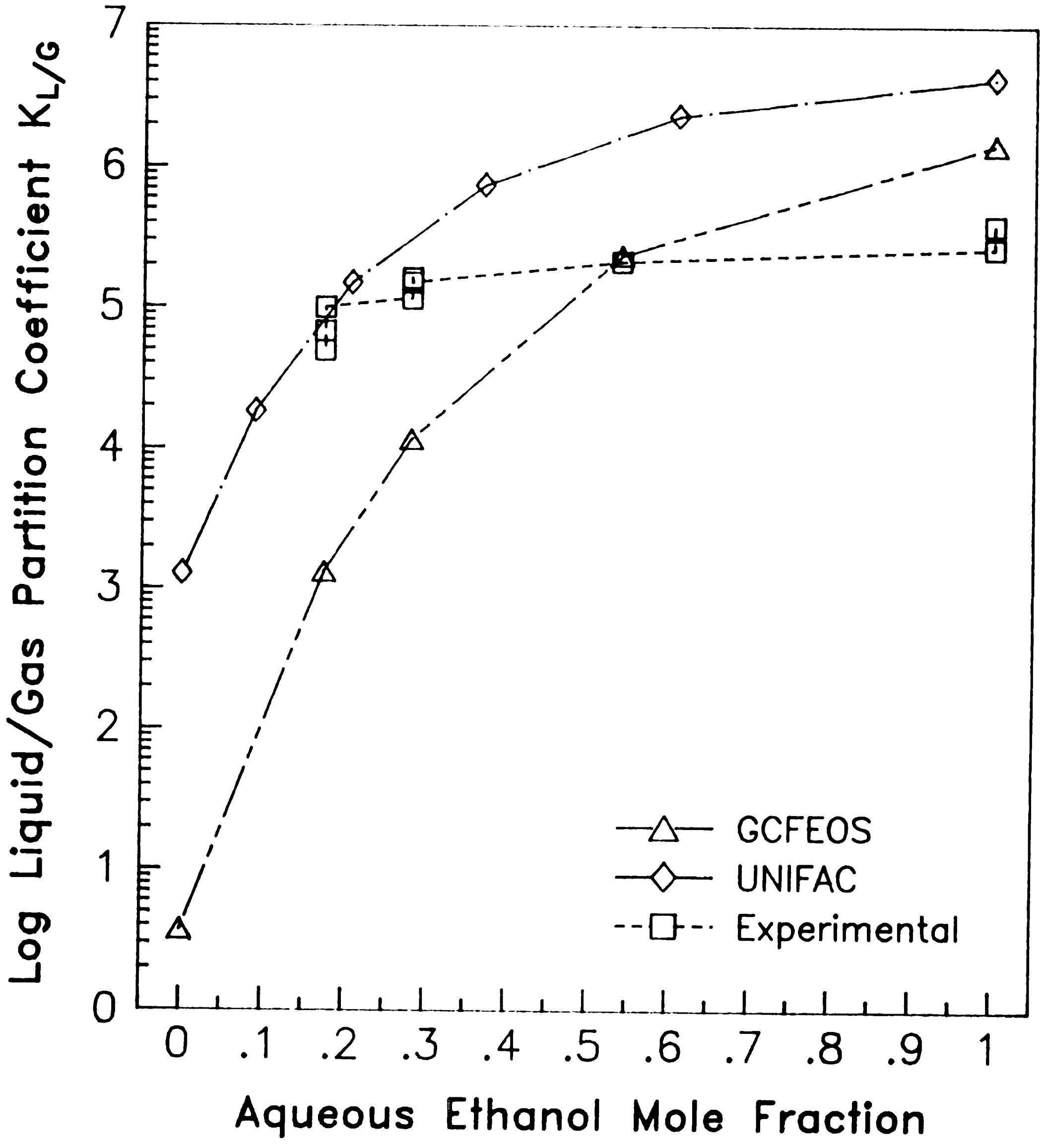

Figure 25. Citronellol: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

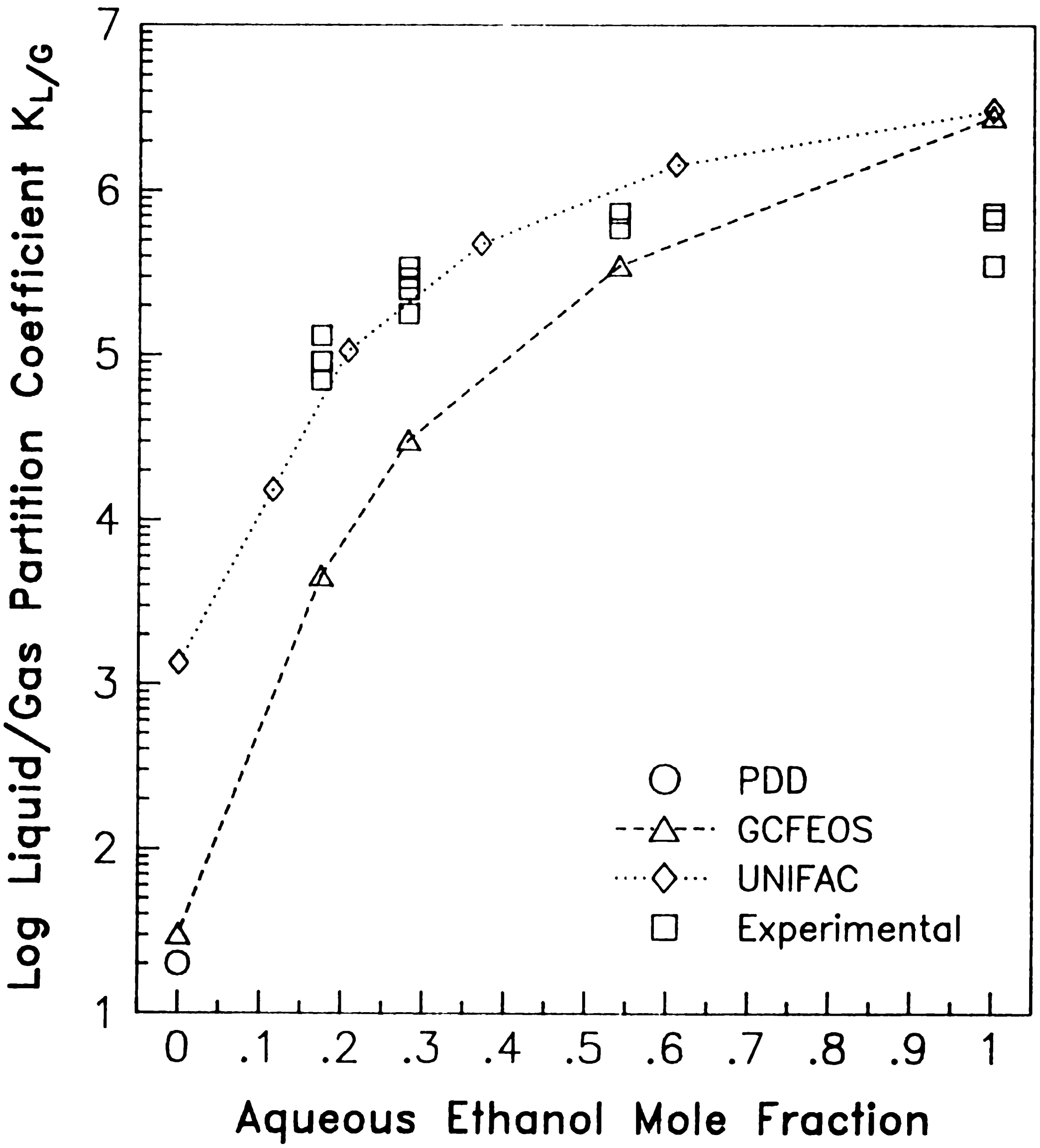

Figure 26. Dimethylbenzylcarbinol: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

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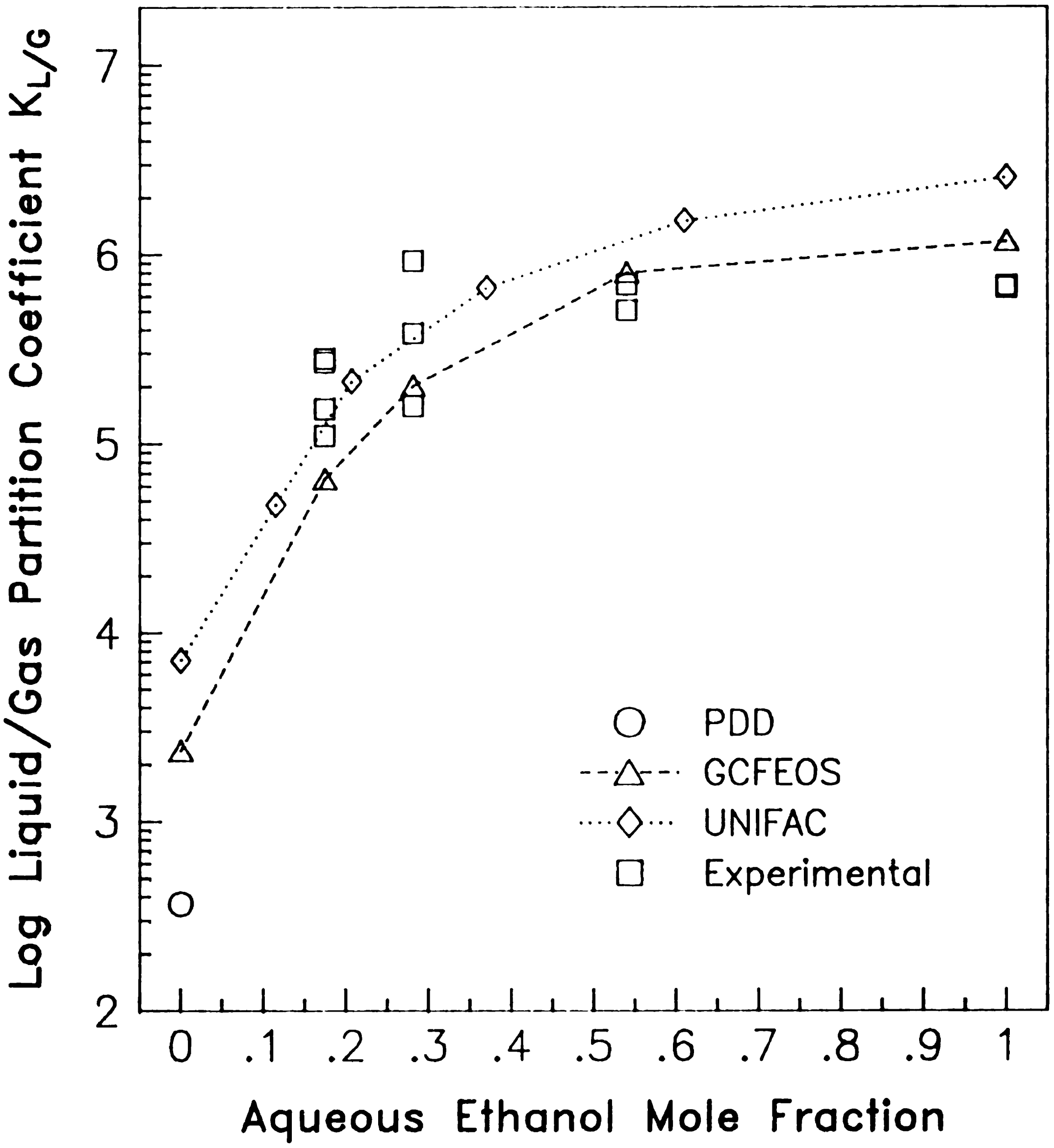

Figure 27. Phenylethylalcohol: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

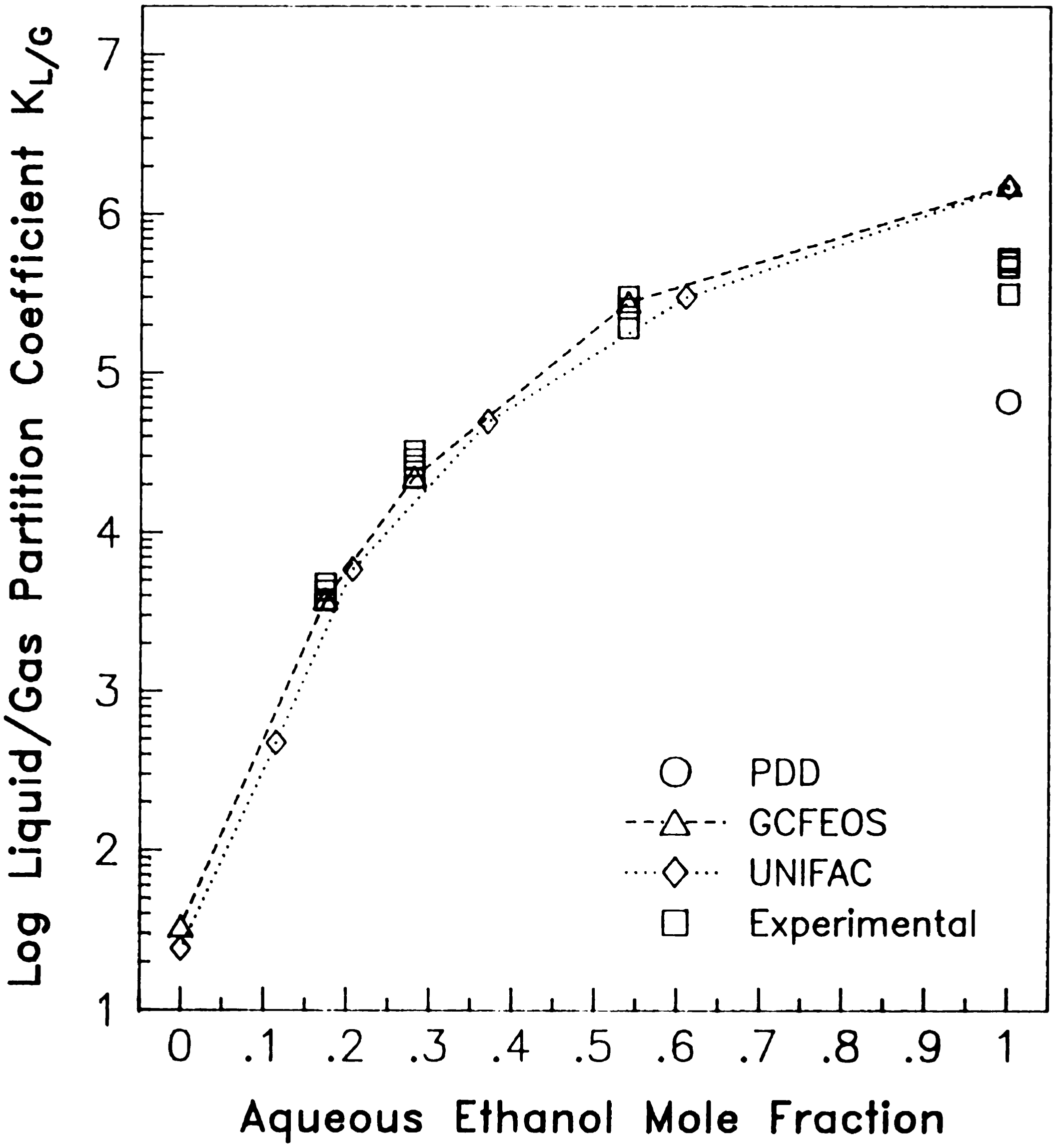

Figure 28. Diphenylmethane: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

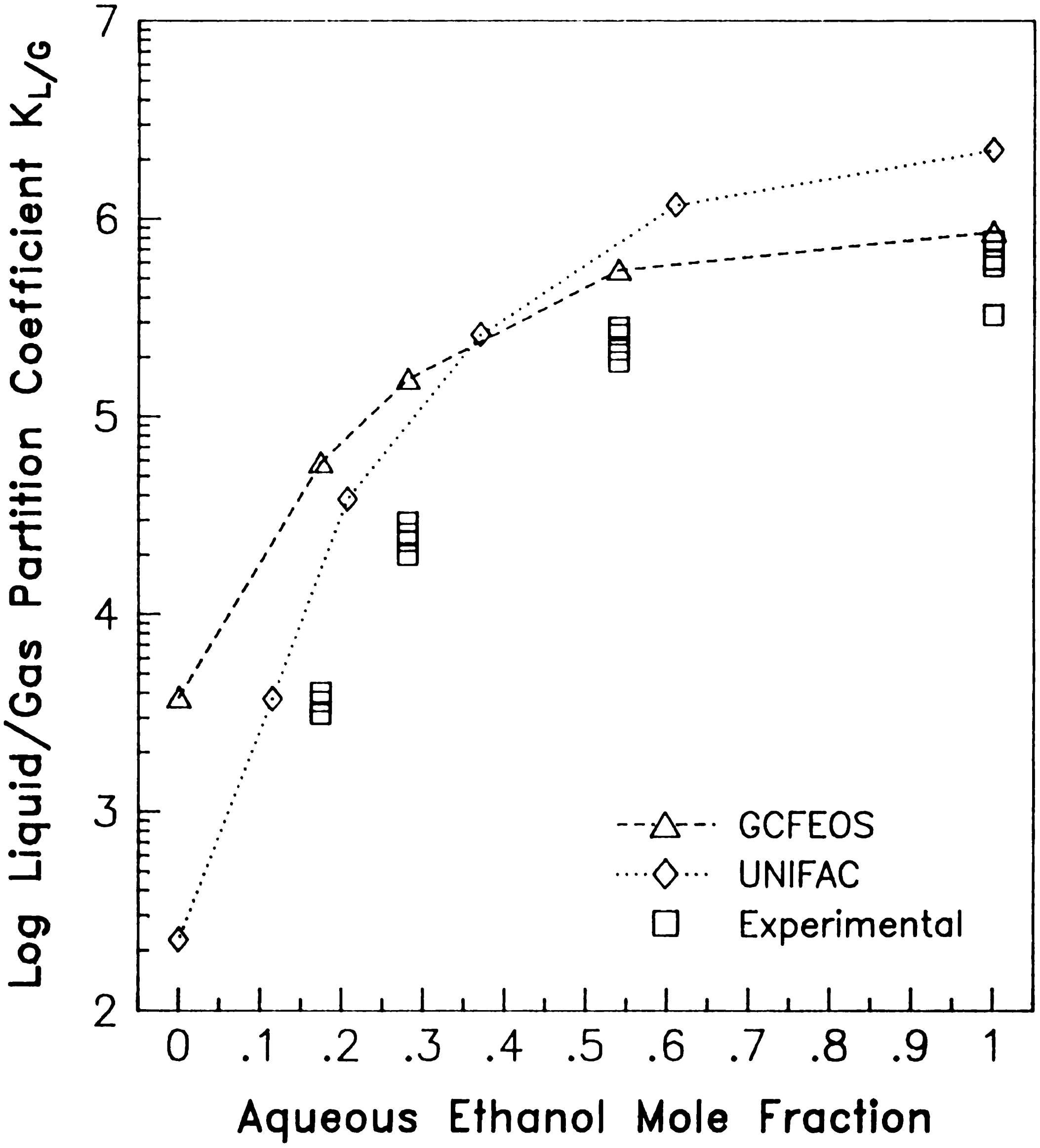

Figure 29. Diphenyloxide: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

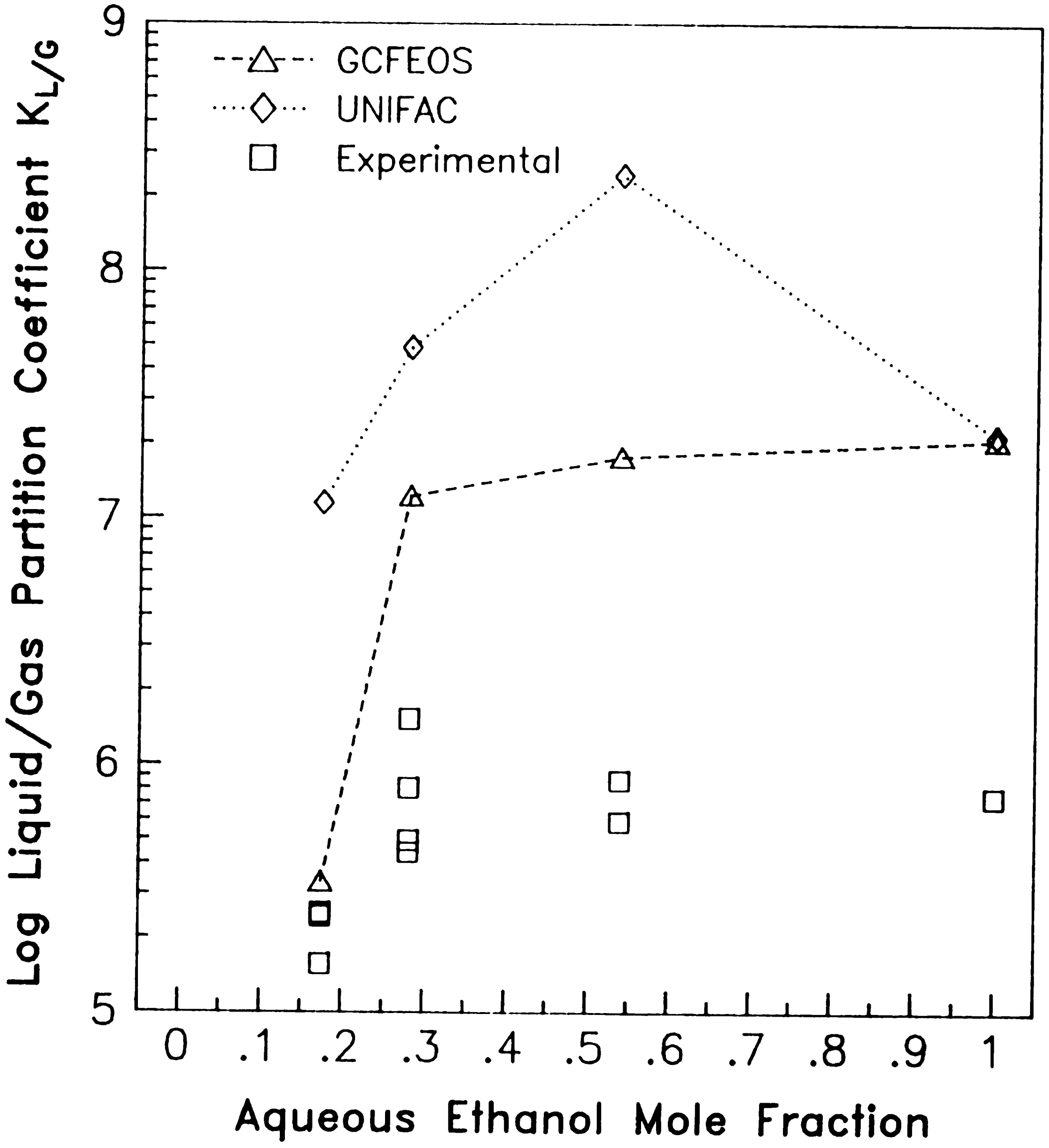

Figure 30. Eugenol: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

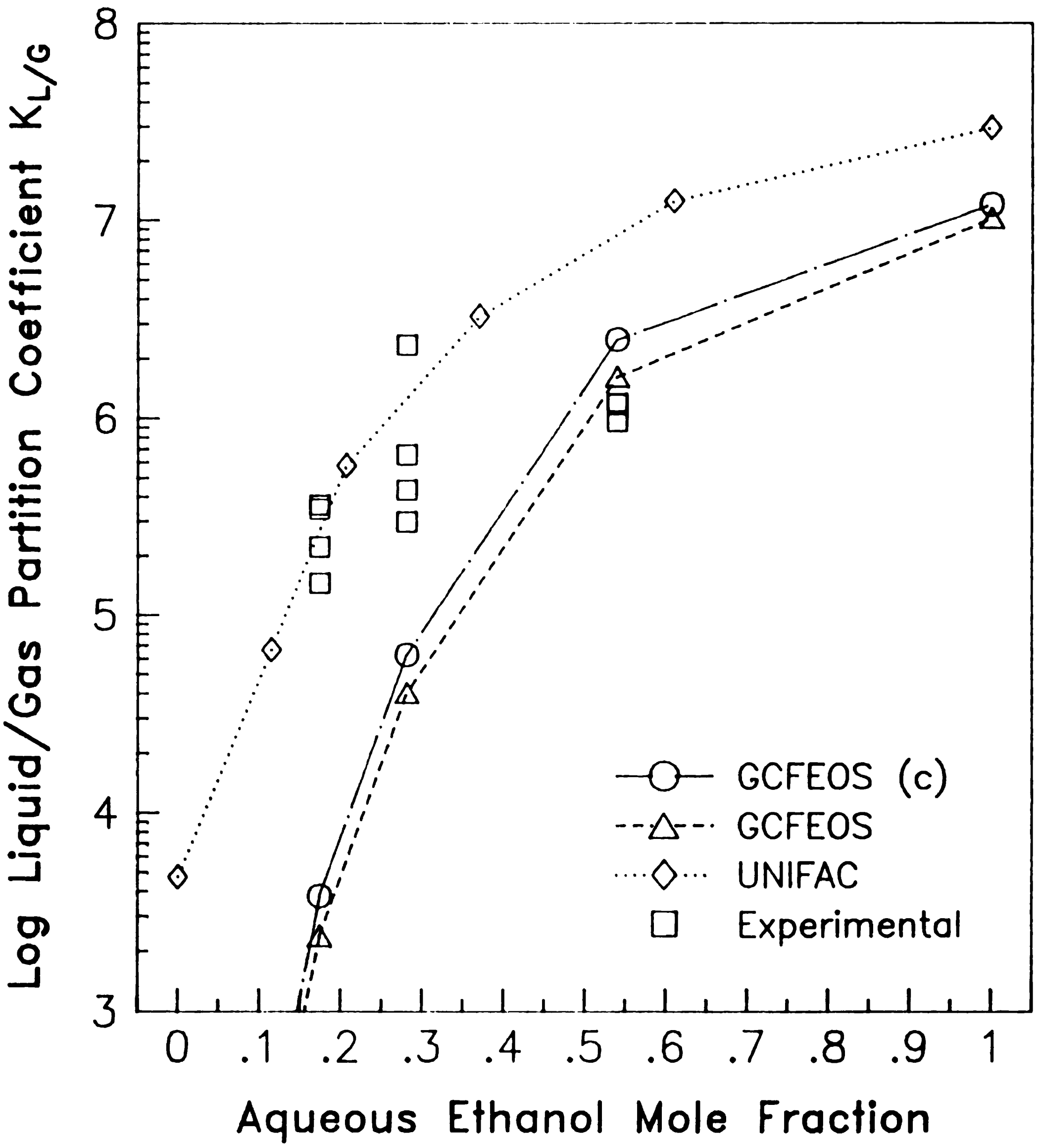

Figure 31. τ-Undelactone: Experimental $K_{L/G}$ versus UNIFAC and GCFEOS

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mass balances increased with increasing aqueous content. The literature contains very little partition coefficient data for these compounds. A partition coefficient could be calculated for isoamylacetate in water using infinite dilution activity coefficient data from Voilley et al. (1991). The correlations developed by Pierotti et al. (1959) were used for estimating infinite dilution activity coefficients for alcohols and n-acetates in water and alkanes in ethanol. The polar aromas were more difficult to measure than the alkanes because they have a greater affinity for the liquid phase, therefore, the difference in the liquid phase before and after stripping was too small and the $K_{L/G}$ difference calculation method could not used. The alcohols and less volatile aromas such as eugenol and τ-undelactone were particularly difficult to measure and their concentrations in the solvent trap were often not detectable or very near the detection limit. The effects of lower aroma volatility and their greater alcohol phase affinity can be seen in the increasing coefficients of variation for these compounds compared to the n-alkanes.

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Polymer/Liquid Partition Coefficients

The absorbed ethanol from the liquid phase into the polymer is negligible. No significant ethanol peaks were found in the polymer hexane extract for the 100% ethanol or the aqueous ethanol solutions.

n-Alkanes: Measured Polymer/Liquid Partition Coefficients

In Figures 32 to 35, the log of $K_{P/L}$ for n-alkanes versus n-alkane carbon number (i.e. molecular weight) are plotted showing that the n-alkanes increase linearly with increasing carbon number over the temperature range tested (10 to 40°C) for ethanol and aqueous ethanol liquid phases. $K_{P/L}$ increases with the aqueous content of the liquid phase and decreases with temperature. The linear increase in log $K_{P/L}$ in a homologous series is commonly observed behavior for homologous series of compounds (Pierotti et al., 1959) and can be fitted using linear regression. Table 15 lists the regression equations for the curves in Figures 33, 34 and 35.

Log Partition Coefficient $K_{P/L}$

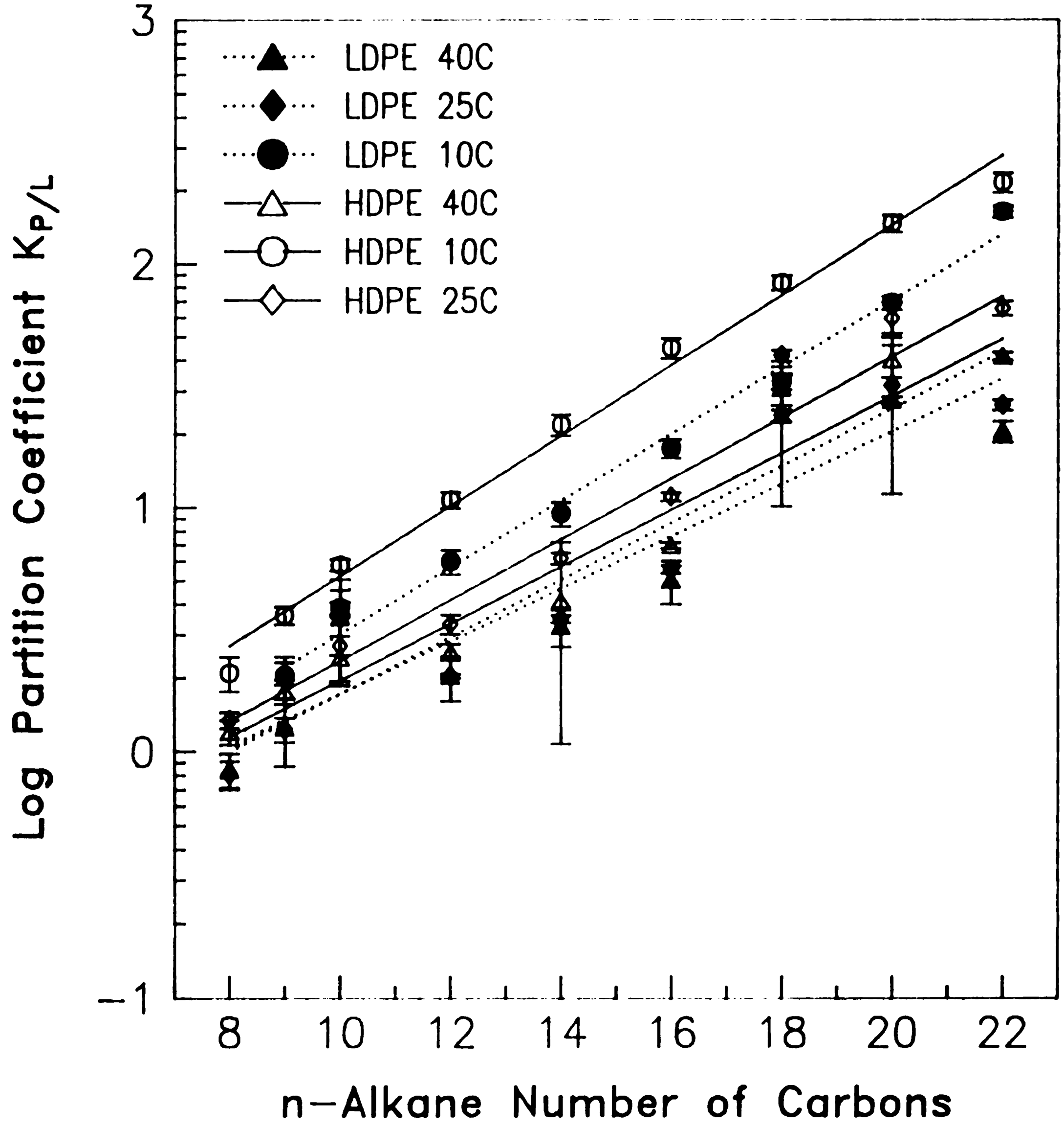

Figure 32. n-Alkanes/100% Ethanol: $K_{P/L}$ Variation with Temperature

Log Partition Coefficient $K_{P/L}$

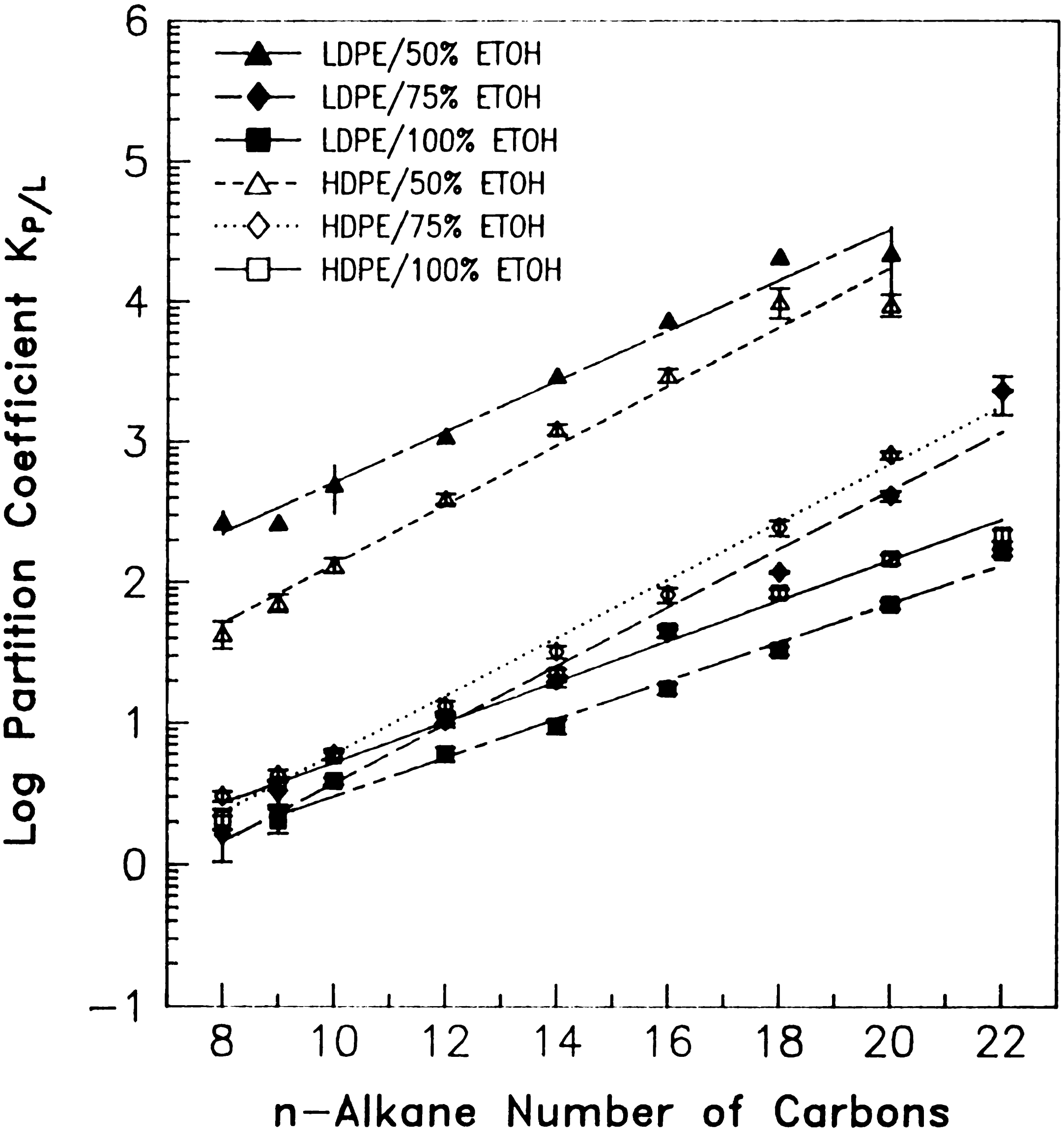

Figure 33. n-Alkanes/10°C: $K_{P/L}$ Variation with Percent Ethanol

Log Partition Coefficient $K_{P/L}$

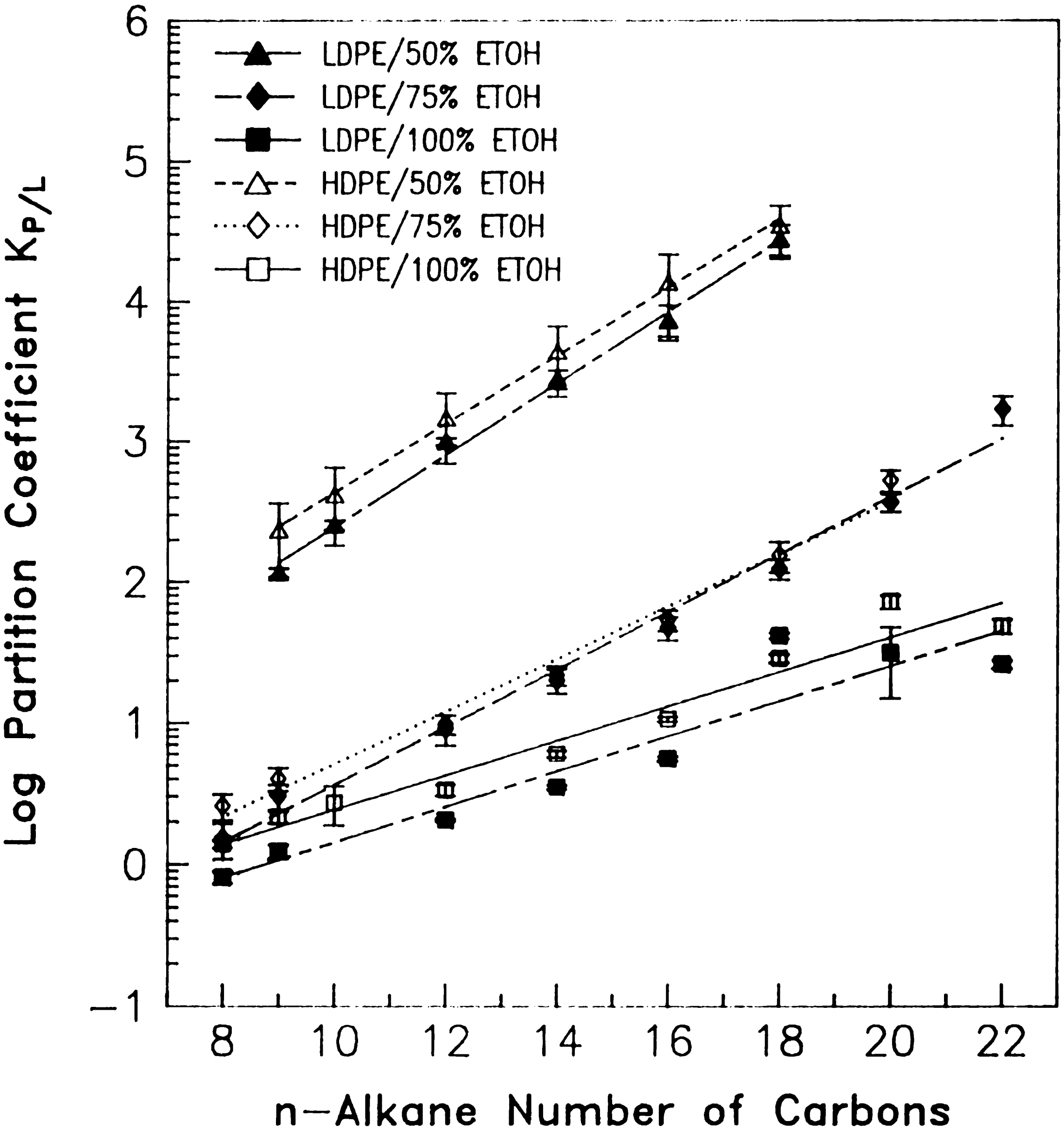

Figure 34. n-Alkanes/25°C: $K_{P/L}$ Variation with Percent Ethanol

Log Partition Coefficient $K_{P/L}$

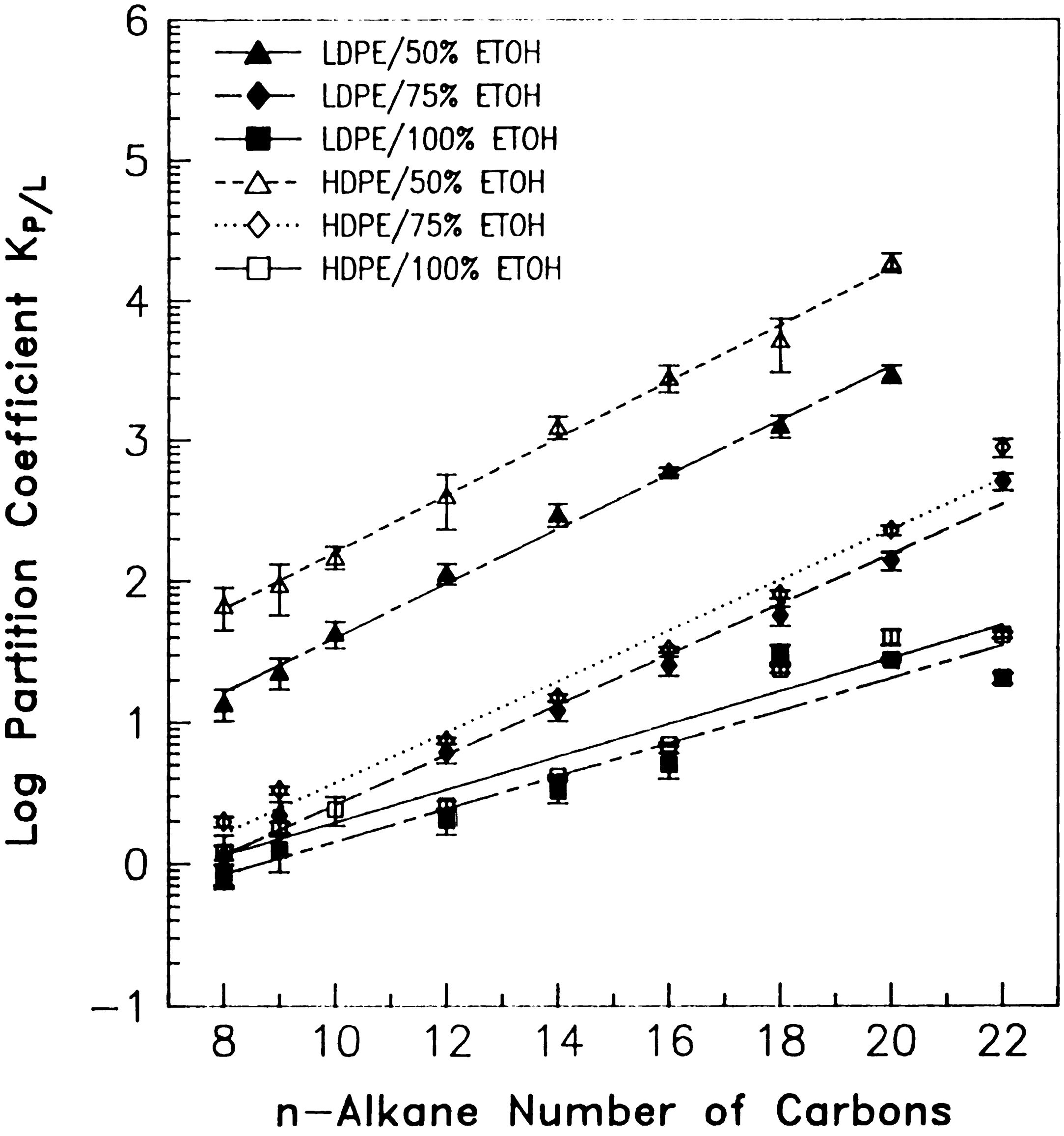

Figure 35. n-Alkanes/40°C: $K_{P/L}$ Variation with Percent Ethanol

Table 15. n-Alkanes $K_{P/L}$ Regression Equations

Liquid Phase[1]	Polymer	T (°C)	Equation	r²
100% Ethanol	HDPE	10	$K_{P/L}$ = .19 EXP(# .33)	.99
	LDPE	10	$K_{P/L}$ = .13 EXP(# .31)	.99
	HDPE	25	$K_{P/L}$ = .14 EXP(# .28)	.96
	LDPE	25	$K_{P/L}$ = .08 EXP(# .29)	.89
	HDPE	40	$K_{P/L}$ = .13 EXP(# .27)	.96
	LDPE	40	$K_{P/L}$ = .10 EXP(# .27)	.90
75% Ethanol	HDPE	10	$K_{P/L}$ = .05 EXP(# .47)	.99
	LDPE	10	$K_{P/L}$ = .03 EXP(# .48)	.98
	HDPE	25	$K_{P/L}$ = .07 EXP(# .43)	.98
	LDPE	25	$K_{P/L}$ = .03 EXP(# .47)	.99
	HDPE	40	$K_{P/L}$ = .06 EXP(# .41)	.98
	LDPE	40	$K_{P/L}$ = .04 EXP(# .41)	.99
50% Ethanol	HDPE	10	$K_{P/L}$ = 1.03 EXP(# .49)	.98
	LDPE	10	$K_{P/L}$ = 8.11 EXP(# .42)	.98
	HDPE	25	$K_{P/L}$ = 1.58 EXP(# .56)	1.0
	LDPE	25	$K_{P/L}$ = .68 EXP(# .59)	1.0
	HDPE	40	$K_{P/L}$ = 1.52 EXP(# .47)	1.0
	LDPE	40	$K_{P/L}$ = .47 EXP(# .44)	.99

r² = coefficient of determination

1 = w/w percentage ethanol in aqueous solution

= number of carbon atoms in n-alkane

Table 15 (cont.): Comparison of n-Alkane K(P/L): Dodecane

	HDPE	c_i^P	LDPE	c_i^P	HDPE/LDPE
100% Ethanol					
10°C	9.97	8.4E-05	5.36	4.8E-05	1.86
25°C	4.03	5.0E-05	2.60	4.6E-05	1.55
40°C	3.32	3.9E-05	2.55	4.6E-05	1.30
75% Ethanol					
10°C	14.1	3.0E-04	9.52	7.1E-05	1.48
25°C	12.2	2.4E-04	8.44	2.0E-04	1.44
40°C	8.22	1.8E-04	5.48	1.5E-04	1.50
50% Ethanol					
10°C	369	6.3E-04	1253	8.3E-04	0.29
25°C	1310	6.9E-04	808	8.6E-04	1.62
40°C	428	5.2E-04	92.3	6.7E-04	4.64

c(i,p) = concentration (g/mL) dodecane in polymer

Figures 33, 34, 35 and Table 15 show how the $K_{P/L}$'s for LDPE and HDPE in the 100% and 75% solutions are essentially the same at all three temperatures. In Table

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15 the ratio of HDPE and LDPE dodecane $K_{P/L}$ calculated from the regression curves in Table 15 are calculated. In general HDPE had a larger partition coefficient than LDPE. However, only in the 50% solution were the polymer's $K_{P/L}$'s found to be significantly different at 10°C and 40°C (but not at 25°C). Without the data at higher water content aqueous ethanol solutions it is unsure if this is a real effect or an analytical artifact. The 35% aqueous ethanol solution $K_{P/L}$'s could not be accurately measured and are not reported because the partition coefficients were so great that practically all the n-alkanes partitioned into the polymer phase at equilibrium. Measurements for Decane, Eicosane and Docosane tend to have the largest deviations from the homologous series regression lines because of analytical problems. A complete listing of all the treatment measurements with means, standard deviations and coefficients of variation are found in Appendix C.

The variation of the log of the n-alkane's partition coefficients with the inverse Kelvin temperature did not exhibit an Arrhenius relationship in the temperature range from 10°C to 40°C. Figure 32 shows the effect of temperature on $K_{P/L}$ between HDPE and LDPE and 100% ethanol. Here each measurement mean is plotted with error bars signifying two standard deviations (95% probability limits). Within the total uncertainty of the measurements which ranges from 19 to 42%, and which depends on the treatment (see error analysis), the $K_{P/L}$'s for LDPE and for HDPE are not different from one another at 25°C and 40°C. The slopes of the lines for both polymers at 25°C are not significantly different at the 95% level of significance. The slopes of the regression lines for LDPE and HDPE at all three temperatures are not significantly different from one another at the 95% level of significance. However, the slopes of both polymer's regression lines at 10°C are significantly different from those at 25°C and 40°C at the 95% level of significance. At 10°C the $K_{P/L}$ for HDPE are significantly different than those for LDPE. Similar partitioning patterns and significant relationships are repeated in the 75% aqueous ethanol solution although the slopes of the regression lines are greater. At 25°C the 50% aqueous ethanol solution had its largest slope whereas the 100% and 75% solutions had theirs at 10°C.

Aromas: Measured Polymer/Liquid Partition Coefficients

Figures 36 to 47 plot the variation in aroma $K_{P/L}$ for both polyethylenes at all three temperatures as a function of percentage aqueous ethanol. The measured data for the aromas along with their means of four replicates, standard deviations and coefficient of variations are found in Appendix C. The data points shown in the figures are means

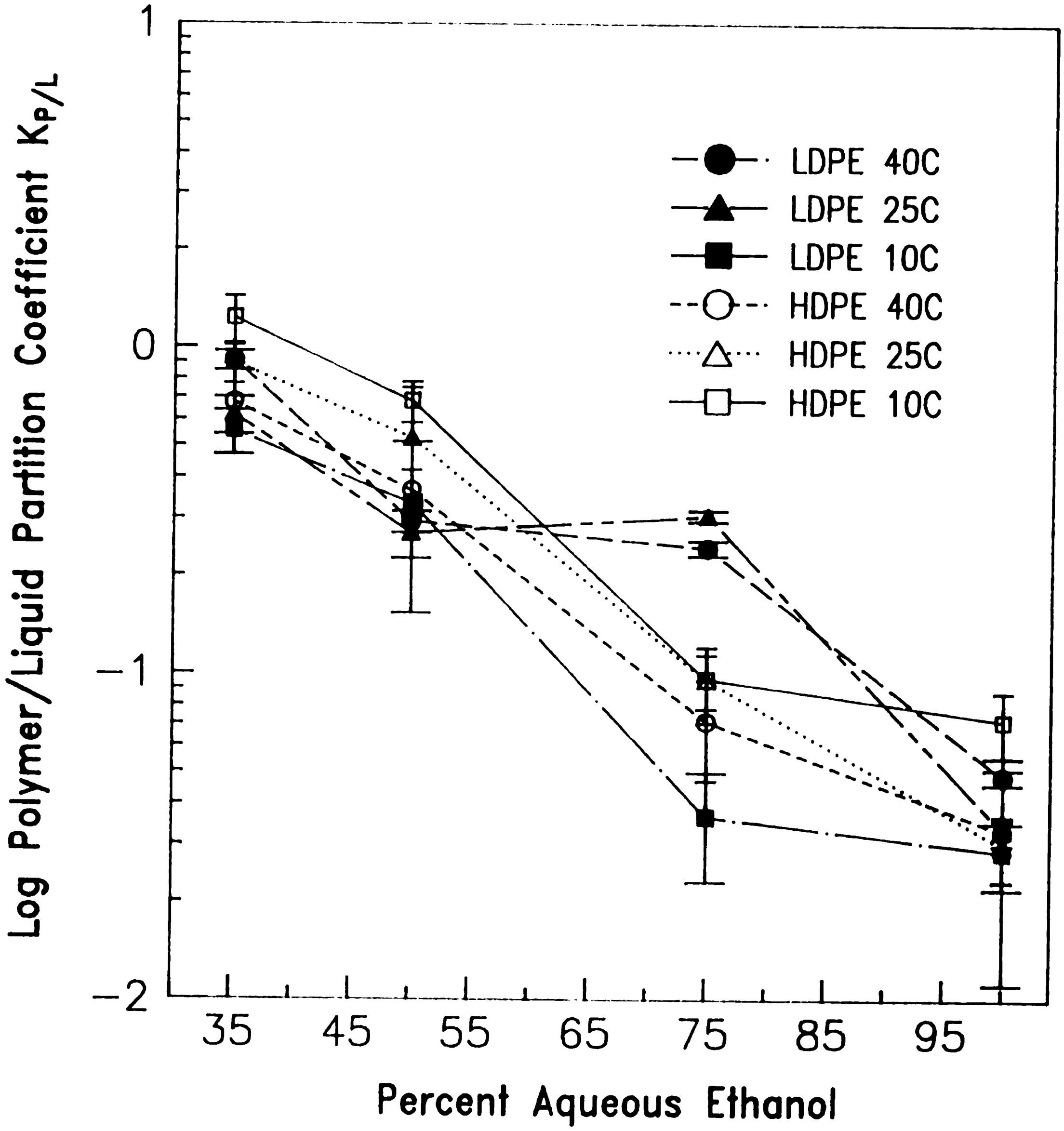


Figure 36. Isoamylacetate: Experimental $K_{P/L}$ Variation with Percent Ethanol

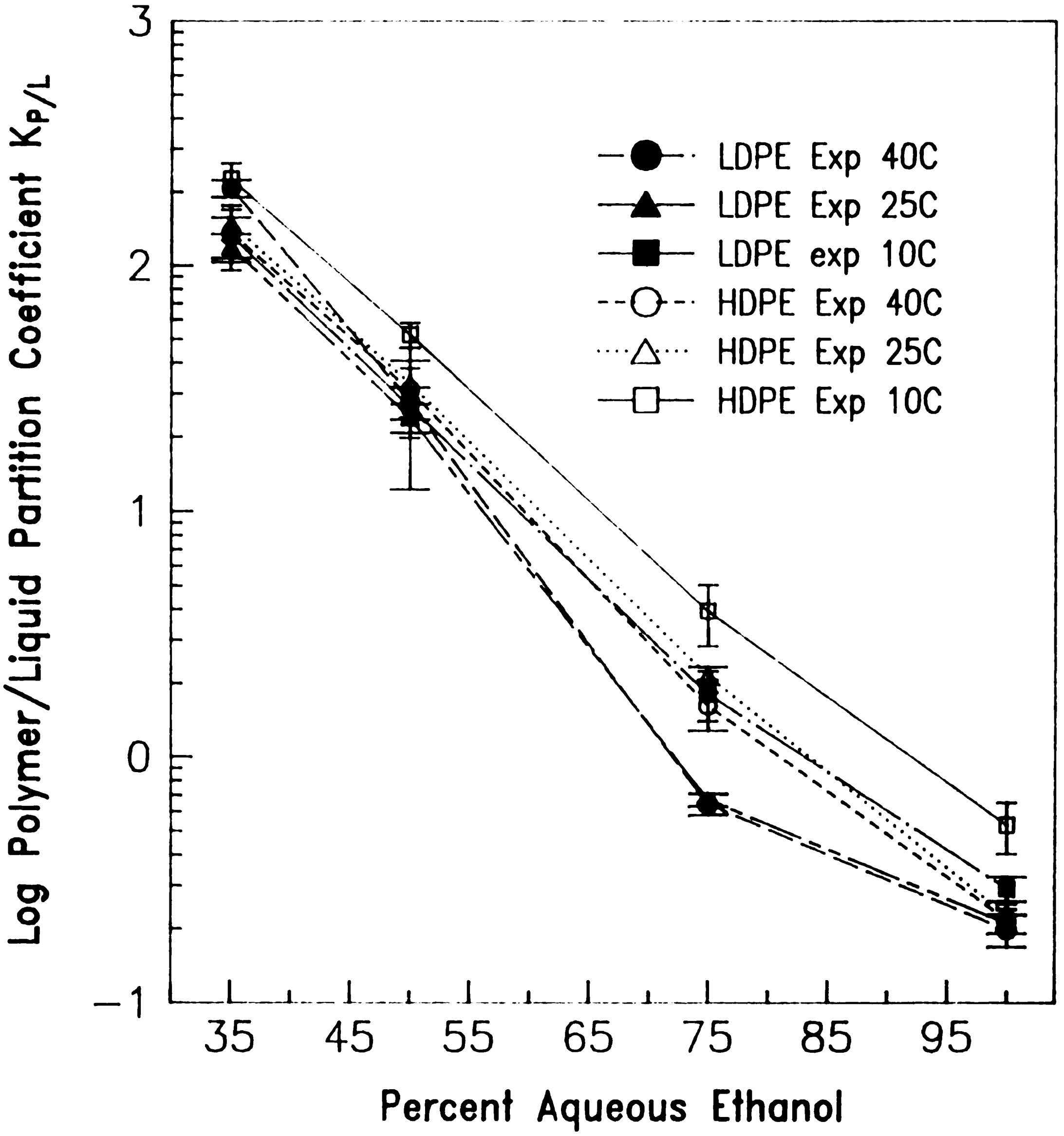


Figure 37. **d-limonene:** Experimental $K_{P/L}$ Variation with Percent Ethanol

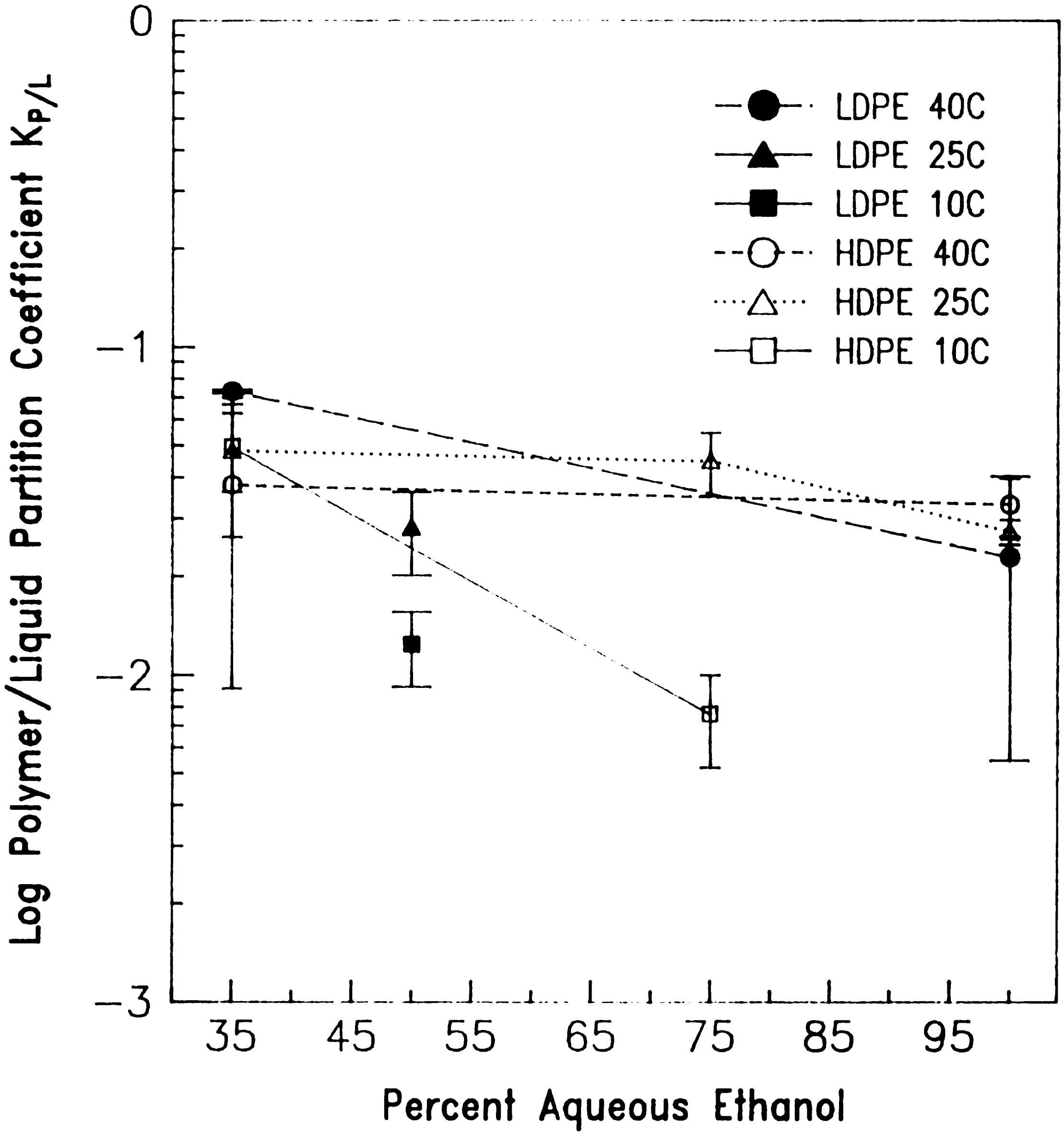


Figure 38. cis-3-Hexenol: Experimental $K_{P/L}$ Variation with Percent Ethanol

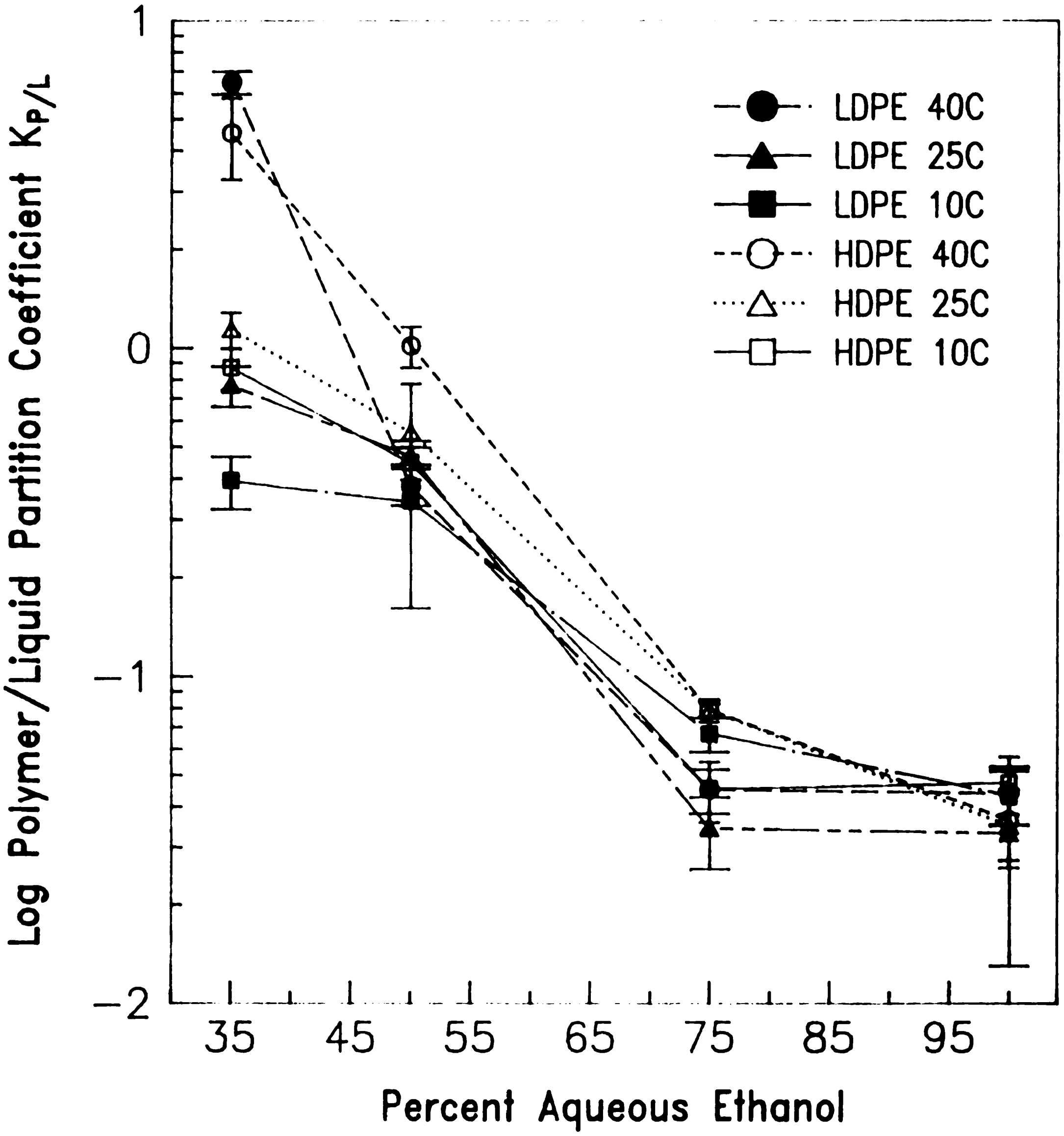


Figure 39: Camphor: Experimental $K_{P/L}$ Variation with Percent Ethanol

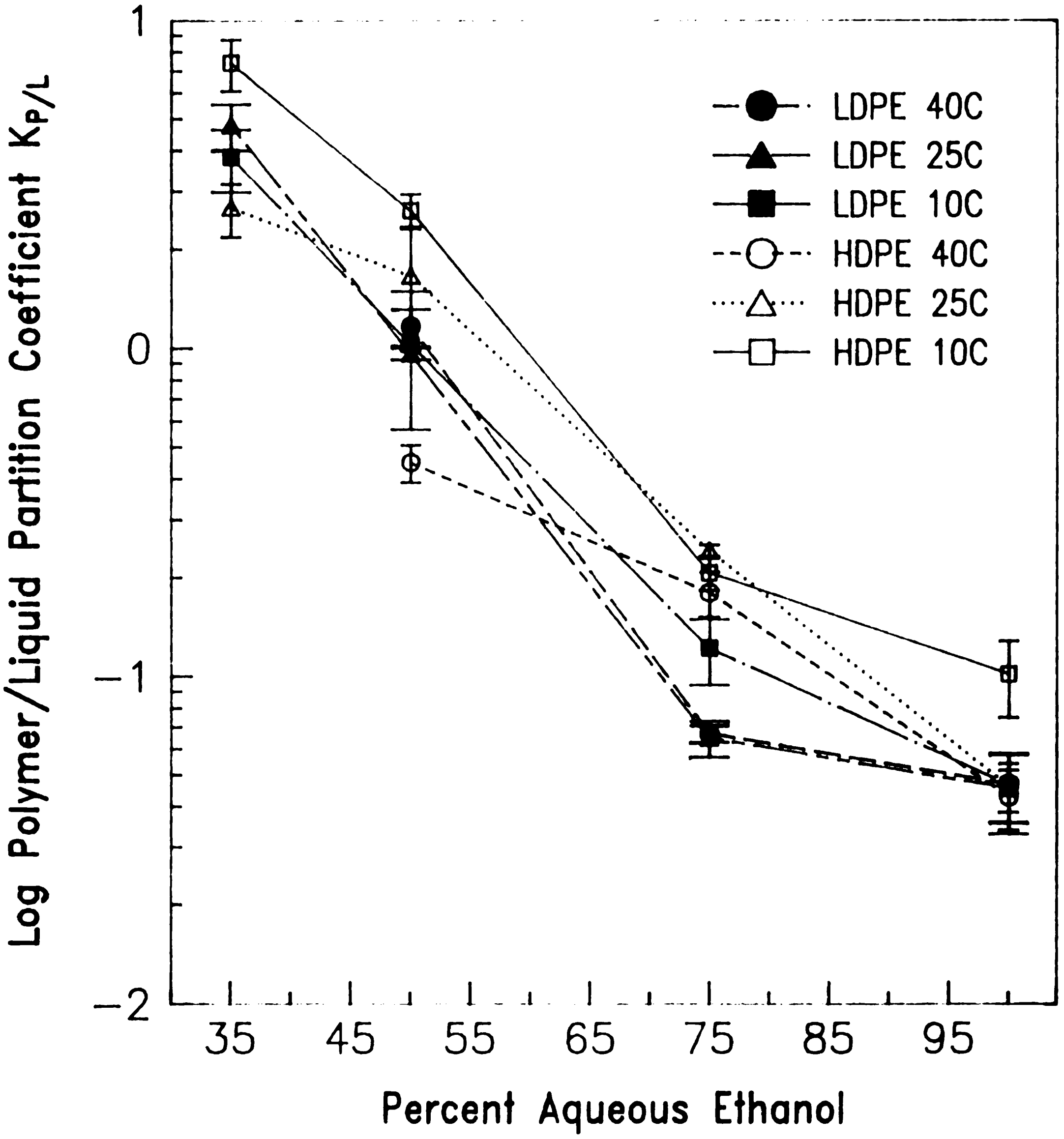


Figure 40. Linalylacetate: Experimental $K_{P/L}$ Variation with Percent Ethanol

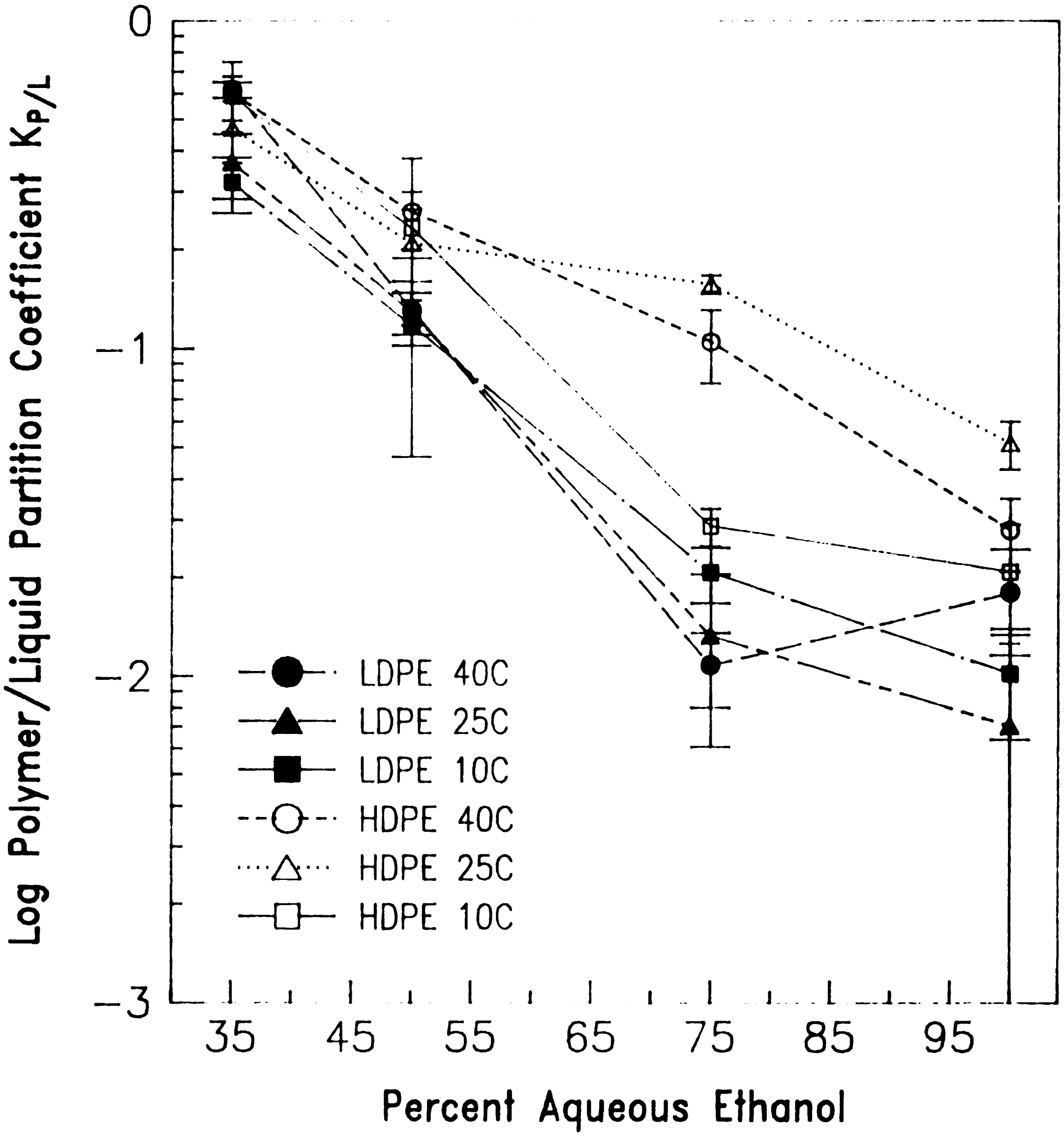


Figure 41. Menthol: Experimental $K_{P/L}$ Variation with Percent Ethanol

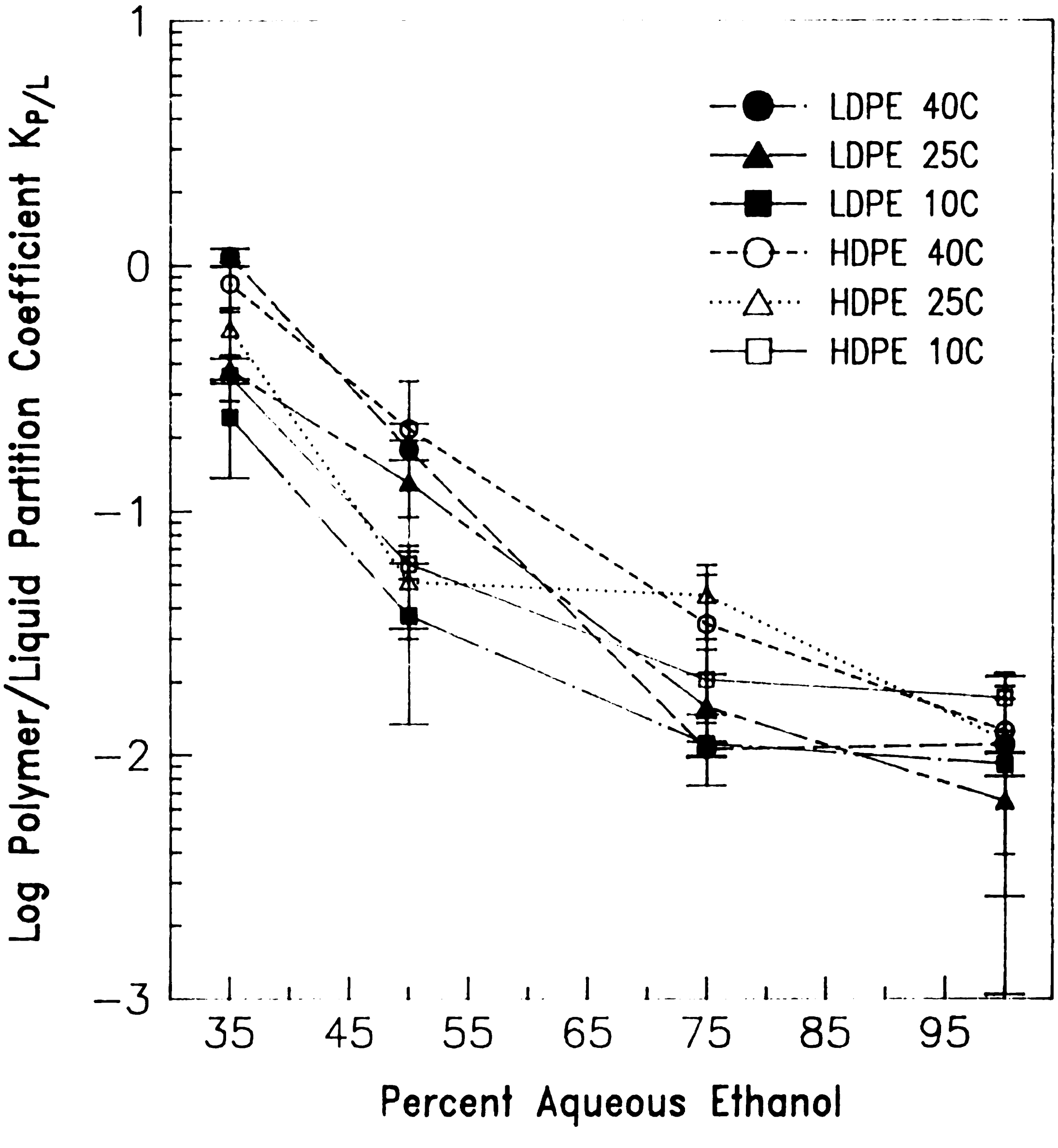


Figure 42. Dimethylbenzylcarbinol: Experimental $K_{P/L}$ Variation with Percent Ethanol

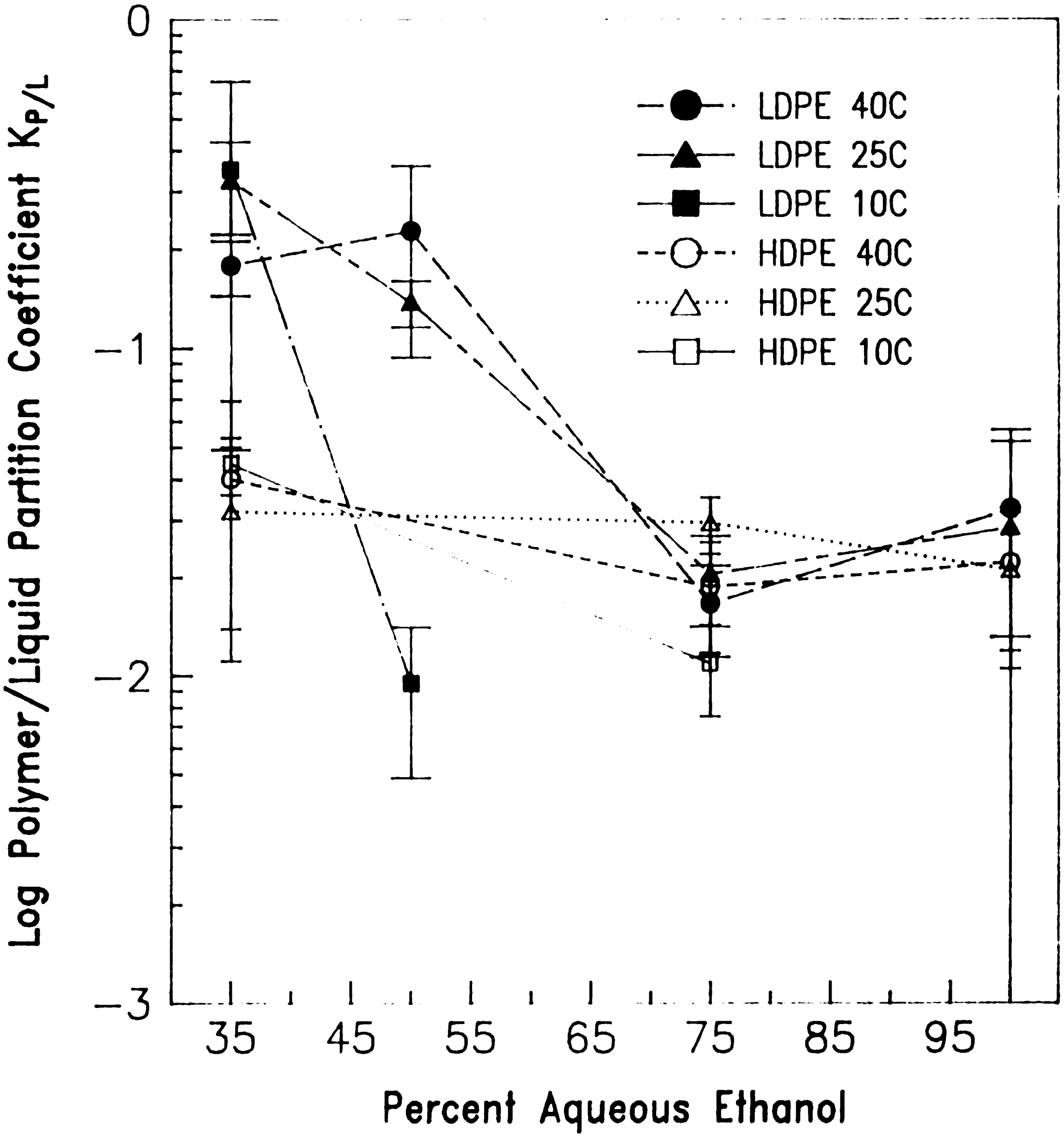


Figure 43. Phenylethylalcohol: Experimental $K_{P/L}$ Variation with Percent Ethanol

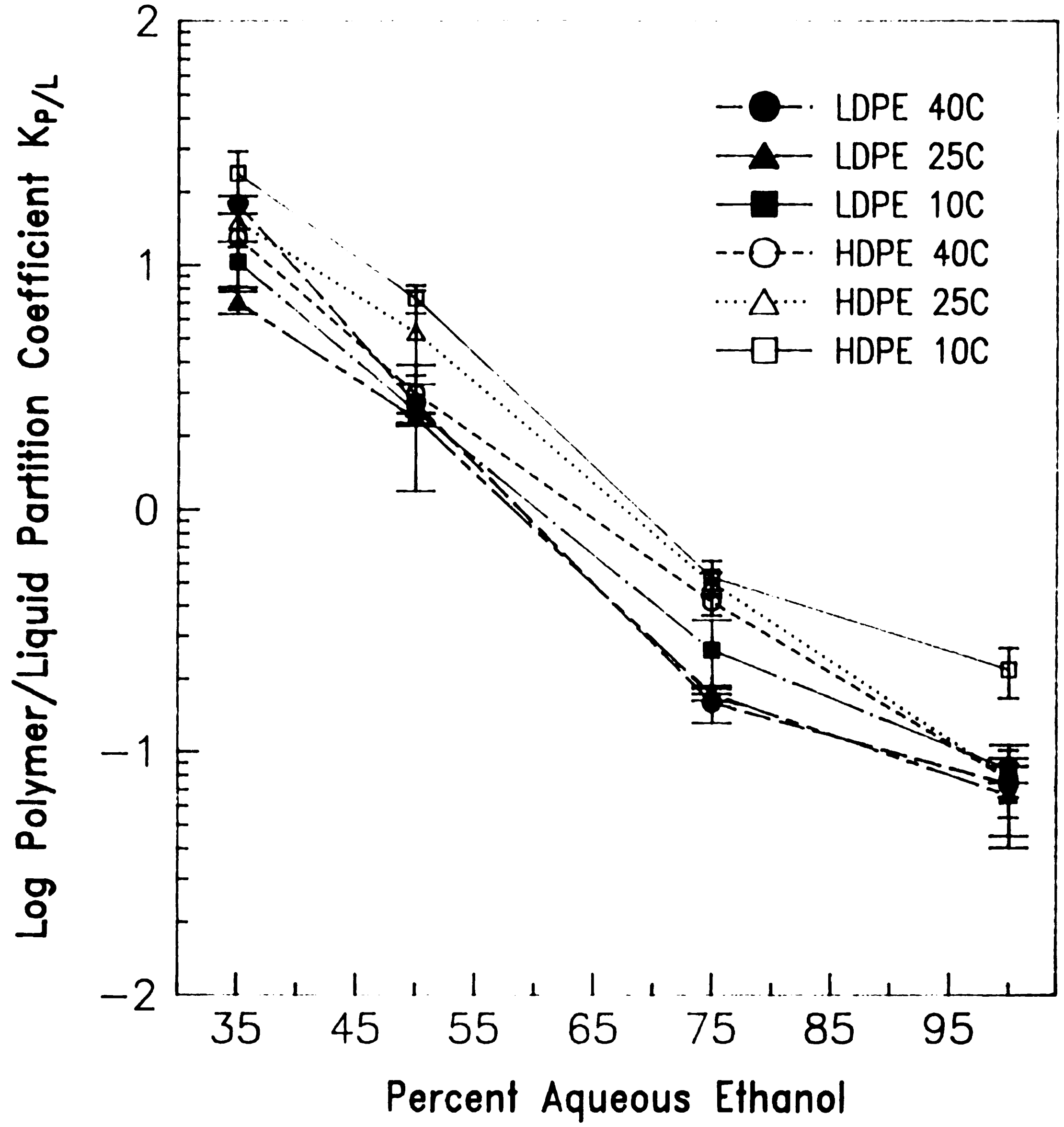


Figure 44. Diphenylmethane: Experimental $K_{P/L}$ Variation with Percent Ethanol

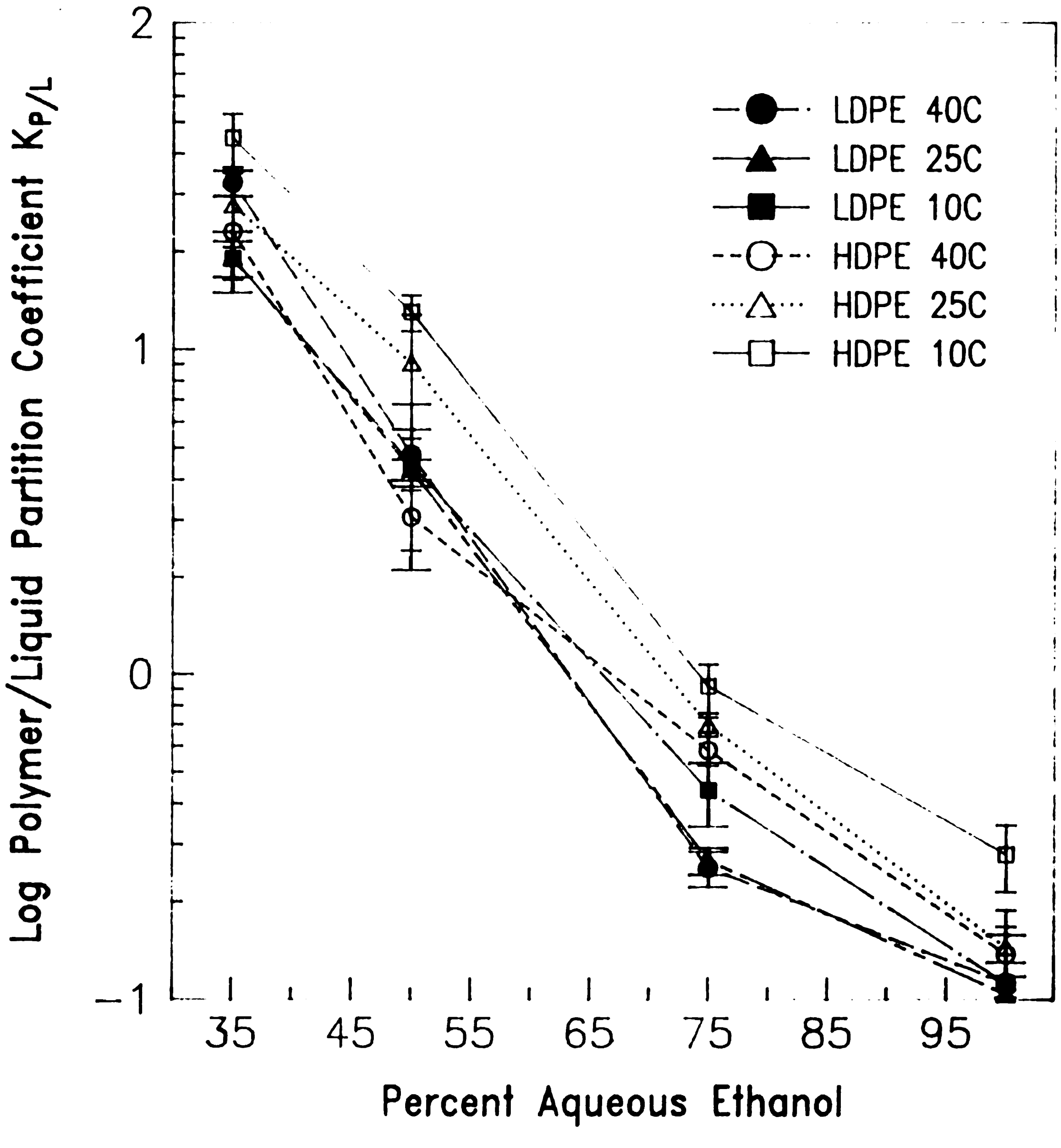


Figure 45. Diphenyloxide: Experimental $K_{P/L}$ Variation with Percent Ethanol

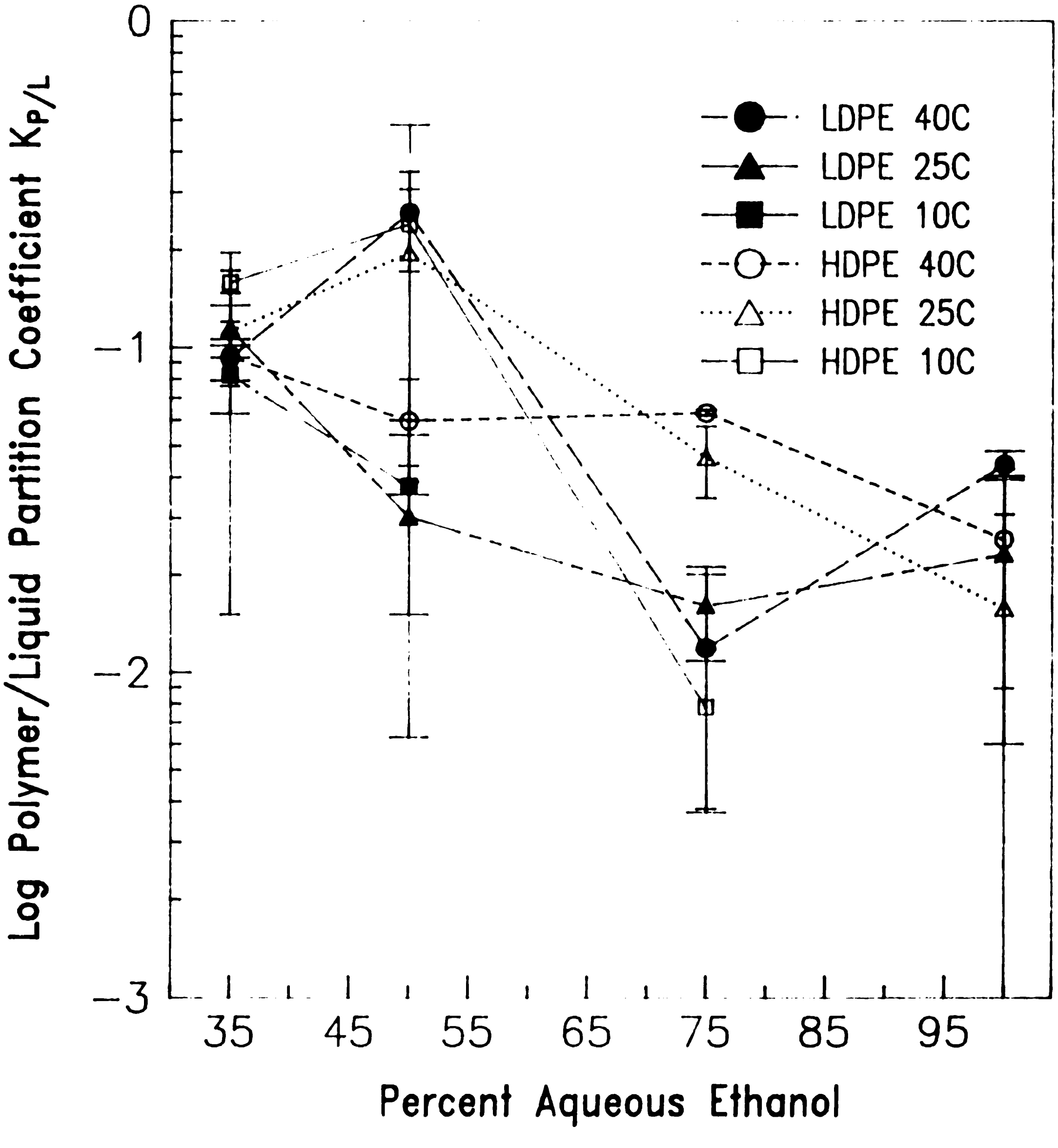


Figure 46. Eugenol: Experimental $K_{P/L}$ Variation with Percent Ethanol

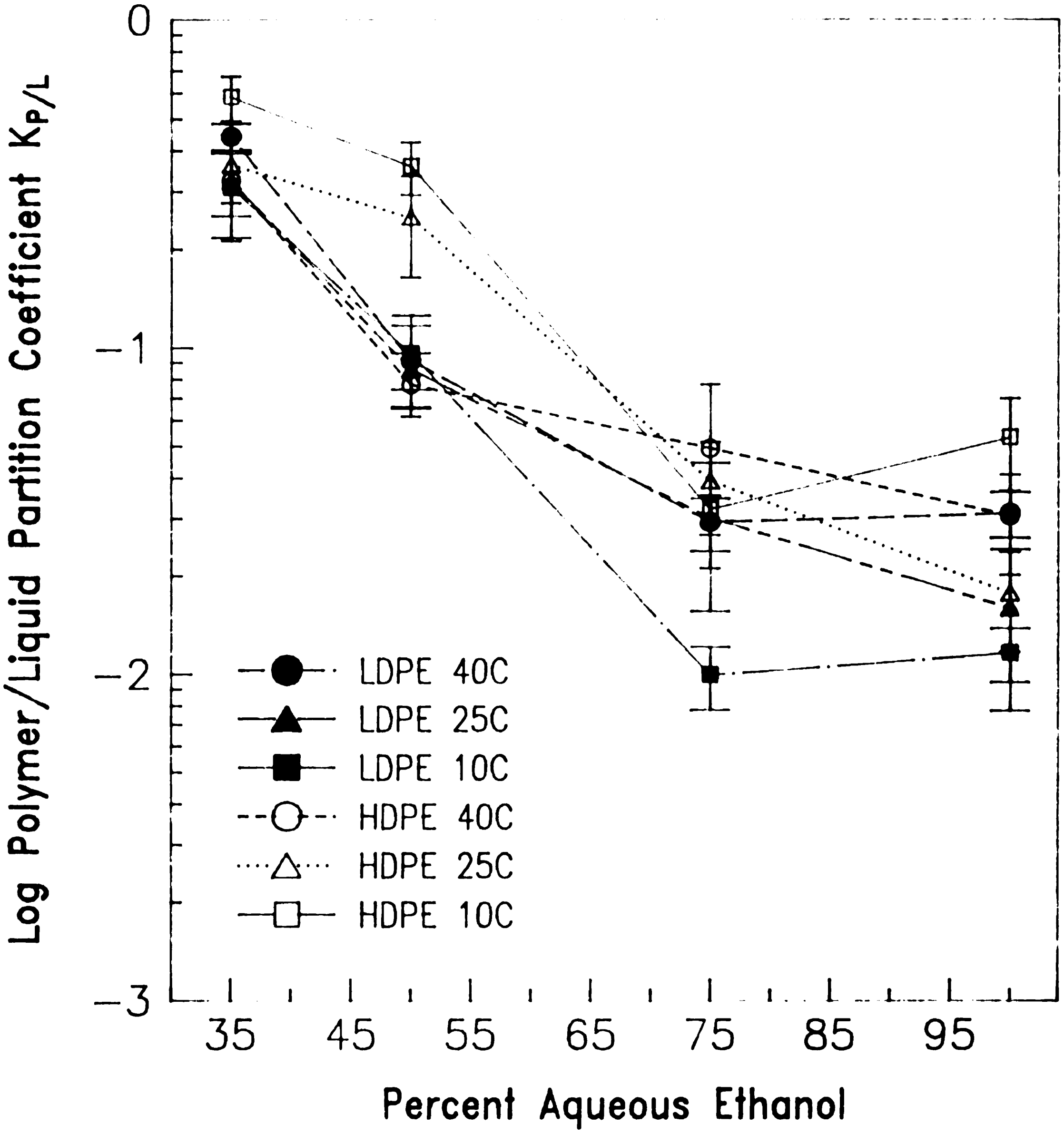


Figure 47. γ-Undelactone: Experimental $K_{P/L}$ Variation with Percent Ethanol

and the error bars represent two standard deviations of the mean (a 95% confidence interval for the mean). There are some apparent trends in the data variation of the aromas with temperature and polymer density which are similar to those observed for the n-alkanes. In general HDPE had larger partition coefficients than LDPE and the partition coefficients for a given polymer decreased with increasing temperature so that HDPE at 10°C had the largest partition coefficients and LDPE at 40°C had the smallest. However, in most cases the differences between the $K_{P/L}$'s for the two polymers and between the different temperatures were not large enough and consistent enough to make significant statistical observations when the total uncertainty of the measurements are taken into account (see Error Analysis). The total uncertainty (two standard deviations plus the systematic uncertainty combined in quadrature) of the means ranged from 19 to 31% depending on the aroma and the ethanol solution measured. The measurement difficulty (or increased random error uncertainty) and potential systematic uncertainty increased as the partition coefficient became smaller. For partition coefficients below 0.1 the concentration of aromas in the hexane extract were often at or near the analytical detection limit. Camphor and linalylacetate, started decomposing in the 35% aqueous ethanol solutions at 40°C and 25°C, otherwise no other decompositions were detected for other aromas. The partitioning behavior of an aroma is largely decided by its polarity relative to the polymer and liquid phases.

Referring to Figure 48 the non-polar hydrocarbon molecules, d-Limonene and diphenylmethane, have the largest partition coefficients overall and had the largest increase as the aqueous content of the liquid phase increased. The non-polar hydrocarbons partition more favorably in the non-polar polyethylenes relative to the polar liquid phase. Diphenyloxide, which has a stearically hindered ketone functional group between two phenyl groups, behaves similarly to the hydrocarbons. Intermediate polar molecules like isoamylacetate, camphor, linalylacetate and τ-undelactone have smaller $K_{P/L}$'s and flatter curves over the percentage ethanol range. The partition coefficients for the intermediate polar aromas are in the order of 10 to 100 times smaller than the hydrocarbons and increase 100 times on the average over the range from 100% to 35% ethanol. The intermediate polar aromas show practically no partitioning difference between the 100% and 75% ethanol phases. The highly polar aromas, i.e. the alcohols and aromas with multiple functional groups (Eugenol), have the smallest partition coefficients and the least variance with percentage ethanol. Because of their low partition coefficients and subsequent high random error, the alcohols had the largest uncertainties and variance. The alcohol aroma $K_{P/L}$ varied on average

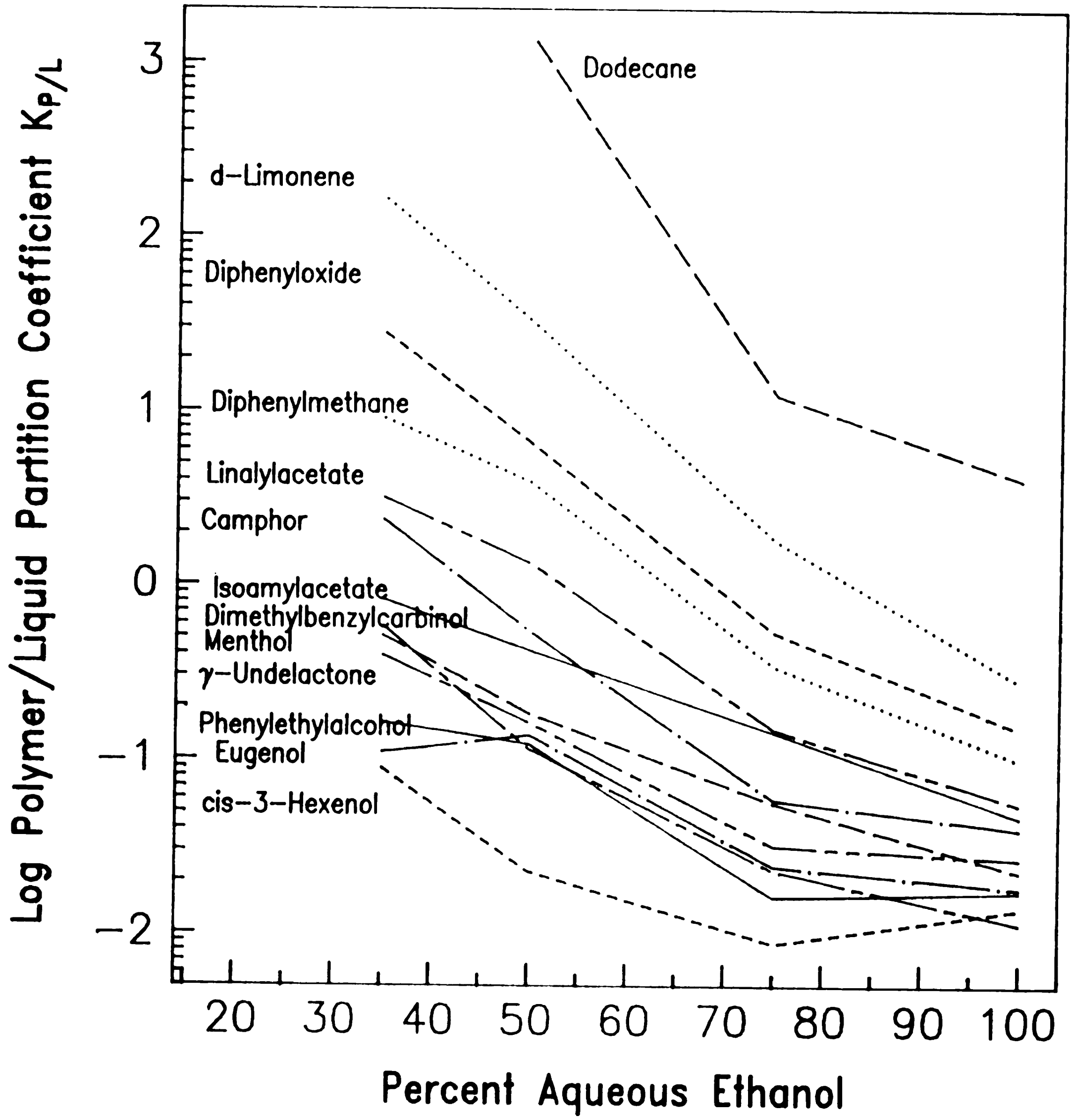


Figure 48. Comparison of Relative Aroma $K_{P/L}$

less than 10 times over the aqueous ethanol range. When the alcohol aroma has a primary alcohol group and low molecular weight, the variation in the partition coefficient with percent ethanol was smaller. For example the small primary alcohols, cis-3-hexanol and phenylethyl alcohol have practically flat curves compared to the larger molecular weight secondary alcohols menthol and dimethylbenzylcarbinol.

The temperature dependence of the partitioning process showed some general differences and trends but in general the partitioning process was relatively temperature insensitive in the temperature range from 10°C to 40°C. In general the measurements at 25°C and 40°C were not significantly different from one another and between the two polymers over the entire range of ethanol concentration studied. At 10°C the HDPE $K_{P/L}$'s represent the upper bounds and the LDPE $K_{P/L}$'s represent the lower bounds for all $K_{P/L}$ measurements for the partitioning of several aromas at 10°C.

Given that the differences between the polymers and temperatures measured were not significant their partition coefficients can be averaged for each percent ethanol liquid solution. Table 16 lists average values for the combined average polymer/liquid partition coefficients for LDPE and HDPE at temperatures of 10°, 25° and 40°C as a function of the percent ethanol in the liquid phase.

Table 16. Aromas $K_{P/L}$: Polyethylene/Ethanol at 10°C - 40°C

Aroma	Percent Aqueous Ethanol Liquid Phase			
	100%	75%	50%	35%
Isoamylacetate	0.0464	0.141	0.416	0.813
d-Limonene	0.278	1.80	32.4	161
cis-3-Hexenol	0.0139	0.0087	0.0224	0.0880
Camphor	0.0397	0.0581	0.534	2.359
Linalylacetate	0.0549	0.147	1.32	3.14
Menthol	0.0225	0.0557	0.180	0.507
Dimethylbenzylcarbinol	0.0113	0.0228	0.113	0.575
Phenylethylalcohol	0.0174	0.0160	0.121	0.161
Diphenylmethane	0.0992	0.339	3.86	8.99
Diphenyloxide	0.148	0.526	6.45	27.6
Eugenol	0.0181	0.0241	0.137	0.109
γ-Undelactone	0.0267	0.0316	0.160	0.391

Table of averages of aroma $K_{P/L}$ across 10°C, 25°C, 40°C and LDPE and HDPE combined.

% Aqueous ethanol (w/w)

Error Analysis

The error analysis was conducted using the principles outlined in Taylor (1982). The error analysis is essentially an estimate of the uncertainty (δq) of a measurement (q). The propagation of uncertainties in sums and differences is calculated by the quadratic sum of the uncertainties:

$$\delta q = \sqrt{(\delta x)^2 + (\delta y)^2 + \ldots} \qquad (53)$$

The propagation of uncertainties in products and quotients is the sum in quadrature of the original fractional uncertainties:

$$\delta q/|q| = \sqrt{(\delta x/x)^2 + (\delta y/y)^2 + \ldots} \qquad (54)$$

Where the fractional uncertainty ($\delta q/|q|$) is the measurement uncertainty divided by the measurement's best estimate.

The error analysis contains both systematic and random errors. Random errors are determined by repeated measurements of a measured quantity. The coefficient of variance is an example of a random error fractional uncertainty. Systematic errors are estimated from the uncertainty with which quantities can be measured.

Liquid/Gas Partition Coefficients

The following assumptions were made: There were no concentration effects on the liquid/gas partition coefficient by the concentration of the solute in the liquid phase. Within the flow rate ranges of the gas and liquid flows there was no effect on the partition coefficient. The measurement uncertainties are listed in Table 17. Table 18 lists the total relative uncertainties for $K_{L/G}$ according to the different solutes and the partition calculation method used.

Table 17. Liquid/Gas Partition Coefficient Measurement Uncertainties

Uncertainty		Absolute	Relative
Systematic Measurement Uncertainties:			
Gas flow rate.		-	0.1%
Time	(900 min)	2	.00222
Volume 1	(100 mL)	0.5	.005
Volume 2	(100 mL)	0.5	.005
GC area units		-	2.5% to 5.0%
GC calibration		-	3.29% to 5.44%
Total systematic uncertainty:			7.5%

Random Uncertainties:		**Range of c.v.%**
Solvent Trap Data (Eq 36)[1]		
n-Alkanes	100% Etoh	9.7 to 36%
	66% Etoh	8.8 to 32%
	33% Etoh	4.8 to 43%
Aromas	100% Etoh	6.7 to 33%
	75% Etoh	9.3 to 20%
	50% Etoh	11 to 66%
	33% Etoh	5.7 to 36%
Concentration Difference Data (Eq 38)[1]		
n-Alkanes	100% Etoh	6.5 to 21%
	66% Etoh	13 to 44%
	33% Etoh	2.7 to 42%

c.v.% = coefficient of variation, percent standard deviation of the mean.

1 = range of c.v.% taken from Tables 33-39.

Table 18. Liquid/Gas Partition Coefficient Total Relative Uncertainties.

Solute	Ethanol %	Range
Solvent Trap Measurements		
n-Alkanes	100%	12.1 to 37.8%
	66%	11.4 to 34.0%
	33%	8.72 to 44.5%
Aromas	100%	9.89 to 35.0%
	75%	11.8 to 23.0%
	50%	13.2 to 67.0%
	35%	9.24 to 38.1%
Concentration Difference Measurements		
n-Alkanes	100%	18.0 to 24.0%
	66%	15.3 to 45.6%
	33%	7.76 to 43.6%

Polymer/Liquid Partition Coefficients

Table 19 lists the systematic measurement uncertainties for the polymer/liquid partition coefficient measurements.

Table 19. Polymer/Liquid Partition Coefficient Systematic Measurement Uncertainties.

Uncertainty	Absolute	Relative
Polymer Weight	.0002 g	.053%
Polymer Density	.01 g/mL	1%
Volume of Hexane	.1 mL	.67%
GC area counts	-	8%
GC calibration Ethanol	-	10.7%
GC calibration Hexane	_	12.8%
Total Systematic Relative Uncertainty:		18.5%

Average random uncertainties for $K_{P/L}$ are based on four replicate samples per treatment and are listed according to solutes and ethanol solutions in Table 20. A complete tabulation of standard deviations for means for each treatment is given in Appendix B.

Table 20. Polymer/Liquid Partition Coefficient Measurement Average Random Uncertainties.[1]

By Aroma:	c.v.%	By n-Alkane	c.v.%
Isoamylacetate	15.3%	C8	17.5%
d-Limonene	8.3%	C9	13.0%
cis-3-Hexanol	11.9%	C10	23.5%
Camphor	9.9%	C12	10.3%
Linalylacetate	9.9%	C14	11.3%
Menthol	15.0%	C16	11.5%
Dimethylbenzylcarbinol	18.2%	C18	10.9%
Phenylethylalcohol	25.0%	C20	9.07%
Diphenylmethane	10.9%	C22	12.8%
Diphenyloxide	10.0%		
Eugenol	21.5%		
gamma-Undelactone	13.3%		

By Percent Aqueous Ethanol:

	Aroma c.v.%	n-Alkanes c.v.%
100% Ethanol	7.2-24%	4-9%
75% Ethanol	8.2-12%	6-19%
50% Ethanol	10-25%	8-38%
35% Ethanol	5-22%	15-35%

c.v.% = coefficient of variation, percent standard deviation of the mean.
1 = for c.v.% see Tables 40 and 41.

The total estimated uncertainty of $K_{P/L}$ is dependent on the coefficient of variance of the treatment measurements. The total uncertainty obtained by combining the systematic and random uncertainties by quadrature fall in a range between 19% and 31% of a measured value for the flavors and 19% and 42% of a measured value the n-alkanes.

Calculation Results

Estimation of $K_{L/G}$ With UNIFAC and GCFEOS

n-Alkanes: Comparison of Estimated with Experimental $K_{L/G}$

Calculations were carried out with UNIFAC and GCFEOS using identical concentrations to those used in the liquid/gas partition coefficient measurements. Figure 49 compares the UNIFAC and GCFEOS estimations for n-alkanes partitioned between 100% ethanol and air with experimental measurements. The experimental regression lines lie exactly in-between the regression lines of the two estimation techniques. UNIFAC tends to overestimate the $K_{L/G}$ and GCFEOS to underestimate the $K_{L/G}$. Table 21 compares the regression line equations of the experimental results with the two estimations.

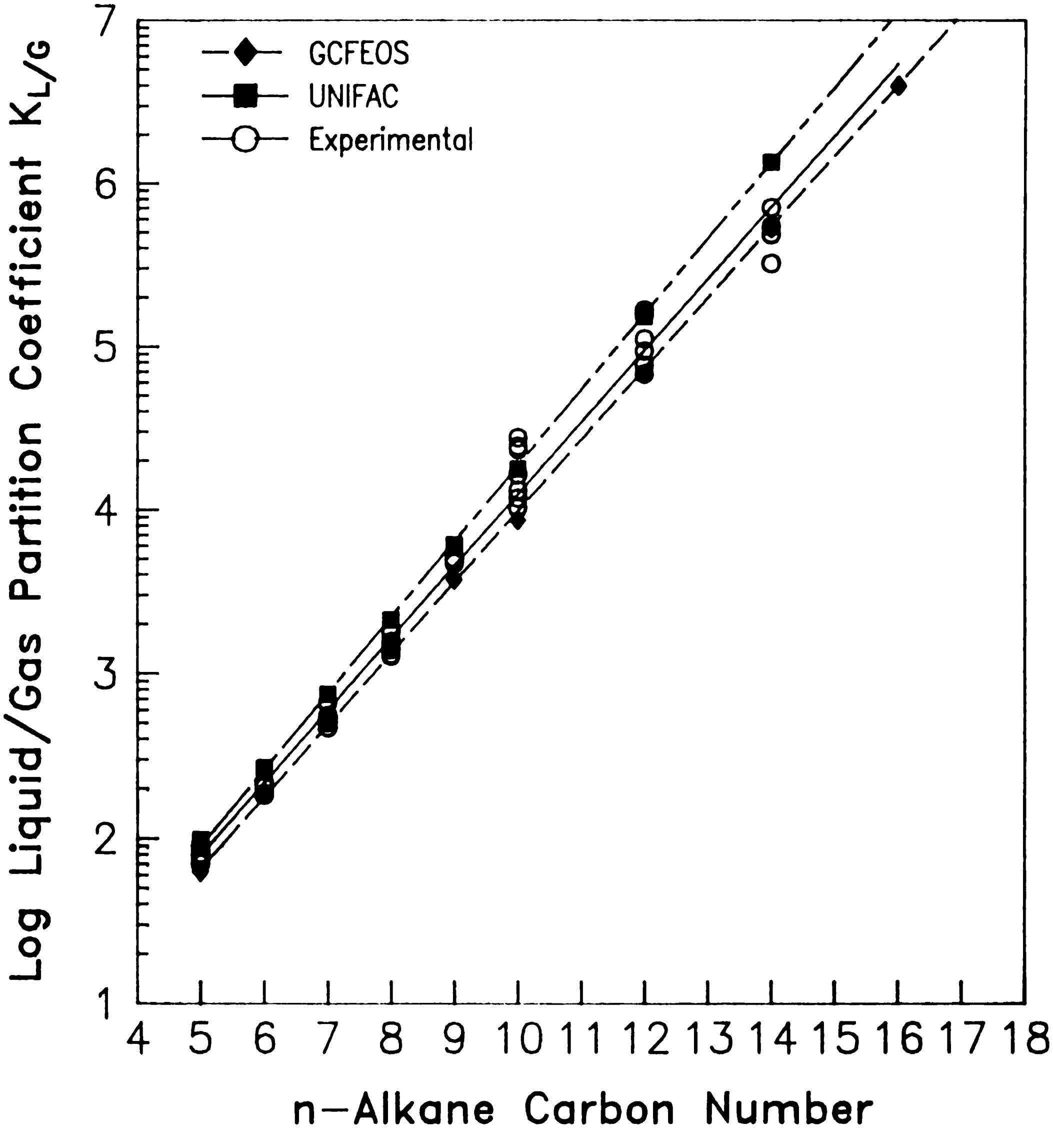


Figure 49. $K_{L/G}$: n-Alkanes/100% Ethanol/25°C
Estimated versus Experimental

Table 21. n-Alkanes/100% Ethanol $K_{L/G}$ at 25°C: Estimations versus Experimental Measurements.

Measurement or Estimation	Equation	r^2
Experimental (this work)	$K_{L/G}$ = 0.5 EXP(# 1.01)	.99
Cori & Delogu (1986)	$K_{L/G}$ = 0.31 EXP(# 1.06)	1
Pierotti et al. (1959)	$K_{L/G}$ = 0.28 EXP(# 1.07)	1
UNIFAC	$K_{L/G}$ = 0.42 EXP(# 1.07)	1
GCFEOS	$K_{L/G}$ = 0.43 EXP(# 1.0)	1

is the number of carbon atoms in the n-alkane.

UNIFAC and GCFEOS fit the lower molecular weight n-alkane's experimental data the closest and then diverge as the molecular weight increases. $K_{L/G}$ estimations for n-alkanes were quite acceptable for 100% Ethanol with the GCFEOS model giving somewhat better estimations. Figures 10 to 18 show how well the models estimate $K_{L/G}$ for n-alkanes in aqueous ethanol solutions. As previously mentioned, UNIFAC overestimated and GCFEOS underestimated the $K_{L/G}$. As the aqueous content of the liquid phase increased the estimation's deviations became greater. The uncertainty (9 to 67%, see Error analysis) of the experimental measurements is much smaller than the difference between the models and the experimental means. The experimental data relates well to the experimental data of Drozd et al. (1982) who measured $K_{L/G}$ for hexane,

heptane and octane in water. In the Figures data points attributed to Drozd et al. for n-alkanes larger than octane or smaller than hexane are extrapolated estimations. The data points at 100% ethanol and water attributed to PDD (Pierotti et al., 1959) are from that work's correlations. GCFEOS estimations were best for pentane to octane. The best estimations of UNIFAC converged at nonane and then diverged at higher molecular weights. Neither UNIFAC nor GCFEOS gave good estimations for Drozd et al.'s and Pierotti et al.'s n-alkane partition coefficients in water. An average of the UNIFAC and GCFEOS estimations
would result in estimations very close to the experimental data.

Aromas: Comparison of Estimated with Experimental $K_{L/G}$

Figures 19 to 31 compare the UNIFAC and GCFEOS $K_{L/G}$ estimations with experimental measurements for the 13 aromas measured in ethanol and aqueous ethanol. In general, the models estimated the hydrocarbon $K_{L/G}$ best followed by the acetates with some good estimations for the alcohols. Since the models estimate activity coefficients it is necessary to use the pure component vapor pressures of the aromas to calculate the partition coefficients. The uncertainty for some of the vapor pressures could range as high as 50% depending on how the vapor pressure was estimated. In particular, the vapor pressures for cis-3-Hexanol, Dimethylbenzylcarbinol, Diphenyloxide and τ-Undelactone have some of the largest probable errors. Figures 19 to 31 show all the experimental data points which demonstrates the range of the random uncertainty of the measurements. The systematic uncertainty is approximately 7.5% and the total uncertainty ranges from 9 to 67% depending on the aroma and liquid phase measured (see Error Analysis). Almost no other experimental data for the partitioning of these aromas was found in the literature. An experimental point was found for isoamylacetate and some estimations were made using PDD's correlations (Pierotti et al., 1959).

GCFEOS has both cyclic and aliphatic methyl groups. Calculations were made using both of these groups for the cyclic aroma molecules. In general, the calculations using the cyclic groups (c) showed a marked improvement over the aliphatic (a) results with the exception of methanol. In UNIFAC the best fit to the experimental diphenyloxide data was obtained using the secondary ether group as the ether group contribution and then using one less aromatic carbon group contribution (e.g. 10 aromatic CH, 1 aromatic C, 1 CHO). Eugenol is an example of a molecule containing multiple functional groups that challenges the group-contribution additive assumptions in both models. The eugenol molecule with its two munctional groups, aromatic ring and unsaturation has some stearic hindrance so that the behavior of the functional groups are different than if they were part of an mono-functional group aliphatic molecule. The Eugenol experimental data, although very weak, shows there may be large variations in the model's estimation ability.

Table 22 summarizes the fit of the UNIFAC and GCFEOS estimations with the experimental data using somewhat subjective criterea. Keeping in mind the potentially large vapor pressure uncertainties of some of the aromas, if the estimations matched the experimental data values within 50% over the whole ethanol mole fraction range then the estimation was judged to be 'good'. If the estimations followed the trend of the experimental data but had variations of up to an order of magnitude then the fit was judged to be satisfactory or 'O.K.'. If the estimations showed deviations larger than an order of magnitude or could not predict the shape of the experimental curve then the data was judged to be 'poor'. In cases where the experimental data was weak, such that no judgement of the estimations could be made, a question mark was assigned. In general where the model had a poor fit (deviations greater than one order of magnitude) the estimation in 100% ethanol was better than for the aqueous solutions. The 100% ethanol solution experimental data were also the most difficult to measure analytically and should contain the largest potential systematic errors.

Table 22. Aromas: $K_{L/G}$ Estimations versus Experimental at 25°C

Aroma	**UNIFAC**	**GCFEOS**
Isoamylacetate	Good/O.K.	Good/O.K.
d-Limonene	Good	Good
cis-3-Hexenol+	Good	Good
Camphor	Good	Poor
Linalylacetate	Good	Good
Menthol	Good	Poor
Citronellol	?	?
Dimethylbenzyl-carbinol+	Good	Poor
Phenylethylalcohol	Good	Good
Diphenylmethane	Good	Good
Diphenyloxide+	Good?	Good?
Eugenol	?	?
τ-Undelactone	?	?

+ = estimated vapor pressure used has potentially large errors.

Estimation of $K_{P/L}$ using UNIFAC and GCFEOS

n-Alkanes: Comparison of Estimations with Experimental $K_{P/L}$

Figure 50 shows the UNIFAC and GCFEOS estimations for n-alkane $K_{P/L}$'s compared to the limits of the experimental uncertainty for the measured $K_{P/L}$'s at 25°C. The limits of experimental uncertainty are defined here as two standard deviations, which are maximum standard deviations of the LDPE and HDPE $K_{P/L}$ measurements, combined in quadrature with the estimated systematic uncertainty plus or minus the values of the experimental data regression lines. The estimated values are calculated using the experimental weight and mole fractions. The liquid phase weight or mole fraction was calculated using the starting concentrations. The error created by doing this is negligible because the estimated activity coefficients are relatively insensitive to small changes in concentration in this concentration range. For example, UNIFAC estimated activity coefficients for tetradecane in 100% ethanol at 25°C decreased by .15% between mole fractions ranging from $1x10^{-7}$ to $1x10^{-4}$ and by 1.5% from $1x10^{-7}$ to $1x10^{-3}$. GCFEOS estimated the weight activity coefficients decreased by 0.01% between weight fractions ranging from $1x10^{-7}$ to $1x10^{-3}$ for tetradecane in 100% ethanol at 25°C. Similar observations were made for activity coefficient estimations for the polyethylenes.

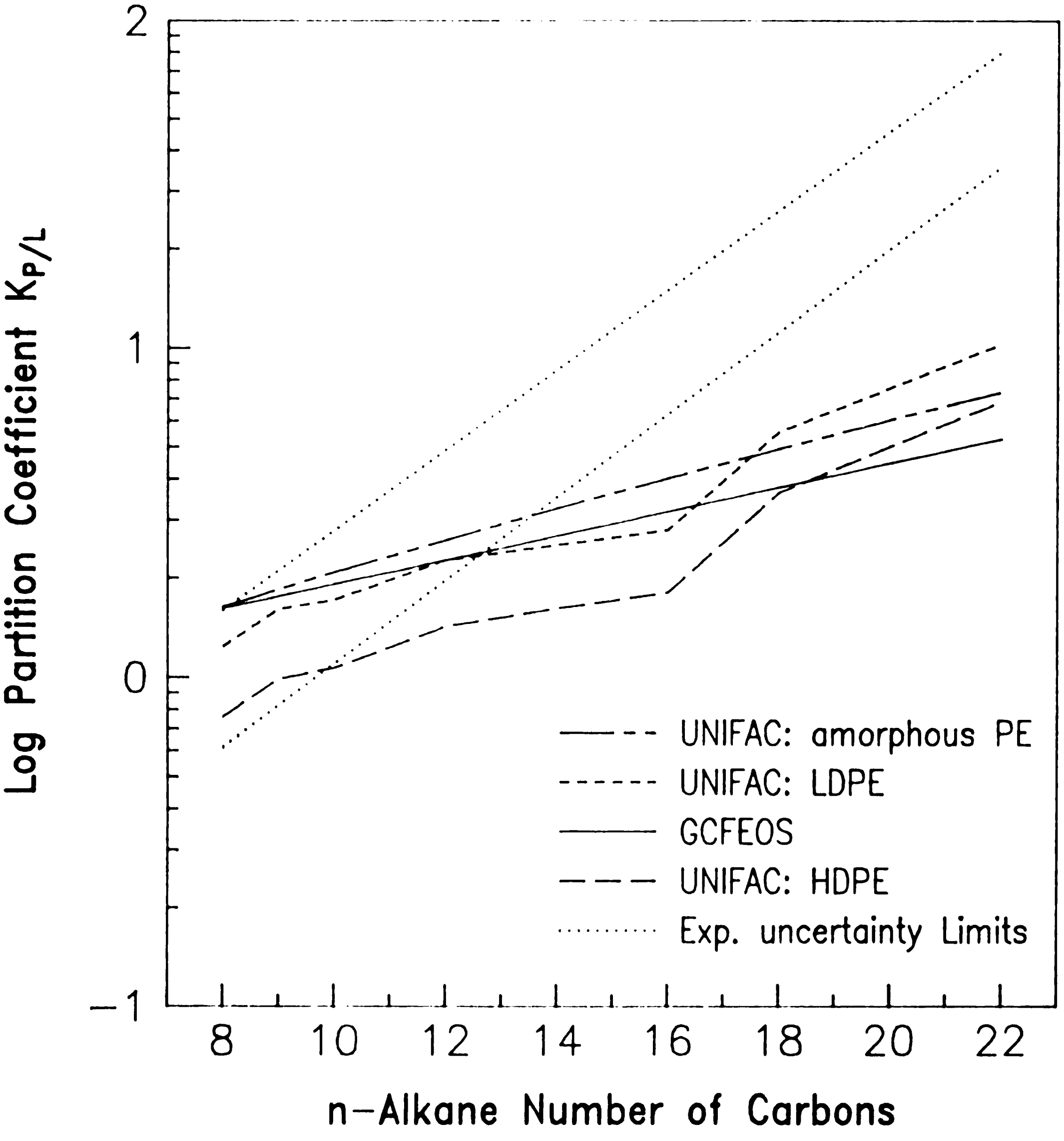


Figure 50. n-Alkanes/100% Ethanol: Estimated $K_{P/L}$ versus Experimental

The UNIFAC and GCFEOS weight activity coefficient estimations for tetradecane in HDPE at 25°C decreased by 3% and .19% between weight fractions ranging from 1×10^{-8} to 1×10^{-3}. The UNIFAC and GCFEOS estimations used in Figures 50 to 53 are given in Appendices D and E.

Figure 50 compares the effect of different polymer densities on the UNIFAC estimations. The UNIFAC free volume correction requires input of polymer density which is how the distinction between LDPE and HDPE is made in the method. Calculations using the density of amorphous polyethylene were compared to those using the semi-crystalline polymer densities. The amorphous density results are almost the same as if no free volume correction was used. The results show polymer activity coefficients decrease with decreasing density up to a limit where there is no free volume correction. GCFEOS requires no density inputs and thus makes no distinction between varying polymer crystallinities, assuming in affect that all polymers are amorphous.

The best $K_{P/L}$ estimations in 100% ethanol for both models are for n-alkanes in molecular weight up to dodecane (MW = 170.4) after which subsequent estimations for larger n-alkanes are underestimated and continue to diverge from the experimental data. The UNIFAC $K_{P/L}$ estimations for 75% ethanol in Figure 51 are comparable with the 100% ethanol

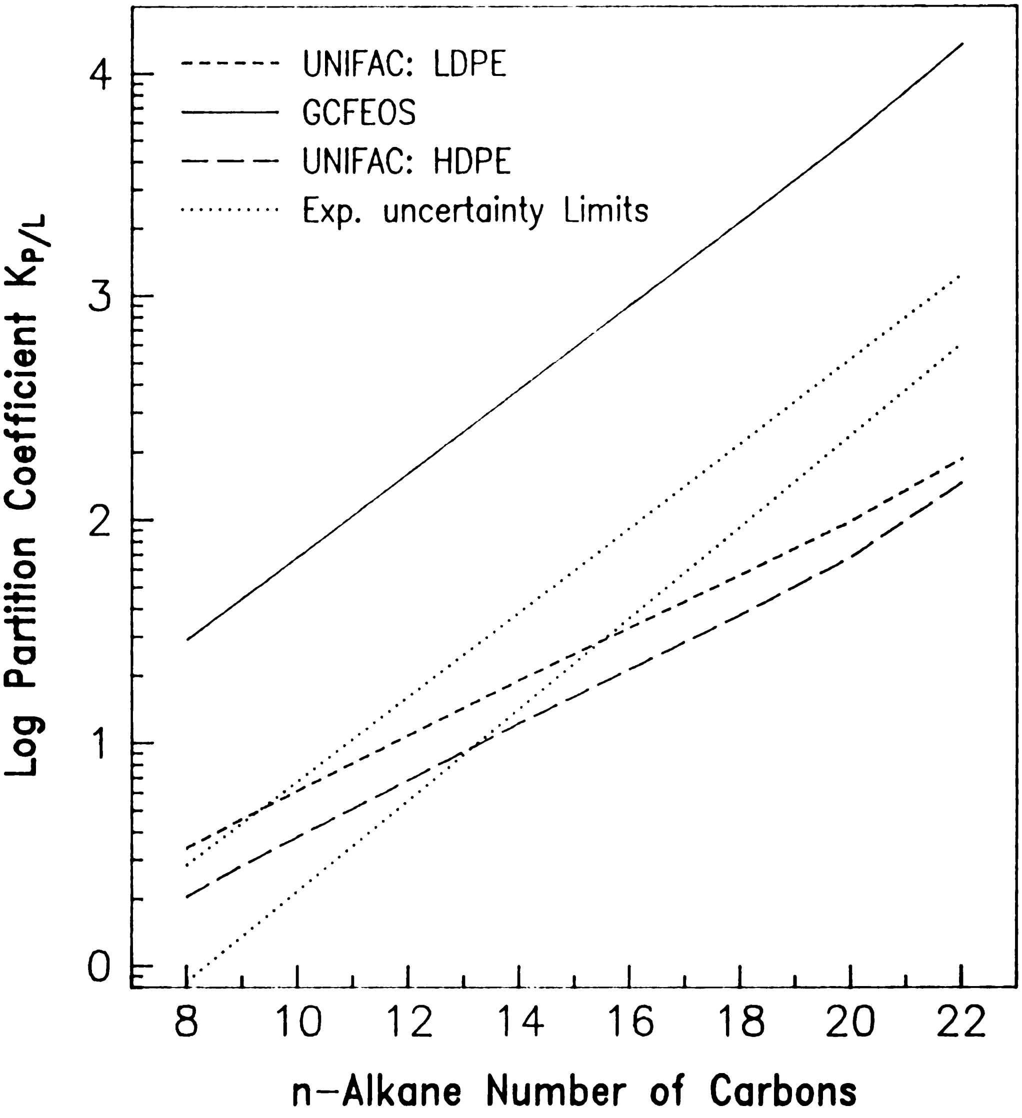


Figure 51. n-Alkanes/75% Ethanol: Estimated $K_{P/L}$ versus Experimental

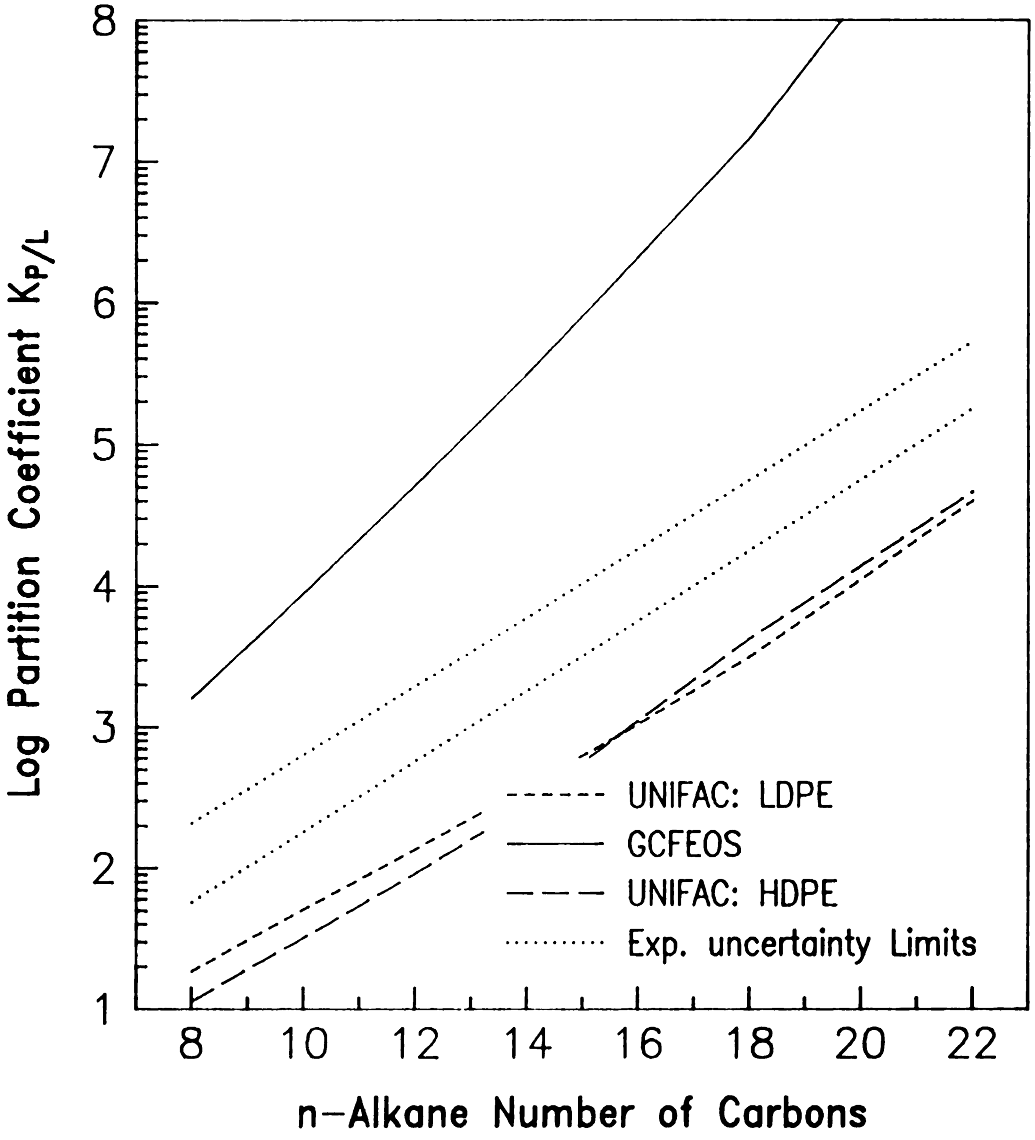


Figure 52. n-Alkanes/50% Ethanol: Estimated $K_{P/L}$ versus Experimental

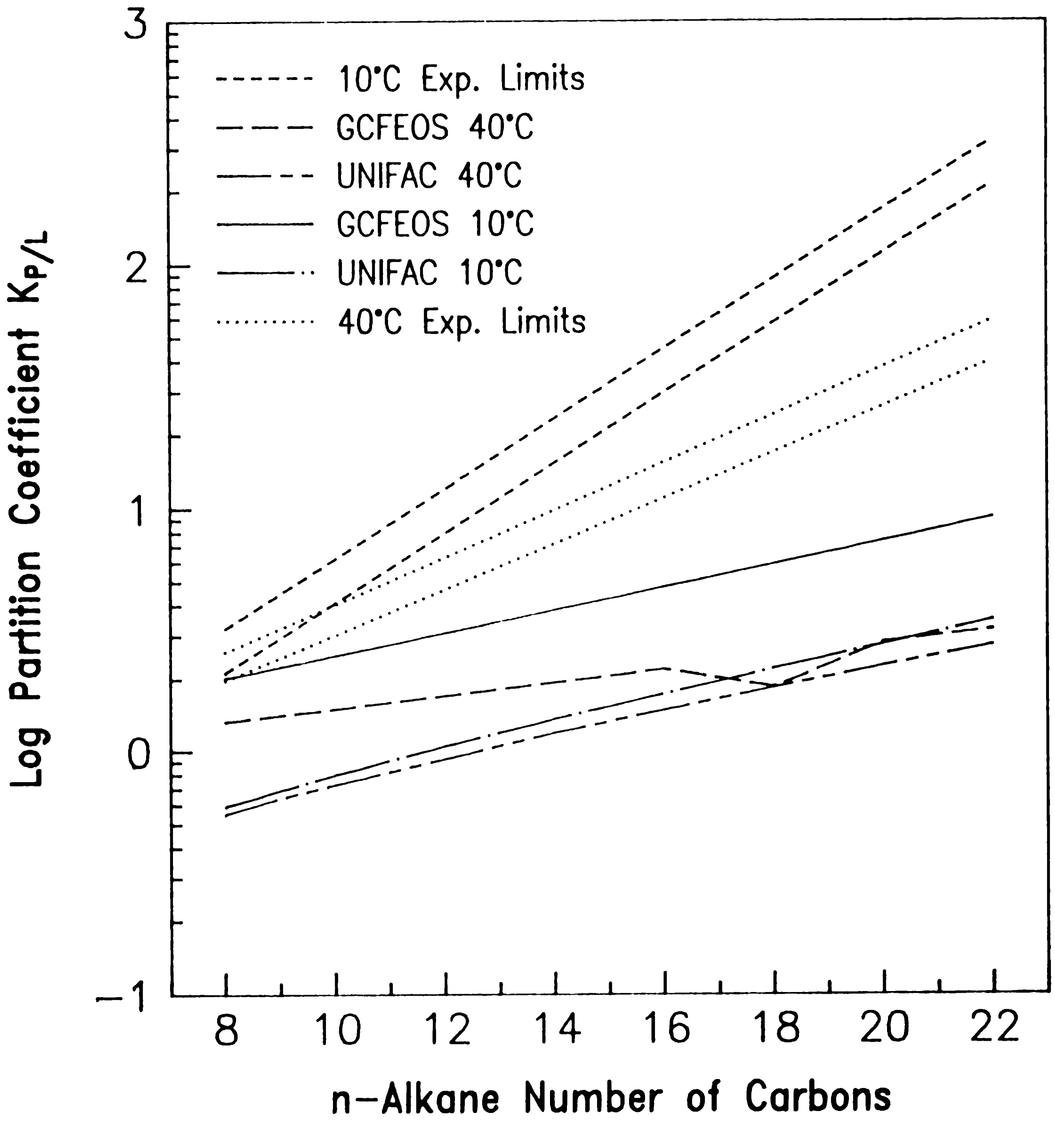


Figure 53. n-Alkanes/100% Ethanol: Estimated $K_{P/L}$ versus Experimental Variation with Temperature

results. GCFEOS overestimates the 75% ethanol experimental data by an order of magnitude but has a similar slope. The 50% ethanol $K_{P/L}$ data in Figure 52 were not estimated satisfactorily by either model. The UNIFAC model consistently underestimates the experimental data by 50% and GCFEOS overestimates octane by 90% and then becomes worse for the higher n-alkanes.

Figure 53 shows how well UNIFAC and GCFEOS estimate the partitioning of n-alkanes between 100% ethanol and HDPE at temperatures of 10°C and 40°C. Neither method estimated the experimental measurements quantitatively. The models showed the correct shifts in their estimations with temperature, GCFEOS had a better temperature effect estimation than UNFIAC. Agreement of their slopes with the experimental measurements were worse at 10°C than at 40°C.

Aromas: Comparison of Estimations with Experimental $K_{P/L}$

Figures 54 to 65 compare the UNIFAC and GCFEOS estimations with the experimental uncertainty limits for the 12 aromas. The limits of uncertainty are defined here as two standard deviations, of the maximum standard deviation from both the LDPE and HDPE $K_{P/L}$ measurements, combined in quadrature with the estimated systematic uncertainty plus or minus the average experimental value. Neither model is clearly better than the other for all aromas. Often, one

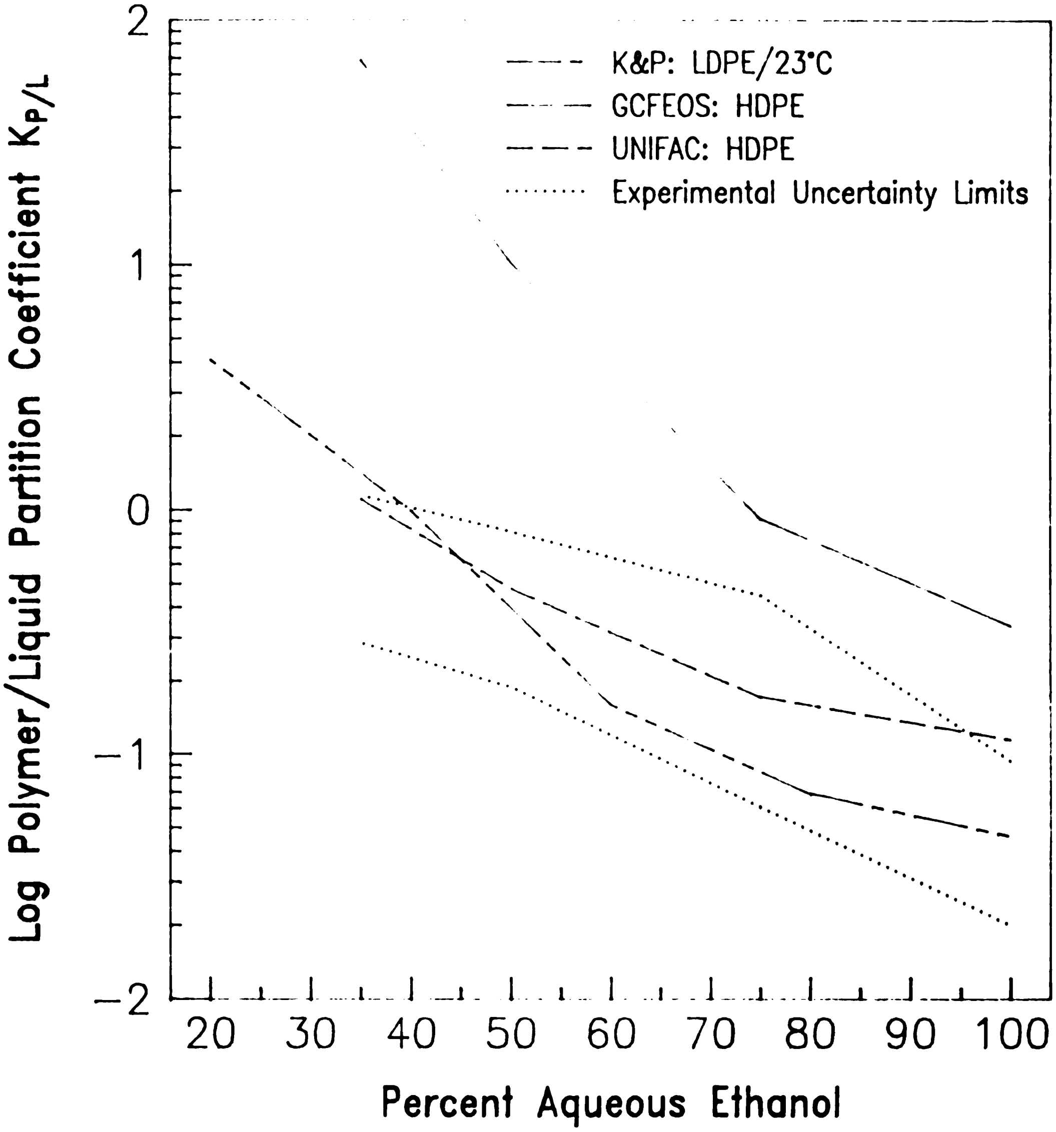


Figure 54. Isoamylacetate: Experimental $K_{P/L}$ versus Estimated

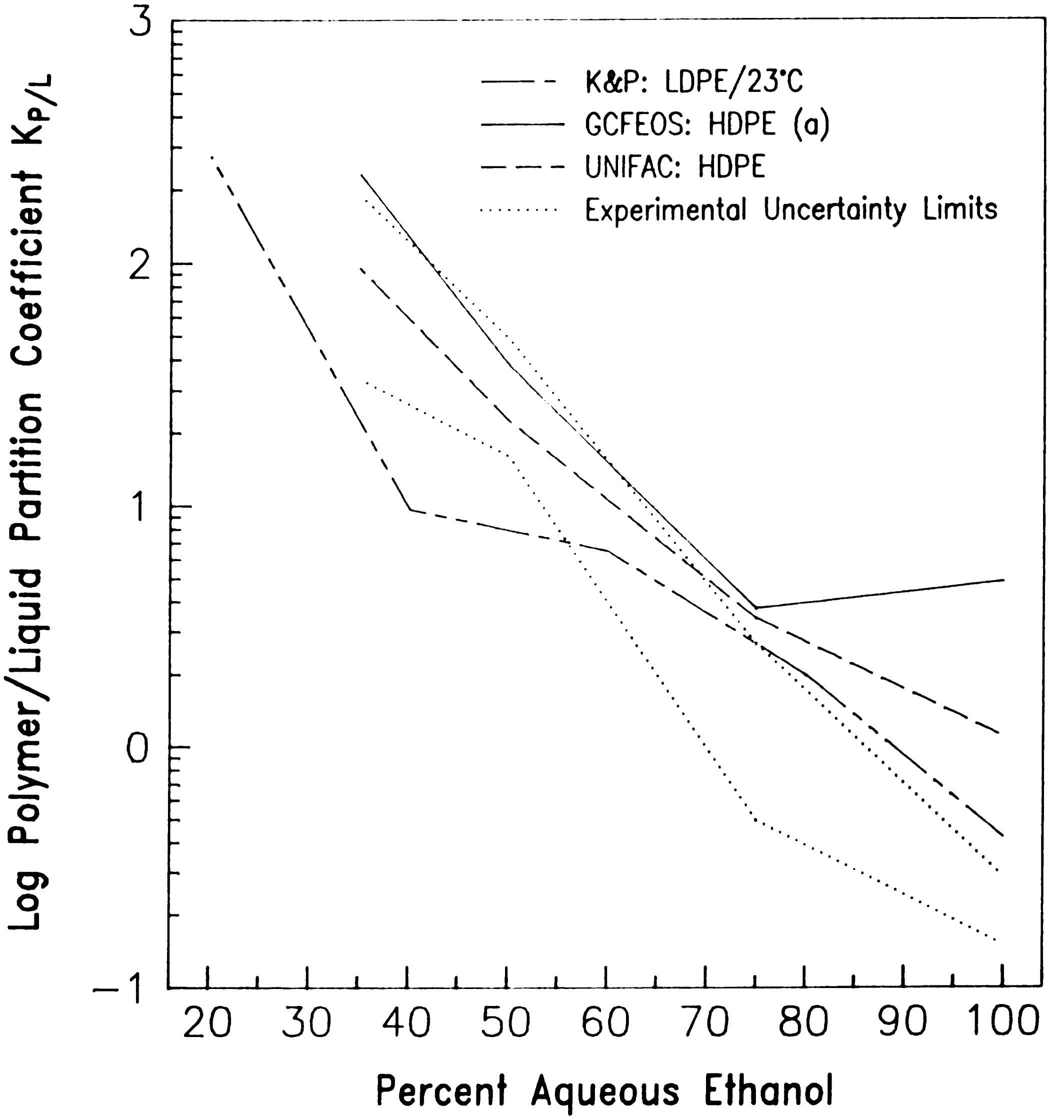
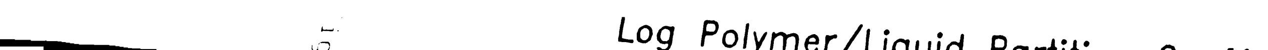


Figure 55. d-Limonene: Experimental $K_{P/L}$ versus Estimated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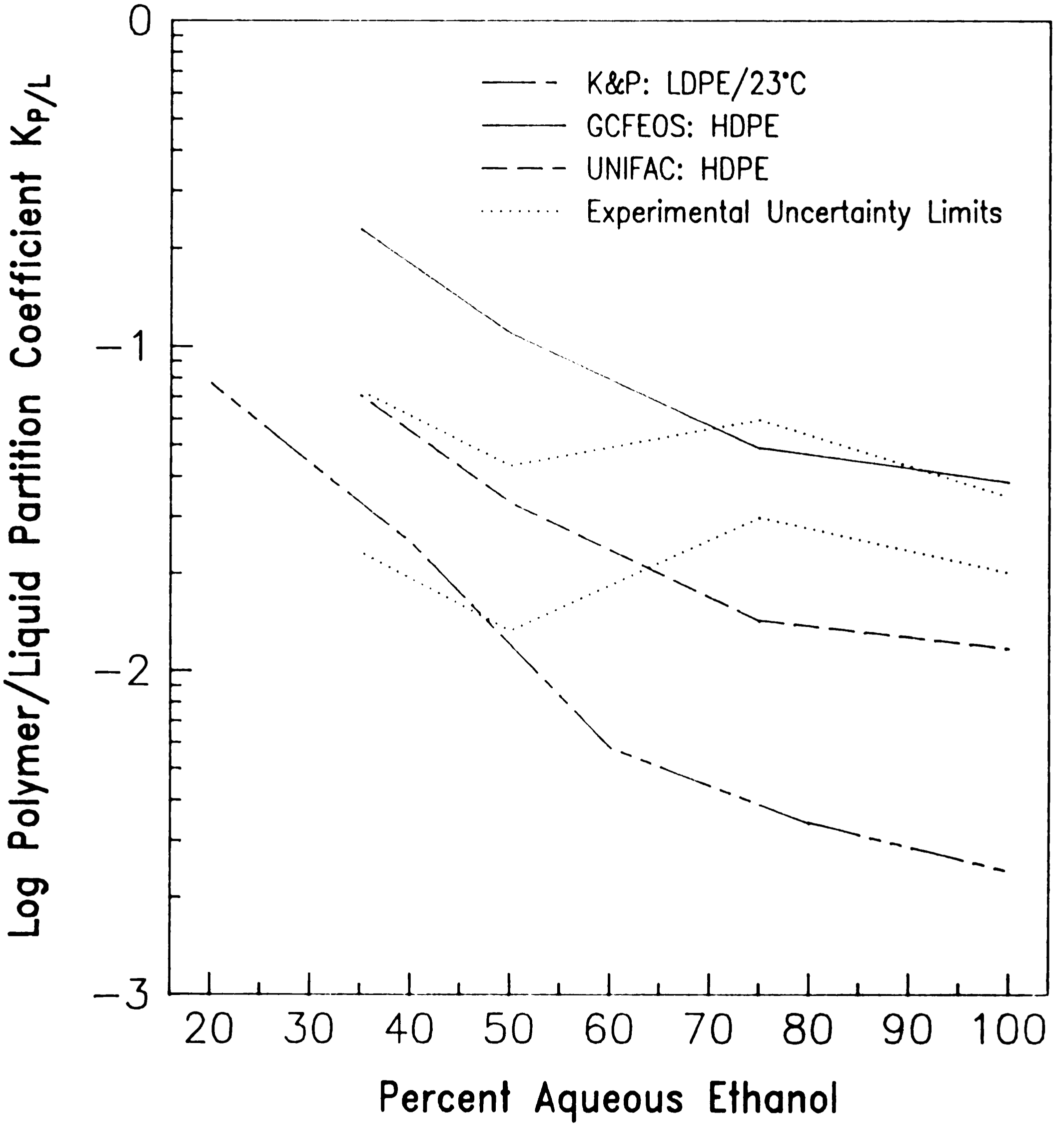

Figure 56. cis-3-Hexenol: Experimental $K_{P/L}$ versus Estimated

Log Polymer/Liquid Partition Coefficient $K_{P/}$

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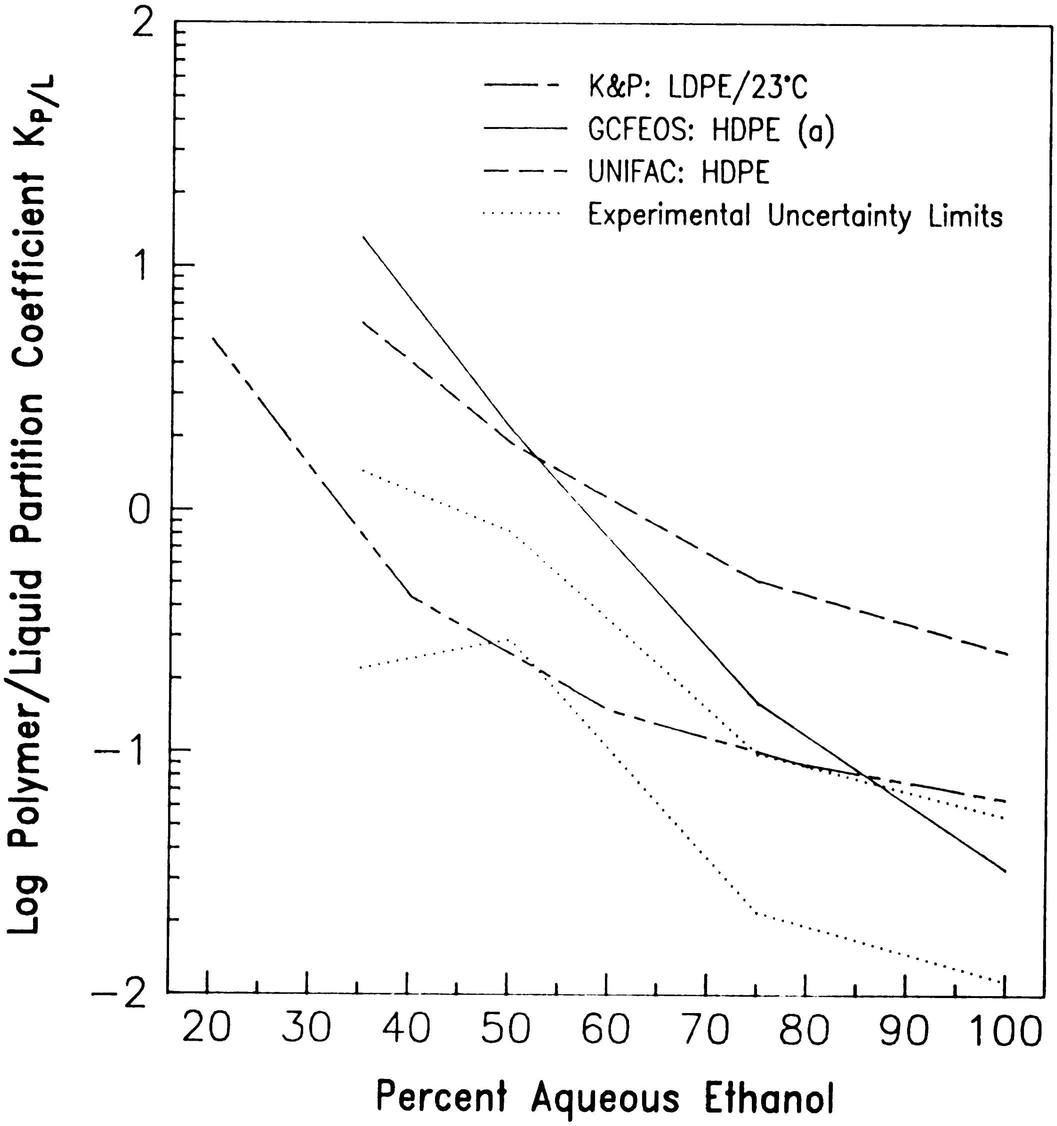

Figure 57. Camphor: Experimental $K_{P/L}$ versus Estimated


Log Polymer/Liquid Partition Coefficient $K_{P/L}$

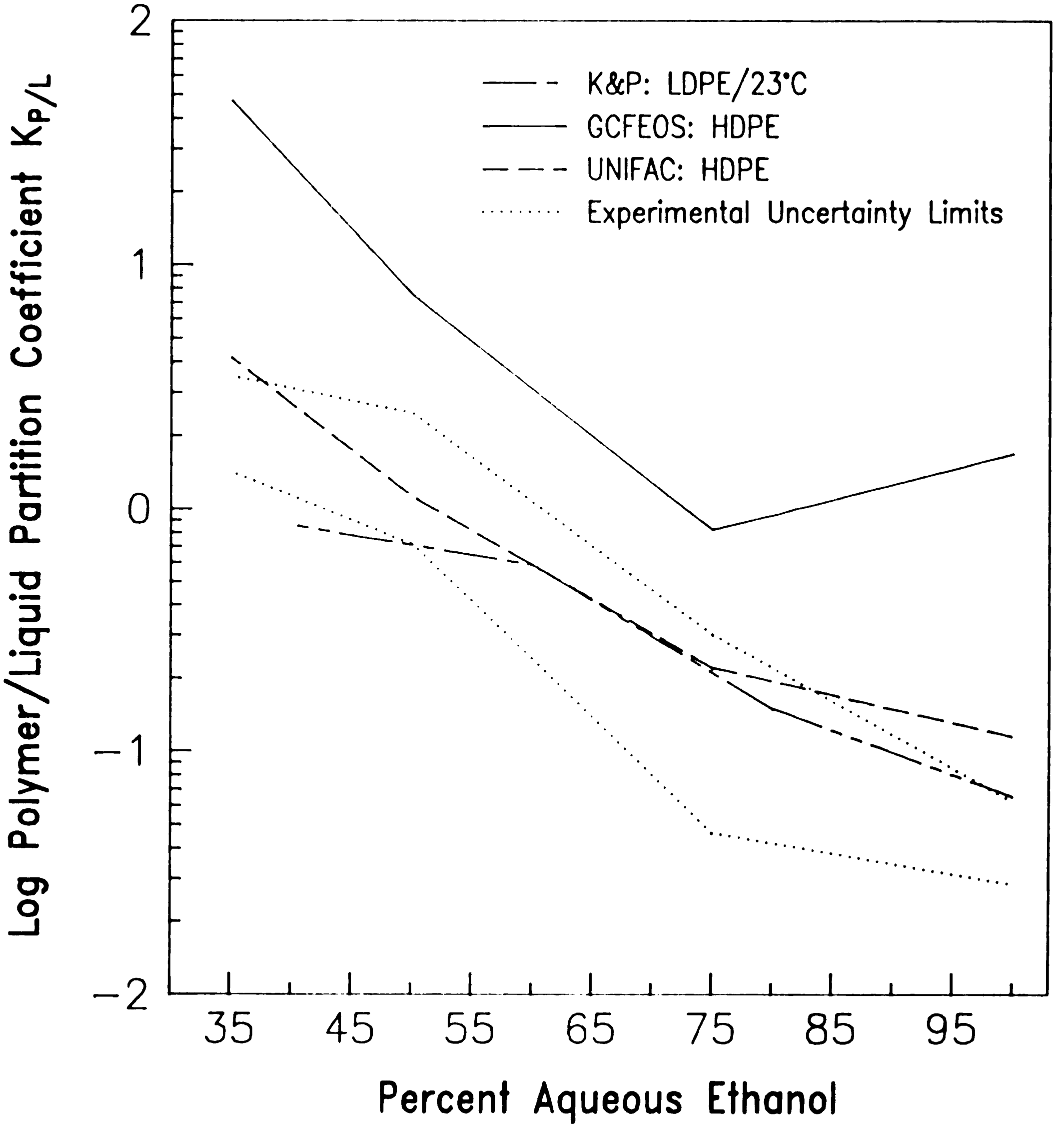

Figure 58. Linalylacetate: Experimental $K_{P/L}$ versus Experimental

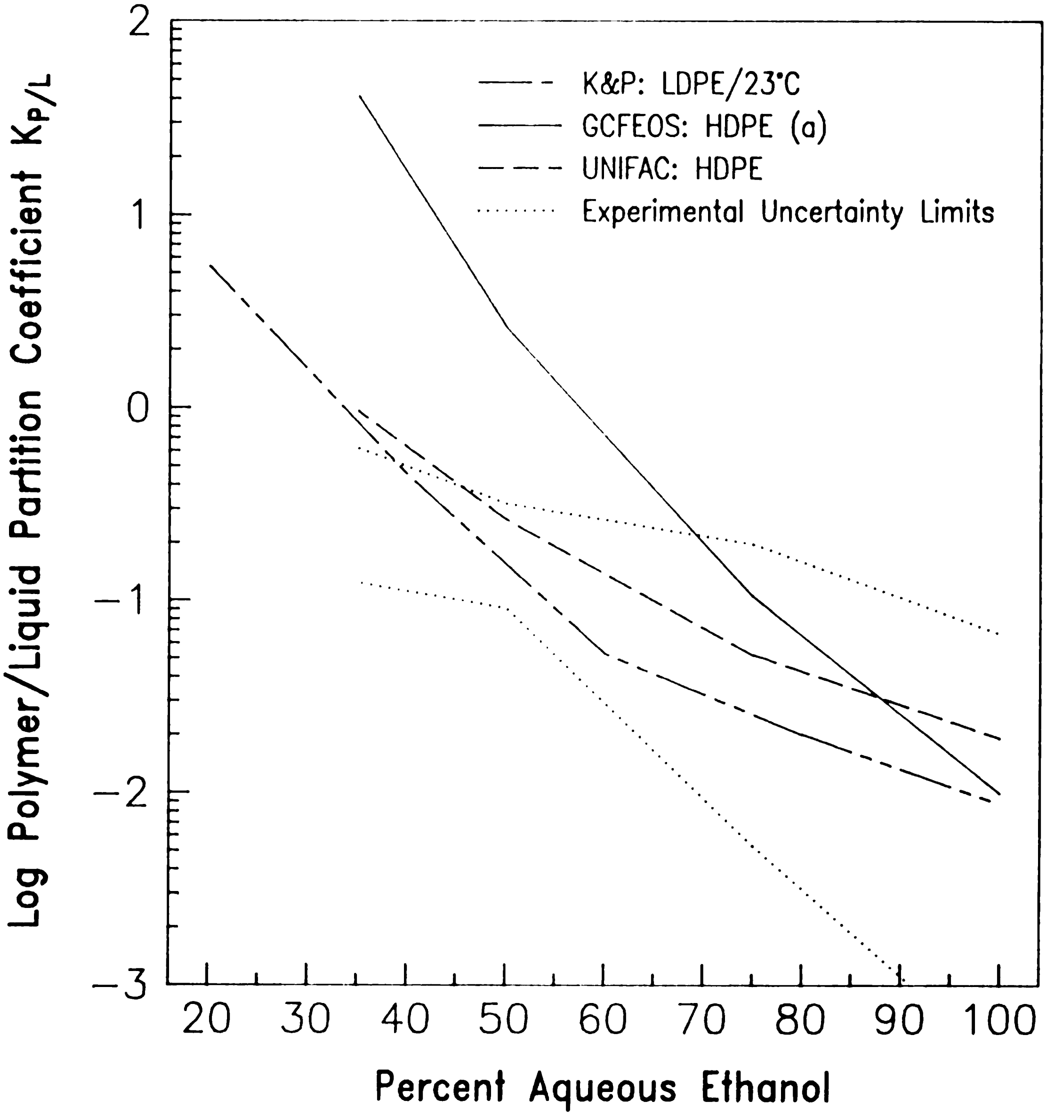

Figure 59. Menthol: Experimental $K_{P/L}$ versus Estimated

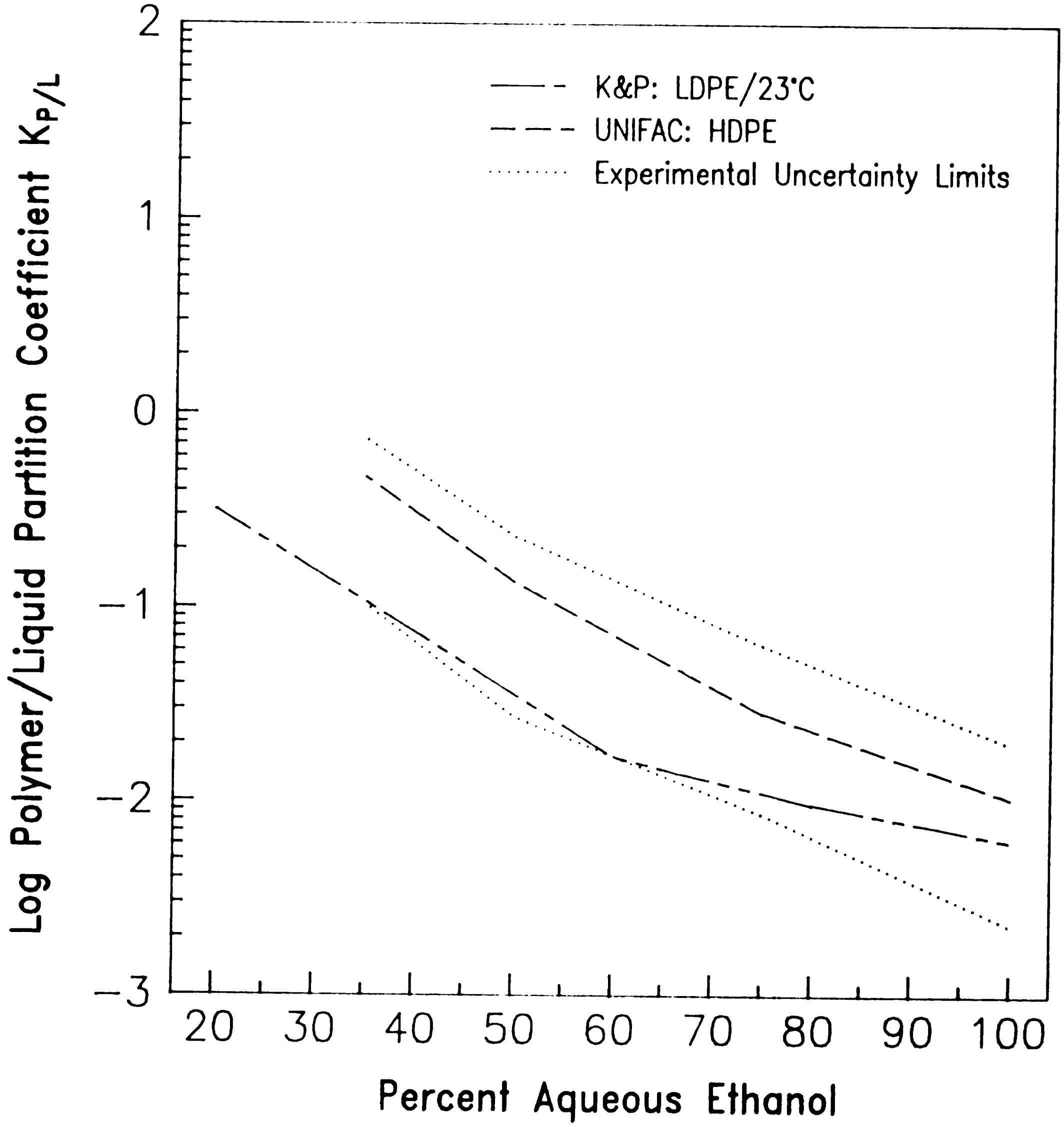

Figure 50. Dimethylbenzylcarbinol: Experimental $K_{P/L}$ versus Estimated

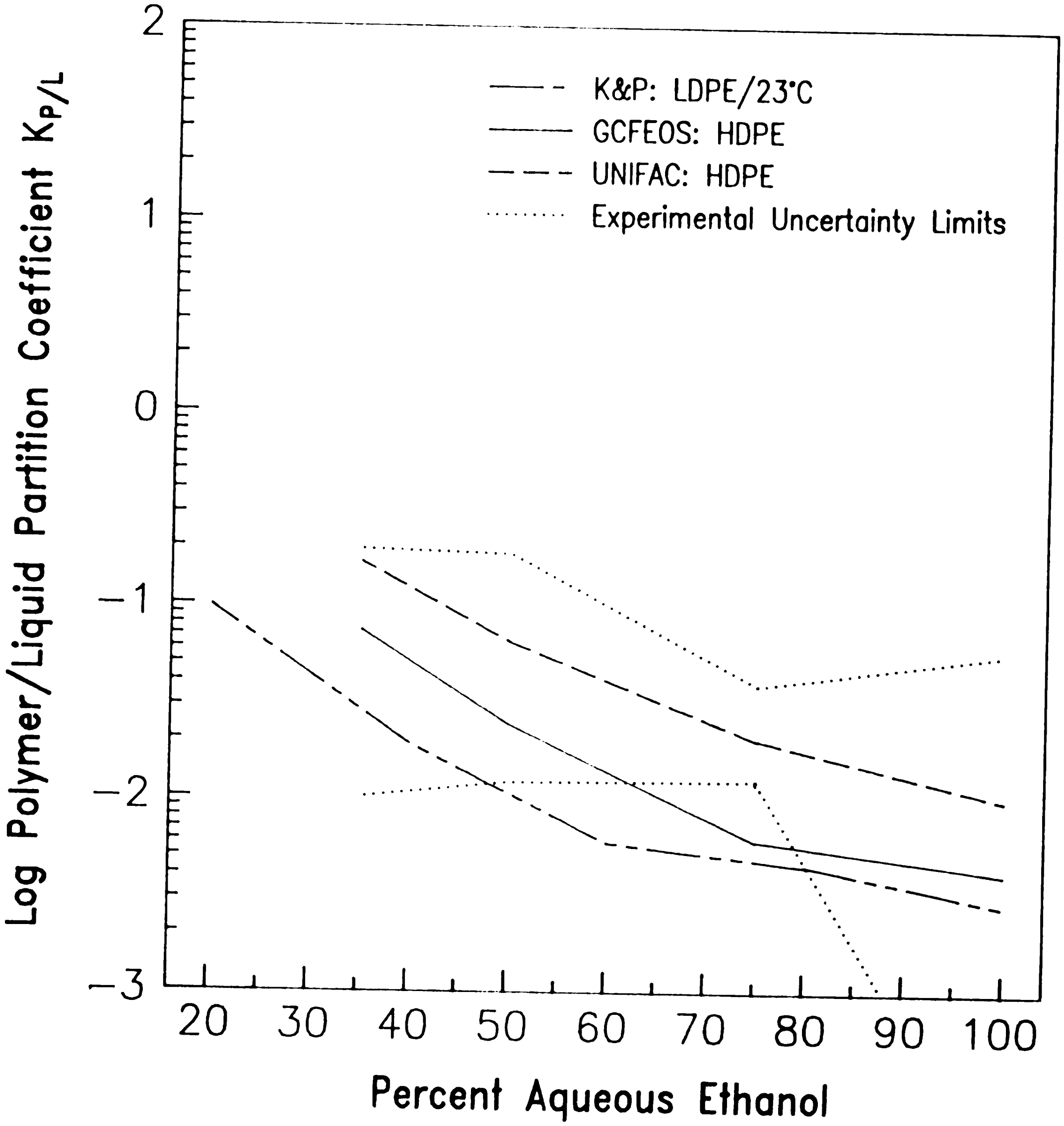

Figure 61. Phenylethylalcohol: Experimental $K_{P/L}$ versus Estimated

Partition Coefficient $K_{P/L}$

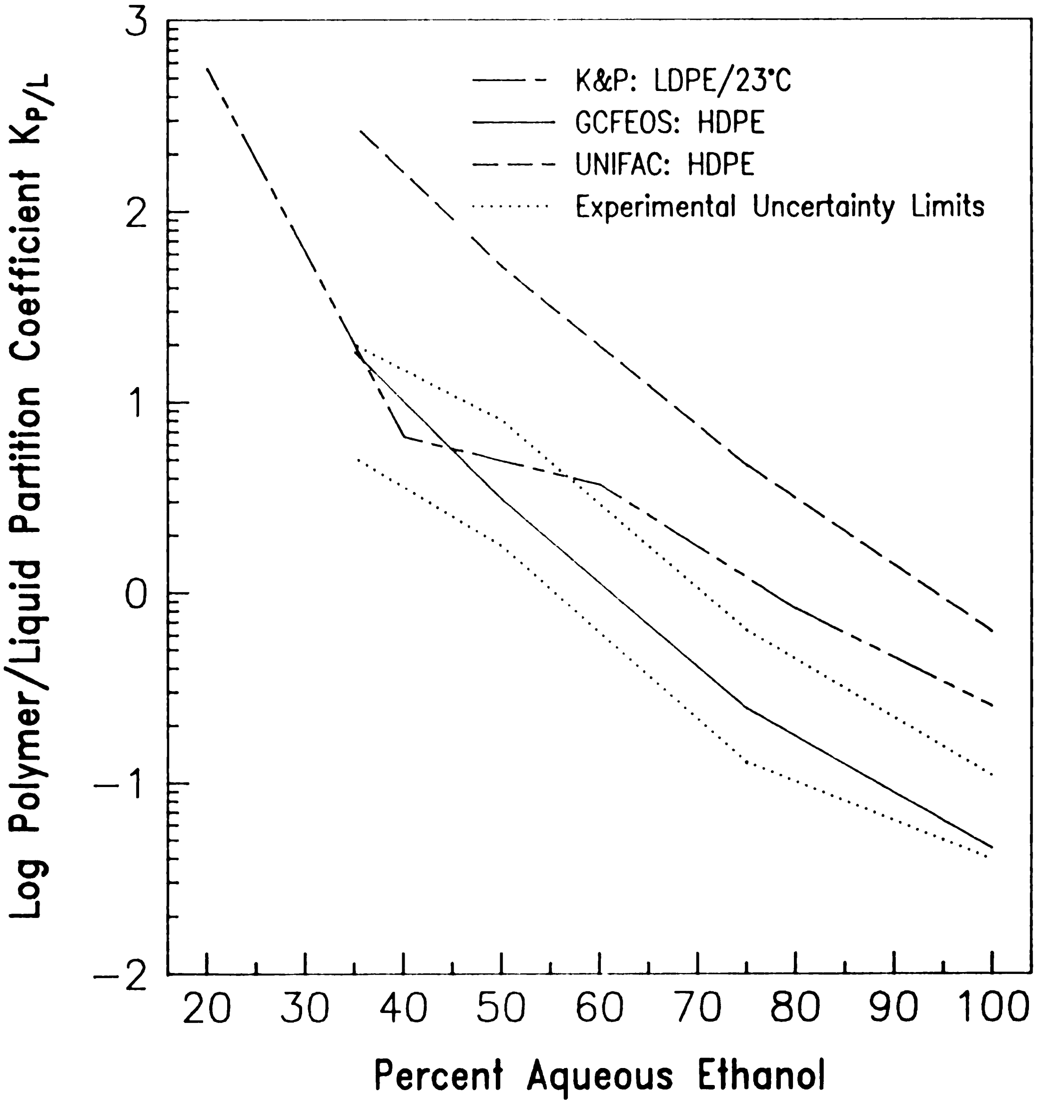

Figure 62. Diphenylmethane: Experimental $K_{P/L}$ versus Estimated

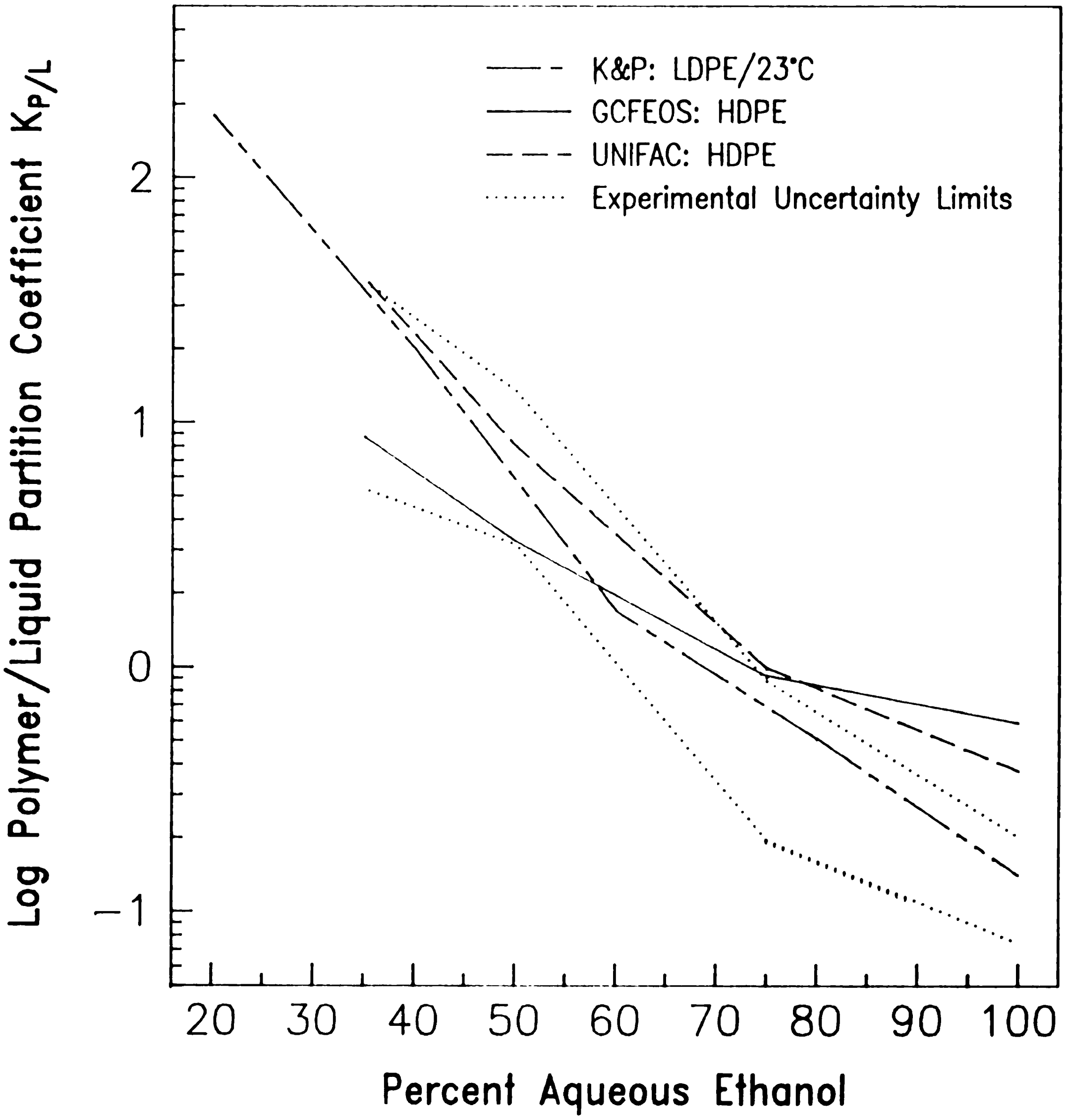

Figure 63. Diphenyloxide: Experimental $K_{P/L}$ versus Estimated

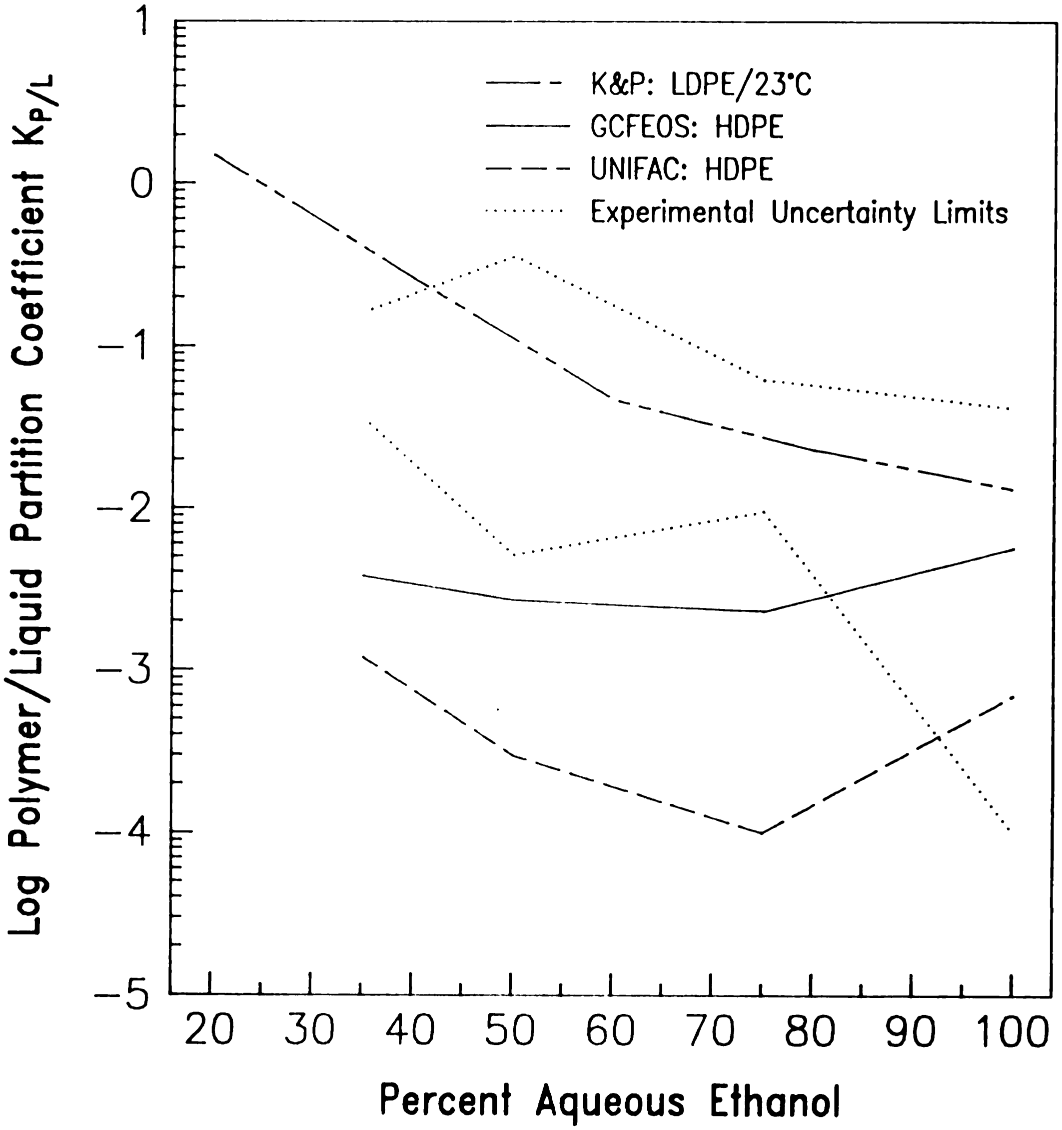

Figure 64. Eugenol: Experimental $K_{P/L}$ versus Estimated

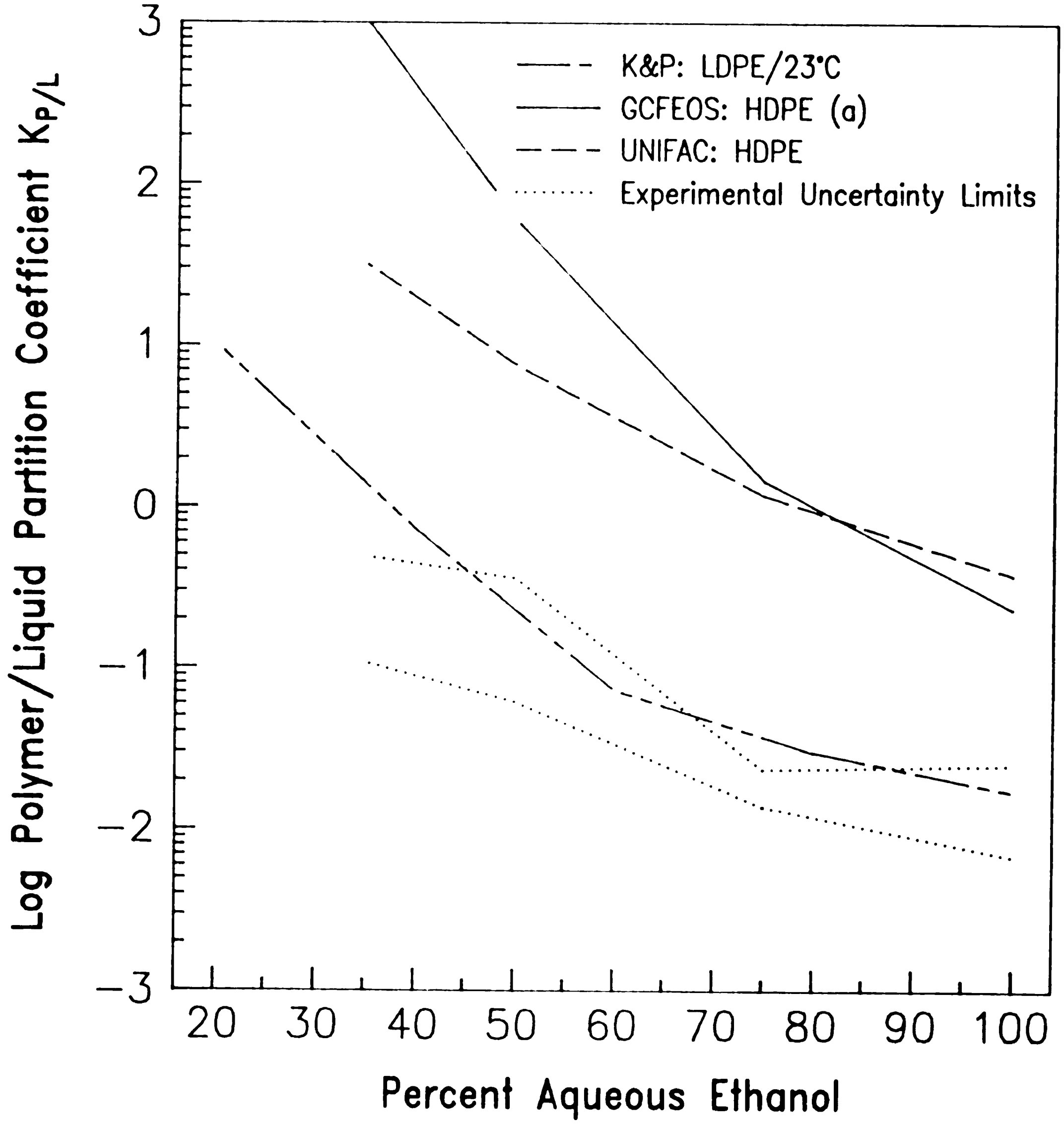

Figure 65. γ-Undelactone: Experimental $K_{P/L}$ versus Estimated

model predicts better than the other at one ethanol percentage but does not follow the variation in the $K_{P/L}$ over the whole ethanol range. The UNIFAC and GCFEOS estimations in Figures 54 to 65 are presented in Tables in Appendices D and E. Figures 54 to 65 also compare the experimental data with that from Koszinowski and Piringer (1989). With the exception of cis-3-hexenol and diphenylmethane there were no large discrepencies between their data and this data. The discrepency for cis-3-hexenol is likely an error in these measurements since the cis-3-hexanol liquid concentration used here is lower and the concentration of sorbed cis-3-hexanol was at the GC detection limit in the hexane extract. No explanation can be given for the diphenylmethane differences except there may be an analytical error in one of the measurement sets.

Table 23 summarizes Figures 54 to 65 by listing how well the estimations of the two models approximate the experimental data. A somewhat subjective grading system has been assigned the following meanings in Table 23: 'Excellent' means the estimations are within the measurement uncertianties over the whole ethanol range. 'Good' means the estimations are within the measurment certainties for over three quarters of the ethanol range. 'O.K.' means the estimations were within the measurement uncertainties for half of the ethanol range without any order of magnitude deviations. 'Fair' means the estimations were within the measurement uncertainties at one point or were outside the uncertainties but within 25% of the experimental uncertainties. Bad means the estimations were outside the measurement uncertainty limits over the range of ethanol solutions measured. A question mark (?) qualifies the observation that the experimental data may contain appreciable systematic measurement errors not taken into account here.

Table 23. Aromas: $K_{P/L}$ Estimations versus Experimental at 25°C

Aroma	**UNIFAC**	**GCFEOS**
Isoamylacetate	Good	Bad
d-Limonene	Good	Good
cis-3-Hexenol	Good?	Good?
Camphor	Bad	Fair
Linalylacetate	O.K.	Bad
Menthol	Good	O.K.
Dimethylbenzylcarbinol	Excellent	Bad
Phenylethylalcohol	Excellent	Good
Diphenylmethane	Bad	Excellent
Diphenyloxide	Good	Good
Eugenol	Fair?	Fair?
γ-Undelactone	Bad	Bad

The rankings in Table 22 for the $K_{L/G}$ and Table 23 for the $K_{P/L}$ do not correlate with one another for all aromas. UNIFAC correlated $K_{L/G}$ with the $K_{P/L}$ for all aromas except camphor, linalylacetate and diphenylmethane, GCFEOS correlates $K_{L/G}$ with $K_{P/L}$ for all except the acetates and dimethylbenzylcarbinol.

Each model appears to have specific strengths and weaknesses made apparent by these calculations. The GCFEOS model does not estimate the acetates well and gives an estimate for the activity coefficient of dimethylbenzylcarbinol in the polyethylenes that was many orders of magnitude too small. The GCFEOS model's cyclic (c) methyl group-contributions gave poorer $K_{P/L}$ estimations than the aliphatic groups (a). Therefore, the aliphatic estimations are used for d-limonene, camphor, menthol and τ-undelactone. Both models poorly estimated $K_{P/L}$'s for the complex ring stuctures of camphor and τ-undelactone but did better with the simple ring structres of menthol and d-limonene. The estimations for Eugenol with its multiple functional groups were the only aroma to have underestimated $K_{P/L}$'s. The poorest predictions for GCFEOS were usually for the 50% and 35% aqueous ethanol solutions.

Partition Coefficients of Aroma Compounds between Polyethylene and Aqueous Ethanol and Their Estimation Using UNIFAC and GCFEOS

By

Albert Lawrence Baner III

Volume II

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Food Science and Human Nutrition
and
Department of Agricultural Engineering

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Discussion

Experimental Results: Discussion of $K_{L/G}$ Method

The $K_{L/G}$ measurements show that the gas-stripping column method gives comparable results to other liquid/gas partition coefficient measurement methods. The results also show that mixtures of solutes in dilute solutions can be used in this method without significant interaction effects relative to the measurement uncertainties. This significantly reduces the work needed to measure a series of solutes. There are optimization parameters such as gas and liquid flow that must be optimized for the solutes being measured. The partition of solutes between the liquid and gas phase is determined mainly by the vapor pressure of the substance and its solubility in the liquid phase. It is advisable to select a series of solutes for use in a mixture which have similar vapor pressures and solubilites in the liquid phase (while still remaining separable analytically), so that they have similar partition coefficients. Solutes with widely varying partition coefficients cause analytical problems when one substance is minimally found in the gas trap while the other has saturated the solvent in the trap after a given measurement time period. Concentration effects appear to be negligible compared to the uncertainties of the measurements in dilute concentrations with mole fractions less than 1×10^{-4}.

Experimental Results: Significance of $K_{L/G}$ Data

$K_{L/G}$ partition coefficients for n-alkanes between aqueous ethanol solutions and nitrogen have not been found to be previously reported in the literature. Also the $K_{L/G}$ data for the 13 aromas in 100% ethanol and aqueous ethanol solutions have not been previously reported in the literature.

Experimental Results: $K_{P/L}$ Measurement Method

Polymer/Liquid partition coefficients for n-alkanes (C8-C22) and 12 different aromas partitioning between polyethylenes and ethanol/aqueous ethanol liquid phases in the dilute concentration range ($x_i < 1 \times 10^{-4}$) have been measured using an equilibrium sorption technique. The use of mixtures of solutes in the dilute concentration range produced no significant errors within the measurement uncertainty of the method. The use of mixtures allows a significant reduction in the number of samples needed for $K_{P/L}$ measurements with many solutes. When selecting mixtures the solutes should be grouped together based on their expected partitioning behavior to allow optimization of the extraction step. This means using less extraction

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solvent for solutes with small partition coefficients and using more extraction solvent for solutes with large partition coefficients. It may be necessary to increase initial liquid phase concentrations of solutes with extremely small partition coefficients to increase the relative amount sorbed in the polymer so it can be better measured.

Surface effects were also tested and found to be insignificant relative to the uncertainty of the method. Sorption experiments therefore can use as large a surface area of polymer to volume of solution ratio as the method allows in order to increase measurement sensitivity for solutes with low partition coefficients. The surface effects test may not have detected these since the same polymer surface area to mass ratio was used in the tests. A better test would be to use the same polymer material but with varying thicknesses so that different surface area to mass ratios are tested.

Significant concentration effects were observed for n-alkanes partitioning between HDPE and 100% ethanol, however, the experimental data for aromas agrees (within the experimental uncertainty) with the data of Koszinowski and Piringer (1989) using the same technique at concentrations up to 10 - 20 times higher (0.1-2% w/w = greater than 800 ppm (μg/ml)). The lack of significant

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surface effects and interactions with mixtures of solutes lends greater credibility to the data published by others using similar equilibrium sorption techniques with ethanol/aqueous ethanol liquid phases (Becker et al., 1983, Koszinowski and Piringer, 1989 and 1990). These conclusions may not necessarily apply to pure aqueous solutions.

The results from the surface effects test justify the analytical advantages of increasing the polymer surface area to liquid volume without effecting the $K_{P/L}$. Furthermore, the volume of hexane used in the extraction step should be as small as possible relative to the polymer weight, and which will still allow effective extraction of the polymer in order to reach a high enough concentration to detect with GC. cis-3-Hexenol had such a small partition coefficient that the polymer extract aroma concentration of the aroma was below the GC detection limit and thus its detection limit could benefit from using a smaller hexane extraction volume.

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Experimental Results: Significance of $K_{P/L}$ Measurements.

$K_{P/L}$ Temperature Dependence

One of the most significant contributions of these $K_{P/L}$ data is derived from the study of the effects of temperature. Until now, this has only been done for solubility coefficients calculated indirectly from permeation experiments using the measured permeability and calculated diffusion coefficients. Polymer/liquid partition coefficient temperature differences between 25°C and 40°C were shown to be insignificant for all n-alkanes and aromas. Temperature differences between 10°C and 25°C (and 40°C) were significant for the n-alkanes but show no significant differences within the measurement uncertainties for the aromas. For practical purposes, the $K_{P/L}$'s for aromas between polyethlylenes and ethanol/aqueous ethanol solutions in a temperature range between 10°C and 40°C are essentially constant. The temperature effects are a mixture of concurrent effects between the solubility of the solute in the liquid phase and that in the polymer phase. This finding when applied to partition data for other solutes in the literature considerably increases their utility because they are not likely to show similar temperature behavior.

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Effect of Polymer Crystallinity on $K_{P/L}$

There were no polymer crystallinity effects observed between the LDPE and HDPE that were greater than the uncertainty of the measurements. This observation appears to be contrary to the conclusions of Ikegami et al. (1987) for distribution ratios (μL film / μL liquid) in package systems containing polyethylenes of varying crystallinities. However, the data presented by Ikegami et al. has no supporting statistics and the magnitude of the measurement uncertainty is not given. It is possible that with better control of the systematic errors through tighter analytical procedures (e.g. greater numbers of GC injections and smaller calibration uncertainties) that a significant difference could be observed here. However, a counter-argument pertinent to the effect of crystallinity on sorption and partitioning can be made. Sorption in the polymer is largely an interactive thermodynamic process which is determined by the chemical nature of the solute and the polymer. Whether or not the polymer is in a semi-crystalline or crystalline form does not change the polymer chemical environment that a solute molecule sees.

If anything one could speculate, crystallinity increases the density of polymer chain packing and increases the intensity of the chemical attraction per volume of polymer. This is perhaps the only explanation for why the HDPE n-

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alkane partition coefficients are larger than those for LDPE in Figures 32-34 and Table 15. Table 15 shows that the concentration of dodecane in the polymer is low enough to be considered infinitely dilute which would rule out concentration effects. Surface effects could be involved in these differences because HDPE and LDPE had different thicknesses (100μm versus 50μm) been used. Surface effects in PE are likely to be due to oxidation which increases the polarity of the polymer surface which would thus decrease the partitioning of the non-polar n-alkanes into the LDPE since it has a higher surface area to mass ratio than the HDPE. The partitioning of the polar aroma compounds showed similar behavior to the n-alkanes. The increased partitioning and sorption in the HDPE compared to LDPE is opposite of the widely observed phenomena that less sorption occurs with higher polymer crystallinity (Rogers et al. 1960, Shimoda et al, 1988).

It should be pointed out that the effect of polymer crystallinity is most significant for kinetic type parameters such as permeation and diffusion. Becker et al. (1983), Koszinowski (1986a) and Koszinowski and Piringer (1989) have also observed that polyethylene crystallinity had little or no effect on the polymer/liquid partition coefficients.

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Rogers et al. (1960) and others have seen effects of polymer crystallinity on the sorption of organic solutes in polymers which were not observed in this study. The measurements by Rogers et al. may be valid only for low molecular weight solutes, (up to MW = 114 for Octane) however the more likely reason is that crystalline effects were dependent on the solute concentrations in the polymer. The measurements in this study were carried out at very dilute concentrations. The highest average weight concentrations measured were for the n-alkanes which partitioned into HDPE and ranged from $1x10^{-5}$ to $2x10^{-4}$ for the 100% ethanol liquid phase and from $3x10^{-4}$ to 0.1 (which is no longer inifitely dilute) for the 50% ethanol phase. The relatively high concentrations of n-alkanes which partitioned into the polymer may in part help explain the differences seen between LDPE and HDPE $K_{P/L}$. The aromas reached a maximum weight fraction of 0.01 for d-limonene in the 35% aqueous ethanol solution and a minimum of $7x10^{-7}$ for cis-3-hexenol in the 100% ethanol solution in HDPE. The low aroma compound polymer concentrations may be a possible reason as to why there was practicaly no difference between LDPE and HDPE $K_{P/L}$'s.

The solute weight fraction in polymer for the solubility correlations in Rogers et al. (1960) are greater than 0.01. In the concentration range measured by Rogers et al. it is likely that swelling of the polymer matrix began to occur and that the effect of crystallinity becomes important as the crystals in the polymer matrix restrain swelling of the matrix and thus sorption of the solute. The polymer/liquid partition data for two polyethylenes with crystallinities of 0.26 (LDPE) and 0.58 (HDPE) (determined by DSC) showed no significant crystalline effect in the partitioning of dilute solutions of n-alkanes or the aromas at 25°C. $K_{P/L}$'s calculated by Koszinowski (1986a) from permeation and diffusion measurements of n-alkanes in 100% ethanol at 23°C for the same LDPE and HDPE films also showed no significant crystallinity effects. To test this further, a polymer/gas partition coefficient was calculated for d-Limonene to be 6900 at a concentration in nitrogen of 0.3 ppm (μg/mL) and a weight fraction of 0.0022 in a HDPE structure (derived from gravimetric data in Mohney et al. (1988)). Calculated $K_{P/G}$'s from UNIFAC and from GCFEOS which assume no polymer crystalline effects were 9274 and 3532. These results suggest that the effect of polymer crystallinity on the sorption of solutes is important only at relatively high concentrations of sorbed solutes ($w(i) > 0.01$). At dilute solute concentrations ($w(i) = 0.0001$) in the polymer, crystalline effects can be assumed to be insignificant.

The semi-crystalline UNIFAC correction factor for polyethylene (Doong and Ho, 1991) was applied by them to high concentrations of aromatic hydrocarbons with molecular weights up to 140. The weight fractions of solute in the polymer in this research were 10 to 100 times smaller than the lowest weight fraction measured by Dong and Ho. Their semi-crystalline correction factor does not apply here since no significant crystalline effects were found in the experimental data.

Effect of System Components on $K_{P/L}$

The most significant experimental effects observed for the $K_{P/L}$ measurements were due to the liquid phase, the nature of the solute molecule's functional groups and the solute's molecular weight and shape. Becker et al. (1983), and Koszinowski and Piringer (1989, 1990) have also made similar observations for partitioning between different polymers and methanol, ethanol, ethanol and water, and aqueous foods. The logarithmic variation of $K_{P/L}$ with n-alkane homologous series between LDPE and aqueous ethanol solvents has also been observed by Koszinowski and Piringer (1989).

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UNIFAC and GCFEOS $K_{P/L}$ Estimations

UNIFAC and GCFEOS $K_{P/L}$ Estimations: Significance of Calculations

The application of UNIFAC and GCFEOS activity coefficient estimations for calculating partition coefficients in polymer/liquid systems has not been previously reported. Furthermore, UNIFAC and GCFEOS have not previously been used for estimating activity coefficients of molecules other than low molecular weight solvents. In general the UNIFAC and GCFEOS models were found to be qualitatively correct with their $K_{L/G}$ and $K_{P/L}$ estimations. The models were able to distinguish between the behavior of solutes with different functional groups in the ethanol and aqueous ethanol phases. The models correctly predicted that $K_{P/L}$ increases with increasing aqueous content and they show correct shifts in their estimations with temperature. UNIFAC and GCFEOS do not take into consideration the effect of polymer crystallinity on activity estimations, for dilute concentrations this is correct. The effect (or in this case the non-effect) of polymer crystallinity on the estimated activity coefficients of these models has not been discussed in the literature. UNIFAC and GCFEOS have only been tested for low molecular weight hydrocarbon solvents in polyethylene (Chen et al., 1990, Doong and Ho, 1991).

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The models show varying degrees of success in quantitatively estimating the partitioning of solutes between the ethanol liquid phases and the polyethylenes. The advantage in estimating partition coefficients with these models is that they are essentially a ratio of estimated activity coefficients. Even though the models may make quantitatively poor activity coefficient estimations the qualitative relationships are correct so that the poor quantitative effects are lessened or offset in the ratios of the two activity coefficients.

The experimental data presented here is in the very dilute or infinitely dilute concentration range. Infinitely dilute concentrations are loosely defined in the literature to be the concentration where a solute molecule 'sees' only solvent molecules and is dependent on the nature of the solute and solvent. In the literature, solutions are generally referred to as infinitely dilute at mole fractions below 1×10^{-4} for solutions containing associating species (e.g. hydrogen bonding, dimerization) (Alessi et al., 1991). The infinite dilution range represents the maximum deviation from ideal solution behavior for most binary systems (except for associating systems). These estimations then represent the limits of the activity coefficient estimations for these models and in this concentration range the model's are often less accurate. This is especially true for UNIFAC because the

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combinatorial term is known to give questionble estimations at dilute concentrations, especially for mixtures of molecules very different in size (Weidlich and Gmehling, 1987). This data, in the dilute concentration region, is then a severe test for the UNIFAC and GCFEOS methods.

Significance of n-Alkane $K_{P/L}$ Estimations

The n-alkanes, because they are a homologous series and are non-polar enable characterization of the behavior of UNIFAC and GCFEOS over a large molecular weight range. The n-alkanes are at one extreme of the partition interactions studied and represent the upper limits for partition coefficients for these liquid/polymer systems. The n-alkanes are practically insoluble in polar ethanol and aqueous ethanol liquid phases compared to the non-polar polyethylene polymer phase and thus partition heavily into the polymer phase. The activity coefficients of the n-alkanes in the polyethylenes have the smallest estimated activity coefficients of all solutes and their liquid activity coefficients were the largest estimated by the models.

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UNIFAC: n-Alkane $K_{P/L}$ Estimations

UNIFAC overestimates the liquid/gas partition coefficients for the n-alkanes. If the polymer/liquid partition coefficients are calculated using Eq 23b:

$$K_{P/L} = K_{P/G} / K_{L/G} \qquad (23b)$$

It then follows that the predicted $K_{P/L}$ will be too small if $K_{L/G}$ is overestimated. The overestimation of $K_{L/G}$, for n-alkanes by UNIFAC becomes worse as the aqueous content of the liquid phase increases. However, there is also a second effect coming from the estimated $K_{P/G}$ partition coefficient. If the experimental $K_{L/G}$ is multiplied by the experimental $K_{P/L}$ then an estimate of an 'experimental' $K_{P/G}$ is obtained. In Table 24 this experimental $K_{P/G}$ is compared to the UNIFAC estimated $K_{P/G}$. The table shows that the UNIFAC $K_{P/G}$ estimations are also contributing to the UNIFAC $K_{P/L}$ estimation error.

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Table 24. n-Alkane: Comparison of Experimental $K_{P/G}$ with UNIFAC at 25°C

n-alkane	$K_{P/G}$ 'Exp'	$K_{P/G}$ UNIFAC	Ratio UNIFAC/'Exp'
C8	2123	970	.457
C9	7714	2913	.378
C10	28022	8678	.310
C12	369808	77321	.209
C14	4.88E6	704638	.144
C16	6.44E7	6.36E6	.0988
C18	8.50E8	5.80E7	.0682
C20	1.12E10	5.31E8	.0473
C22	1.48E11	4.86E9	.0328

The accuracy of the estimated $K_{P/G}$ is dependent on the molecular weight of the n-alkane. The greater the molecular weight the poorer the estimation so that the ratio of UNIFAC to the 'Exp' $K_{P/G}$ decreases by over an order of magnitude with a molecular weight increase from 114 to 310.

UNIFAC: n-Alkanes $K_{P/L}$ Estimations: Effect of Free Volume

Underestimation of $K_{P/G}$ by UNIFAC means that the estimated solu

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solute activity coefficient in the polymer is too large (see Eq 52). The UNIFAC free volume correction has a significant effect on the predicted $K_{P/G}$ (activity coefficient) as shown in Figure 50 (where the amorphous PE line is almost the same as the UNIFAC estimations without the free volume correction). Without the free volume correction the activity coefficient is smaller and the UNIFAC $K_{P/L}$ estimation is 60% higher in relation to the UNIFAC estimation line for HDPE with the free volume correction. Without the free volume correction the prediction is better overall for the higher molecular weight alkanes (MW>114) than for the lower molecular weight n-alkanes (MW< 114) when the regression line for estimations without free volume is extrapolated to lower molecular weights. Changing the polymer density from .956 (HDPE) to .918 (LDPE) increases the estimated $K_{P/L}$ for the n-alkanes by 40%. The forty to 60% increases in the estimated $K_{P/L}$ which occurs due to varying the polyethylene density in the free volume term are still small in comparison with the total estimation error of UNIFAC for the n-alkanes.

Oishi and Prausnitz (1978) suggested in their initial paper on UNIFAC-FV that the empirical c_i term in Eq 30 may need to be increased for large solute molecules since c_i was optimized for small solute molecules. Thus increasing the size of the free volume contribution is not desirable because the activity coefficient is already too large.

UNIFAC n-alkanes $K_{P/L}$ Estimations: Errors in Combinatorial Term

Considering the small size of the free volume contribution the failure of UNIFAC to predict n-alkane activity coefficients in polyethylene suggests an error exists in the combinatorial or residual activity contributions (Eq 29). The residual term in Eq 29 can be eliminated from consideration because the group interaction parameter for a group interacting with itself (CH_2 vs CH_2) is zero. This leaves the combinatorial term remaining as the source of error. Weidlich and Gmehling (1987) and Larsen et al. (1987) have proposed modifications fo the UNIFAC combinatorial term that improve the VLE estimations for hydrocarbons significantly and slightly for semi-polar and polar molecules. Although these new combinatorial terms require new interaction parameters they can be used for hydrocarbon mixtures since the residual terms are zero. Activity coefficient estimations for n-alkanes in polyethylene were calculated using the combinatorial terms from Weidlich and Gmehling and from Larsen et al. and were several orders of magnitude larger than those from the original UNIFAC combinatorial term. This was the expected result of using these combinatorials for polymers as pointed out by Fredenslund (1990). Park et al. (1991)

believes that a more important problem than the combinatorial term in n-alkane activity coefficient estimations is the residual term where the dispersions of the CH_2 and CH_3 groups are considered equal. The assumption of equal dispersions for CH_2 and CH_3 is fundamentally incorrect and to improve alkane-alkane predictive accuracy separate interaction parameters for these groups must be assigned (Park et al., 1991).

Before going further with this discussion a word of caution concerning this experimental data should be made. It was observed in the Method Development section that the measured $K_{P/L}$ for the alkanes in 100% ethanol showed a dependency on the liquid phase concentration. Figure 66 shows the UNIFAC and GCFEOS estimations compared to the n-alkane $K_{P/L}$ data from Koszinowski (1986a). Koszinowski's data is smaller by a factor of two than this experimental data although it has a similar slope. With respect to Koszinowski's data, the activity coefficient estimations are too small for C12-C18. However, the trend in Koszinowski's data again shows UNIFAC overestimating the activity coefficients of the n-alkanes above docosane. Koszinowski estimated these partition coefficients from permeation and diffusion data which does not rule out the presence of different systematic errors. At this point the discussion remains unresolved without stronger certainty to where exactly the UNIFAC estimations lie with respect to

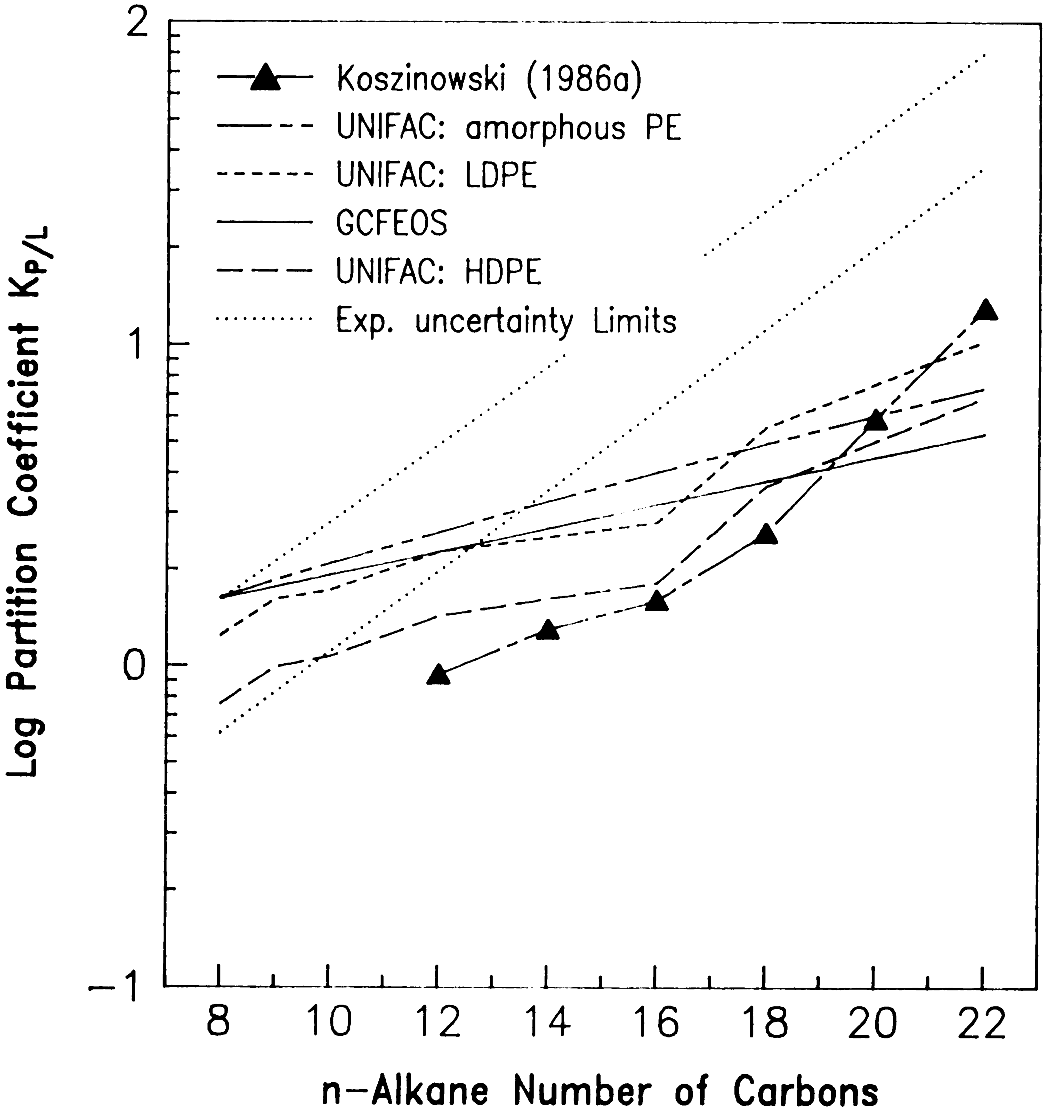

Figure 66. n-Alkane/100% Ethanol: Effect of Polymer Density on Estimations

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the experimental data. The polymer/liquid partition coefficient data for the n-alkanes should be carefully remeasured using the sorption equilibrium method to carefully controll any possible systematic errors that might be present for the n-alkane measurements. The acceptable magnitude of the $K_{P/L}$ estimation error is discussed later in the chapter on $K_{P/L}$ application to food/package systems.

GCFEOS: n-Alkanes $K_{P/L}$ Estimations

GCFEOS underestimates the n-alkane liquid/gas partition coefficients over the entire measured aqueous ethanol range as noted in the results. The underestimation is relatively small for 100% ethanol and becomes progressively worse as the aqueous content increases. The underestimation of the $K_{L/G}$ in the aqueous ethanol solutions dominates in the overestimation error of the $K_{P/L}$. In the 100% ethanol liquid phase GCFEOS underestimates the experimental $K_{P/L}$ which suggests that the polymer/gas partition coefficient could be too small. The flatness of the regression line slope indicates a molecular weight effect as well. This is the case when GCFEOS $K_{P/G}$ are compared to experimental ('Exp') $K_{P/G}$ values for the n-alkanes in 100% ethanol at 25°C (Table 25).

Table 25. n-Alkane: Comparison Experimental $K_{P/G}$ with GCFEOS at 25°C

n-alkane	$K_{P/G}$ 'Exp'	$K_{P/G}$ GCFEOS	Ratio GCFEOS/'EXP'
C8	2123	2131	1.003
C9	7714	6258	.811
C10	28022	18413	.657
C12	369808	160688	.435
C14	4.88E6	1415920	.290
C16	6.44E7	1.27E7	.196
C18	8.50E8	1.13E8	.133
C20	1.12E10	1.02E9	.0909
C22	1.48E11	9.28E9	.0627

The ratios of GCFEOS to experimental $K_{P/G}$ are better than for UNIFAC but in the aqueous ethanol solutions the underestimation of the $K_{L/G}$ by GCFEOS reduces this advantage. The molecular weight dependence is also not as extreme as in UNIFAC, the ratio decreases by less than an order of magnitude from octane to docosane. The $K_{P/G}$ estimations for octane and nonane are the same as the expeimental data. Unlike UNIFAC, free volume considerations are taken into account in the GCFEOS model for both the solvent and the polymers activity coefficients. When GCFEOS estimations are compared with Koszinowski's n-alkane data (Figure 66) the comparison is similar to that for UNIFAC. GCFEOS underestimates the polymer phase activity coefficient up to eisosane. However, the curves then cross over and it begins to overestimate it. In both UNIFAC and GCFEOS, regardless of the magnitude of the $K_{P/L}$, the slopes of the estimated $K_{P/L}$ are flat compared to the experimental data.

The inaccuracies of the UNIFAC and GCFEOS estimations are especially surprising because the sorption of n-alkanes in polyethylene form a very simple chemical system for modeling. Only dispersive forces are present between the n-alkanes and polyethylene and the two substances are composed of methyl (CH_2 and CH_3) groups, the fundamental building blocks of all aliphatic molecules. This failure is surprising because GCFEOS starts with the Flory equation of state which is a widely used model for polymer solutions. The apparent failure of both GCFEOS and UNIFAC similarly for n-alkane activity coefficient estimation in polyethylene may warrant remeasuring of the experimental $K_{P/L}$ data to re-test these estimation methods.

The molecular weight of the polymer, the only user supplied parameter in GCFEOS, does not have an appreciable effect on the estimated polymer activity coefficient. An average number molecular weight for polyethylene was estimated to be 30,000. The molecular weight ranges quoted by Brydson for LDPE varied from 20,000 to 48,000. Over this range the estimated activity coefficient for tetradecane varied by 1.1% at a tetradecane weight fraction of $1x10^{-5}$.

Significance of Aroma Compound $K_{P/L}$ Estimations

The aroma compound mixture used represents a mixture of different commonly occurring food aroma compound structures and contains most of the important functional groups occurring in food aromas. The aldehydes, an important class of aromas, are not represented in this mixture. However, the group-contribution parameters for aldehydes are not currently available for GCFEOS so they could have only been tested for UNIFAC. The mixture chosen was mainly because of its precedence established in previous studies (Becker et al, 1983, Koszinowski and Piringer, 1989). The aromas represent solutes with partition coefficients ranging from the upper limits of the hydrocarbons to the lower limits of the alcohols. The aromas are unsaturated, have complicated ring structures and sometimes multiple functional groups. In the following section the limitations and advantages of the UNIFAC and GCFEOS models will be discussed using this group of aromas.

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UNIFAC: Aroma $K_{P/L}$ Estimations

In the results section it was shown that the UNIFAC estimations for $K_{L/G}$ do not correlate in all cases with the $K_{P/L}$ estimations. This suggests that the polymer/gas partition coefficients are not always well predicted by UNIFAC. Table 27 shows UNIFAC estimated $K_{P/G}$'s for HDPE compared with $K_{P/G}$'s calculated by taking the product of the experimental $K_{P/L}$ and $K_{L/G}$ at 25°C in the 35% liquid ethanol phase. The 35% ethanol data was used for this example because the experimental data has the smallest systematic error compared to measurements at the other ethanol concentrations. The polymer/gas partition coefficient itself changes very little (e.g. 5.4% difference for d-limonene weight fractions of $1.6x10^{-5}$ in 100% Ethanol and $1..2x1-^{-2}$ in 35% Ethanol) with the absorbed solute weight fraction ranges observed for the different ethanol solutions. These experimental $K_{P/G}$ values are representative for all liquid phases tested.

Table 26 shows that UNIFAC, within the uncertainties of the pure aroma saturated vapor pressures used, best predicts $K_{P/G}$ in HDPE for the polar alcohols, overestimates slightly for the hydrocarbons followed by greater overestimations for the intermediate polar compounds. The $K_{P/G}$ prediction for cis-3-hexenol, diphenyloxide, and eugenol are likely to have the largest errors introduced by the vapor pressure

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Table 26. Aromas: Comparison of Experimental K(P/G) with UNIFAC

Aroma	Exp K(P/G)	UNIFAC K(P/G)	Ratio UNIFAC/exp
d-Limonene	5562	9803	1.76
Diphenylmethane	37373	397184	10.63
Linalylacetate	7233	38563	5.33
Camphor	14101	41189	2.92
Diphenyloxide	95851	384359	4.01
Isoamylacetate	306	1437	4.69
gamma-undelactone	121179	3841882	31.70
Eugenol	26460	14010	0.53
Citronellol	-	19555	-
Dimethylbenzyl-carbinol	54893	16199	0.30
Menthol	10951	15075	1.38
Phenylethylalcohol	32724	4075	0.12
cis-3-Hexenol	1121	2765	2.47
		Average:	5.49
		Standard Deviation	8.38

K(P/G) for polyethylene
Exp = experimental data estimated from experimental K(P/L) and K(L/G) data.
UNIFAC estimations using PE density = .956 (HDPE) at 25C
Temperature = 25C

estimations used. Nonetheless, the d-limonene and isoamylacetate vapor pressures are taken from experimental data in the literature but their estimations are not appreciably better than the other non-polar and intermediate polarity aromas. The vapor pressure error introduced in the $K_{P/G}$ calculations is not a factor in the $K_{P/L}$ calculations (see Eq 23). The polymer/gas partition coefficient is inversely related to the size of the estimated activity coefficient (see Eq 52) thus the $K_{P/G}$ overestimations are due to underestimated activity coefficients. Without the UNIFAC free volume correction, the activity coefficients would be even smaller.

Underestimation of the activity coefficients is opposite of that for the n-alkanes where the activity coefficient was overestimated by UNIFAC. This could be due to the group-contribution parameters themselves. For example, the partition coefficients for alcohols with a variety of structures, are well predicted for both the liquid and polymer phases. The greater accuracy of the alcohol aroma estimations in polyethylene is surprising because they are nonideal. However, in highly associated systems like alcohols in ethanol, UNIFAC is known to make good estimations (Fredenslund, 1989) so that the estimations of $K_{L/G}$ are good as expected. The intermediate polarity aromas tend to have well predicted liquid partition coefficients but not polymer phase partition coefficients. This could be cause

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The tendency to overestimate the polymer partition coefficient coincides with the tendency for UNIFAC to overestimate the liquid partition coefficients. The net effect is a canceling out of some errors in the predicted polymer/liquid partition coefficient. However, in cases where the liquid/gas partition coefficients are well predicted by UNIFAC, the error from the polymer/gas estimation carries through to the overestimation of the polymer/liquid partition coefficient. This is the case for diphenylmethane, camphor and γ-undelactone. In only one case did UNIFAC underestimate the $K_{P/L}$. This was for eugenol, where the $K_{L/G}$ was overestimated and the $K_{P/G}$ was underestimated. The $K_{L/G}$ error had the larger effect on the eugenol estimation.

UNIFAC Aromas $K_{P/L}$ Estimations: Effect of User Inputs

UNIFAC requires the input of polymer and solute densities for the free volume activity calculation. These were not always found at 25°C and some substances are solid at 25°C (camphor, menthol, diphenylmethane, and diphenyloxide). In these cases the densities were estimated (Fedors 1974a,b). The sensitivity of UNIFAC-FV to variations in density were car

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carried out with γ-undelactone, one of the aromas with an estimated density and the aroma with the largest overestimated $K_{P/G}$. HDPE had a solute weight fraction of 4×10^{-4}. For γ-undelactone a 5% increase in the density increases the estimated $K_{P/G}$ (or decreases the activity coefficient) by approximately 30%. A 5% decrease in the density decreases the $K_{P/G}$ by 30%. The effect of density, although significant, cannot entirely explain the overestimation by UNIFAC. These calculations also show that the use of estimated liquid densities for crystalline aroma densities is acceptable and any density estimation errors are within the estimation error of the UNIFAC method itself. Errors in the polymer phase partition coefficients but not in the liquid phase partition phase coefficients suggest an error in the formulation of the free volume activity contribution. Iwai et al. (1991) developed a new free volume activity contribution equation which they have shown to be useful for predicting the solubilites of hydrocarbon vapors in various polymers for finite solute weight fraction ranges ($w_i = 0.01 - 0.2$).

The polyethylene density has an effect on the size of the $K_{P/L}$ calculations. The lower LDPE density (0.918 versus 0.956 for HDPE) increases UNIFAC $K_{P/L}$ estimations from 8 to 43% depending on the solute. Using the amorphous density of the polymer in the free volume calculations can increase the $K_{P/L}$ estimates by 8 to 60% and not using any free

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volume correction at all can increase the $K_{P/L}$ estimation by 9 to 62%. Clearly there is a polymer crystallinity effect included in the polymer density input but as concluded for the n-alkanes and for the individual solute densities, the effect of density is minimal compared to the size of the error of the UNIFAC estimations themselves.

UNIFAC Aroma $K_{P/L}$ Estimations: Effect of Polymer Crystallinity

Polymer crystallinity is not a likely cause of the overestimation of the polymer/gas partition coefficients because not all solutes are equally overestimated. Concentration effects in the experimental measurements would increase the experimental partition coefficient and cause UNIFAC to underestimate the polymer/gas partition coefficient. All polymer/solute activity coefficients were calculated as binary solutions and the effect of any sorbed ethanol in the polymer was not considered significant. Preliminary calculations with mixtures of solutes at these concentrations in the polymer had no effect on the UNIFAC estimated activity coefficients. Additionally, the method development results show interaction effects were insignificant for these dilute polymer solute concentrations. Effects of the sorption of the ethanol phase into the polymer can also be ruled out as discussed in the results. An estimated $K_{P/L}$ for ethanol in LDPE at

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23°C in 100% ethanol was obtained by extrapolating $K_{P/L}$'s for higher molecular weight n-alcohols from Koszinowski (1986b). The estimated $K_{P/L}$ for ethanol is 0.001. In pure ethanol this is essentially a weight fraction of 0.001. This number is the upper limit for the amount of ethanol absorbed by the LDPE and at the upper limit for the dilute concentration range.

UNIFAC Aromas $K_{P/L}$ Estimations: Discussion of Model Deficiencies

Having systematically quantified the possible sources of error in these UNIFAC $K_{P/L}$ calculations the only remaining source of estimation error in UNIFAC resides with UNIFAC itself, its empirical group-contribution parameters and its inherent assumptions. Even when the reported 20 to 30% deviation of UNIFAC activity coefficients from experimental measurements and the uncertainties created by the estimation of densities in the free volume correction are considered, the magnitude of some variations from the experimental data cannot be fully explained. Stearic hindrances found in eugenol could be a partial explanation for its poor estimation. Stearic hindrances lead to the underestimation of $K_{P/L}$ by UNIFAC because its solution of groups group-contribution assumptions are violated. The group contributions are assumed to be additive and activity coefficients in mixtures are related to the interactions betw

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between structural groups. In UNIFAC there is no differentiation between shielded functional groups and non-shielded ones. Hence, UNIFAC underestimates the activity coefficient for eugenol because the hydroxyl and ether groups are viewed by UNIFAC as though they have no hindrance and have a greater affinity for the ethanol phase then it really has and overestimates the activity coefficient in the non-polar polymer phase. A more likely reason for UNIFAC's underestimation of the eugenol partition coefficient is that the alcohol group contribution term is not the same for phenolic compounds as it is for non-aromatic structures. Table 28 and Figure 67 show that the magnitude of the UNIFAC estimation error for eugenol lies in the range of other phenolic compounds. It is recommended that UNIFAC add an additional group contribution component for phenolic alcohol groups. Molecules with ring structures like camphor and τ-undelactone also violate the group contribution assumptions because the CH_2 group in a ring structure behaves differently than one in an aliphatic molecule. UNIFAC made particularly high $K_{P/L}$ estimations for these two molecules. UNIFAC may need a cyclic methyl group-contribution parameter like GCFEOS. However, this observation does not always hold true because menthol is also a cyclic molecule and has a satisfactorily estimated $K_{P/L}$.

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Some improvement in the UNIFAC $K_{P/L}$ estimations may be made by using either of the modified UNIFAC versions (Weidlich et al. 1987, or Larsen et al. 1987) to estimate the liquid phase activity coefficient and UNIFAC-FV to estimate the polymer phase activity coefficient. However, only marginal improvement is expected using the modified UNIFACs (Fredenslund et al. 1990) and the modifications are not as widely applicable as the original UNIFAC version (because they cannot be applied to polymers and have fewer group contribution groups).

The UNIFAC combinatorial term, (from the non-polar n-alkane in polyethylene $K_{P/G}$ observations in Table 24) appears to overpredict the activity coefficient in the aroma molecular weight range from 120-200. UNIFAC tended to overpredict the $K_{P/G}$ for the semi-polar aromas in polyethylene in Table 26 which means the activity coefficient is underpredicted. The underprediction of the semi-polar aroma polymer activity coefficient is due not so much to the free volume contribution, which increases the size of the activity coefficient, or the combinatorial term, which has a tendency to overpredict the activity coefficient, but to the residual term which is underpredicted. The $K_{L/G}$ is generally overpredicted by UNIFAC which means the activity coefficient is underpredicted. The UNIFAC aroma activity coefficient estimation in the aqueous ethanol is dominated by the residual term. It appears that the best chance for improving UNIFAC $K_{P/L}$ predictions for semi-polar and polar molecules is developing better empirical interaction parameters. These empirical parameters will be discussed later in greater detail.

GCFEOS: Aroma Compound $K_{P/L}$ Estimations

In the Results section it was shown that the GCFEOS estimations for $K_{L/G}$ do not correlate completely with the $K_{P/L}$ estimations for all aroma compounds. In spite of liquid/gas partition coefficients for aqueous ethanol solutions which tended to be underestimated (activity coefficients overestimated) some polymer/liquid partition coefficients were overestimated. This suggests there are instances where GCFEOS overestimated polymer/gas partition coefficients. Table 27 shows a GCFEOS estimated $K_{P/G}$ in HDPE compared with experimental $K_{P/G}$ estimated from experimental data as previously described in the UNIFAC aroma discussion.

Table 27 shows that GCFEOS, within the uncertainties of the pure aroma compound saturated vapor pressures used, estimates $K_{P/G}$'s best for hydrocarbons and greatly overestimates them for acetates. The estimations of partition coefficients for other aroma compounds appears to be mixed. The experimental vapor pressure used for calculating the $K_{P/G}$ of isoamylacetate lends credibility to

Table 27. Aromas: Comparison of Experimental K(P/G) with GCFEOS

Aroma	Exp K(P/G)	GCFEOS K(P/G)	Ratio GCFEOS/EXP
d-Limonene	5562	3790	0.68
Diphenylmethane	37373	69090	1.85
Linalylacetate	7233	66595	9.21
Camphor	14101	2170	0.15
Diphenyloxide	95851	510931	5.33
Isoamylacetate	306	3670	11.98
gamma-Undelactone	121179	2338296	19.30
Eugenol	26460	46747	1.77
Citronellol	—	75620	—
Dimethylbenzyl-carbinol	54893	—	—
Menthol	10951	8544	0.78
Phenylethylalcohol	32724	4824	0.15
cis-3-Hexenol	1121	10662	9.52
gamma-Undelactone (c)	121179	3400960	28.07
Camphor (c)	14101	5985	0.42
Menthol (c)	10951	15141	1.38
		Average :	5.52
		Standard Deviation	5.97

K(P/G) for polyethylene
Exp = experimental data estimated from experimental K(P/L) and K(L/G) data.
GCFEOS estimations using PE density = .956 (HDPE) at 25C
(c) = cyclic paramters used
Temperature = 25C

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the idea that the cause of overestimation for the acetates rests with GCFEOS group contribution groups. The use of cyclic group-contribution parameters greatly improve the estimation of the camphor partition coefficient, but makes the estimation for menthol worse and greatly increases the overestimation of τ-undelactone. The estimated partition coefficients for dimethylbenzylcarbinol and for d-limonene calculated are many orders of magnitude too high using cyclic parameters. The phenylethyl alcohol partition coefficient estimation is underestimated suggesting an error in the vapor pressure used because the estimated polymer/liquid partition is quite good. Eugenol is surprisingly well predicted despite its structural complexities. The overestimation of $K_{P/G}$ of a primary alcohol like cis-3-hexenol is somewhat surprising because the structure is so simple and well defined. The effect of the overestimated $K_{P/G}$ carried through to the $K_{P/L}$ estimation.

GCFEOS, like UNIFAC, has examples where the activity coefficient estimations for polymer and liquid phases have offsetting quantitative errors (e.g. diphenyloxide and eugenol). However, more often than with UNIFAC one or the other activity coefficient estimations carries through into the polymer/liquid partition coefficient estimation. With the GCFEOS model there are no user inputs with external sources of error like the density component in the UNIFAC

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free volume correction. The estimation problems experienced in GCFEOS are likely to reside in the group-contributions. In particular, the group contribution for water and acetates should be re-evaluated. Calculations with aromas partitioned in polypropylene have shown GCFEOS to have instances like those for dimethylbenzylcarbinol and d-limonene (both with cyclic groups) where the estimations were completely unreasonable.

Confirmation of Hypothesis

It was hypothesized that the UNIFAC and GCFEOS activity coefficient estimation methods can be used to estimate polymer/liquid partition coefficients that are more accurate than the activity coefficient estimations for the polymer and liquid phases separately. Tables 28 and 29 compare the error ratio (estimated partition coefficient / experimental partition coefficient) for the liquid/gas and polymer/gas partition coefficients with the polymer/liquid partition coefficients. Note that the liquid/gas and polymer/gas partition coefficients reflect the liquid and polymer activity coefficient estimations and the polymer/liquid partition coefficient is a ratio of the polymer and liquid activity coefficients estimations (Eq 23a).

Table 28. Comparison of $K_{P/L}$ Estimations versus $K_{P/G}$ and $K_{L/G}$ Estimations: 100% Ethanol.

		$K_{P/L}$	$K_{P/G}$ *	$K_{L/G}$
d-limonene	U	3.94	1.76	(1.88)
	GC	17.4	(1.47)	1.06
diphenylmethane	U	6.25	10.6	1.20
	GC	2.22	1.85	2.89
linalylacetate	U	2.09	5.33	1.00
	GC	30.8	9.21	(8.33)
camphor	U	6.52	2.92	1.21
	GC	1.20	(6.66)	(2.0)
diphenyloxide	U	2.53	4.01	1.64
	GC	3.97	5.33	1.5
isoamylacetate	U	2.47	4.69	(1.06)
	GC	7.24	12.0	(1.22)
γ-undelactone	U	14.0	31.7	-
	GC	8.61	19.3	-
eugenol	U	(25.0)	(1.89)	29.0
	GC	(3.13)	1.77	11.0
citronellol	U	(1.12)	-	3.94
	GC	3.07	-	4.43
dimethybenzylcarbinol	U	(1.09)	(3.33)	2.43
	GC	!	!	4.43
menthol	U	(1.18)	1.38	1.12
	GC	(2.27)	(1.28)	(1.60)
phenylethylalcohol	U	(1.75)	(8.33)	(1.63)
	GC	(4.17)	(6.66)	1.74
cis-3-hexenol	U	(1.19)	2.47	1.73
	GC	2.75	9.52	2.05
dodecane	U	(3.37)	(4.78)	2.61
	GC	(1.47)	(2.30)	(1.43)

UNIFAC (U): 9 of 14 $K_{P/L}$ measurements are better or not worse (by 50%) than the $K_{P/G}$ and $K_{L/G}$ estimations.
GCFEOS (GC): 9 of 13 $K_{P/L}$ measurements are better or not worse (by 50%) than the $K_{P/G}$ and $K_{L/G}$ estimations.

! = values could not be estimated
() = value is inverse (ratio is smaller than one)
- = experimental value not available
* = $K_{P/G}$ estimated experimental values (Table 26, 27)

Table 29. Comparison of $K_{P/L}$ Estimations versus $K_{P/G}$ and $K_{L/G}$ Estimations: 35% Ethanol.

		$K_{P/L}$	$K_{P/G}$ *	$K_{L/G}$
d-limonene	U	(1.69)	1.76	2.98
	GC	1.44	(1.47)	(2.11)
diphenylmethane	U	31.4	10.6	(2.94)
	GC	2.03	1.85	(1.10)
linalylacetate	U	1.33	5.33	3.83
	GC	15.1	9.21	(1.72)
camphor	U	2.50	2.92	1.31
	GC	5.56	(6.66)	(3.23)
diphenyloxide	U	1.40	4.01	2.71
	GC	3.13	5.33	16.8
isoamylacetate	U	1.36	4.69	3.45
	GC	84.5	12.0	(7.04)
γ-undelactone	U	80.5	31.7	(2.56)
	GC	2530	19.3	(125)
eugenol	U	(88.5)	(1.89)	46.6
	GC	(28.6)	1.77	50.0
citronellol	U	-	-	(2.78)
	GC	-	-	(55.6)
dimethybenzylcarbinol	U	(1.22)	(3.33)	(2.78)
	GC	!	!	20.8
menthol	U	1.90	1.38	(1.39)
	GC	81.3	(1.28)	(100)
phenylethylalcohol	U	1.03	(8.33)	(8.33)
	GC	(2.17)	(6.66)	(3.12)
cis-3-hexenol	U	(1.25)	2.47	3.07
	GC	2.60	9.52	3.66

UNIFAC (U): 9 of 12 $K_{P/L}$ measurements are better or not worse (by 50%) than the $K_{P/G}$ and $K_{L/G}$ estimations.
GCFEOS (GC): 6 of 11 $K_{P/L}$ measurements are better or not worse (by 50%) than the $K_{P/G}$ and $K_{L/G}$ estimations.

! = values could not be estimated
() = value is inverse (ratio is smaller than one)
- = experimental value not available
* = $K_{P/G}$ estimated experimental values (Table 26, 27)

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The results in Tables 28 and 29 support the hypothesis. Comparison of results for 75% and 50% aqueous ethanol liquid phases gave similar results as the 100% and 35% aqueous ethanol phases with 8 out of 12 for UNIFAC and 7 and 9 out of 11 for GCFEOS. The hypothesis is not true in all cases but in approximately 75% of the cases for these substances it is true.

Comparison of UNIFAC and GCFEOS Estimations

Discussion of Semi-Empirical Nature of Methods

Before questioning the assumptions and theories underlying the derivations of GCFEOS or UNIFAC it should be pointed out that the first question should ask, how good are the group-contribution parameters? In both, UNIFAC and GCFEOS experimental data is reduced to give empirical group-contribution parameters for the models. If good quality experimental data is not available then the group-contribution parameters will be somewhat compromised. In short, UNIFAC and GCFEOS are essentially empirical in nature because they need to use experimental data to obtain their group-contribution parameters. The first place to look in questioning the shortcomings of the models relates to the kinds of data needed for the model's empirical parameters.

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GCFEOS relies on thermal expansivity and thermal pressure coefficients of pure liquids and on VLE data for binary mixtures of components with low molar mass to determine the group- contribution parameters. The problem that the authors of GCFEOS had with their approach was most likely finding necessary thermodynamic data which is not available for many compounds. It can be inferred from the number of group-contribution functional groups offered in GCFEOS compared to UNIFAC that much of the experimental data needed for GCFEOS group-contribution parameters is simply not available. GCFEOS is also a relatively new model whereas UNIFAC has undergone five revisions of the group-contribution parameters. It will likely take some time before the model is tested enough so weaknesses in the group-contribution parameters can be sorted out.

UNIFAC has a much simpler data reduction task in that it only needs to use binary VLE data to obtain its group-contribution parameters. The availability of VLE data is much larger and more complete than for the other data needed by GCFEOS. As a consequence UNIFAC has 50 groups and GCFEOS has only 26. The majority of this VLE data is from low molecular weight solutes. This is because most VLE measurements are made using low molecular weight compounds because they are simply easier to work with than larger less volatile molecules (like aroma compounds). The VLE measurement temperature is another factor affecting the accuracy of the interaction parameters. According to Park et al. (1991) UNIFAC uses parameters estimated from VLE data in the 40°C to 80°C range and consequently is not especially accurate outside this range. Temperature dependence is one of UNIFAC's weak points claimed to have been improved in GCFEOS. The vast majority of VLE data used for UNIFAC estimations were made at relatively high concentrations (mole fractions > 0.05) where chemical associations between solutes can take place so that the same paramters poorly predict infinite dilutions (Park et al. 1991). It is very likely that GCFEOS has incorporated many of the same errors in its parameters because both methods use the same VLE data base.

The UNIFAC and GCFEOS models are similar in that both have been constructed around theories based on interactions between small molecular weight molecules in solvent and polymer solutions and empirical group-contribution parameters calculated from small molecular weight molecules. UNIFAC is based on statistical mechanical theory and its free volume correction term is based on Flory's equation-of-state theory (leaving out the interaction parameter). Flory's equation-of-state is derived from statistical mechanics and is supported by observations of polymer solutions in low molecular weight solvents (Flory, 1970). GCFEOS starts with the concepts in the Flory equation-of-state, improves the free volume portion of the equation, changes the interaction term and then fits it all with group-contribution parameters.

Comparison of UNIFAC and GCFEOS Estimations: The Presence of Molecular Weight Effects in the Models.

The molecular weights of most aromas range between 100 and 200 which are two to three times the weights of normal solvents from which most of the UNIFAC and GCFEOS group-contribution parameters were estimated. The GCFEOS and UNIFAC estimations of n-alkanes showed a definite molecular weight effect but the aroma molecules data showed no strong correlation. Belfiore et al. (1988) identified a molecular weight effect present in the residual term of UNIFAC as they tried to model phase behavior of polymer-polymer blends. To test the presence of an estimation problem at large molecular weights in UNIFAC and GCFEOS, estimations for the partitioning of phenols and phenolic polymer additives between LDPE and 100% ethanol at 23°C were compared to data from Koszinowski (1986b).

Table 30 shows the UNIFAC estimations. GCFEOS estimations are not reported because the estimated polymer phase activity coefficients for substituted phenols are severely underestimated apparently due to inaccurate group-contribution parameters. The partition coefficients are either severely overestimated for phenol and Topanol or

Table 30. Comparison of Phenol Experimental K(P/L) with UNIFAC

Phenol	MW	UNIFAC K(P/L) w/FV	UNIFAC K(P/L) no FV	Exp. K(P/L) (1)	ratio calc/exp w/FV	ratio calc/exp no FV
Phenol	94	0.63	0.72	0.0026	243.3	276.9
p-Cresol	108	0.093	0.094	0.0056	16.67	16.84
2,4,6	136	0.0026	0.0030	0.019	0.14	0.16
2,3,5,6	150	0.00050	0.00067	0.030	0.017	0.022
2,4	206	1.3	1.3	0.016	81.7	81.8
2,6	206	1.3	1.3	0.13	10.2	10.2
BHT	220	0.37	0.47	0.19	1.95	2.48
Tinuvin 120	450	0.019	0.70	0.045	0.433	15.5
Topanol	544	6.7E-05	0.011	0.00031	0.216	35.8
				ave:	38.4	48.8
				std dev.	76.2	84.2

LDPE = density = .918, thickness = 50 micrometer
(1) = experimental data from Koszinowski (1986b),
CL = 1270 ppm (w/v), at 23C
w/FV = with free volume correction
no FV = no free volume correction
2,4,6 = Trimethylphenol
2,3,5,6 = 2,3,5,6-Tetramethylphenol
2,4 = 2,4-Di-t-butylphenol
2,6 = 2,6-Di-t-butylphenol
BHT = 2,6 Di-t-butyl-4-methyl phenol
Tinuvin 120 = 3,5-Di-t-butyl-4-hydroxy-benzoic acid--(2,4-di-t-butyl-phenyl)-ester
Topanol = 1,1,3-Tris(2-methyl-4 hydroxy-5-t-butylphenyl) butane

severely underestimated for the substituted phenols. This appears to be another GCFEOS group-contribution parameter problem. Table 30 shows UNIFAC overestimates the phenol partition coefficient and tends underestimate the substituted phenols as the degree of substitution increases. The underestimation of the phenols is especially noticeable in phenol molecules with 4 substitutions on the aromatic ring. Calculating the partition coefficients without using the free volume correction increases the estimated partition coefficients and the estimations are somewhat worse overall than those made using the free volume correction. There are likely to be stearic hindrance effects present in these phenols that play a role in causing UNIFAC to underestimate the partition coefficients of the substituted phenols.

In Figure 67, the log error ratio (estimated K/experimental K) versus Van der Waals molar volume for aroma compounds between 100% ethanol and HDPE at 25°C is plotted. The Van der Waals molar volumes were estimated using the group contribution estimation procedure of Van Krevelen (1990). It is clearly shown that both UNIFAC and GCFEOS have molecular weight dependent estimation errors. The error ratio is best (≈ 1) for the smaller molecular volumes and diverges as the size of the molecule increases. The increasing underestimation of $K_{P/L}$ above a molecular weight

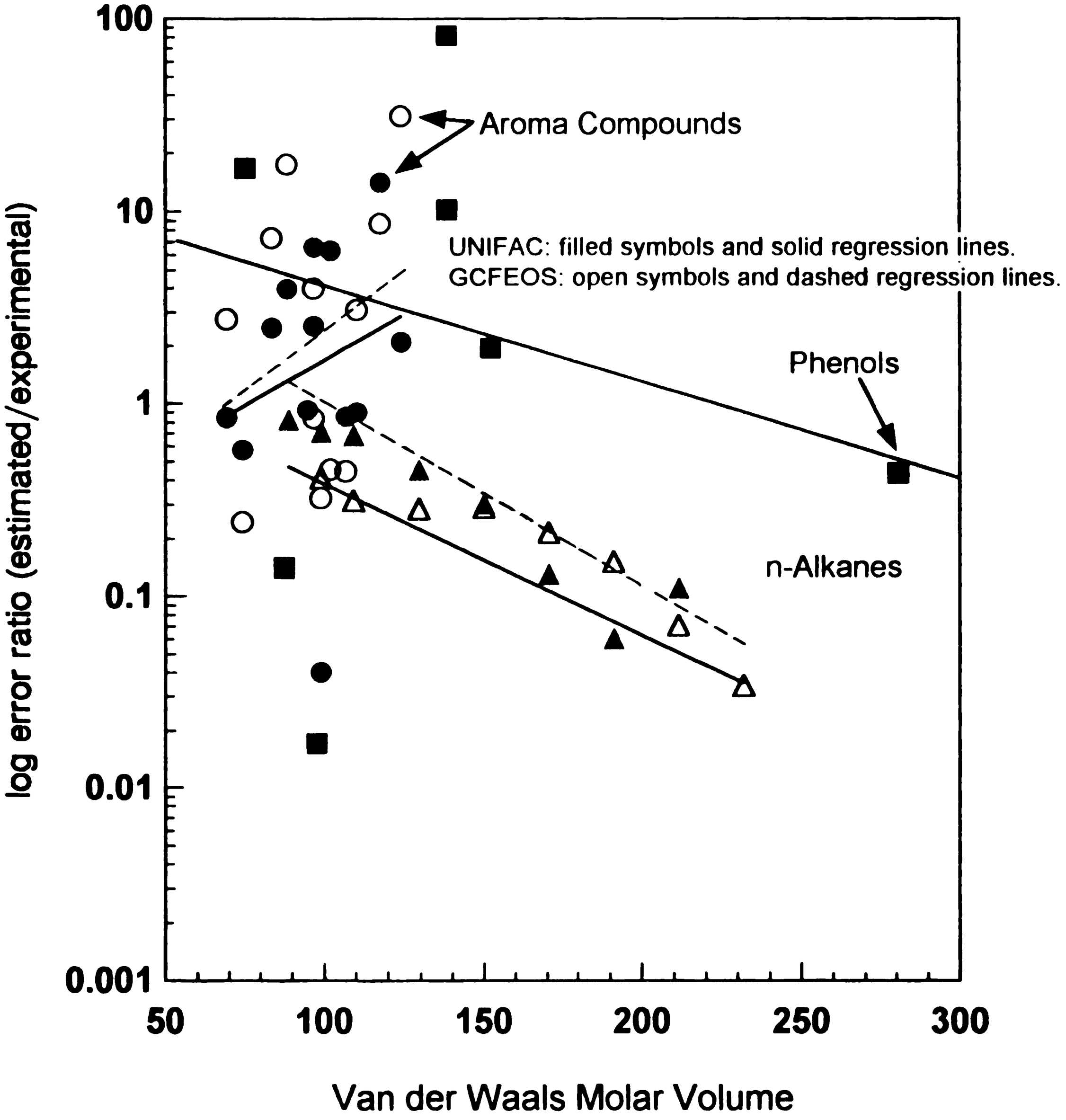

Figure 67. UNIFAC and GCFEOS $K_{P/L}$ Error vs Van der Waals Molar Volume: aroma compounds at 25°C between HDPE and 100% Ethanol

of 140 is especially noticeable for UNIFAC estimations of n-alkanes and phenols. GCFEOS has trends similar to UNIFAC but does not underestimate as much. Similar trends in underestimation with molecular weight are observed for the UNIFAC and GCFEOS aroma compound aqueous ethanol $K_{P/L}$ estimations. Figure 68 summarizes the trends for UNIFAC and GCFEOS n-alkane HDPE/aqueous ethanol $K_{P/L}$ estimations. UNIFAC has a consistent increasing $K_{P/L}$ underestimation with molecular volume for the liquid phase compositions. GCFEOS has similar trends for 100% ethanol but overpredicts for aqueous ethanol solutions which can be attributed to the poor water group contribution interaction terms.

The increasing overestimation by UNIFAC and GCFEOS of the polymer activity coefficient (and subsequent underestimation of $K_{P/G}$) as molecular weight increases should be further investigated. It may also be useful to find out if a molecular weight cut off point for the use of the free volume correction exists.

The addition of interaction parameters for CH_2 and CH_3 in UNIFAC as suggested by Park et al. (1991) may or may not improve the $K_{P/L}$ estimation for high molecular weight solutes in polymers depending on whether they would be positive or negative. GCFEOS is similar to UNIFAC in that it also has no interaction parameters between CH_2 and CH_3. According to the experimental n-alkane/polyethylene $K_{P/G}$

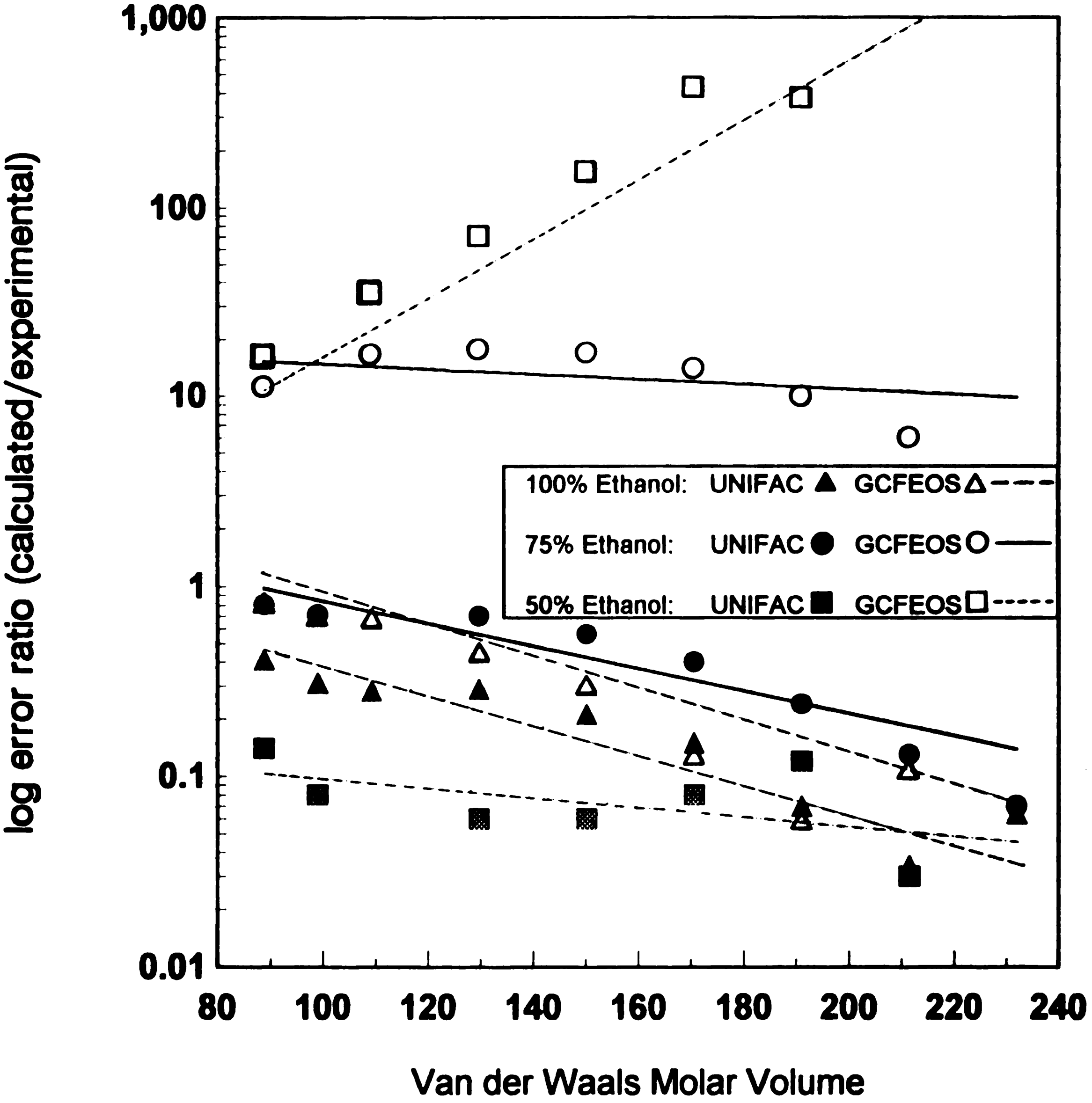

Figure 68. UNIFAC & GCFEOS K(P/L) Error vs Van der Waals Molar Volume: n-Alkanes at 25°C between HDPE and Aqueous Ethanol

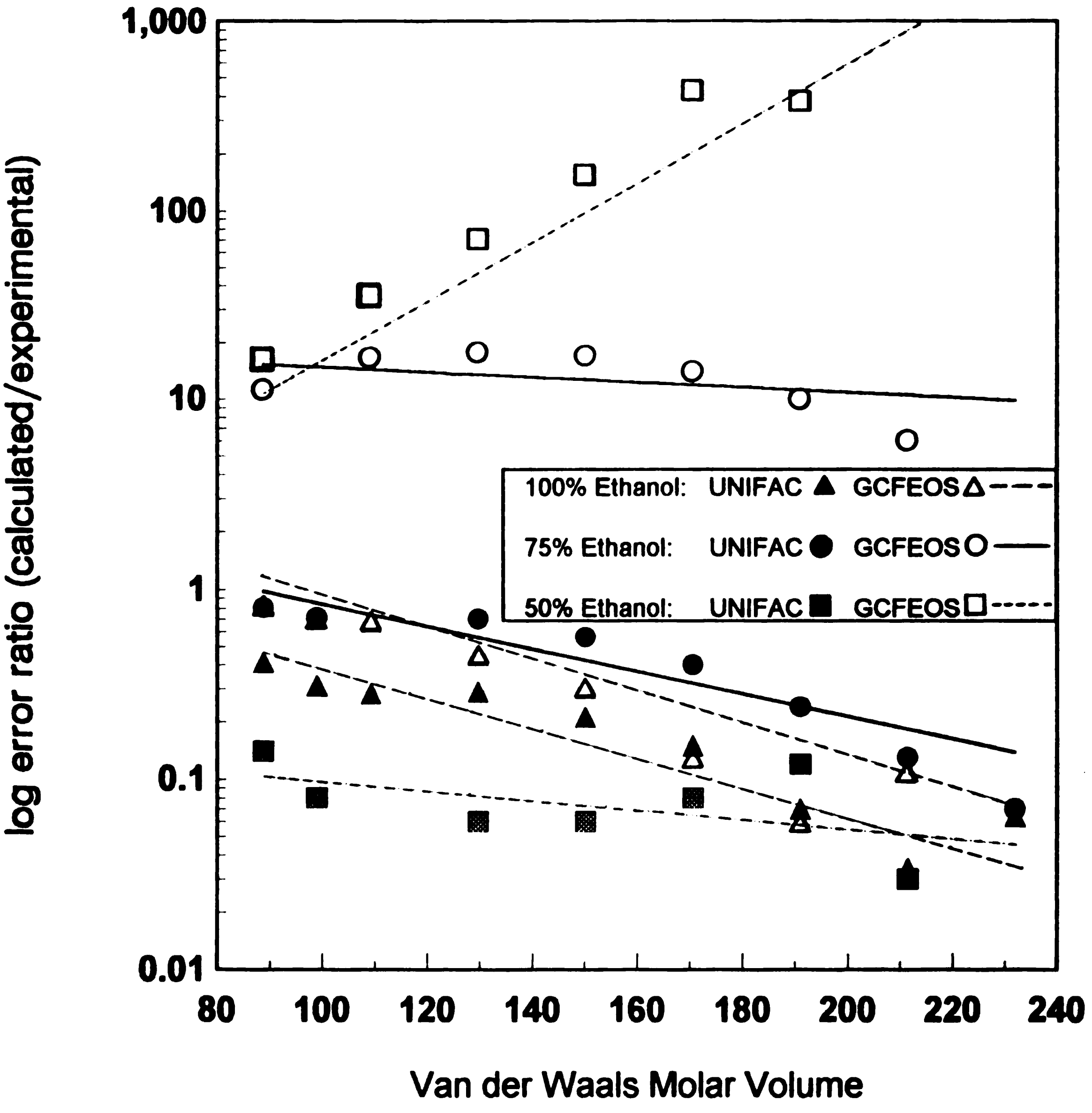

Figure 68. UNIFAC & GCFEOS K(P/L) Error vs Van der Waals Molar Volume: n-Alkanes at 25°C between HDPE and Aqueous Ethanol

calculated from $K_{P/L}$ and $K_{L/G}$ measurements, the underestimated $K_{P/G}$ of UNIFAC and GCFEOS suggests that the interaction parameter between CH_2 and CH_3 should be negative so that the estimated activity coefficient would be smaller. The CH_3 group is a relatively minor group compared to the number of CH_2 groups in high molecular weight n-alkanes (e.g. 10% for eicosane) where the underprediction is the worst but it could have more importance for substituted larger molecular weight molecules like polymer additives. The estimation of $K_{P/L}$'s for substituted n-alkanes in polyethylene may be a good starting point to investigate this further.

Summary of UNIFAC and GCFEOS Estimations

Table 31 summarizes the estimation abilities of UNIFAC and GCFEOS for $K_{P/L}$ between polyethylene and aqueous ethanol liquid phases. The table lists the average ratios of the estimated $K_{P/L}$ to the experimental data for the aroma compounds listed in Table 7 and the tetradecane estimation to the experimental regression line $K_{P/L}$. Two averages are given for the aromas, one with the ratios of γ-undelactone and Eugenol included and one without.

Table 31 **Comparison of UNIFAC and GCFEOS $K_{P/L}$ Estimations**

Ratio estimated / Experimental

Liquid	**UNIFAC**	**GCFEOS**
100%		
Aromas	3.22	6.35
w/o	2.53	6.72
C14	0.23	0.38
75%		
Aromas	5.95	6.75
w/o	3.41	3.02
C14	0.43	13.3
50%		
Aromas	6.06	38.7
w/o	2.55	6.78
C14	0.070	76.5
35%		
Aromas	10.3	247
w/o	4.31	21.5
C14	-	-

C14 = tetradecane
w/o = without ratios for eugenol and τ-undelactone
Liquid = percent w/w aqueous ethanol
- not measured

The estimation error ratio's for UNIFAC and GCFEOS in addition to being correlated with the Van der Waals molar volumes of the solutes (Figures 67 and 68) can be correlated with an interaction term using the regular solution theory solubility parameters. Since the polymer phase measured here is always PE, the interaction term need only consider the differences between the solutes and the changes in the liquid contacting phase. An interaction parameter (I.P) derived from the regular solution theory for predicting the activity coefficient of the solute in the liquid phase would be (Baner and Piringer, 1991):

$$I.P. = \underline{V}_i^W \Phi_L^2 (\delta_i - \delta_L)^2 \qquad (55)$$

Where $\underline{V}_i^W$ is the Van der Waals molar volume calculated from the group contribution method in Van Krevelen (1990), δ_i and δ_L are the Hildebrand (or total) solubility parameters for the solute and liquid calculated from the group contribution method of Hoy (1985). Eq 55 is derived from the regular solution theory estimation of liquid phase activity coefficients for solutes at infinite dilution (the volume fraction of the liquid phase ≈ 1). The solubility parameters for aqueous ethanol mixtures were estimated as the sum of the molar volume fractions (θ) of the liquid phase components times their solubility parameters:

$$\delta_L = \theta_{H2O}\ \delta_{H2O} + \theta_{Ethanol}\ \delta_{Ethanol} \qquad (56)$$

where the molar volume fraction for component 1 in a binary mixture is defined as:

$$\theta_1 = \underline{V}_1 x_1 / (\underline{V}_1 x_1 + \underline{V}_2 x_2) \qquad (57)$$

The interaction parameter gives a general correlation for the similarities of the solute and liquid phase. The smaller the interaction parameter the more similar the chemical natures of the two compounds and thus the more ideal the system is likely to be. When the log of the estimation error ratio is plotted versus the interaction parameter in Figures 69 and 70 broad correlations are seen. Both GCFEOS and UNIFAC follow similar trends where the smaller the interaction parameter the smaller the estimation error. One group of exceptions to this are the phenol estimations by UNIFAC and GCFEOS which are obviously in error. The GCFEOS ester partition coefficient estimations and the γ-undelactone estimations for both models are other outliers. Figures 69 and 70 could be used to help define boundaries for the UNIFAC and GCFEOS model accuracies. If a factor of plus or minus 10 were used as a criteria for estimation acceptability then a interaction parameter of 20,000 might be used as a cut off point for both UNIFAC and GCFEOS. Above 20,000 the estimation models' accuracy is not good enough to be considered useful. Figures 69 and 70 also allow comparison of the accuracy of the two models. On a strict probability basis, out of the 75 or more plotted data points, UNIFAC has more estimations within an order of magnitude of the experimental partition coefficient than does GCFEOS.

With respect to these comparisons and previous discussion points, UNIFAC appears to give more consistent and more accurate estimations than GCFEOS for ethanol and aqueous ethanol liquid/gas partition coefficients, for polyethylene polymer/gas partition coefficients and for

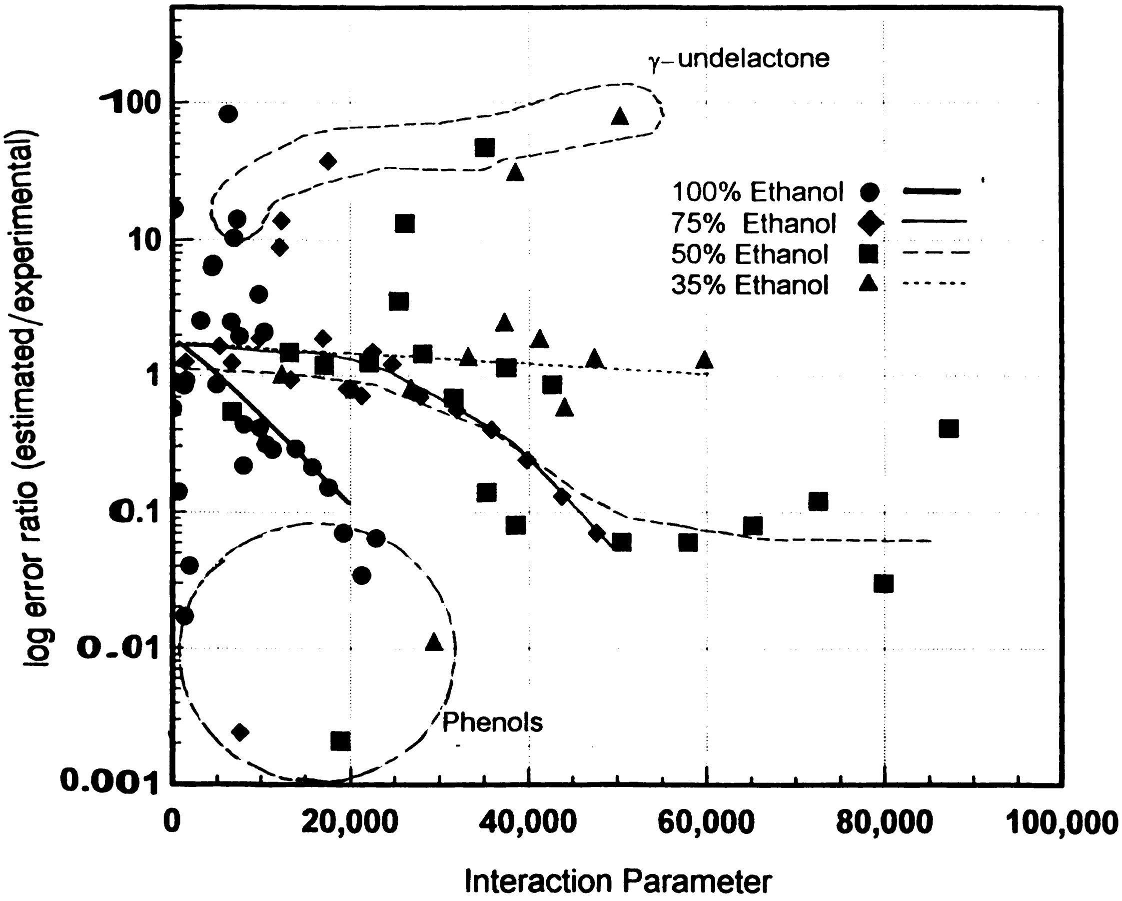

Figure 69. Log UNIFAC errror ratio vs interaction parameter HDPE/Aroma Compounds at 25°C

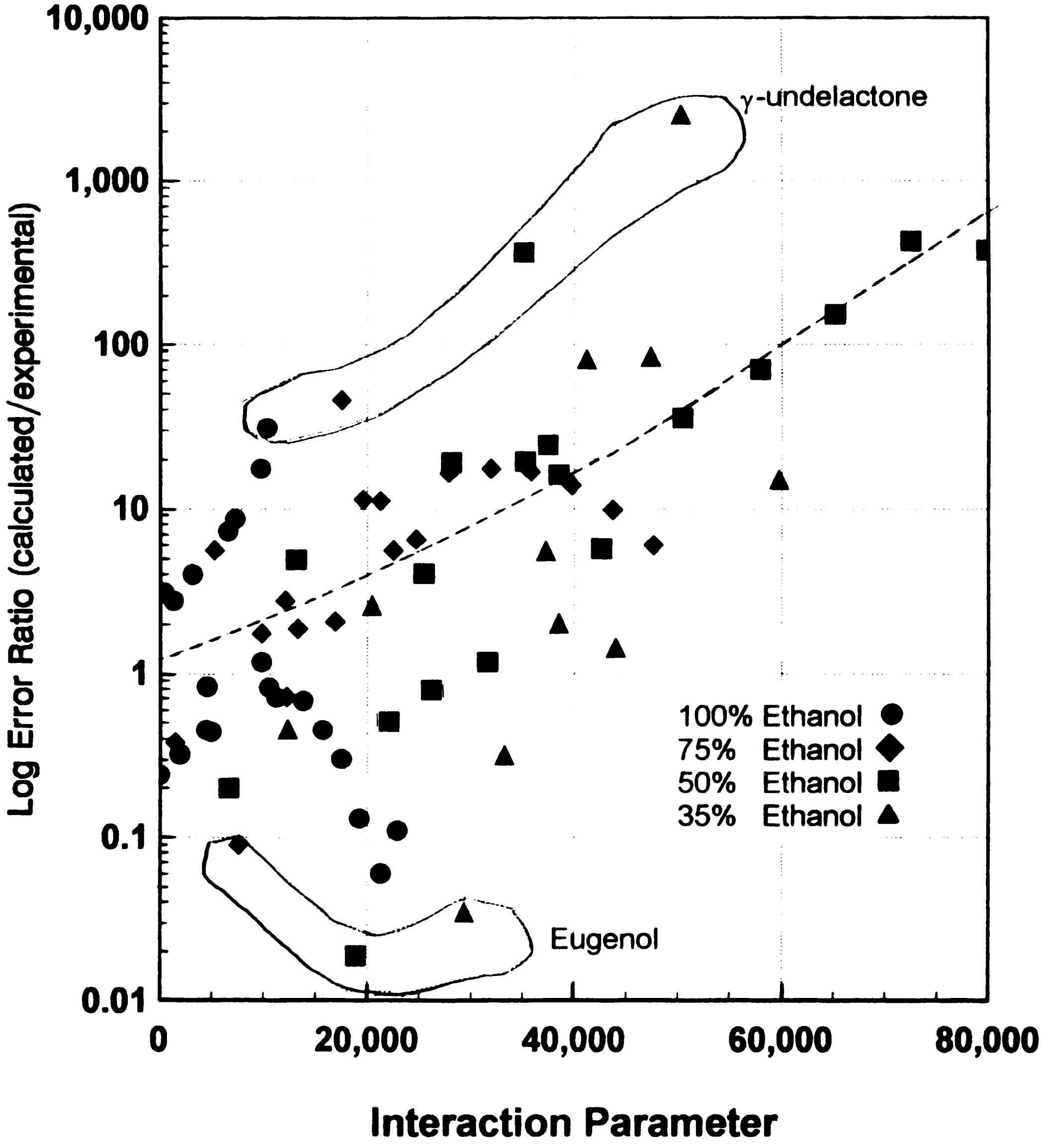

Figure 70. Log GCFEOS errror ratio vs interaction parameter HDPE/Aroma Compounds at 25°C

polyethylene/ethanol and aqueous ethanol polymer/liquid partition coefficients. These calculations have shown that both UNIFAC and GCFEOS estimations can be excellent as well as terrible. The user of these methods should always compare the estimated result with what a reasonable estimate might be based on the polarity of the polymer and liquid phases. Outlier estimations can be eliminated by comparing the estimations with expected partition coefficient upper and lower limits. For example, the upper and lower limits for an aqueous ethanol / polyolefine system are the n-alkanes and primary alcohols.

Other estimates of partition coefficients in polymer/liquid systems can be made by using a ratio of activity coefficients, ie. solute liquid activity coefficient to solute activity coefficient in a phase with similar polarity to the polymer phase in question. For example, activity coefficient data exist for many solvents in ethanol as well as in hydrocarbons. A ratio of the solute's ethanol to hydrocarbon activity coefficient would give an upper limit for the $K_{P/L}$ of the solvent partitioned between the liquid and polyethylene (activity coefficients in a hydrocarbon solvent will be smaller than those in polyethylene). Suitable solvent simulants for other polymers could be correlated using solubility parameters or consulting reference books for suitable polymer solvents.

Figures 71 and 72 give rough predictions for the expected magnitudes of estimated partition coefficients by correlating experimental $K_{P/L}$ data with interaction parameters. Figures 71 and 72 correlate the log of the polyolefin/aqueous ethanol or 100% methanol partition coefficient with the interaction parameter (Eq 55). The figures include the experimental partition coefficients for LDPE, HDPE and polypropylene based on the observations by Becker et al. (1983) and Koszinowski and Piringer (1989). The partition coefficients for a given solute are practically the same regardless of the polyolefin polymer measured. Figure 71 correlates partition coefficient data for solutes partitioned between polyolefins and aqueous ethanol from this work as well as from Becker et al. (1983), Koszinowski (1986a, 1986b), and Koszinowski and Piringer (1989) at 23-25°C. Figure 72 correlates partition coefficient data for solutes between polyolefins and 100% methanol from Becker et al. (1983), Koszinowski (1986b), and Koszinowski and Piringer (1990) at 23°C. The linear regression lines for the data are plotted with their 95% confidence intervals. The regression line equations are:

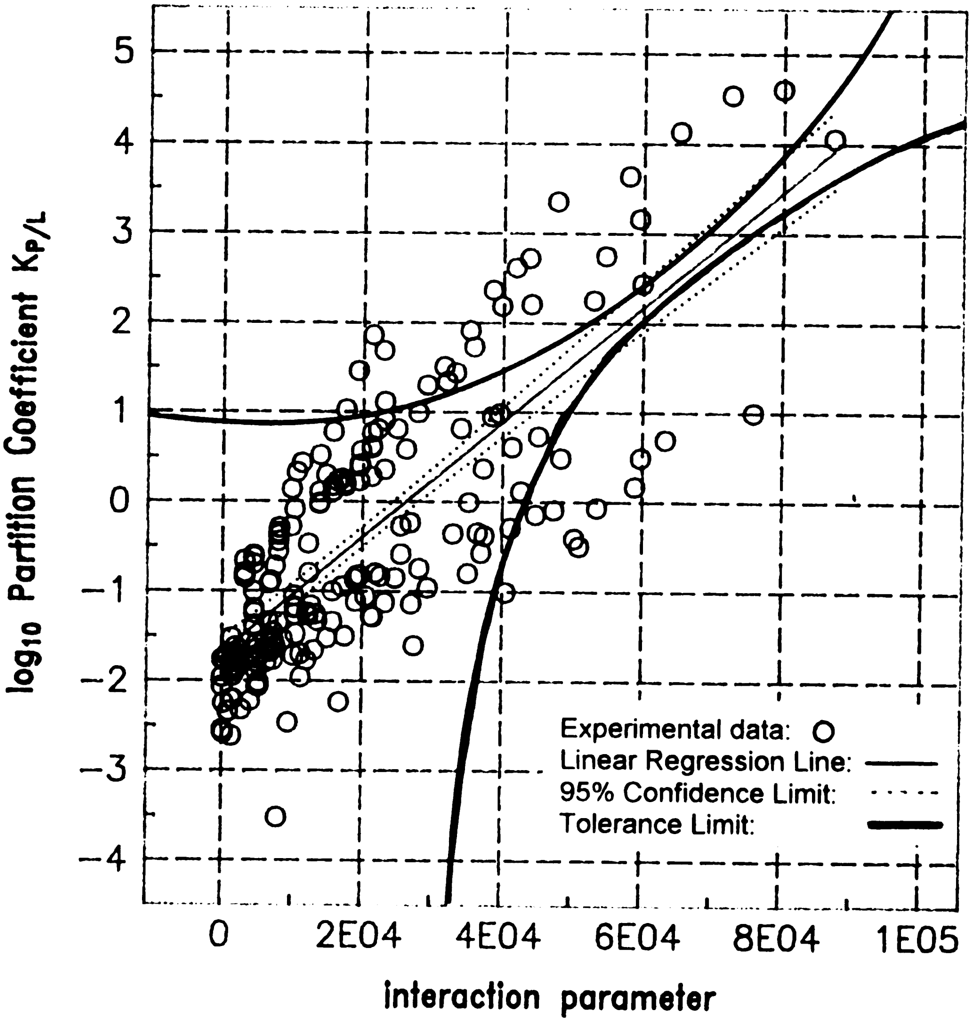

Figure 71. Log_{10} polymer/liquid partition coefficient versus interaction parameter (Eq 55).

Solutes partitioned between polyolefins and aqueous ethanol at 23 - 25°C (this work, Koszinowski 1986a,b, Koszinowski and Piringer, 1989). 195 experimental data points.

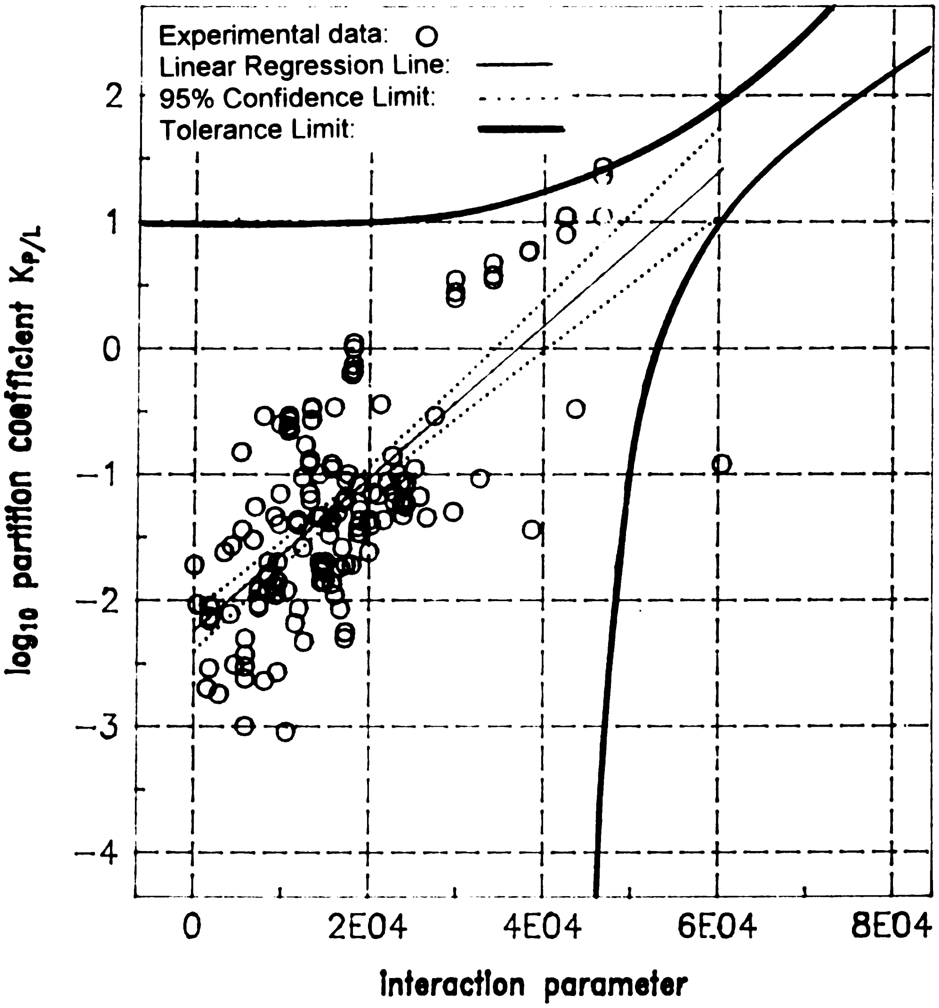

Figure 72. Log_{10} polymer/liquid partition coefficient versus interaction parameter (Eq 55).

Solutes partitioned between polyolefins and methanol at 23°C (Becker et al. 1983, Koszinowski and Piringer 1989). 157 experimental data points.

Polyolefin/Aqueous Ethanol:

$$\log_{10}(K_{P/L}) = 6.43E-5(I.P.) - 1.681219; \quad r^2=0.60 \tag{58}$$

Polyolefin/100% Methanol:

$$\log_{10}(K_{P/L}) = 6.06E-5(I.P.) - 2.239233; \quad r^2=0.51 \tag{59}$$

Using Figures 71 and 72 as rough guides, significant outlier estimations by UNIFAC and GCFEOS can be recognized and rejected. In Figures 71 and 72, two lines are drawn signifying the limits of allowable partition coefficient limits about the linear regression line for the one liter aseptic package application, discussed in the following chapter. These limits are drawn so that partition coefficients falling in this range cause no more than a 5 to 10% change in the migration estimation. Using these partition coefficient limits UNIFAC and GCFEOS estimations can be evaluated. For example the partition coefficient estimations for eugenol and τ-undelactone by UNIFAC and GCFEOS, (two of the aroma compounds that were not well estimated) showed that the estimations (see appendix) are acceptable for 100%, 75%, 50% and 35% ethanol for both compounds except for the GCFEOS estimations for τ-undelactone in 50% and 35% ethanol. Although the partition coefficient for eugenol was always orders of magnitude underestimated this does not matter in terms of migration or sorption because in this partition coefficient range and package/food volume ratio essentially all of the eugenol will remain in the food phase (see Figure 73). The tetradecane partition coefficient estimations were likewise evaluated and only the GCFEOS estimations for 50% and 35% ethanol fell outside the limits. These limits are dependent on the package/food application and the size of the partition coefficient. Naturally this method of evaluation is constrained by the availability of experimental partition coefficients in order to make the necessary correlations.

The most important questions that must be answered by the users of these estimation methods pertains to what accuracy is needed. For qualitative estimations these models (in particular UNIFAC) can be recommended. If the user can live with estimations that range as high as 2 to as much as 10 times greater, then both of these methods can be recommended. These methods are less important for polyolefin $K_{P/L}$ estimations because the partition behavior of aromas in polyolefins can be estimated by simply using the large amount of experimental data available in the literature. Other polymers that are not as well studied may benefit from estimations using UNIFAC and GCFEOS. However, this may not matter for polymers like polyamides which seldom come in direct contact with food or for polyesters which absorb very little aroma regardless of the system (they always have small partition coefficients). However, the methods should be investigated for polymer/polymer partition coefficient estimations which would be of more importance in this case. The accuracy and reliability of these methods is such that they cannot be accepted in place of laboratory measurements for regulatory purposes. The role of such estimation method remains of interest for package designers and for first approximations for those concerned with food/package interaction problems. The use of estimation methods such as these always comes back to the same point, that they give estimations and are not complete substitutes for experimental data.

The Application of Partition Coefficient Estimations to Food/Package Interaction Problems

When applying partition coefficients to food/polymer package systems it is important to remember that the partition coefficient is defined as the ratio of the equilibrium concentration of the solute in the polymer phase to that in the food phase. The total amount of solute that can migrate from the polymer or be sorbed into the polymer is determined by the partition coefficient, the total amount of solute in the system and the volumes of the package material and the food. Whereas the partition coefficient describes the equilibrium condition, Eqns 8 and 12 describe the the mass transfer processes as the system approaches equilibrium. The partition coefficient can be used to calculate the equilibrium concentrations of solute in the food/package system given the initial amount of solute. In the following example the use of the partition coefficient is applied to possible of mass transfer problem in a food/package system.

Example: 1 Liter Aseptic Package

A 1 liter aseptic package is typically constructed from a laminate of PE/Paperboard/Aluminum foil/ionomer/PE and has the approximate dimensions, 9.5 x 6 x 16.5 cm (L x W x H), and following specifications:

$A = 625.5$ cm²

$d = 0.0053$ cm

$V_F = 1000$ mL

$V_P = 4.91$ mL

$c_{i,o}^P = 0.001$ g/mL

$c_{i,o}^F = 0$ g/mL

$D_P = 1\text{x}10^{-10}$ cm²/sec

The equilibrium concentration of the solute in the polymer and food can be calculated using the partition coefficient and the solute mass balance using Eq 60.

$$K_{P/F} = c_{i,\infty}^{\ \ P} / c_{i,\infty}^{\ \ F} = \frac{m_{i,\infty}^{\ \ P}}{V_P} \Big/ \frac{m_{i,\infty}^{\ \ F}}{V_F} \qquad (60)$$

where Σm_i is the total mass of solute in the food/package system and $m_{i,\infty}^{\ \ P}$ is the equilibrium mass of solute in the polymer phase at equilibrium. From the solute mass balance: $\Sigma m_i = m_{i,\infty}^{\ \ P} + m_{i,\infty}^{\ \ F}$, the equilibrium solute mass in the food $m_{i,\infty}^{\ \ F}$ is:

$$m_{i,\infty}^{\ \ F} = \Sigma m_i - m_{i,\infty}^{\ \ P} \qquad (61)$$

Solving Eq 60 for $m_{i,\infty}^{\ \ P}$ then gives:

$$m_{i,\infty}^{\ \ P} = \frac{K_{P/L}\ (V_P/V_F)\ \Sigma m_i}{(K_{P/F}\ V_P/V_F) + 1} \qquad (62)$$

Figure 73 shows the effect of the size of the partition coefficients on $m_{i,\infty}^{\ \ P}$ and $m_{i,\infty}^{\ \ F}$ relative to the total mass, Σm_i (here Σm_i = 0.00491 g). It is important to note that the large food to package material volume ratio here, (V_F/V_P > 200), is common to most food/package systems. A large food to package volume ratio means that unless the partition coefficient is very large most of the solute

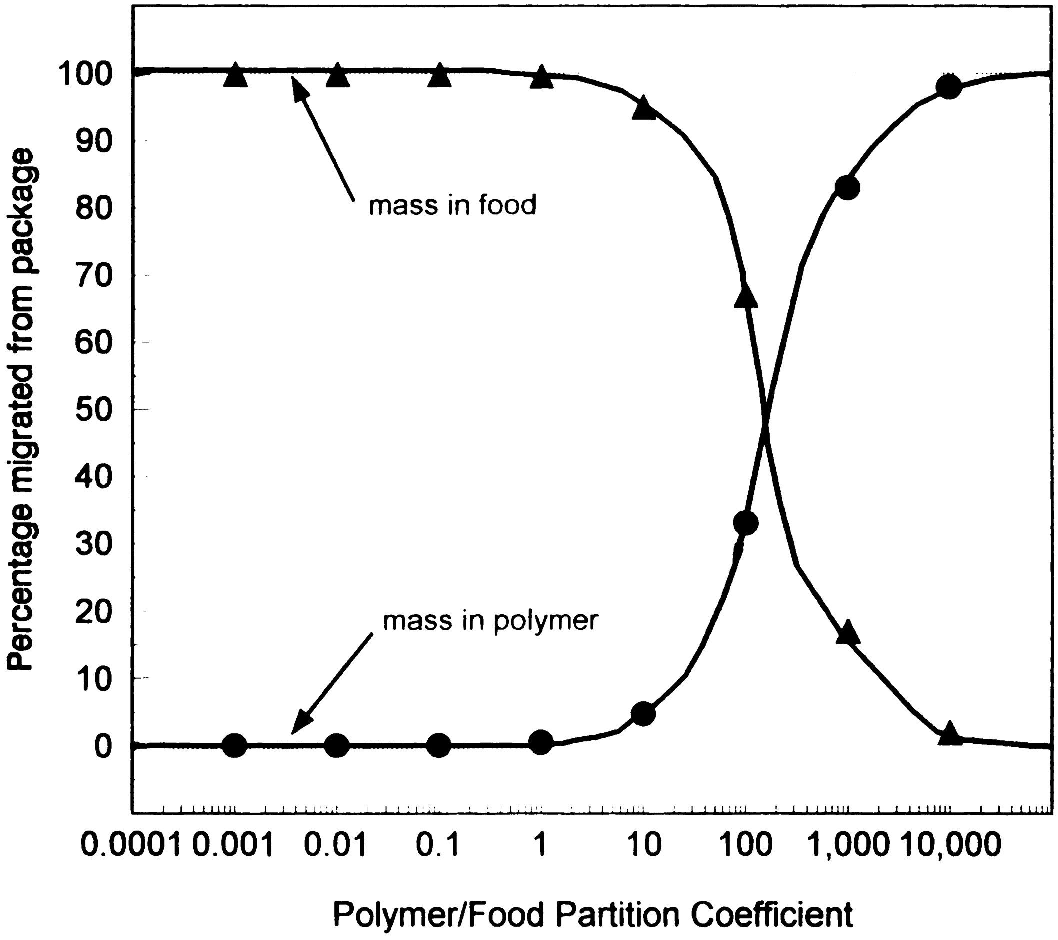

Figure 73. Effect of Partition Coefficient Magnitude on Solute Partition: Aseptic Carton Example

migrates into or remains in the food phase. The consequence for migration is most solute in the polymer will migrate into the food for solutes with small partition coefficients. Oil or fatty foods packed in this system will have smaller partition coefficients ($K_{P/F} \approx 1$) so that practically all the polymer additives will migrate into the food phase. Conversely, for aqueous foods packed in this package, the partition coefficients for large molecular weight relatively unpolar polymer additives will be large because they will favor the unpolar PE over very polar aqueous food. Thus, in aqueous food systems the polymer additives will remain in the this polymer phase. With respect to small molecular weight polar aroma compounds, the partition coefficients will be smaller than the polymer additives. The small partition coefficients for flavor compounds coupled with the large food to package volume means they will tend to remain in the food phase.

In contrast to the equilibrium state in Figure 73, Figure 74 shows the effect of the partition coefficient magnitude for a liquid food on the variation of the migrated solute mass into a polymer with time as the aseptic food/package system approaches equilibrium using Eq 12. It can be seen in Figure 74 that until the partition coefficient is larger than 10 there is very little effect on the system's approach to equilibrium. This is because the polymer diffusion coefficient is controlling the rate at which the

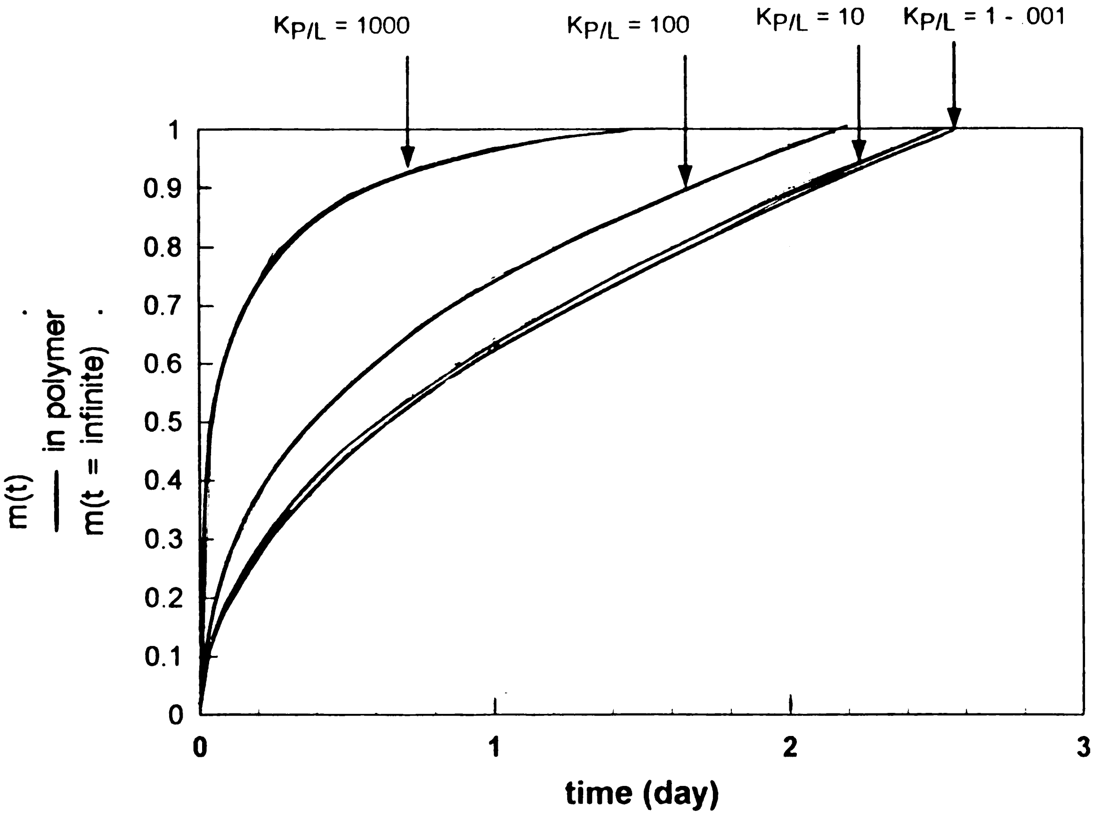

Figure 74. Migration or Sorption between a Polymer Sheet and Fluid Food, D_p=1E-10 (cm^2/sec).

system approaches equilibrium. Partition coefficients larger than 100 approach equilibrium very rapidly because very little solute must be transferred for the system to reach its equilibrium concentration. Note that the shape of the curves show appreciable error because the assumptions of an infinite thickness polymeric sheet are violated when 40% of the solute is transferred to the food.

When the aseptic package is filled with solid or semi-solid food then Figure 75 shows the mass transfer approach to equilibrium using Eq 8. In Eq 8 small $K_{P/L}$ ($K_{P/L} = 0.001$ to $K_{P/L} = 0.1$) mean that $\beta >> 1$ so that $\beta/(1+\beta) \approx 1$ so that Eq 8 simplifies to Eq 63.

$$m_{t,\infty} /A = 2\ c_{i,o}^{\ P}\ (D_P\ t\ /\ \pi)^{\frac{1}{2}} \qquad (63)$$

In this case the partitioning process is controlled by diffusion in the polymer. In the case when $K_{P/L} > 1.0$ then $\beta/(1+\beta) \approx \beta$ which means the diffusion process in the food controls the mass transfer and Eq 8 simplifies to Eq 64.

$$m_{t,\infty} /A = 2\ c_{i,o}^{\ P}\ 1/K_{P/L}\ (D_F\ t\ /\ \pi)\tfrac{1}{2} \qquad (64)$$

The reason why the curves for $K_{P/L} > 10$ in Figure 75 take such a long time to reach equilibrium compared to the times seen in Figure 74 is that the migration is dependent on the food phase diffusion coefficient and the food phase is

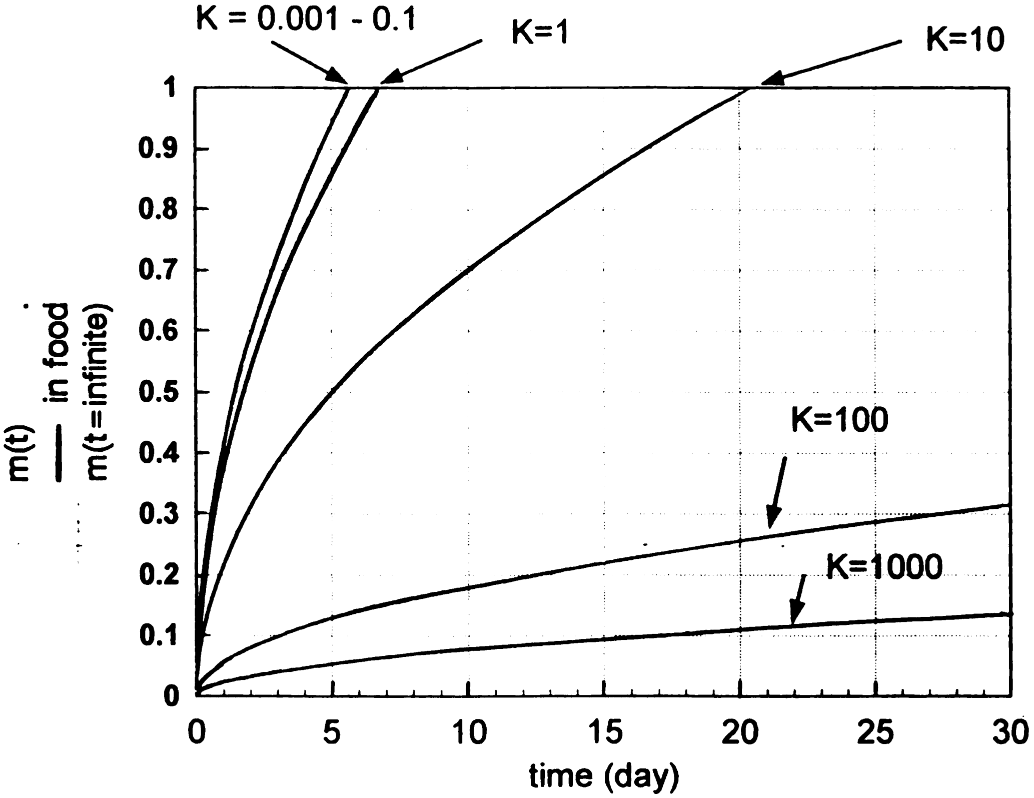

Figure 75. Migration into semi-solid food from polymer. D_p=1E-10 (cm^2/sec), D_F=1E-8 (cm^2/sec)

thousands of times thicker than the polymer phase. Even when the food phase diffusion coefficient is greater than that of the polymer it still takes a much longer time for the food phase to reach equilibrium due to the thickness of the food phase.

Effect of Partition Coefficient Estimation Error on Mass Transfer Calculations

For a given food/package system the partition coefficient is an important determinate for how much mass transfer of a given solute occurs between the food and package phases. The magnitude of the partition coefficient estimation error is directly related to the accuracy of the estimated mass transfer calculations. In Figure 73 an error of 10 times for a small partition coefficient ($K_{P/L}$ = 0.001-0.1) has practically no effect on the amount of transferred solute at equilibrium and similarly has no effect in Figures 74 and 75 for unsteady-state mass transfer in package systems containing liquid and solid foods. However, an error of 10 times for large $K_{P/L}$'s (>10) has a large effect on both equilibrium and unsteady-state calculations. Looking at the average relative estimation errors in Table 29 (less eugenol and γ-undelactone for the aroma compounds) UNIFAC errors range from 2.5 to 4.31 for aroma compounds and 0.23 to 0.07 for n-alkanes and GCFEOS errors range from 3.02 to 21.5 and 0.38 to 77. Several general comments can be made about these estimation errors in terms of mass transfer estimations.

In mass transfer calculations the underestimation of $K_{P/L}$ is less serious than overestimation. When $K_{P/L}$ is underestimated there is a safety factor for migration estimates because more solute is predicted to migrate than actually does. Underestimation of $K_{P/L}$ leads to underestimation of sorption which is a less serious error for health reasons and because sorption mass transfer estimations change by smaller amounts as the $K_{P/L}$'s become smaller (because the polymer phase volume is so much smaller). Overestimation of $K_{P/L}$ is more of a problem in migration estimations for health reasons because more solute is predicted to remain in the polymer than actually does. Overestimation becomes especially significant for $K_{P/L} > 1$ because the magnitude of the error becomes quite large and thus error in the estimated amount of transferred material becomes quite significant. In terms of the partition coefficients of the soutes between polyethylene and the liquid phases measured here, the UNIFAC and GCFEOS 100% ethanol estimation errors are unimportant because the partition coefficients are so small ($K_{P/L} < 1$). The estimation errors for 75% ethanol are also relatively unimportant for the aroma compounds because the partition coefficients are less than 5. The estimation errors for the n-alkanes in 75% ethanol are a more serious because the partition coefficients are larger (up to 500) however they are underestimated which is not as serious an error as overestimation. The estimation errors in the 35% and 50% ethanol solutions depend more on the magnitude of the actual partition coefficient for $K_{P/L} > 10$. In such a case Figures 71 and 72 are useful for evaluating the significance of the errors because they show the expected range that the actual $K_{P/L}$ would fall in.

Intuitive evaluation of the estimated partition coefficients can also help identify possible outlier estimations. By classifying solute molecules with similar masses on the basis of their polarity they can be ranked according to the relative size of their partition coefficients. For example one can rank solute partition coefficients in polyolefin/aqueous ethanol systems from largest to smallest in terms of the molecules polarity as:

n-alkane > hydrocarbon > ether > ester > ketone > aldehyde > alcohol > acid

This also fits what is intuitively expected since n-alkanes are the most chemically similar to the polyolefins they would partition out of the polar liquid phase. For other polymers the same reasoning can be used to evaluate the potentially validity of a partition coefficient estimation by UNIFAC or GCFEOS.

For qualitative estimations these models (in particular UNIFAC) is recommended. If the user can live with estimations that range as high as 2 to as much as 10 times greater then these methods can be recommended. The importance of these methods for polyolefins is less so because the partition behavior of aromas in polyolefins can be estimated by simply using the large amount of experimental data available in the literature. Other polymers that are not as well studied may benefit from estimations using UNIFAC and GCFEOS. However, this may not matter for polymers like polyamides which seldom come in direct contact with food or for polyesters which absorb very little aroma. The accuracy and reliability of these methods is such that they cannot be accepted in place of laboratory measurements. These models need to be compared with partition data for high molecular weight solutes (e.g. polymer additives MW>300) as definite trends in estimation error with molecular weight have been observed. The use of estimation methods such as these always comes back to the same point, that they give estimations and are not complete substitutes for experimental data.

Conclusions

Measurments of liquid/gas partition coefficients for n-alkanes (octane to tetradecane) and 13 aroma compounds partitioned between ethanol, aqueous ethanol solutions and nitrogen have been made in the infinite dilution concentration range. This is the first time partition data over a range of ethanol and aqueous ethanol concentrations have been measured for these substances and allow insights into the estimation of polymer/liquid partition coefficient estimations.

Measurements of polymer/liquid partition coefficients for n-alkanes (octane to docosane) and 12 aromas were measured for the polymers, LDPE and HDPE, and the liquid phases, ethanol and aqueous ethanol (35%, 50%, 75%). The partition coefficients were measured in the infinite dilution concentration range. Measurements of partition coefficients for n-alkanes and 12 different aromas between polyethylenes and ethanol and aqueous ethanol liquid phases between 10° and 40°C showed no significant variation with temperature within the uncertainty of these measurements. At these dilute concentration ranges there were no significant effects on the partition of solutes in the semi-crystalline polyethylenes within the uncertainty of these measurements. This is in contrast to observations by others at finite concentrations who have observed that increased polymer crystallinity inhibits the sorption of solutes by the polymer.

The measured liquid/gas partition coefficients were used together with the measured polymer/liquid partition coefficients to systematically analyze the polymer/liquid partition coefficient estimations of the UNIFAC and GCFEOS activity coefficient estimation methods. This is the first time UNIFAC and GCFEOS have been used to estimate partition coefficients in polymer/liquid systems. GCFEOS was used to estimate weight fraction activities for liquid/gas and polymer/gas systems which were then combined to estimate polymer/liquid partition coefficients. The original UNIFAC model, estimates activity coefficients on a mole fraction basis and was used to estimate liquid/gas activity coefficients. Original UNIFAC was then combined with UNIFAC-FV, which estimates weight activity coefficients for polymer/gas systems, to estimate polymer/liquid partition coefficients and polymer/gas partition coefficients.

With respect to their current development and with respect to their ability to quantitatively estimate solute partition coefficients between polyethylenes and ethanol and aqueous ethanol solutions, the UNIFAC is better than

GCFEOS in several aspects. UNIFAC is more applicable to a wider range of solutes and on average predicted their polymer/liquid partition coefficients better. UNIFAC also had fewer estimations having greater than an order of magnitude error for the estimations of the solutes tested. UNIFAC can estimate aqueous ethanol liquid activity coefficients better than GCFEOS which had large deviations as the more aqueous the solution became. Both are comparable for ease of use. Both methods had particular problems with ring structures and multi-functional group solutes. The effect of user inputs into these two models (polymer and solute density for UNIFAC and polymer molecular weight for GCFEOS) had insignificant effects relative to the size of the estimation error. In general, with UNIFAC the simpler the solute structure the better chance of a good partition coefficient estimation. GCFEOS showed no systematic variation in its ability to estimate different molecular structures. It is suggested that UNIFAC add a phenolic group contribution and GCFEOS re-evaluate the ester and water group contribution groups. For these reasons UNIFAC is recommended over GCFEOS for the estimation of polymer/liquid partition coefficients.

The user of these methods should be critical of their estimations and be aware of the potential for significant variation from experimental data. It is suggested that the users of these methods compare the order of magnitude of these estimations to experimental data for similar systems. This can be done either by comparing estimations to partition coefficient data for two liquids which are similar in polarities to the polymer/liquid system used, comparing them to data for similar polymer/liquid systems or through intuitive comparisons of the magnitudes of the estimated partition coefficients for solutes with different polarities.

Appendices

Appendix A

Tables of Pure Vapor Pressures and Their Estimation

Vapor Pressures of pure substances at 25°C.

Table 32. Pure Vapor Pressures of n-Alkanes at 25°C

n-Alkanes	Reid[1] atm	Perry[2] atm
Pentane	0.7244	0.6739+
Hexane	0.1950	0.1992+
Heptane	0.05878	0.06026+
Octane	0.01662	0.01844+
Nonane	3.683E-3[R]	6.272E-3
Decane	-	2.342E-3
Dodecane	-	2.603E-4[R]
Tetradecane	-	3.106E-5[R]
Hexadecane	-	2.644E-6[R]
Octadecane	-	-
Eicosane	-	-
Docosane	-	-

1) Reid et al. (1987) Equation for Temperature dependence of vapor pressure.
2) Experimental Data from Perry's (1989) fitted with Antoine equation.
3) Boublík et al. (1984): Experimental data fitted with Antoine equation.
4) Ambrose and Walton (1989) vapor pressure curves
R) Data point estimated out of the range of the Antoine Equation.
+) Value used for partition coefficient calculations
Note: conversion atm to MPa: multiply by 0.1013253

Table 32. (cont.)

n-Alkanes

	Boublik[3] atm	Ambrose[4] atm
Pentane	0.6744	0.6744
Hexane	0.1995	0.1992
Heptane	0.06011	0.06024
Octane	1.835E-2[R]	0.0185
Nonane	5.622E-3[R]	5.761E-3
Decane	1.713E-3[R]	2.052E-3
Dodecane	-	1.832E-4
Tetradecane	-	1.915E-5
Hexadecane	-	2.029E-6
Octadecane	-	2.586E-7
Eicosane	-	2.415E-8
Docosane	-	-

Table 33. Regressed n-Alkane Pure Vapor Pressures at 25°C

	Reid Corr[1]	Perry's Corr[2+]	
	atm	atm	ppm[3]
Pentane	0.709	0.6217	2949
Hexane	0.2027	0.1990	700.9
Heptane	0.0580	0.0637	260.9
Octane	0.0166	0.02039	95.19
Nonane	4.73E-3	6.527E-3	34.22
Decane	1.35E-3	2.089E-3	12.15
Dodecane	1.11E-4	2.141E-4	1.491
Tetradecane	9.02E-6	2.194E-5	0.1779
Hexadecane	7.37E-7	2.248E-6	0.02080
Octadecane	6.02E-8	2.303E-7	2.396E-3
Eicosane	4.92E-9	2.369E-8	2.726E-4
Docosane	4.02E-10	2.418E-9	3.0698E-5

1) Correlation of Reid et al.'s data: log vapor pressure vs n-Alkane carbon number. r = .99986

2) Correlation of Perry's data: log vapor pressure vs n-Alkane carbon number. r = .99925.

3) ppm (g/mL) calculated using ideal gas law.

+) n-alkanes >C9 vapor pressures used for partition coefficient calculations.

Table 34. Aroma Pure Vapor Pressures at 25°C

	Perry[1]		Boublík[2]	
	atm	ppm	atm	ppm
d-Limonene	2.68E-3[+]	14.9	-	
Diphenymethane	4.54E-5[R]	0.312	5.42E-7[R]	0.00373
Linalylacetate	1.37E-4[R]	1.10	-	
Camphor	4.06E-4[R]	2.53	6.98E-5[R]	0.435
Diphenyoxide	-		-	
Isoamylacetate	7.13E-3[+]	38.0	7.57E-3	40.3
γ-Undelactone	-		-	
Eugenol	2.40E-5[R]	0.162	-	
Citronellol	5.65E-5[R]	0.361	-	
Dimethylbenzlcarbinol[5]	-		-	
L-Menthol	1.61E-4[R]	1.03	-	
Phenylethylalcohol	1.05E-4[R]	0.525	-	
cis-3-Hexenol[*]	1.32E-3[+]	5.39	-	

1) Antoine equation estimate using experimental data from Perry (1984)
2) Boublík et al. (1973) reported antoine equation constants.
3) RI = retention indices vapor pressure estimation method using retention indices from Jennings and Shibamoto (1980) and the n-alkane Perry vapor pressures Table 31.
4) Estimated using Miller equation as described in Bertucco et al. (1991) using Perry (1984) vapor pressure data.
5) ethylbenzylcarbinol used to estimate dimethylbenzylcarbinol v.p.

R = The value reported is outside of the temperature range for the antoine equation and could contain considerable error.
* = estimated from vapor pressure of 1-hexanol ppm = (μg/mL)
\+ = used for partition coefficient calculations

Table 34. (cont.)

	RI[3]		Miller[4]
	atm	ppm	atm
d-Limonene	1.65E-4	9.18	2.687E-3
Diphenymethane	3.23E-5	0.222^+	4.547E-5
Linalylacetate	1.31E-4	1.052^+	1.400E-4
Camphor	4.54E-4	2.82^+	4.097E-4
Diphenyoxide	2.66E-5	0.185^+	-
Isoamylacetate	9.82E-3	52.3	7.135E-3
γ-Undelactone	4.51E-6	0.0339^+	-
Eugenol	3.86E-5	0.259^+	2.599E-5
Citronellol	1.87E-4	1.19^+	5.785E-5
Dimethyl-benzlcarbinol	1.72E-4	1.06^+	-
Menthol	3.05E-4	1.95^+	1.588E-4
Phenylethyl-alcohol	6.54E-4	3.26	1.103E-4
cis-3-Hexenol*	1.13E-2	46.3	1.377E-3

Retention Indices Vapor Pressure Estimation Method.

The vapor pressure estimation method using retention indices was suggested by Piringer (1992) and is analogous to the molecular retention index, $Me_i^{(p)}$, equation for a solute i on the chromatographic stationary liquid stationary phase p.

$$Me_i^{(p)} = 14 \frac{\log_{10} P^{\circ}{}_i - \log_{10} P^{\circ}{}_n}{\log_{10} P^{\circ}{}_{n+1} - \log_{10} P^{\circ}{}_n} + M_n = 0.14\ I_i^{(p)} + 2 \tag{65}$$

Where $Me_i^{(p)}$ is the molecular retention index for a solute i on the chromatographic stationary phase p, P° is the saturated vapor pressure of a substance at temperature of interest, n is an n-alkane with n carbons and n+1 is the next n-alkane in the homologous series, M_z is the relative molecular weight and $I_i^{(p)}$ is the KOVATS index of the solute i on phase p. The retention indices for many aromas and other substances for the chromatographic stationary phases OV-101 and Carbowax 20M are found in Jennings and Shibamoto (1980) the saturated vapor pressures for n-alkanes can be found in Perry's (1984).

Appendix B

Raw $K_{L/G}$ Data

Table 35. n-Alkanes Experimental K(L/G) 100% Ethanol

alkane	Avg. x(i) (x10E+4)	Avg. ppm (g/mL)		Measurement 1	2	3	4
C5	1.05	129	trap	80.3	74.4	69.8	90.1
	(.037)	(4.5)	mass bal	1.16	4.13	1.52	3.3
			diff.	88.8	110	79.6	75.8
C6	1.04	152	trap	215	203	184	182
	(.048)	(7.1)	mass bal	1.19	1.48	1.69	1.83
			diff.	283	154	276	222
C7	1.01	173	trap	661	537	470	465
	(.0055)	(1.1)	mass bal	0.214	6.01	0.667	3.53
			diff.	760		352	
C8	1.05	204	trap	1770	1550	1450	1270
	(.052)	(9.7)	mass bal	0.0018	1.5	0.288	3.34
			diff.	1780		1006	
C9	1.02	223	trap	4920	4980	4680	
	(.011)	(2.3)	mass bal	0.099	1.32	0.348	
			diff.	3070	2770		2730
C10	1	244	trap	24400	23300	27400	16300
	(.016)	(4.5)	mass bal	0.108	3.55	0.77	0.642
			diff.				
C12	1.01	294	trap	156200	166400	156400	76300
	(.013)	(3.5)	mass bal	0.621	0.907	1.74	0.073
			diff.				
C14*	1	340	trap	320800	540400	484900	478600
	(.0048)	(1.5)	mass bal	2.56	0.904	0.896	2.12
			diff.				
C16*	1	392	trap	842400	2E+06		
	(-)	(-)	mass bal	2.72	4.32		
			diff.				

- not determined
( ) = standard deviation
* high analytical uncertainty
x(i) = mole fraction
trap = measurements using solvent trap
diff. = measurements using liquid phase conc. differences
avg = average
mass bal. = mass balance absolute diff. from initial input
s.d. = standard deviation
c.v. = percent coefficient of variation (s.d./average)

Table 35. (cont.)

	Measurement							
alkane	5	6	7	8	9	Average	s.d.	c.v.
C5						78.65	7.59	9.6
						2.53	1.23	48.7
	63.2	73.4	93	97		85.10	14.01	16.5
C6	214					199.60	14.21	7.1
	7.77					2.79	2.50	89.5
	161	191	216	249		219.00	45.60	20.8
C7	505	549				531.17	65.84	12.4
	3.89	2.33				2.77	1.98	71.3
	487	487	602	679		561.17	135.30	24.1
C8	1400	1300				1456.67	168.09	11.5
	8.8	1.54				2.58	2.98	116
		1100	1560	1370		1363.20	286.13	21.0
C9						4860.00	129.61	2.7
						0.59	0.53	89.4
						2856.67	151.73	5.3
C10	13100	10200	10300	11800	16400	17022.2	6117.7	35.9
	1.74	1.4	2.21	1.65	4.87	1.88	1.42	75.2
			3560	9670	4250	5826.67	2732.2	46.9
C12	67200	93800	111300			118229	38221	32.3
	0.957	2.07	4.64			1.57	1.40	88.8
C14*	707400					364940	196583	53.9
	4.76					2.25	1.42	63.1
C16*						1522200	679800	44.7
						3.52	0.80	22.7

Table 36. n-Alkanes Experimental K(L/G) 66% Ethanol

				Measurement		
n-alkane	Avg. x(i) (x 10E+5)	Avg. PPM (g/mL)		1	2	3
C5	4.02	84.2	trap	8.85	11.6	9.22
	(.29)	(.47)	mass bal	23.9	9.15	17.3
			diff.	7.45	10.3	7.23
C6	2.4	59.6	trap	15.5	21.7	17
	(.13)	(2.6)	mass bal	5.47	2.12	1.55
			diff.	14.2	21	17.4
C7	1.63	46.6	trap	30.9	44.2	39.2
	(.14)	(3.2)	mass bal	3.99	3.5	0.31
			diff.	28.5	41.3	39.5
C8	0.966	31.7	trap	139	264	192
	(.079)	(2.1)	mass bal	6.11	2.94	38.5
			diff.	127		41.4
C9	0.633	22.8	trap	1010	1310	
	(.065)	(2.2)	mass bal	12.9	27.2	
			diff.	160	89.5	
C10	0.387	15.5	trap	448	498	367
	(.037)	(1.4)	mass bal	0.65	5.75	0.55
			diff.	433	423	348
C12	0.18	8.08	trap	1790	2100	2080
	(.037)	(1.9)	mass bal	3.2	1.17	3.31
			diff.			
C14	0.07	3.59	trap	8260	8380	11522
	(.021)	(1.2)	mass bal	5.04	7.48	0.246
			diff.			
C16	0.031	1.78	trap	15300	3800	
	(.01)	(.65)	mass bal	3.89	2.53	
			diff.			

- not determined
( ) = standard deviation
* high analytical uncertainty
x(i) = mole fraction
trap = measurements using solvent trap
diff. = measurements using liquid phase conc. differences
avg = average
mass bal. = mass balance absolute diff. from initial input
s.d. = standard deviation
c.v. = percent coefficient of variation (s.d./average)

Table 36 (cont.)

alkane	4	5	6	7	Average	s.d.	c.v.
C5	8.42				9.52	1.2	12.9
	13				15.84	5.5	34.6
	8.67				8.41	1.2	14.5
C6	15.2				17.35	2.6	15.0
	11.7				5.21	4.0	77.5
	16.1				17.18	2.5	14.5
C7	29.8				36.03	6.0	16.5
	1.08				2.22	1.6	70.2
	36.5				36.45	4.9	13.4
C8	225	180.1			200.02	42.2	21.1
	17.1	3.59			13.65	13.4	98.4
	80.2	151	48.9	85.6	89.02	39.3	44.1
C9					1160.00	150.0	12.9
					20.05	7.1	35.7
					124.75	35.3	28.3
C10	347	424			416.80	54.7	13.1
	1.19	6.35			2.90	2.6	89.4
	385	567			431.20	74.3	17.2
C12	2240	1980	1740		1988.33	175.7	8.8
	2.25	0.865	5.23		2.67	1.5	55.0
C14*	6620	3900			7736.40	2489	32.2
	34.4	3.21			10.08	12.4	123.0
C16*					9550.00	5750	60.2
					3.21	0.7	21.2

Table 37. n-Alkanes Experimental K(L/G) 33% Ethanol

n-alkane	Avg. x(i) (x10E+6)	Avg. ppm (g/mL)		Measurement			
				1	2	3	4
C5	19.3	58.4	trap	0.293	0.257	0.296	0.103
	(4.1)	(12)	mass bal	30.3	67.1	69.4	58.4
			diff.	0.284	0.169	0.343	0.165
C6	7.53	30.5	trap	0.2	0.197	0.179	
	(3.0)	(7.2)	mass bal	43.3	69.2	67.6	
			diff.	0.292	0.288	0.307	
C7	4.5	18.9	trap	0.48	0.223	0.617	0.366
	(2.3)	(9.5)	mass bal	25.9	91.8	24.7	46.7
			diff.			0.451	0.355
C8	3.63	11.9	trap	0.501			0.728
	(2.3)	(-)	mass bal	20.1			83.3
			diff.	0.608	0.861	0.678	
C9	3.63	8.56	trap	6.613	3.14	6.44	2.55
	(2.0)	(-)	mass bal	62	63.1	59.2	41.1
			diff.	1.19	0.85	1.52	1.25
C10	1.07	6.4	trap	1.489			
	(-)	(-)	mass bal	16.6			
			diff.	1.66	1.89	1.26	
C12	0.674	4.8	trap	8.03	5.82	14.3	4.41
	(-)	(-)	mass bal	25.1	63.5	8.84	27.6
			diff.	10.9	9.38	16.15	4.56
C14	0.327	2.72	trap	24.81	20.9	9.55	15.7
	(-)	(-)	mass bal	22.1	48.1	60.5	21.6
			diff.	29.4	24.9	22.2	9.49
C16	0.073	0.77	trap	52.2	31.2	94.7	62.7
	(-)	(-)	mass bal	26.4	40	19.1	0.007
			diff.	83			63

- not determined
( ) = standard deviation
* high analytical uncertainty
x(i) = mole fraction
trap = measurements using solvent trap
diff. = measurements using liquid phase conc. differences
avg = average
mass bal. = mass balance absolute diff. from initial input
s.d. = standard deviation
c.v. = percent coefficient of variation (s.d./average)

Table 37. (cont.)

Alk	5	6	7	8	Ave.	s.d.	c.v.
C5					0.19	0.12	62.3
					56.30	15.56	27.6
					0.24	0.08	31.7
C6					0.14	0.08	58.0
					60.03	11.85	19.7
					0.30	0.01	2.8
C7	0.275				0.33	0.20	59.8
	44.8				46.78	24.31	52.0
	0.407				0.40	0.04	9.7
C8	0.432	0.621			0.46	0.25	54.7
	56.2	32.1			47.93	24.21	50.5
	0.708	0.853			0.74	0.10	13.4
C9					3.75	2.50	66.8
					56.35	8.92	15.8
					1.20	0.24	19.8
C10					0.74		
					16.60		
					1.60	0.26	16.2
C12	6.27	6.04			6.41	3.97	62.0
	46.4	1.63			28.85	21.08	73.1
		6.26			9.45	4.03	42.6
C14	10.4	13.8	22		14.65	7.56	51.6
	46.2	0.471	10.8		29.97	20.33	67.8
	25	13.7	13.4		19.73	6.92	35.1
C16	42.4	44.1	62.4		48.71	25.62	52.6
	24.2	1.97	6.45		16.88	13.62	80.7
		56		45.7	67.33	11.44	17.0

Table 38. Aroma Experimental K(L/G): 100% Ethanol, 25C

Aroma	Ave. x(i) (x10E+6)	Ave. ppm g/mL		Measurement 1	Measurement 2
Isoamylacetate	7.7	16.88	K(L/G)	15500	16300
			mass bal	1.15	1.81
d-Limonene	7.7	16.96	K(L/G)	19200	19700
			mass bal	0.75	1.65
Cis-3-Hexenol	7.7	12.4	K(L/G)	183000	90400
			mass bal	2.15	3.94
Camphor	7.7	18.72	K(L/G)	133000	144000
			mass bal	3.9	2.7
Linalylacetate	7.7	23.73	K(L/G)	239000	341000
			mass bal	4.94	2
Menthol	7.7	20.28	K(L/G)	865000	334000
			mass bal	1.34	4.5
Citronellol	14.3	38	K(L/G)	393000	269000
			mass bal	1.72	3
Dimethylbenzyl-carbinol	7.7	19.76	K(L/G)	350000	668000
			mass bal	4.53	1.85
* Phenylethyl-alcohol	7.7	16.16	K(L/G)	671000	678000
			mass bal	0.51	1.84
Dimethylmethane	7.7	20.9	K(L/G)	504000	889000
			mass bal	3.14	1.09
Diphenyloxide	7.7	19.76	K(L/G)	325000	574000
			mass bal	4.7	1.9
* Eugenol	7.7	21.67	K(L/G)	738000	
			mass bal	4.28	
* gamma-undelactone	7.7	23.77	K(L/G)		
			mass bal. %		

* results highly uncertain, large error likely
Gas flow (100-300 mL/min), Liquid flow (1-3 mL/min)
Ratio gas/liquid flow = 63-190
x(i) = mole fraction
mass bal. = mass balance absolute percent deviation from 100%
s.d. = standard deviation
c.v. = percent coefficient of variation (s.d./average)

Table 38 (cont.)

Measurement						
3	4	5	6	Average	s.d.	c.v.
12300	11300	12800	12000	13366.7	1859.8	14
0.287	2.9	7.72	3.16	2.8	2.4	84
14700	13400	15200	13400	15933.3	2574.0	16
0.59	2.95	7.33	3.3	2.8	2.3	83
132000	148000	126000		135880.0	30160.5	22
3.2	7.38	3.21		4.0	1.8	45
160000	150000			146750.0	9782.0	7
7.81	4.03			4.6	1.9	42
343000	348000			317750.0	45537.8	14
8.48	4.49			5.0	2.3	46
623000	900000	773000		699000.0	206123.3	29
2.03	7.95	4.45		4.1	2.3	57
				331000.0	62000.0	19
				2.4	0.6	27
728000	818000			641000.0	176286.7	28
7.08	4.3			4.4	1.9	42
666000				671666.7	4921.6	1
4.33				2.2	1.6	71
314000	464000	468000	523000	527000.0	175313.1	33
4.74	1.91	6.4	5.47	3.8	1.9	50
764000	619000			570500.0	158174.7	28
7.21	4.18			4.5	1.9	42
				738000.0		
				4.3		

Table 39. Aroma Experimental K(L/G): 75% Ethanol, 25 C

Aroma	Avg. x(i) (x10E+6)	Avg. ppm g/mL		Measurement 1	Measurement 2
Isoamylacetate	7.7	16.88	K(L/G)	5850	6070
			mass bal.	0.058	5.26
d-Limonene	7.7	16.96	K(L/G)	12400	9870
			mass bal.	2.46	1.47
Cis-3-Hexenol	7.7	12.4	K(L/G)	99300	118600
			mass bal.	2.38	5.2
Camphor	7.7	18.72	K(L/G)	95900	112000
			mass bal.	2.63	5.54
Linalylacetate	7.7	23.73	K(L/G)	136000	161000
			mass bal.	3.17	4.65
Menthol	7.7	20.28	K(L/G)	633000	783000
			mass bal.	3.12	6.82
Citronellol	14.3	38	K(L/G)	213000	213000
			mass bal.	2.75	2.78
Dimethylbenzyl-carbinol	7.7	19.76	K(L/G)	729000	587000
			mass bal.	17.6	5.6
Phenylethyl-alcohol	7.7	16.16	K(L/G)	691000	503000
			mass bal.	17.1	5
Dimethylmethane	7.7	20.9	K(L/G)	303000	254000
			mass bal.	2.69	5.81
Diphenyloxide	7.7	19.76	K(L/G)	282000	260000
			mass bal.	1.83	5.52
* Eugenol	7.7	21.67	K(L/G)	477000	585000
			mass bal.	1.7	18
* gamma-undelactone	7.7	23.77	K(L/G)	963000	1173000
			mass bal.	1.39	19.9

* results highly uncertain
Gas flow (100-300 mL/min)
Liquid flow (1-3 mL/min)
ratio gas flow / liquid flow = 56-100

Table 39 (cont.)

Measurement				
3	4	Average	s.d.	c.v.
5470	4470	5465.0	613.2	11
13.5	5.18	6.00	4.82	80
11500		11256.7	1047.1	9
3.66		2.53	0.90	35
83500	79100	95125.0	15495.5	16
16.4	5.02	7.25	5.40	74
99000	81600	97125.0	10808.6	11
17.7	4.96	7.71	5.87	76
143000	89700	132425.0	26299.1	20
18.7	4.43	7.74	6.35	82
593000		669666.7	81785.6	12
17.5		9.15	6.10	67
		213000.0	0.0	0
		2.77	0.01	1
		658000.0	71000.0	11
		11.60	6.00	52
		597000.0	94000.0	16
		11.05	6.05	55
218000	192000	241750.0	41655.6	17
18.1	5.47	8.02	5.95	74
217000	188000	236750.0	36588.1	15
18.2	4.92	7.62	6.27	82
862000		641333.3	162144.7	25
3.95		7.88	7.21	91
1182000		1106000.0	101183.0	9
9.3		10.20	7.58	74

Table 40. Aroma Experimental K(L/G): 50% Ethanol, 25 C.

Aroma	Avg. x(i) (x10E+6)	Avg. ppm g/mL		Measurement	
				1	2
Isoamylacetate	7.7	16.88	K(L/G)	1160	1180
			mass bal	5.4	8.25
d-Limonene	7.7	16.96	K(L/G)	224	258
			mass bal	7.89	6.29
Cis-3-Hexenol	7.7	12.4	K(L/G)	33500	31200
			mass bal	2.48	0.256
Camphor	7.7	18.72	K(L/G)	24900	22400
			mass bal	29.8	4.64
Linalylacetate	7.7	23.73	K(L/G)	17500	16300
			mass bal	43.8	0.061
Menthol	7.7	20.28	K(L/G)	120000	114000
			mass bal	28.2	0.384
Citronellol	14.3	38	K(L/G)	151000	161000
			mass bal	2.97	0.25
Dimethylbenzylcarbinol	7.7	19.76	K(L/G)	293000	251000
			mass bal	2.03	1.34
Phenylethylalcohol	7.7	16.16	K(L/G)	382000	157000
			mass bal	11.8	0.563
Dimethylmethane	7.7	20.9	K(L/G)	28900	26200
			mass bal	33.3	0.09
Diphenyloxide	7.7	19.76	K(L/G)	25600	23400
			mass bal	35.1	0.017
* Eugenol	7.7	21.67	K(L/G)	439000	491000
			mass bal	7.44	2.56
* gamma-undelactone	7.7	23.77	K(L/G)	652000	297000
			mass bal	40.8	0.46

* results highly uncertain
Gas flow (100-300 mL/min)
Liquid flow (1-3 mL/min)
ratio gas flow / liquid flow = 58-61

Table 40 (cont.)

Measurement				
3	4	Average	s.d.	c.v.
868	1490	1174.5	220.1	19
0.42	5.41	4.87	2.82	58
168	290	235.0	45.2	19
11.5	2.35	7.01	3.29	47
31400	42000	34525.0	4408.7	13
1.49	0.76	1.25	0.84	67
19500	27000	23450.0	2802.2	12
0.83	4.93	10.05	11.52	115
13200	20900	16975.0	2756.2	16
1.73	0.11	11.43	18.70	164
103000	139000	119000.0	13057.6	11
1.95	0.54	7.77	11.81	152
116000		142666.7	19293.1	14
6.52		3.25	2.57	79
177000	342000	265750.0	60520.1	23
1.3	1.38	1.51	0.30	20
926000		488333.3	322821.2	66
0.095		4.15	5.41	130
22000	32300	27350.0	3769.9	14
1.64	0.207	8.81	14.15	161
19900	29100	24500.0	3344.4	14
1.75	0.964	9.46	14.82	157
801000	1520000	812750.0	431147.5	53
3.16	1.28	3.61	2.31	64
431000	2340000	930000.0	823874.1	89
1.88	1.22	11.09	17.16	155

Table 41. Aroma Experimental K(L/G): 35%, 25 C.

Aroma	Avg. x(i) (x10E+6)	Avg. ppm g/mL		Measurement 1	Measurement 2
Isoamylacetate	7.7	16.88	K(L/G)	399	348
			mass bal. %	13.2	3.84
d-Limonene	7.7	16.96	K(L/G)	39.8	30
			mass bal. %	11.2	0.25
Cis-3-Hexenol	7.7	12.4	K(L/G)	13900	12000
			mass bal. %	17.7	2.14
Camphor	7.7	18.72	K(L/G)	6570	5690
			mass bal. %	16.2	2.43
Linalylacetate	7.7	23.73	K(L/G)	2520	2160
			mass bal. %	16.2	0.971
Menthol	7.7	20.28	K(L/G)	22200	23600
			mass bal. %	0.682	18.3
Citronellol	14.3	38	K(L/G)	100000	49400
			mass bal. %	2.67	2.83
Dimethylbenzyl-carbinol	7.7	19.76	K(L/G)	69800	131000
			mass bal. %	1.44	11.4
Phenylethyl-alcohol	7.7	16.16	K(L/G)	152000	110000
			mass bal. %	2.06	3.3
Dimethylmethane	7.7	20.9	K(L/G)	4770	4330
			mass bal. %	1.12	16.3
Diphenyloxide	7.7	19.76	K(L/G)	4020	3610
			mass bal. %	3.92	14.2
Eugenol	7.7	21.67	K(L/G)	250000	241000
			mass bal. %	8.8	4.86
gamma-undelactone	7.7	23.77	K(L/G)	222000	345000
			mass bal. %	11.5	3.86

Gas flow (100-300 mL/min)
Liquid flow (1-3 mL/min)
ratio gas flow / liquid flow = 45-71

Table 41. (cont.)

Measurement				
3	4	Average	s.d.	c.v.
385		377.3	21.5	6
8.85		8.63	3.82	44
33.8		34.5	4.0	12
5.6		5.68	4.47	79
12300		12733.3	834.0	7
10.1		9.98	6.35	64
5670		5976.7	419.6	7
5.81		8.15	5.86	72
2220		2300.0	157.5	7
13.4		10.19	6.62	65
20300	20300	21600.0	1391.0	6
0.273	11.6	7.71	7.62	99
68100		72500.0	20890.3	29
6.32		3.94	1.68	43
90200	90600	95400.0	22208.1	23
6.71	5.9	6.36	3.53	56
269000	281000	203000.0	73637.6	36
0.017	15.1	5.12	5.88	115
3740	3780	4155.0	424.8	10
0.72	22.5	10.16	9.50	93
3110	3130	3467.5	376.6	11
1.37	5.46	6.24	4.82	77
244000		245000.0	3741.7	2
1.85		5.17	2.85	55
363000		310000.0	62657.8	20
2.7		6.02	3.90	65

Appendix C

Raw $K_{P/L}$ Data

Table 42. n-Alkane Experimental K(P/L) Data

Partitioned between 100% Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C8						
1	2.22	-	1.38	-	1.18	-
2	2.29	-	1.29	-	1.09	-
3	1.92	-	1.40	-	1.24	-
4	1.92	-	1.31	-	1.27	-
Average	2.09		1.34		1.20	
Std. Dev.	0.17		0.05		0.07	
% c.v.	8.04		3.38		6.01	
C9						
1	3.63	-	2.16	-	1.70	-
2	3.75	-	1.91	-	1.63	-
3	3.70	-	2.14	-	1.90	-
4	3.37	-	2.15	-	1.79	-
Average	3.61		2.09		1.76	
Std. Dev.	0.15		0.10		0.10	
% c.v.	4.08		4.98		5.74	
C10						
1	5.89	37.5	3.33	85.6	2.36	86.6
2	6.00	37.3	2.57	99.6	2.88	71.9
3	5.75	39.4	2.75	96.7	2.23	91.2
4	5.58	39.3	2.16	109.0	2.16	92.2
Average	5.81	38.4	2.70	97.7	2.41	85.5
Std. Dev.	0.16	1.0	0.42	8.3	0.28	8.1
% c.v.	2.74	2.6	15.47	8.5	11.80	9.5

Table 42. (cont.)

Partitioned between 100% Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C12						
1	11.24	41.3	3.42	69.7	2.57	72.9
2	11.04	41.3	3.37	71.5	2.38	70.5
3	10.28	43.4	3.42	71.9	2.57	71.0
4	10.38	43.5	3.07	71.8	2.64	71.7
Average	10.73	42.4	3.32	71.2	2.54	71.5
Std. Dev.	0.41	1.1	0.15	0.9	0.10	0.9
% c.v.	3.84	2.6	4.44	1.3	3.75	1.2
C14						
1	22.64	49.6	6.33	75.8	4.06	77.9
2	23.13	48.1	6.18	75.2	4.16	75.9
3	21.08	52.3	6.27	77.5	4.18	76.1
4	20.50	51.7	5.90	77.6		45.1
Average	21.84	50.4	6.17	76.5	4.13	68.7
Std. Dev.	1.08	1.7	0.16	1.0	0.05	13.7
% c.v.	4.96	3.3	2.66	1.4	1.28	19.9
C16						
1	46.02	63.3	11.28	81.1	6.83	81.5
2	47.70	61.6	10.84	82.8	6.95	79.5
3	43.60	66.5	11.23	83.1	6.89	79.8
4	42.27	65.7	10.80	83.4	7.10	81.0
Average	44.90	64.3	11.04	82.6	6.94	80.4
Std. Dev.	2.10	2.0	0.22	0.9	0.10	0.8
% c.v.	4.69	3.1	2.02	1.1	1.45	1.0

Table 42. (cont.)

Partitioned between 100% Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C18						
1	86.62	81.2	24.17	95.0	24.24	104.8
2	85.79	80.8	24.89	98.9	24.26	102.1
3	81.07	84.2		117.1	22.66	101.3
4	80.06	84.0	23.33	96.4	23.62	103.6
Average	83.38	82.5	24.13	101.9	23.70	103.0
Std. Dev.	2.86	1.5	0.64	8.9	0.65	1.4
% c.v.	3.43	1.9	2.65	8.8	2.75	1.3
C20						
1	151.33	103.7	66.12	133.7	41.66	115.9
2	152.00	103.4	58.70	127.5	42.04	112.7
3	140.19	105.6	56.21	120.8	40.35	112.6
4	139.72	105.9	56.44	126.3	35.83	106.4
Average	145.81	104.7	59.37	127.1	39.97	111.9
Std. Dev.	5.86	1.1	4.02	4.6	2.47	3.4
% c.v.	4.02	1.1	6.77	3.6	6.18	3.1
C22						
1	224.74	121.4	67.27	73.3	40.70	67.3
2	225.85	121.6	65.36	73.5	42.37	66.1
3	202.93	121.9	68.14	73.9	39.89	65.4
4	208.27	122.7	60.52	72.5	42.27	67.4
Average	215.45	121.9	65.33	73.3	41.31	66.5
Std. Dev.	10.03	0.5	2.95	0.5	1.05	0.8
% c.v.	4.66	0.4	4.51	0.7	2.55	1.3

Table 42. (cont.)

Partitioned Between 100% Ethanol and LDPE

n-Alkane replicate	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
C8						
1	-	-	0.74	-	0.73	-
2	-	-	0.81	-	0.86	-
3	-	-	0.84	-	0.91	-
4	-	-	0.85	-	0.85	-
Average			0.81		0.84	
Std. Dev.			0.04		0.07	
% c.v.			5.46		8.15	
C9						
1	1.85	-	1.27	-	0.98	-
2	2.15	-	1.32	-	1.22	-
3	1.84	-	1.16	-	1.50	-
4	2.32	-	1.17	-	1.28	-
Average	2.04		1.23		1.25	
Std. Dev.	0.20		0.07		0.19	
% c.v.	9.92		5.49		15.07	
C10						
1	3.73	37.2	3.05	149.2	3.93	101.3
2	3.87	36.2	3.82	116.0	2.65	93.8
3	3.82	36.4	2.54	149.0	3.50	93.0
4	4.04	36.8	4.59	88.9	4.00	85.4
Average	3.87	36.6	3.50	125.8	3.52	93.4
Std. Dev.	0.11	0.4	0.78	25.2	0.54	5.6
% c.v.	2.97	1.1	22.18	20.1	15.26	6.0

Table 42. (cont.)

Partitioned Between 100% Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C12						
1	5.41	38.4	2.06	71.8	1.72	74.2
2	6.28	37.3	2.03	71.9	1.92	68.2
3	6.20	36.9	2.04	72.3	2.27	66.2
4	6.05	38.0	2.01	72.2	2.15	67.9
Average	5.98	37.6	2.03	72.0	2.02	69.1
Std. Dev.	0.34	0.6	0.02	0.2	0.21	3.0
% c.v.	5.69	1.5	0.84	0.3	10.49	4.4
C14						
1	8.48	39.4	3.55	72.6	2.83	74.9
2	9.71	38.2	3.51	73.0	3.11	68.8
3	9.59	38.7	3.39	72.9	3.55	66.5
4	9.86	39.1	3.44	72.7	3.45	68.9
Average	9.41	38.9	3.48	72.8	3.24	69.8
Std. Dev.	0.54	0.5	0.06	0.2	0.29	3.1
% c.v.	5.76	1.2	1.76	0.2	8.86	4.5
C16						
1	16.32	41.9	5.57	73.5	4.25	75.4
2	18.39	40.9	5.61	73.9	4.84	69.7
3	17.26	41.1	5.38	74.0	5.62	64.7
4	17.78	41.6	5.62	73.7	5.28	69.7
Average	17.44	41.4	5.54	73.8	5.00	69.9
Std. Dev.	0.76	0.4	0.10	0.2	0.51	3.8
% c.v.	4.37	1.0	1.78	0.2	10.26	5.4

Table 42. (cont.)

Partitioned Between 100% Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C18						
1	30.93	45.8	39.96	101.5	30.87	98.2
2	34.03	45.3	42.33	103.3	31.09	89.9
3	32.48	45.5	41.93	103.9	33.32	89.5
4	32.91	46.1	42.59	101.9	27.23	84.6
Average	32.59	45.7	41.70	102.7	30.63	90.5
Std. Dev.	1.11	0.3	1.03	1.0	2.18	4.9
% c.v.	3.41	0.7	2.48	0.9	7.13	5.4
C20						
1	65.59	55.6	17.21	72.9	27.53	86.0
2	71.72	56.8	35.48	88.5	27.61	79.2
3	69.86	56.2	37.67	90.7	27.31	76.7
4	68.42	56.6	35.15	86.4	26.69	78.4
Average	68.90	56.3	31.38	84.6	27.29	80.1
Std. Dev.	2.24	0.5	8.24	6.9	0.36	3.5
% c.v.	3.25	0.8	26.25	8.2	1.33	4.4
C22						
1	160.15	76.1	25.50	60.9	18.26	62.6
2	168.86	80.6	27.50	62.2	20.16	59.3
3	164.53	79.7	25.27	61.3	21.86	57.9
4	156.92	79.5	26.21	60.6	21.34	58.9
Average	162.62	79.0	26.12	61.3	20.41	59.7
Std. Dev.	4.51	1.7	0.87	0.6	1.38	1.7
% c.v.	2.77	2.1	3.32	1.0	6.78	2.9

Table 42. (cont.)

Partitioned Between 75% (w/w) Aqueous Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C8						
1	3.16	-	2.92	-	0.86	-
2	2.82	-	2.68	-	1.00	-
3	2.99	-	2.46	-	1.16	-
4	3.01	-	2.18	-	1.47	-
Average	2.99		2.56		1.12	
Std. Dev.	0.12		0.27		0.23	
% c.v.	4.02		10.65		20.53	
C9						
1	4.53	-	4.64	-	1.93	-
2	4.02	-	3.81	-	1.97	-
3	4.19	-	3.91	-	2.19	-
4	4.23	-	3.69	-	2.61	-
Average	4.24		4.01		2.18	
Std. Dev.	0.18		0.37		0.27	
% c.v.	4.31		9.22		12.41	
C10 *			*		*	
1	6.36	112.8	11.59	116.42	2.91	97.48
2	5.71	116.0	10.12	126.71	5.68	106.22
3	5.85	119.6	14.30	131.59	16.14	112.92
4	5.93	111.6	20.84	158.60	16.77	108.43
Average	5.97	115.0	14.21	133.33	10.38	106.26
Std. Dev.	0.24	3.1	4.11	15.58	6.16	5.62
% c.v.	4.05	2.7	28.91	11.69	59.38	5.29

Table 42. (cont.)

Partitioned Between 75% (w/w) Aqueous Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C12						
1	14.09	116.0	11.03	109.55	5.63	102.08
2	12.63	116.0	8.94	117.49	5.63	105.32
3	12.68	121.2	9.68	114.41	6.22	101.99
4	13.01	114.1	9.60	122.34	6.78	99.82
Average	13.10	116.8	9.81	115.95	6.07	102.30
Std. Dev.	0.59	2.7	0.76	4.65	0.48	1.96
% c.v.	4.48	2.3	7.71	4.01	7.92	1.92
C14						
1	34.54	115.3	24.50	107.24	10.97	100.55
2	30.86	110.8	19.86	113.31	11.46	102.38
3	30.43	114.9	21.74	110.92	12.45	98.73
4	31.61	109.9	21.36	118.27	13.39	98.97
Average	31.86	112.7	21.87	112.44	12.07	100.16
Std. Dev.	1.60	2.4	1.68	4.00	0.93	1.46
% c.v.	5.03	2.1	7.67	3.56	7.70	1.46
C16						
1	89.12	118.8	60.68	108.07	22.72	93.25
2	79.41	109.7	49.35	110.34	24.11	94.11
3	76.30	113.6	54.18	110.57	25.99	90.91
4	78.52	108.5	50.62	116.72	27.84	92.43
Average	80.84	112.6	53.71	111.43	25.17	92.67
Std. Dev.	4.92	4.0	4.40	3.21	1.93	1.18
% c.v.	6.08	3.6	8.19	2.88	7.68	1.27

Table 42. (cont.)

Partitioned Between 75% (w/w) Aqueous Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C18						
1	269.82	115.4	176.85	107.74	51.02	89.04
2	243.35	103.7	144.96	105.33	54.08	89.06
3	231.76	110.5	156.67	108.18	58.59	86.83
4	230.11	102.5	140.38	112.58	62.43	88.56
Average	243.76	108.0	154.72	108.46	56.53	88.37
Std. Dev.	15.89	5.2	14.09	2.62	4.34	0.91
% c.v.	6.52	4.8	9.11	2.41	7.68	1.03
C20						
1	774.29	99.6	597.63	103.93	126.38	87.57
2	776.93	90.8	505.78	97.98	132.73	88.35
3	803.94	104.4	542.11	104.01	143.63	84.98
4	832.85	102.2	471.67	106.10	153.56	86.31
Average	797.00	99.2	529.30	103.01	139.08	86.80
Std. Dev.	23.73	5.2	46.66	3.03	10.39	1.28
% c.v.	2.98	5.2	8.82	2.94	7.47	1.47
C22						
1	2370.44	86.6	2756.00	96.57	467.11	91.29
2	2355.43	81.8	1970.47	89.79	476.01	96.25
3	2567.49	92.2	2406.81	102.62	531.19	85.30
4	1659.31	89.5	1904.64	98.05	548.95	83.52
Average	2238.17	87.5	2259.48	96.76	505.82	89.09
Std. Dev.	344.52	3.9	345.57	4.60	34.97	5.04
% c.v.	15.39	4.4	15.29	4.75	6.91	5.66

Table 42. (cont.)

Partitioned Between 75% (w/w) Aqueous Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C8						
1	1.13	-	1.19	-	0.86	-
2	1.73	-	1.75	-	1.00	-
3	1.72	-	1.44	-	1.16	-
4	1.88	-	1.62	-	1.47	-
Average	1.62		1.50		1.12	
Std. Dev.	0.29		0.21		0.23	
% c.v.	17.77		13.95		20.53	
C9						
1	2.75	-	2.63	-	1.93	-
2	3.34	-	3.47	-	1.97	-
3	3.19	-	2.86	-	2.19	-
4	3.55	-	3.07	-	2.61	-
Average	3.21		3.01		2.18	
Std. Dev.	0.30		0.31		0.27	
% c.v.	9.24		10.22		12.41	
C10 *						
1	6.51	22.92	2.46	86.25	2.91	97.48
2	12.43	24.04	8.71	88.91	5.68	106.22
3	27.81	30.23	5.22	97.52	16.14	112.92
4	27.78	28.97	25.25	111.29	16.77	108.43
Average	18.63	26.54	10.41	95.99	10.38	106.26
Std. Dev.	9.40	3.12	8.85	9.76	6.16	5.62
% c.v.	50.44	11.74	85.00	10.17	59.38	5.29

Table 42. (cont.)

Partitioned Between 75% (w/w) Aqueous Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C12						
1	9.42	29.85	8.45	89.25	5.63	102.08
2	10.38	29.95	11.04	87.88	5.63	105.32
3	10.16	32.11	8.35	98.45	6.22	101.99
4	10.66	31.26	8.65	98.98	6.78	99.82
Average	10.16	30.79	9.12	93.64	6.07	102.30
Std. Dev.	0.46	0.94	1.11	5.10	0.48	1.96
% c.v.	4.55	3.07	12.20	5.45	7.92	1.92
C14						
1	18.36	30.15	18.81	84.04	10.97	100.55
2	20.39	30.94	23.42	83.86	11.46	102.38
3	19.76	32.60	18.44	92.41	12.45	98.73
4	20.65	32.29	19.74	89.96	13.39	98.97
Average	19.79	31.49	20.10	87.57	12.07	100.16
Std. Dev.	0.89	1.00	1.97	3.72	0.93	1.46
% c.v.	4.48	3.17	9.81	4.25	7.70	1.46
C16						
1	41.24	27.83	45.78	80.74	22.72	93.25
2	44.25	29.44	54.65	82.87	24.11	94.11
3	43.24	30.38	42.89	87.29	25.99	90.91
4	44.81	30.77	45.89	86.88	27.84	92.43
Average	43.39	29.60	47.30	84.45	25.17	92.67
Std. Dev.	1.36	1.13	4.41	2.75	1.93	1.18
% c.v.	3.14	3.83	9.32	3.26	7.68	1.27

Table 42. (cont.)

Partitioned Between 75% (w/w) Aqueous Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C18						
1	116.73	26.90	122.71	80.04	51.02	89.04
2	115.61	28.99	140.20	83.61	54.08	89.06
3	117.23	29.31	112.97	83.04	58.59	86.83
4	118.55	30.19	119.12	85.43	62.43	88.56
Average	117.03	28.85	123.75	83.03	56.53	88.37
Std. Dev.	1.06	1.21	10.11	1.94	4.34	0.91
% c.v.	0.90	4.18	8.17	2.34	7.68	1.03
C20						
1	439.64	29.57	377.94	81.62	126.38	87.57
2	398.12	31.50	407.67	85.19	132.73	88.35
3	404.91	31.02	337.04	79.35	143.63	84.98
4	398.93	31.98	353.98	85.84	153.56	86.31
Average	410.40	31.02	369.16	83.00	139.08	86.80
Std. Dev.	17.09	0.90	26.56	2.65	10.39	1.28
% c.v.	4.16	2.91	7.20	3.19	7.47	1.47
C22						
1	2878.19	43.38	1490.49	82.34	467.11	91.29
2	2152.07	46.59	1709.44	81.22	476.01	96.25
3	2185.78	41.86	2004.01	73.14	531.19	85.30
4	1972.22	41.18	1551.77	83.98	548.95	83.52
Average	2297.06	43.25	1688.93	80.17	505.82	89.09
Std. Dev.	345.19	2.08	198.67	4.18	34.97	5.04
% c.v.	15.03	4.82	11.76	5.21	6.91	5.66

Table 42. (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C8						
1	40.64	74.1	79.8	43.1	83.0	42.0
2	50.93	67.8	58.9	48.7	53.2	43.0
3	40.84	73.7	110.5	39.8	60.1	29.5
4	39.06	76.7	80.3	44.7	72.2	38.6
Average	42.87	73.1	82.4	44.1	67.1	38.3
Std. Dev.	4.71	3.3	18.4	3.2	11.4	5.3
% c.v.	10.98	4.5	22.3	7.3	17.0	13.9
C9						
1	70.37	82.7	230.2	56.2	62.5	35.8
2	79.44	79.9	148.9	61.4	99.1	59.3
3	69.19	81.1	331.7	54.6	109.1	51.2
4	65.99	83.1	220.5	57.9	106.3	57.8
Average	71.25	81.7	232.8	57.5	94.2	51.0
Std. Dev.	5.00	1.3	65.2	2.6	18.7	9.3
% c.v.	7.01	1.6	28.0	4.4	19.8	18.2
C10						
1	132.17	142.0	409.9	111.9	128.3	86.1
2	143.99	139.3	261.9	117.2	148.8	114.4
3	130.07	137.4	590.8	109.2	166.5	109.2
4	122.10	139.5	397.2	114.3	149.4	115.3
Average	132.08	139.5	414.9	113.2	148.3	106.2
Std. Dev.	7.83	1.6	116.9	2.9	13.6	11.9
% c.v.	5.93	1.2	28.2	2.6	9.1	11.2

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C12
1

2

3

4

Average
Std. De
% c.v.

C14
1

2

3

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Averag
Std. De
% c.v.

C16
1

2

3

4

Avera
Std. D
% c.v

Table 42. (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C12						
1	393.85	156.0	1456.4	143.7	261.8	77.0
2	414.77	154.5	924.6	147.2	444.7	142.3
3	387.87	149.7	1996.0	142.9	485.6	145.1
4	369.45	148.9	1438.4	145.5	409.3	145.1
Average	391.49	152.3	1453.8	144.8	400.3	127.4
Std. Dev.	16.17	3.1	378.9	1.7	84.4	29.1
% c.v.	4.13	2.0	26.1	1.1	21.1	22.9
C14						
1	1228.25	167.7	4061.3	168.9	1400.7	163.9
2	1293.85	168.5	2911.6	171.8	1188.6	164.4
3	1209.46	162.2	6111.9	166.8	1276.4	167.5
4	1145.93	157.5	4352.0	172.2	1091.6	166.8
Average	1219.37	163.9	4359.2	169.9	1239.3	165.6
Std. Dev.	52.72	4.5	1146.3	2.2	113.8	1.5
% c.v.	4.32	2.7	26.3	1.3	9.2	0.9
C16						
1	2866.45	183.3	13841.1	189.8	3194.7	185.2
2	3130.57	186.8	8513.5	191.3	2697.6	185.9
3	3103.14	178.0	19629.2	190.1	2884.2	191.6
4	2754.01	168.3	12321.1	192.9	2358.7	186.2
Average	2963.54	179.1	13576.2	191.0	2783.8	187.2
Std. Dev.	158.68	7.0	3997.3	1.2	302.9	2.5
% c.v.	5.35	3.9	29.4	0.6	10.9	1.4

Table 42. (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C18						
1	8404.4	185.0	33181.0	190.7	6141.3	189.0
2	10405.1	187.0	25284.3	192.1	6403.3	186.0
3	11697.4	181.0	35851.8	192.7	4212.1	193.0
4	9515.3	167.0	44134.4	191.9	4010.0	188.0
Average	10005.5	180.0	34612.9	191.9	5191.7	189.0
Std. Dev.	1206.9	7.8	6731.8	0.7	1086.9	2.5
% c.v.	12.1	4.3	19.4	0.4	20.9	1.3
C20						
1	8953.9	139.0	403403	188.4	20294.6	184.6
2	8261.4	143.0	417000	190.3	19540.7	182.1
3	10473.3	151.0	393654	190.1	16798.2	188.2
4	9933.6	140.0	398396	188.5	1750.4	184.2
Average	9405.5	143.3	403113	189.3	14596.0	184.8
Std. Dev.	856.1	4.7	8727.2	0.9	7529.7	2.2
% c.v.	9.1	3.3	2.2	0.5	51.6	1.2
C22						
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-

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C8
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2

3

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Ave
Std.
% C

C
1

2

3

4

Ave
Std.
%

1

2

3

4

Av
Std
%

Table 42. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C8						
1	100.9	-	18.3	-	16.4	-
2	160.9	-	15.1	-	13.1	-
3	687.5	-	18.3	-	11.6	-
4	118.2	-	61.6	-	13.4	-
Average	266.9		28.3		13.6	
Std. Dev.	243.8		19.2		1.7	
% c.v.	91.4		67.9		12.8	
C9						
1	185.2	-	121.3	-	27.5	-
2	235.1	-	114.0	-	21.8	-
3	440.5	-	111.8	-	19.9	-
4	197.8	-	311.7	-	21.6	-
Average	264.7		164.7		22.7	
Std. Dev.	103.2		84.9		2.8	
% c.v.	39.0		51.6		12.6	
C10						
1	418.5	55.4	268.0	50.0	50.2	119.7
2	487.7	55.1	246.3	44.7	40.4	117.8
3	648.2	55.5	247.5	54.2	39.1	114.4
4	419.7	58.1	643.2	48.8	40.3	121.2
Average	493.5	56.0	351.3	49.4	42.5	118.2
Std. Dev.	93.6	1.2	168.8	3.4	4.5	2.5
% c.v.	19.0	2.2	48.0	6.9	10.5	2.2

Partitio

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replicat

C12
1

2

3

4

Averag
Std. De
% c.v.

C14
1

2

3

4

Averag
Std. De
% c.v.

C16
1

2

3

4

Avera
Std. D
% c.v

Table 42. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C12						
1	1060.7	101.8	1004.1	90.2	129.5	143.9
2	1130.1	100.4	925.5	79.2	109.9	133.6
3	1135.7	104.0	1042.8	95.9	107.6	136.3
4	1017.3	103.3	2663.2	93.8	106.4	133.1
Average	1085.9	102.4	1408.9	89.8	113.3	136.7
Std. Dev.	49.5	1.4	725.4	6.4	9.4	4.3
% c.v.	4.6	1.3	51.5	7.2	8.3	3.2
C14						
1	2951.7	126.0	2738.4	117.1	343.2	147.0
2	3040.7	124.9	2539.1	101.2	276.0	135.7
3	2972.3	128.6	3058.5	123.6	285.0	140.3
4	2776.7	125.6	6424.0	124.1	281.2	130.3
Average	2935.4	126.3	3690.0	116.5	296.3	138.4
Std. Dev.	97.3	1.4	1589.3	9.3	27.2	6.1
% c.v.	3.3	1.1	43.1	7.9	9.2	4.4
C16						
1	7724.6	139.6	6501.0	134.4	578.9	159.4
2	7366.8	138.2	6643.3	114.7	597.6	141.0
3	7487.3	143.6	8739.9	140.1	626.1	147.9
4	6854.6	137.7	15667.0	141.6	590.8	133.8
Average	7358.3	139.8	9387.8	132.7	598.4	145.5
Std. Dev.	318.0	2.3	3732.1	10.7	17.4	9.5
% c.v.	4.3	1.7	39.8	8.1	2.9	6.5

Partitio

n-Alkane
replicat

C18
1

2

3

4

Average
Std. De
% c.v.

C20
1

2

3

4

Averag
Std. De
% c.v.

C22
1

2

3

4

Table 42. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

	10C		25C		40C	
n-Alkane replicate	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
C18						
1	21138.9	147.6	22584.3	142.8	1133.0	167.0
2	20771.7	145.1	25313.7	122.0	1165.9	147.2
3	20620.5	150.8	31096.9	148.0	1335.5	154.7
4	20841.6	146.0	31073.3	149.8	1404.4	132.7
Average	20843.2	147.4	27517.1	140.7	1259.7	150.4
Std. Dev.	188.5	2.2	3696.3	11.0	113.5	12.4
% c.v.	0.9	1.5	13.4	7.9	9.0	8.3
C20						
1	12144.2	140.0	628251	150.6	2947.8	136.4
2	22271.9	127.0	525213	128.6	3092.2	123.7
3	26527.2	129.0	620636	155.7	2606.9	137.5
4	26836.3	129.0	619793	156.8	3179.4	124.8
Average	21944.9	131.3	598473	148.0	2956.6	130.6
Std. Dev.	5938.9	5.1	42424.6	11.4	218.2	6.4
% c.v.	27.1	3.9	7.1	7.7	7.4	4.9
C22						
1	-	-	-	-	-	-
2	-	-	-	-	-	-
3	-	-	-	-	-	-
4	-	-	-	-	-	-

Table 42.

K(P/L) =
cP = conc
cL = conc
C = numbe
HDPE = de
LDPE = de
* = analy

Table 42. Table Descriptors and Abbreviations

K(P/L) = polymer/liquid partition coefficient
cP = concentration of solute in polymer (w/v)
cL = concentration of solute in liquid (w/v)
C = number of carbons in n-alkane
HDPE = density = 0.956
LDPE = density = 0.918
* = analytical problem separating with C10 from Ethanol

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Table 43. Aroma Experimental K(P/L) Data, 25C

Table Descriptors and Abbreviations

Initial concentrations used: ppm (microgram/mL)

Ethanol solutions:		100%	35%
ELUTION #	**NAME**	**PPM**	**(W/V)**
1	ISOAMYLACETATE	73.79	79.52
2	LIMONENE	67.56	79.74
3	CIS-3-HEXENOL	49.99	56.93
4	CAMPHOR	76.34	95.83
5	LINALYLACETATE	94.69	108.43
6	MENTHOL	81.58	92.84
7	DIMETHYLBENZYLPHENOL	79.04	88.51
8	PHENYLETHYLALCOHOL	65.59	75.89
9	DIPHENYLMETHANE	93.13	105.07
10	DIPHENYLOXIDE	99.34	108.07
11	EUGENOL	86.09	98.15
12	C14 ALDEHYDE	95.25	108.15

Sum of all 12 aromas in mixture = 4 x 10-4 mole fraction.
75%, 50% Ethanol conc. are approximately equal to 100% conc.

Key to Table:

repl. = replicate measurement
K(P/L) = polymer/liquid partition coefficient
cP = concentration in polymer (g/mL)
cL = concentration in liquid (g/mL)
Mass Balance = gram polymer + gram liquid phase/(initial grams)
(1) = aroma has likely decomposed data has large error
* = Data is significant to 2 significant figures only, more than 2 figures shown in this table have no significance.
(+) = concentration of aroma in polymer hexane extract is at or near the GC detection limit
(++) = aroma peak is overlayed or not well separated from polymer oligomer peak.
stnd.dev. = standard deviation of the mean
% c.v. = coefficient of variation (% stnd. dev. of mean)
(2) = Data measured using 21 polymer disks, all other 14 disks

Ta

Arom
repl

Isoam
1

2

3

4

Avera
Stnd
% c

d-Li
1

2

3

4

Aver
Stnd
% c

cis-
1

2

3

4

Aver
Stnd
% c

Table 43. Aroma Experimental K(P/L) Data, 25C

Partitioned between 100% Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate (+)						
1	0.0613	94.3	0.0257	105.3	0.0327	102.8
2	0.0667	96.0	0.0317	103.2	0.0354	105.0
3	0.0796	97.9	0.0345	101.6	0.0316	104.5
4	0.0798	105.7	0.0279	101.8	0.0322	102.6
Average:	0.0719	98.5	0.0300	103.0	0.0330	103.7
Stnd.dev	0.0081	4.3	0.0034	1.5	0.0015	1.1
% c.v.	11.2371	4.4	11.3178	1.4	4.4318	1.0
d-Limonene						
1	0.4309	105.3	0.2369	104.8	0.2294	102.5
2	0.5125	106.1	0.2391	102.8	0.2257	104.5
3	0.5894	109.6	0.2231	101.3	0.2121	104.2
4	0.5743	117.3	0.2077	101.2	0.2020	102.2
Average:	0.5268	109.6	0.2267	102.5	0.2173	103.3
Stnd.dev	0.0624	4.8	0.0126	1.5	0.0109	1.0
% c.v.	11.8397	4.4	5.5501	1.4	5.0270	1.0
cis-3-Hexenol (++)						
1	-	162.6		105.4	0.0319	102.9
2	-	163.0		103.5	0.0357	104.9
3	-	169.0	0.0261	101.9	0.0363	104.6
4	-	179.2	0.0285	102.1	0.0280	102.7
Average:		168.4	0.0273	103.2	0.0330	103.8
Stnd.dev.		6.7	0.0012	1.4	0.0033	1.0
% c.v.		4.0	4.2980	1.3	10.1360	0.9

Arom
repl

Camph
1

2

3

4

Avera
Stnd.
% c

Lina
1

2

3

4

Aver
Stnc
%

Men
1

2

3

4

Av
St
%

Table 43. (cont.)

Partitioned between 100% Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Camphor						
1	0.0392	100.6	0.0316	105.2	0.0421	102.6
2	0.0484	101.3	0.0411	103.4	0.0361	104.7
3	0.0496	104.7	0.0370	101.6	0.0372	104.5
4	0.0519	111.5	0.0297	101.7	0.0295	102.8
Average:	0.0473	104.5	0.0349	103.0	0.0363	103.6
Stnd.dev	0.0048	4.3	0.0045	1.5	0.0045	0.9
% c.v.	10.1848	4.1	12.8856	1.4	12.4203	0.9
Linalylacetate						
1	0.0795	83.1	0.0470	106.2	0.0493	103.4
2	0.1021	83.6	0.0500	104.0	0.0384	105.2
3	0.1130	86.5	0.0484	102.5	0.0444	105.3
4	0.1115	92.0	0.0395	102.9	0.0389	103.1
Average:	0.1015	86.3	0.0462	103.9	0.0427	104.3
Stnd.dev	0.0134	3.5	0.0040	1.5	0.0045	1.0
% c.v.	13.1906	4.1	8.7376	1.4	10.4504	1.0
Menthol (+)						
1	0.0142	86.8	0.0526	106.3	0.0299	103.1
2	0.0205	87.4	0.0576	104.2	0.0291	106.0
3	0.0245	90.5	0.0461	102.6	0.0306	105.2
4	0.0239	96.1	0.0489	102.8	0.0219	103.1
Average:	0.0208	90.2	0.0513	104.0	0.0279	104.3
Stnd.dev	0.0041	3.7	0.0043	1.5	0.0035	1.3
% c.v.	19.5717	4.1	8.4227	1.4	12.6016	1.2

Ar
re

Dim
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2

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4

Ave
Stn
%

Phe
1

2

3

4

Ave
Stn
%

Dip
1

2

3

4

Ave
Stn
%

Table 43. (cont.)

Partitioned between 100% Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Dimethylbenzylcarbinol (+)						
1	**0.0147**	101.4	0.0080	106.2	0.0119	103.5
2	**0.0151**	102.4	0.0157	103.9	0.0150	104.8
3	**0.0184**	106.0	0.0149	102.3	0.0139	105.4
4	**0.0201**	112.8	0.0074	102.1	0.0091	103.1
Average:	**0.0171**	105.7	0.0115	103.6	0.0125	104.2
Stnd.dev	**0.0023**	4.5	0.0038	1.6	0.0022	0.9
% c.v.	**13.2695**	4.2	33.1997	1.6	17.8856	0.9
Phenylethylalcohol (++)						
1	-	107.2	0.0178	106.2	0.0243	104.0
2	-	108.5	0.0177	104.3	0.0299	106.1
3	-	111.7	0.0303	102.9	0.0172	105.8
4	-	118.2	0.0185	102.9	0.0177	103.6
Average:		111.4	0.0211	104.1	0.0223	104.9
Stnd.dev.		4.2	0.0053	1.4	0.0052	1.1
% c.v.		3.8	25.2301	1.3	23.4101	1.0
Diphenylmethane						
1	**0.1775**	86.9	0.0931	106.4	0.0778	103.9
2	**0.2125**	86.4	0.0722	104.5	0.0807	106.5
3	**0.2437**	89.7	0.0838	102.4	0.0822	104.1
4	**0.2351**	96.5	0.0611	102.0	0.0669	103.5
Average:	**0.2172**	89.8	0.0775	103.8	0.0769	104.5
Stnd.dev	**0.0256**	4.0	0.0120	1.8	0.0060	1.2
% c.v.	**11.7831**	4.5	15.5329	1.7	7.7587	1.1

Ar
re

Dip
1

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Ave
Stn
%

Eug
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Ave
Stn
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1

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Ave
Stnd
% c

Table 43. (cont.)

Partitioned between 100% Ethanol and HDPE

		10C		25C		40C
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Diphenyloxide						
1	0.2295	80.8	0.1430	104.2	0.1197	101.3
2	0.2709	81.3	0.1781	101.9	0.1260	103.7
3	0.3130	83.6	0.1403	100.1	0.1559	104.3
4	0.3024	89.6	0.1173	100.6	0.1487	101.7
Average:	0.2789	83.8	0.1447	101.7	0.1376	102.7
Stnd.dev	0.0325	3.5	0.0217	1.6	0.0151	1.3
% c.v.	11.6469	4.2	15.0144	1.6	10.9777	1.3
Eugenol (++)						
1	-	82.2		106.3	0.0170	102.7
2	-	82.1	0.0056	103.4	0.0339	104.9
3	-	85.2	0.0260	101.9	0.0176	105.0
4	-	91.5		101.5	0.0344	103.0
Average:		85.3	0.0158	103.3	0.0257	103.9
Stnd.dev.		3.8	0.0102	1.9	0.0084	1.0
% c.v.		4.5	64.3915	1.8	32.7722	1.0
gamma-Undelactone (+)						
1	0.0420	71.4	0.0206	104.9	0.0279	101.1
2	0.0518	71.5	0.0187	102.9	0.0377	103.1
3	0.0652	73.7	0.0127	101.5	0.0234	104.0
4	0.0534	78.0	0.0187	101.4	0.0329	102.0
Average:	0.0531	73.7	0.0177	102.7	0.0305	102.6
Stnd.dev	0.0083	2.7	0.0030	1.4	0.0054	1.1
% c.v.	15.5390	3.6	16.7951	1.4	17.6013	1.1

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Av
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%

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Ave
Stn
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cis

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Ave
Stn
%

Table 43. (cont.)

Partitioned between 100% Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate (+)						
1	0.0305	92.3	0.0556	103.7	0.0506	97.4
2	0.0261	101.9		104.6	0.0478	102.3
3	0.0328	90.0	0.0778	101.8	0.0481	103.4
4	0.0245	98.8		104.1	0.0473	104.8
Average:	0.0285	95.8	0.0667	103.6	0.0485	102.0
Stnd.dev	0.0033	4.8	0.0111	1.1	0.0013	2.8
% c.v.	11.6620	5.0	16.6204	1.0	2.5992	2.8
d-Limonene						
1	0.2844	102.1	0.2131	103.2	0.1993	97.4
2	0.2679	114.1	0.2060	104.2	0.1906	102.1
3	0.3127	100.7	0.2286	101.1	0.1795	103.2
4	0.2995	109.2	0.1891	103.8	0.2190	104.8
Average:	0.2912	106.5	0.2092	103.1	0.1971	101.9
Stnd.dev	0.0167	5.4	0.0142	1.2	0.0145	2.8
% c.v.	5.7507	5.1	6.7848	1.2	7.3344	2.7
cis-3-Hexenol (+)						
1	-	156.0	-	104.5		97.1
2	-	174.8	-	105.1	0.0202	102.5
3	-	152.7	-	102.9	0.0324	104.0
4	-	168.0	-	104.8	0.0160	105.7
Average:		162.9		104.3	0.0229	102.3
Stnd.dev.		8.9		0.8	0.0069	3.2
% c.v.		5.5		0.8	30.2959	3.1

Table 43. (cont.)

Partitioned between 100% Ethanol and LDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Camphor						
1	0.0414	95.3	0.0244	105.6	0.0423	97.1
2	0.0392	107.6	0.0310	104.5	0.0406	102.3
3	0.0501	94.4	0.0267	101.7	0.0410	103.4
4	0.0418	103.6	0.0498	104.6	0.0515	104.6
Average:	0.0431	100.2	0.0330	104.1	0.0439	101.9
Stnd.dev	0.0041	5.6	0.0100	1.5	0.0044	2.9
% c.v.	9.5917	5.6	30.2343	1.4	10.0928	2.8
Linalylacetate						
1	0.0455	79.3	0.0353	104.2	0.0546	96.5
2	0.0403	88.5	0.0451	104.9	0.0407	103.1
3	0.0554	78.4	0.0515	102.8	0.0421	104.0
4	0.0449	85.8	0.0497	105.5	0.0495	105.4
Average:	0.0465	83.0	0.0454	104.3	0.0468	102.3
Stnd.dev	0.0055	4.3	0.0063	1.0	0.0056	3.4
% c.v.	11.8713	5.1	13.8525	1.0	12.0702	3.3
Menthol (+)						
1	0.0118	81.5	0.0123	103.6	0.0234	97.7
2	0.0105	91.5	0.0042	105.0	0.0089	103.1
3	0.0114	80.7	0.0069	102.6	0.0084	104.1
4	0.0070	88.2	0.0047	106.1	0.0315	105.3
Average:	0.0102	85.5	0.0070	104.3	0.0180	102.5
Stnd.dev	0.0019	4.5	0.0032	1.3	0.0098	2.9
% c.v.	18.3456	5.3	45.6372	1.3	54.5152	2.8

Table 43. (cont.)

Partitioned between 100% Ethanol and LDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Dimethylbenzylcarbinol (+)						
1	0.0100	97.3	0.0078	104.0	0.0097	97.4
2	0.0089	108.8	0.0051	105.3	0.0039	103.2
3	0.0089	94.6	0.0087	102.5	0.0203	103.7
4	0.0087	104.9	0.0041	105.3	0.0102	105.0
Average:	0.0091	101.4	0.0064	104.3	0.0110	102.4
Stnd.dev	0.0005	5.7	0.0019	1.1	0.0059	2.9
% c.v.	5.4392	5.6	29.3450	1.1	53.1344	2.8
Phenylethylalcohol (+)						
1	-	102.6	0.0516	104.5	0.0291	97.6
2	-	114.2	0.0155	105.6	0.0230	103.3
3	-	101.2	0.0266	102.8	0.0292	104.0
4	-	110.6	0.0205	105.3	0.0487	104.7
Average:		107.1	0.0285	104.6	0.0325	102.4
Stnd.dev.		5.4	0.0139	1.1	0.0097	2.8
% c.v.		5.1	48.5603	1.0	29.7419	2.7
Diphenylmethane						
1	0.0850	82.8	0.0489	103.7	0.0696	98.1
2	0.0771	93.0	0.0723	105.0	0.0707	102.8
3	0.0908	82.0	0.0762	102.6	0.0537	104.3
4	0.0845	89.4	0.0667	107.3	0.0997	106.4
Average:	0.0844	86.8	0.0660	104.6	0.0734	102.9
Stnd.dev	0.0049	4.6	0.0105	1.8	0.0166	3.0
% c.v.	5.7969	5.3	15.8483	1.7	22.5640	3.0

Table 43. (cont.)

Partitioned between 100% Ethanol and LDPE

		10C		25C		40C
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Diphenyloxide						
1	0.1141	77.4	0.1033	102.5	0.1043	97.4
2	0.0990	86.6	0.0999	103.5	0.1024	102.5
3	0.1248	76.2	0.1155	100.6	0.0920	102.9
4	0.1099	83.4	0.0967	102.3	0.1515	103.6
Average:	0.1120	80.9	0.1039	102.2	0.1126	101.6
Stnd.dev	0.0092	4.3	0.0071	1.1	0.0230	2.4
% c.v.	8.2520	5.3	6.8478	1.0	20.4032	2.4
Eugenol (+)						
1	-	78.3	0.0112	103.3	0.0458	97.1
2	-	87.2	0.0190	105.6	0.0404	102.4
3	-	77.9	0.0321	101.9	0.0432	103.6
4	-	84.8	0.0306	104.9	0.0456	106.1
Average:		82.0	0.0232	103.9	0.0438	102.3
Stnd.dev.		4.1	0.0086	1.4	0.0022	3.3
% c.v.		4.9	37.0347	1.4	4.9284	3.2
gamma-Undelactone						
1	0.0112	68.2	0.0141	102.9	0.0351	96.5
2	0.0101	75.5	0.0227	104.3	0.0280	102.2
3	0.0121	67.6	0.0149	102.3	0.0310	101.9
4	0.0132	73.4	0.0119	105.3	0.0305	103.7
Average:	0.0116	71.2	0.0159	103.7	0.0311	101.1
Stnd.dev	0.0011	3.4	0.0041	1.2	0.0025	2.7
% c.v.	9.6221	4.7	25.6652	1.1	8.1844	2.7

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate (+)						
1	0.0925	94.3	0.1002	69.5	0.0800	74.5
2	0.0994	80.1	0.1103	68.9	0.0843	77.9
3	0.0839	99.5	0.0969	71.9	0.0681	83.5
4	0.1088	81.4	0.0755	73.6	0.0528	87.4
Average:	0.0962	88.8	0.0957	71.0	0.0713	80.8
Stnd.dev	0.0091	8.3	0.0126	1.9	0.0122	5.0
% c.v.	9.4901	9.4	13.2116	2.7	17.1466	6.2
d-Limonene						
1	3.4419	91.4	2.1930	69.3	1.7715	74.0
2	4.3377	75.9	2.1749	68.7	1.6634	77.7
3	3.3244	95.9	2.1285	71.6	1.5580	83.2
4	4.6002	76.2	2.0836	73.6	1.4774	86.6
Average:	3.9260	84.9	2.1450	70.8	1.6176	80.4
Stnd.dev	0.5524	9.0	0.0425	1.9	0.1107	4.8
% c.v.	14.0689	10.5	1.9835	2.7	6.8410	6.0
cis-3-Hexenol (++)						
1	0.0092	87.5	0.0400	73.8	-	78.9
2	0.0068	76.0	0.0410	73.9	-	82.6
3	0.0066	92.3	0.0525	75.7	-	87.3
4		78.6	0.0452	76.3	-	92.3
Average:	0.0076	83.6	0.0447	74.9		85.3
Stnd.dev	0.0012	6.6	0.0049	1.1		5.0
% c.v.	15.8065	7.9	11.0617	1.5		5.9

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Aver
Stnd
% c

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Camphor						
1	0.0387	96.5	0.0772	71.3	0.0821	73.6
2	0.0523	84.3	0.0804	70.8	0.0777	77.5
3	0.0444	104.6	0.0745	72.7	0.0780	82.5
4	0.0458	89.7	0.0828	72.7	0.0780	86.7
Average:	0.0453	93.8	0.0787	71.9	0.0789	80.1
Stnd.dev	0.0048	7.6	0.0031	0.9	0.0018	5.0
% c.v.	10.6683	8.1	3.9824	1.2	2.3359	6.2
Linalylacetate						
1	0.1996	81.1	0.2473	65.5	0.2040	65.6
2	0.2167	74.1	0.2416	65.7	0.1782	68.9
3	0.1914	87.5	0.2342	67.5	0.1692	73.3
4	0.2197	76.4	0.2441	67.7	0.1696	77.1
Average:	0.2069	79.8	0.2418	66.6	0.1802	71.2
Stnd.dev	0.0118	5.1	0.0048	1.0	0.0142	4.3
% c.v.	5.6950	6.4	1.9935	1.5	7.8654	6.1
Menthol (+)						
1	0.0271	88.3	0.1642	73.0	0.1280	75.4
2	0.0303	79.3	0.1515	72.9	0.0943	79.5
3	0.0265	95.2	0.1583	74.8	0.0968	84.5
4	0.0307	82.8	0.1523	74.3	0.0988	88.6
Average:	0.0287	86.4	0.1566	73.7	0.1045	82.0
Stnd.dev	0.0019	6.0	0.0051	0.8	0.0137	5.0
% c.v.	6.4832	6.9	3.2788	1.1	13.0864	6.1

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Averag
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Average
Stnd.dev
% c.v.

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and HDPE

Aroma repl.	10C K(P/L) (cP/cL)	 Mass Balance %	25C K(P/L) (cP/cL)	 Mass Balance %	40C K(P/L) (cP/cL)	 Mass Balance %
Dimethylbenzylcarbinol (+)						
1	0.0177	88.0	0.0347	72.1	0.0275	74.8
2	0.0188	80.5	0.0477	71.9	0.0315	78.7
3	0.0185	96.1	0.0554	73.3	0.0516	83.2
4	0.0260	82.6	0.0423	73.1	0.0270	87.4
Average:	0.0203	86.8	0.0450	72.6	0.0344	81.0
Stnd.dev	0.0034	6.0	0.0076	0.6	0.0101	4.7
% c.v.	16.6113	6.9	16.8630	0.9	29.2760	5.9
Phenylethylalcohol (++)						
1	0.0082	86.0	0.0311	72.5	0.0187	75.7
2	0.0122	80.8	0.0280	73.0	0.0181	79.5
3	0.0123	94.4	0.0255	74.2	0.0141	83.6
4	0.0111	81.5	0.0330	74.0	0.0239	88.0
Average:	0.0109	85.7	0.0294	73.4	0.0187	81.7
Stnd.dev	0.0017	5.4	0.0029	0.7	0.0035	4.6
% c.v.	15.0986	6.3	9.7791	0.9	18.6163	5.6
Diphenylmethane						
1	0.5012	91.4	0.4696	73.6	0.4417	75.9
2	0.5699	81.4	0.5173	73.7	0.4015	80.0
3	0.4625	98.6	0.5303	75.0	0.4392	84.6
4	0.5678	85.4	0.4782	74.9	0.3813	88.9
Average:	0.5253	89.2	0.4988	74.3	0.4159	82.4
Stnd.dev	0.0456	6.5	0.0256	0.6	0.0255	4.9
% c.v.	8.6805	7.2	5.1249	0.9	6.1396	5.9

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Ave
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Aver
Stnd
% c

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Aver
Stnd.
% c.

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and HDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Diphenyloxide						
1	0.8773	84.1	0.6778	68.2	0.6215	70.2
2	0.9956	75.4	0.7096	68.3	0.5608	73.5
3	0.8058	90.7	0.7227	69.6	0.6004	78.2
4	0.9872	79.1	0.6811	69.2	0.5451	81.5
Average:	0.9165	82.3	0.6978	68.8	0.5819	75.9
Stnd.dev	0.0791	5.8	0.0190	0.6	0.0304	4.3
% c.v.	8.6358	7.0	2.7189	0.9	5.2313	5.7
Eugenol (++)						
1		87.4	0.0542	74.7		76.0
2		80.8	0.0482	74.4		80.0
3	0.0058	96.1	0.0402	75.4	0.0623	84.1
4	0.0097	82.5	0.0410	75.0	0.0634	88.7
Average:	0.0078	86.7	0.0459	74.9	0.0629	82.2
Stnd.dev	0.0020	6.0	0.0057	0.4	0.0006	4.7
% c.v.	25.1994	6.9	12.4450	0.5	0.9112	5.7
gamma-Undelactone (+)						
1	0.0347	88.3	0.0458	76.7	0.0378	74.7
2	0.0304	80.4	0.0299	73.2	0.0730	78.2
3	0.0322	95.8	0.0370	73.8	0.0429	81.7
4	0.0311	82.5	0.0435	73.4	0.0426	85.6
Average:	0.0321	86.8	0.0391	74.3	0.0491	80.0
Stnd.dev	0.0016	6.0	0.0062	1.4	0.0140	4.0
% c.v.	5.0235	6.9	15.9179	1.9	28.4240	5.1

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Avera
Stnd.
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Avera
Stnd.
% c.

cis-
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2

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Avera
Stnd
% c

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate (+)						
1	0.0403	90.2	0.3003	110.9		118.0
2	0.0249	80.9	0.2865	108.3	0.2128	118.3
3	0.0418	79.1	0.2322	111.2	0.1812	108.6
4	0.0385	85.3	0.4024	108.5	0.3348	111.5
Average:	0.0364	83.9	0.3053	109.7	0.2430	114.1
Stnd.dev	0.0067	4.3	0.0615	1.3	0.0662	4.2
% c.v.	18.5058	5.1	20.1527	1.2	27.2538	3.7
d-Limonene						
1	1.4255	86.6	0.6695	109.4		113.6
2	1.6930	73.9	0.6466	106.3	0.6264	114.4
3	2.0833	73.7	0.7007	109.6	0.6106	105.8
4	2.0137	81.2	0.6566	106.0	0.6850	108.9
Average:	1.8039	78.9	0.6683	107.8	0.6407	110.7
Stnd.dev	0.2634	5.4	0.0204	1.7	0.0320	3.5
% c.v.	14.6030	6.9	3.0481	1.6	4.9948	3.2
cis-3-Hexenol (+)						
1	-	83.6	-	111.6	-	120.1
2	-	76.6	-	109.9	-	120.1
3	-	76.1	-	112.5	-	110.7
4	-	79.3	-	109.3	-	113.8
Average:		78.9		110.8		116.2
Stnd.dev.		3.0		1.3		4.1
% c.v.		3.8		1.2		3.5

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Camphor						
1	0.0646	96.1	0.0343	110.9		110.8
2	0.0644	87.4	0.0323	108.2	0.0450	118.8
3	0.0736	84.9	0.0409	110.9	0.0408	109.5
4	0.0642	91.0	0.0291	107.8	0.0492	112.1
Average:	0.0667	89.8	0.0342	109.5	0.0450	112.8
Stnd.dev	0.0040	4.2	0.0043	1.5	0.0035	3.6
% c.v.	5.9958	4.7	12.6564	1.3	7.7109	3.2
Linalylacetate						
1	0.1014	80.5	0.0595	111.8		111.8
2	0.1178	74.8	0.0659	109.0	0.0688	115.3
3	0.1382	73.1	0.0707	112.2	0.0641	106.9
4	0.1301	76.7	0.0627	108.9	0.0675	108.4
Average:	0.1219	76.3	0.0647	110.5	0.0668	110.6
Stnd.dev	0.0139	2.7	0.0041	1.5	0.0020	3.2
% c.v.	11.3828	3.6	6.4042	1.4	2.9528	2.9
Menthol (+)						
1	0.0228	87.3	0.0111	111.6		111.6
2	0.0188	81.7	0.0116	108.4	0.0109	118.6
3	0.0185	79.4	0.0195	111.5	0.0090	109.9
4	0.0226	83.3	0.0109	108.4	0.0124	112.5
Average:	0.0207	82.9	0.0133	110.0	0.0108	113.1
Stnd.dev	0.0020	2.9	0.0036	1.6	0.0014	3.3
% c.v.	9.7672	3.5	27.1328	1.4	12.8200	2.9

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and LDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Dimethylbenzylcarbinol (+)						
1	0.0121	87.6	0.0152	111.6		111.6
2	0.0080	82.1	0.0160	108.3	0.0106	93.0
3	0.0119	79.2	0.0199	111.4	0.0110	110.2
4	0.0123	84.2	0.0117	108.5	0.0101	113.1
Average:	0.0111	83.3	0.0157	110.0	0.0105	107.0
Stnd.dev	0.0018	3.1	0.0029	1.5	0.0004	8.1
% c.v.	15.9478	3.7	18.6335	1.4	3.3241	7.6
Phenylethylalcohol (+)						
1	-	86.7	0.0254	108.3		108.3
2	-	81.7	0.0184	105.4	0.0150	185.0
3	-	80.8	0.0213	107.9	0.0147	106.2
4	-	82.8	0.0171	105.7	0.0203	108.2
Average:		83.0	0.0205	106.8	0.0166	126.9
Stnd.dev.		2.3	0.0032	1.3	0.0026	33.6
% c.v.		2.7	15.4345	1.2	15.4846	26.4
Diphenylmethane						
1	0.1997	90.5	0.1741	113.0		112.8
2	0.2392	83.6	0.1728	109.8	0.1457	128.1
3	0.2996	81.8	0.1773	112.3	0.1526	110.8
4	0.3072	86.0	0.1642	109.7	0.1780	113.4
Average:	0.2614	85.5	0.1721	111.2	0.1588	116.3
Stnd.dev	0.0443	3.3	0.0049	1.5	0.0139	6.9
% c.v.	16.9515	3.8	2.8202	1.3	8.7567	5.9

Table 43. (cont.)

Partitioned between 75% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Diphenyloxide						
1	0.3820	83.3	0.2590	104.5		104.2
2	0.3977	77.2	0.2742	101.4	0.2443	110.5
3	0.4771	75.6	0.2843	104.1	0.2400	102.7
4	0.4950	79.7	0.2519	101.5	0.2757	104.9
Average:	0.4380	78.9	0.2673	102.9	0.2534	105.6
Stnd.dev	0.0488	2.9	0.0127	1.4	0.0159	2.9
% c.v.	11.1480	3.7	4.7366	1.4	6.2805	2.8
Eugenol (+)						
1	-	88.3	0.0180	111.2		111.2
2	-	82.1	0.0191	108.1	0.0062	115.0
3	-	81.2	0.0141	110.4	0.0142	108.8
4	-	83.6	0.0130	108.4	0.0154	110.6
Average:		83.8	0.0161	109.5	0.0119	111.4
Stnd.dev.		2.7	0.0026	1.3	0.0041	2.3
% c.v.		3.2	16.0044	1.2	34.1984	2.0
gamma-Undelactone (+)						
1	0.0097	88.1	0.0313	107.0		106.9
2	0.0088	82.5	0.0413	104.4	0.0283	109.3
3	0.0117	81.1	0.0236	106.6	0.0328	104.3
4	0.0095	84.0	0.0238	104.5	0.0264	105.4
Average:	0.0100	83.9	0.0300	105.6	0.0292	106.5
Stnd.dev	0.0011	2.6	0.0072	1.2	0.0027	1.9
% c.v.	10.9741	3.1	23.9943	1.1	9.2316	1.8

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Aver
Stnd
% c

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Aver
Stnd
% c

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate						
1	0.6171	108.4	0.4418	128.4	0.3505	103.7
2	0.7027	113.3	0.6853	123.3	0.3769	103.0
3	0.7469	121.3	0.6395	126.5	0.3277	108.7
4	0.6656	119.6	0.4367	127.1	0.4023	103.8
Average:	0.6831	115.6	0.5508	126.3	0.3643	104.8
Stnd.dev	0.0477	5.1	0.1127	1.9	0.0280	2.3
% c.v.	6.9880	4.4	20.4669	1.5	7.6751	2.2
d-Limonene						
1	47.9178	130.8	27.7929	143.0	28.7055	113.7
2	54.9248	145.1	41.6977	162.5	34.8114	104.5
3	55.0890	161.8	37.5678	163.9	26.2908	116.7
4	50.0545	148.3	25.8735	141.4	33.8369	122.8
Average:	51.9966	146.5	33.2330	152.7	30.9112	114.4
Stnd.dev	3.1043	11.0	6.5992	10.5	3.5350	6.6
% c.v.	5.9701	7.5	19.8574	6.9	11.4359	5.8
cis-3-Hexenol (++)						
1	-	131.8	-	159.6	0.0850	123.5
2	-	139.3	-	141.4	0.0916	133.1
3	-	145.1	-	159.2	0.1270	131.8
4	-	146.7	-	153.2	0.0722	124.3
Average:		140.7		153.3	0.0940	128.2
Stnd.dev.		5.8		7.3	0.0203	4.3
% c.v.		4.2		4.8	21.6325	3.4

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Men
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Aver
Stnd
% c

Table 43 . (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Camphor					(1)	
1	0.4209	103.8	0.4501	108.2	1.0374	35.4
2	0.4609	108.7	0.6958	100.9	0.9430	36.8
3	0.4817	111.9	0.6352	105.1	0.9498	38.3
4	0.4237	112.2	0.4425	104.4	1.1265	36.1
Average:	0.4468	109.1	0.5559	104.7	1.0142	36.6
Stnd.dev	0.0256	3.4	0.1117	2.6	0.0748	1.1
% c.v.	5.7277	3.1	20.0978	2.5	7.3723	3.0
Linalylacetate						
1	2.4306	116.8	1.3763	133.5	0.4422	103.6
2	2.6876	122.2	2.1521	121.9	0.4920	110.8
3	2.8439	127.2	1.8596	134.2	0.4090	111.1
4	2.5189	128.6	1.3383	129.3	0.4512	117.4
Average:	2.6202	123.7	1.6816	129.7	0.4486	110.7
Stnd.dev	0.1587	4.6	0.3406	4.9	0.0296	4.9
% c.v.	6.0571	3.8	20.2559	3.8	6.5930	4.4
Menthol						
1	0.2127	125.9	0.1723	146.9	0.2119	116.5
2	0.2367	131.1	0.2750	131.1	0.3592	125.8
3	0.2562	135.4	0.2386	145.3	0.2151	125.5
4	0.2223	138.0	0.1669	141.9	0.2509	117.1
Average:	0.2320	132.6	0.2132	141.3	0.2593	121.2
Stnd.dev	0.0164	4.6	0.0455	6.1	0.0597	4.4
% c.v.	7.0547	3.5	21.3416	4.3	23.0190	3.7

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Dimethylbenzylcarbinol						
1	0.0557	125.2	0.0437	149.2	0.1755	121.8
2	0.0630	130.8	0.0684	132.6	0.3191	134.0
3	0.0658	138.3	0.0545	154.2	0.1670	129.0
4	0.0578	144.1	0.0418	145.8	0.2026	121.0
Average:	0.0605	134.6	0.0521	145.5	0.2160	126.5
Stnd.dev	0.0040	7.2	0.0106	8.0	0.0609	5.4
% c.v.	6.6539	5.4	20.3262	5.5	28.2114	4.2
Phenylethylalcohol (++)						
1	0.0877	129.4	0.0919	151.9	0.0352	125.9
2	0.2925	136.1	0.1660	140.6	0.1160	140.5
3	0.1540	139.9	0.0806	160.5	0.1360	130.0
4	0.1256	147.2	0.0548	149.6	0.0599	120.1
Average:	0.1650	138.2	0.0983	150.6	0.0868	129.1
Stnd.dev	0.0773	6.4	0.0413	7.1	0.0408	7.4
% c.v.	46.8681	4.7	42.0251	4.7	47.0352	5.8
Diphenylmethane						
1	6.7702	131.9	4.2517	151.4	2.8139	115.0
2	7.3627	140.4	6.9598	140.1	3.1926	122.9
3	8.0410	146.6	5.9250	153.2	2.5935	122.4
4	6.9757	146.3	4.1416	146.1	3.2914	116.2
Average:	7.2874	141.3	5.3195	147.7	2.9729	119.1
Stnd.dev	0.4843	6.0	1.1816	5.1	0.2824	3.5
% c.v.	6.6458	4.2	22.2126	3.5	9.4981	3.0

Pa

Aron
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Aver
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Ave
Stn
%

gam
1

2

3

4

Ave
Str
%

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Diphenyloxide						
1	12.0970	124.0	7.4246	139.6	2.8511	174.8
2	13.1375	132.5	11.5924	137.4	3.2786	186.2
3	14.2830	139.5	10.2904	143.8	2.6472	185.1
4	12.4679	137.4	7.2480	134.5	3.4537	175.7
Average:	12.9963	133.4	9.1389	138.8	3.0576	180.5
Stnd.dev	0.8312	6.0	1.8615	3.4	0.3228	5.2
% c.v.	6.3956	4.5	20.3685	2.4	10.5571	2.9
Eugenol (++)						
1	0.1897	113.5	0.1251	153.1	0.0616	114.0
2	0.2425	119.9	0.2290	138.1	0.0430	125.4
3	0.2857	126.4	0.3040	165.4	0.0609	118.8
4	0.2380	133.6	0.1230	149.1	0.0717	109.3
Average:	0.2390	123.4	0.1953	151.4	0.0593	116.9
Stnd.dev	0.0340	7.5	0.0760	9.8	0.0103	6.0
% c.v.	14.2291	6.1	38.9255	6.5	17.4122	5.1
gamma-Undelactone						
1	0.3266	119.4	0.1978	151.9	0.0898	151.9
2	0.3843	125.5	0.3177	138.2	0.0740	168.1
3	0.3981	132.3	0.2477	160.1	0.0691	158.6
4	0.3256	140.1	0.2445	149.0	0.0745	150.0
Average:	0.3586	129.3	0.2519	149.8	0.0769	157.1
Stnd.dev	0.0329	7.7	0.0428	7.9	0.0077	7.1
% c.v.	9.1814	6.0	16.9988	5.2	10.0751	4.5

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate						
1	0.4270	116.2	0.2437	119.9	0.2917	113.5
2	0.2520	118.0	0.2533	122.7	0.3069	120.1
3	0.4187	98.4	0.2860	123.5	0.2757	126.2
4	0.2348	125.6	0.2972	112.5	0.2944	120.1
Average:	0.3331	114.5	0.2700	119.7	0.2922	120.0
Stnd.dev	0.0900	10.0	0.0222	4.3	0.0111	4.5
% c.v.	27.0203	8.7	8.2122	3.6	3.7947	3.7
d-Limonene						
1	38.0247	133.4	22.3479	123.2	29.0368	113.7
2	21.9854	119.3	21.4608	124.8	28.4775	120.4
3	26.8646	100.3	23.5678	125.8	23.9485	121.3
4	19.1598	121.7	28.1877	109.8	28.8393	121.1
Average:	26.5086	118.7	23.8910	120.9	27.5755	119.1
Stnd.dev	7.1974	11.9	2.5910	6.5	2.1037	3.1
% c.v.	27.1513	10.0	10.8451	5.4	7.6287	2.6
cis-3-Hexenol (+)						
1	0.0135	141.6		173.9	-	122.8
2	0.0097	143.1	0.0354	165.6	-	127.5
3	0.0127	125.7	0.0295	168.3	-	134.2
4	0.0137	152.2	0.0195	167.8	-	127.5
Average:	0.0124	140.7	0.0281	168.9		128.0
Stnd.dev	0.0016	9.5	0.0066	3.0		4.1
% c.v.	12.8570	6.8	23.2741	1.8		3.2

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Camphor						
1	0.4895	111.1	0.4542	101.0	0.3773	120.7
2	0.2968	111.7	0.4532	97.8	0.3955	126.2
3	0.3255	101.0	0.4844	99.1	0.3403	137.1
4	0.2518	120.3	0.4790	97.8	0.4038	126.2
Average:	0.3409	111.0	0.4677	98.9	0.3792	127.6
Stnd.dev	0.0897	6.8	0.0141	1.3	0.0244	5.9
% c.v.	26.3235	6.1	3.0175	1.3	6.4388	4.6
Linalylacetate					(1)	
1	1.4087	119.6	0.9297	124.7	1.2024	43.7
2	0.9270	119.8	0.9607	117.7	1.2242	46.2
3	0.9821	108.3	0.9855	120.6	1.0347	48.6
4	0.7902	129.2	0.9660	121.0	1.1976	46.2
Average:	1.0270	119.2	0.9605	121.0	1.1647	46.2
Stnd.dev	0.2312	7.4	0.0200	2.5	0.0757	1.7
% c.v.	22.5092	6.2	2.0829	2.1	6.5003	3.8
Menthol						
1	0.1772	132.6	0.1258	141.1	0.1547	121.7
2	0.0978	133.7	0.1243	131.8	0.1176	126.4
3	0.1089	121.1	0.1450	135.3	0.1206	132.5
4	0.0863	145.3	0.1204	137.2	0.1306	126.4
Average:	0.1175	133.2	0.1289	136.3	0.1309	126.8
Stnd.dev	0.0354	8.6	0.0095	3.4	0.0146	3.8
% c.v.	30.0910	6.4	7.3735	2.5	11.1309	3.0

A
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Ave
Str
%

Phe
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2

3

4

Ave
Stn
%

Dip
1

2

3

4

Ave
Stn
%

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Dimethylbenzylcarbinol (+)						
1	0.0587	134.7	0.0944	139.7	0.1837	136.4
2	0.0360	138.5	0.1007	136.1	0.1767	141.6
3	0.0478	118.9	0.1123	139.4	0.1643	147.3
4	0.0271	120.0	0.2141	85.9	0.1849	141.6
Average:	0.0424	128.0	0.1304	125.3	0.1774	141.7
Stnd.dev	0.0119	8.7	0.0487	22.8	0.0082	3.9
% c.v.	28.1016	6.8	37.3874	18.2	4.6186	2.7
Phenylethylalcohol (+)						
1	0.0067	138.5	0.1216	147.3	0.2338	127.6
2	0.0113	143.6	0.1339	145.3	0.2809	131.9
3	0.0120	123.9	0.1442	147.2	0.1157	137.4
4	0.0078	155.2	0.1511	143.8	0.2746	131.9
Average:	0.0095	140.3	0.1377	145.9	0.2262	132.2
Stnd.dev	0.0023	11.2	0.0111	1.5	0.0664	3.5
% c.v.	23.7898	8.0	8.0829	1.0	29.3287	2.7
Diphenylmethane						
1	3.6489	135.8	2.3299	139.6	2.6723	122.6
2	2.1794	134.4	2.2894	132.5	2.8320	127.3
3	2.4434	122.2	2.4409	134.2	2.3147	132.8
4	1.8655	144.0	2.3711	135.3	3.0405	127.7
Average:	2.5343	134.1	2.3578	135.4	2.7149	127.6
Stnd.dev	0.6753	7.8	0.0560	2.6	0.2654	3.6
% c.v.	26.6446	5.8	2.3742	1.9	9.7750	2.8

3

4

A
S

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4

Av
St
%

ga
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2

3

4

Ave
Stn
%

Table 43. (cont.)

Partitioned between 50% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Diphenyloxide						
1	6.3804	124.2	4.0536	126.4	4.8918	113.1
2	3.8541	121.3	4.3474	121.0	4.9822	117.4
3	4.2724	111.2	4.4855	122.3	3.9433	121.6
4	3.2761	130.2	4.2586	123.5	5.1704	117.7
Average:	4.4458	121.7	4.2863	123.3	4.7469	117.5
Stnd.dev	1.1716	6.9	0.1568	2.0	0.4747	3.0
% c.v.	26.3540	5.7	3.6578	1.6	10.0006	2.5
Eugenol (+)						
1	0.0542	124.5	0.0469	141.8	0.3713	128.7
2	0.0301	127.6	0.0169	146.1		132.4
3	0.0408	107.0	0.0354	151.0		137.8
4	0.0248	140.5	0.0210	138.0	0.1473	132.6
Average:	0.0375	124.9	0.0301	144.2	0.2593	132.9
Stnd.dev	0.0112	11.9	0.0119	4.8	0.1120	3.2
% c.v.	30.0047	9.6	39.6695	3.4	43.1973	2.4
gamma-Undelactone						
1	0.1202	131.4	0.0840	140.4	0.0895	125.6
2	0.0797	133.6	0.0770	141.3	0.0847	129.7
3	0.0938	113.3	0.0915	143.4	0.0775	135.5
4	0.0890	145.8	0.0887	137.9	0.1121	129.7
Average:	0.0957	131.0	0.0853	140.8	0.0910	130.1
Stnd.dev	0.0150	11.6	0.0055	2.0	0.0130	3.5
% c.v.	15.7286	8.9	6.4191	1.4	14.2525	2.7

Table 43. (cont.)

Partitioned between 35% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate						
1	1.3195	99.1	0.8228	116.4	0.8100	83.6
2	1.1460	121.0	0.8459	103.2	0.6889	84.0
3	1.1096	108.5	0.9235	102.9	0.5182	96.9
4	1.3375	105.6	0.9737	104.1	0.6883	91.1
Average:	1.2281	108.6	0.8915	106.6	0.6763	88.9
Stnd.dev	0.1014	8.0	0.0604	5.7	0.1039	5.5
% c.v.	8.2532	7.3	6.7741	5.3	15.3635	6.2
d-Limonene						
1	254.0	111.2	140.2	111.3	158.7	105.2
2	214.4	116.7	134.8	92.9	137.3	92.5
3	206.8	107.4	159.5	111.4	103.4	85.1
4	229.5	114.1	157.1	113.1	143.1	99.7
Average:	226.2	112.4	147.9	107.2	135.6	95.6
Stnd.dev	18.0126	3.5	10.6103	8.3	20.1692	7.6
% c.v.	7.9646	3.1	7.1741	7.7	14.8710	7.9
cis-3-Hexenol (+)						
1	0.0604	95.4	0.0401	130.1	0.0626	114.9
2	0.0486	124.8	0.0421	110.0	0.0333	104.7
3	0.0431	109.1	0.0434	105.7	0.0295	125.8
4	0.0453	105.9	0.0668	104.5	0.0263	120.2
Average:	0.0494	108.8	0.0481	112.6	0.0379	116.4
Stnd.dev	0.0066	10.5	0.0109	10.3	0.0144	7.8
% c.v.	13.4635	9.7	22.5921	9.2	38.0596	6.7

Table 43. (cont.)

Partitioned between 35% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Camphor					(1)	
1	0.9566	131.5	1.1214	97.9	5.3209	19.6
2	0.7967	161.6	1.0294	84.3	4.6892	18.3
3	0.8239	143.3	1.1884	83.4	3.5634	20.7
4	0.9017	139.4	1.2134	84.1	4.5124	19.9
Average:	0.8697	144.0	1.1382	87.4	4.5215	19.7
Stnd.dev	0.0633	11.1	0.0712	6.1	0.6295	0.9
% c.v.	7.2742	7.7	6.2583	6.9	13.9231	4.4
Linalylacetate					(1)	
1	8.3896	115.7	2.4722	131.1	0.1241	80.6
2	6.6995	143.0	2.4115	114.6	0.0787	80.4
3	6.9498	127.1	2.7964	112.7	0.0681	92.3
4	7.6561	126.7	3.0183	111.4	0.0807	88.2
Average:	7.4237	128.1	2.6746	117.5	0.0879	85.4
Stnd.dev	0.6588	9.7	0.2465	7.9	0.0214	5.1
% c.v.	8.8738	7.6	9.2181	6.8	24.3909	5.9
Menthol						
1	0.6523	101.3	0.4416	130.6	0.6919	90.4
2	0.5270	128.8	0.3996	118.5	0.6364	83.6
3	0.5705	114.4	0.5050	110.3	0.4919	96.2
4	0.5972	111.1	0.5252	107.8	0.5873	92.5
Average:	0.5868	113.9	0.4678	116.8	0.6019	90.7
Stnd.dev	0.0454	9.9	0.0500	8.9	0.0735	4.6
% c.v.	7.7314	8.6	10.6946	7.6	12.2125	5.0

Table 43. (cont.)

Partitioned between 35% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Dimethylbenzylcarbinol						
1	0.4010	98.1	0.4798	131.4	0.9451	88.7
2	0.3159	128.6	0.5082	109.8	0.8627	85.4
3	0.3218	112.7	0.5968	105.8	0.6854	96.4
4	0.3783	107.6	0.6266	104.7	0.8807	90.5
Average:	0.3542	111.7	0.5528	112.9	0.8435	90.3
Stnd.dev	0.0363	11.1	0.0606	10.9	0.0963	4.0
% c.v.	10.2599	9.9	10.9652	9.6	11.4125	4.4
Phenylethylalcohol						
1	0.0505	95.8	0.0235	129.3	0.0467	90.2
2	0.0382	125.1	0.0462	105.4	0.0229	89.7
3	0.0459	111.7	0.0249	100.2	0.0305	101.6
4	0.0441	106.4	0.0331	100.4	0.0603	93.0
Average:	0.0447	109.7	0.0319	108.8	0.0401	93.6
Stnd.dev	0.0044	10.6	0.0090	12.0	0.0145	4.8
% c.v.	9.9301	9.6	28.2810	11.1	36.1674	5.1
Diphenylmethane						
1	28.5450	84.4	13.1805	107.7	13.5012	85.3
2	22.0699	104.9	13.8017	93.5	15.8960	83.2
3	21.7670	93.3	16.8429	95.8	9.1731	85.3
4	22.8050	93.0	16.4442	95.9	13.2868	84.4
Average:	23.7967	93.9	15.0673	98.2	12.9643	84.5
Stnd.dev	2.7673	7.3	1.5977	5.5	2.4166	0.9
% c.v.	11.6288	7.8	10.6038	5.6	18.6405	1.0

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Ave
Stn
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Euge
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3

4

Avera
Stnd.
% c.

gamma
1

2

3

4

Averag
Stnd.d
% c.v

Table 43. (cont.)

Partitioned between 35% Aqueous Ethanol and HDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Diphenyloxide						
1	49.7370	86.8	23.7934	100.9	24.2520	85.8
2	39.7727	97.5	24.5954	86.3	26.0494	82.6
3	41.2636	89.2	30.6585	91.9	17.4258	83.7
4	47.4214	93.8	31.8733	92.9	24.0880	84.1
Average:	44.5487	91.8	27.7301	93.0	22.9538	84.0
Stnd.dev	4.1465	4.2	3.5730	5.2	3.2830	1.2
% c.v.	9.3077	4.5	12.8849	5.6	14.3027	1.4
Eugenol						
1	0.1681	95.0	0.0895	129.2	0.1595	85.6
2	0.1281	126.6	0.1392	105.0	0.0886	83.7
3	0.1573	112.0	0.1078	100.7	0.0587	97.5
4	0.1793	105.7	0.1105	100.5	0.0688	86.4
Average:	0.1582	109.8	0.1117	108.9	0.0939	88.3
Stnd.dev	0.0190	11.4	0.0178	11.9	0.0394	5.4
% c.v.	12.0423	10.4	15.9508	10.9	41.9308	6.1
gamma-Undelactone						
1	0.6419	93.6	0.3025	128.4	0.3367	87.8
2	0.5269	122.8	0.3442	104.9	0.4045	87.2
3	0.5565	110.3	0.3930	100.3	0.2487	97.5
4	0.6118	104.3	0.4120	99.9	0.3072	90.4
Average:	0.5843	107.8	0.3629	108.4	0.3243	90.7
Stnd.dev	0.0451	10.5	0.0428	11.8	0.0561	4.1
% c.v.	7.7194	9.8	11.7841	10.8	17.3089	4.5

4

A
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d
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2

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4

Av
St
%

cis
1

2

3

4

Ave
Stnd
% c

Table 43. (cont.)

Partitioned between 35% Aqueous Ethanol and LDPE

	10C		25C (2)		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Isoamylacetate						
1	0.5011	96.0	0.5669	95.9	0.9476	79.5
2	0.6029	90.9	0.6352	94.0	0.9136	80.2
3	0.5895	87.1	0.6110	95.9	0.9078	81.7
4	0.5189	98.1	0.5896	93.3	0.8601	88.6
Average:	0.5531	93.0	0.6894	93.0	0.9073	82.5
Stnd.dev	0.0438	4.3			0.0312	3.6
% c.v.	7.9221	4.6	0.6184	94.4	3.4367	4.4
			0.0421	1.2		
			6.8059	1.3		
d-Limonene						
1	123.7	57.2	108.4	54.5	197.8	72.1
2	145.0	59.4	121.6	58.3	216.7	72.1
3	143.7	57.3	111.2	60.9	213.4	56.0
4	116.1	56.2	129.9	53.9	199.8	75.8
Average:	132.10	57.5	121.75	60.7	206.91	69.0
Stnd.dev	12.5059	1.1			8.2298	7.6
% c.v.	9.4670	2.0	118.57	57.7	3.9775	11.1
			7.8189	3.0		
			6.5943	5.1		
cis-3-Hexenol (+)						
1	0.2548	95.7	-	-		106.2
2	0.2925	86.6	-	-		115.0
3	0.2730	84.4	-	-	0.1455	112.8
4	0.1658	100.9	-	-	0.1462	112.4
Average:	0.2465	91.9			0.1458	111.6
Stnd.dev	0.0485	6.7			0.0004	3.3
% c.v.	19.6664	7.3			0.2600	2.9

Table 43. (cont.)
Partitioned between 35% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Camphor					(1)	
1	0.3962	151.3	0.7231	98.7	6.8936	17.8
2	0.4203	142.6	0.7633	97.3	6.1974	20.0
3	0.4252	136.2	0.7812	99.8	6.3883	18.9
4	0.3350	156.8	0.7118	97.2	6.3724	18.8
Average:	0.3942	146.7	0.8639	95.7	6.4629	18.9
Stnd.dev	0.0359	7.9			0.2597	0.8
% c.v.	9.1055	5.4	0.7686	97.7	4.0185	4.2
			0.0540	1.4		
			7.0223	1.4		
Linalylacetate			(1)			
1	3.7353	101.7	4.3618	63.4	0.1066	80.9
2	4.2201	94.0	4.7980	60.8	0.0735	88.5
3	4.1346	91.1	4.6900	64.1	0.1051	84.4
4	3.1752	105.5	4.5256	61.9	0.0841	83.8
Average:	3.8163	98.1	5.4984	60.4	0.0923	84.4
Stnd.dev	0.4129	5.8			0.0140	2.7
% c.v.	10.8192	5.9	4.7747	62.1	15.2037	3.2
			0.3909	1.5		
			8.1866	2.3		
Menthol						
1	0.3242	97.9	0.3455	93.9	0.6346	84.0
2	0.3579	90.0	0.3595	97.1	0.6252	92.4
3	0.3266	87.1	0.3432	99.3	0.5905	87.0
4	0.2715	102.3	0.3418	96.6	0.6106	86.7
Average:	0.3200	94.3	0.4502	94.5	0.6152	87.5
Stnd.dev	0.0310	6.1			0.0166	3.1
% c.v.	9.6995	6.4	0.3680	96.3	2.7038	3.5
			0.0416	1.9		
			11.2970	2.0		

Table 43. (cont.)
Partitioned between 35% Aqueous Ethanol and LDPE

	10C		25C		40C	
Aroma repl.	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %	K(P/L) (cP/cL)	Mass Balance %
Dimethylbenzylcarbinol						
1	0.2171	97.7	0.3482	103.5	1.0754	87.1
2	0.3264	87.5	0.3810	103.0	1.0239	91.7
3	0.2322	85.3	0.3799	104.2	1.1461	85.7
4	0.1880	103.0	0.3574	101.1	1.0958	86.7
Average:	0.2409	93.4	0.4123	100.6	1.0853	87.8
Stnd.dev	0.0518	7.3			0.0438	2.3
% c.v.	21.5188	7.8	0.3758	102.5	4.0363	2.6
			0.0223	1.4		
			5.9270	1.3		
Phenylethylalcohol						
1	0.1021	96.7	0.3780	103.2	0.1973	90.9
2	0.6294	89.1	0.3790	104.5	0.1915	95.9
3	0.5117	84.7	0.3163	108.2	0.1658	90.1
4	0.1529	102.9	0.2984	106.0	0.1574	93.8
Average:	0.3490	93.4	0.2453	102.0	0.1780	92.7
Stnd.dev	0.2261	7.0			0.0168	2.3
% c.v.	64.7849	7.4	0.3234	104.8	9.4423	2.5
			0.0507	2.2		
			15.6746	2.1		
Diphenylmethane						
1	9.8641	84.5	6.8195	80.5	18.3826	71.6
2	11.3845	80.3	7.1123	79.8	16.8113	78.6
3	11.1957	77.6	6.6603	82.1	18.5808	76.2
4	8.6653	87.7	6.9189	79.0	17.2609	76.0
Average:	10.2774	82.5	7.7224	77.9	17.7589	75.6
Stnd.dev	1.0998	3.9			0.7434	2.5
% c.v.	10.7016	4.7	7.0467	79.9	4.1859	3.4
			0.3683	1.4		
			5.2264	1.8		

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Ave
Stn
%

Table 43. (cont.)
Partitioned between 35% Aqueous Ethanol and LDPE

Aroma repl.	10C K(P/L) (cP/cL)	10C Mass Balance %	25C K(P/L) (cP/cL)	25C Mass Balance %	40C K(P/L) (cP/cL)	40C Mass Balance %
Diphenyloxide						
1	18.1915	77.7	18.0083	77.2	34.3699	69.6
2	21.0266	75.0	19.2377	77.0	30.4303	74.7
3	20.6513	72.0	18.1267	78.1	33.3518	74.0
4	16.0333	80.3	18.7530	75.7	31.9717	73.4
Average:	18.9757	76.2	21.3404	76.8	32.5309	72.9
Stnd.dev	2.0178	3.1			1.4816	2.0
% c.v.	10.6339	4.0	19.0932	77.0	4.5546	2.7
			1.2081	0.8		
			6.3276	1.0		
Eugenol (+)						
1	0.0796	99.0	0.1247	98.3	0.0969	84.5
2	0.0812	90.2	0.1141	99.4	0.0812	87.9
3	0.0973	86.4	0.1126	100.4	0.0944	81.9
4	0.0704	106.4	0.1229	96.5	0.0978	85.1
Average:	0.0822	95.5	0.0950	94.3	0.0926	84.9
Stnd.dev	0.0097	7.8			0.0067	2.1
% c.v.	11.7880	8.1	0.1139	97.8	7.2283	2.5
			0.0105	2.2		
			9.2528	2.2		
gamma-Undelactone						
1	0.2804	96.4	0.3323	99.6	0.4457	87.7
2	0.3711	87.0	0.3061	101.1	0.4244	92.4
3	0.3330	84.6	0.2820	101.3	0.4745	86.3
4	0.2519	102.0	0.3087	97.9	0.4217	88.4
Average:	0.3091	92.5	0.3856	96.1	0.4416	88.7
Stnd.dev	0.0461	7.0			0.0212	2.3
% c.v.	14.9250	7.6	0.3230	99.2	4.7902	2.5
			0.0351	2.0		
			10.8783	2.0		

Appendix D

UNIFAC Estimations

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Dim

Men

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Liqu

Table 44. UNIFAC Estimated Aroma K(L/G): 100% Ethanol at 25C

Aroma	x(i) K(L/G)	Act. Coeff UNIFAC	K(L/G) UNIFAC	exp data	Ratio calc/exp
d-Limonene	2.91E-05	18.307	8468	15933	0.53
Diphenylmethane	3.25E-05	20.509	629894	527000	1.20
Linalylacetate	2.83E-05	9.510	319043	317750	1.00
Camphor	2.94E-05	5.782	177547	146750	1.21
Diphenyloxide	3.43E-05	16.775	934626	570500	1.64
Isoamylacetate	3.33E-05	4.664	12529	13366	0.94
gamma-Undelactone	3.03E-05	9.002	10267677		
Eugenol	3.08E-05	0.504	21411051	738000	29.01
Citronellol	2.97E-05	1.713	1304619	331000	3.94
Dimethylbenzyl-carbinol	3.09E-05	1.555	1558915	641000	2.43
Menthol	3.06E-05	1.743	785206	699000	1.12
Phenylethylalcohol	3.15E-05	1.558	409536	671667	0.61
cis-3-Hexenol	2.93E-05	1.340	235603	135880	1.73
			Average :		3.78
			Stnd Dev:		7.66

Liquid phase molar volume: 58.69

Table 45. UNIFAC Estimated Aroma K(L/G): 75% Ethanol at 25C

Aroma	K(L/G) x(i)	UNIFAC Act. Coe	UNIFAC K(L/G)	exp data K(L/G)	Ratio calc/exp
d-Limonene	1.65E-05	85.816	2726	11257	0.24
Diphenylmethane	1.65E-05	231.674	84139	241750	0.35
Linalylacetate	1.65E-05	27.609	165820	132425	1.25
Camphor	1.65E-05	17.185	90135	97125	0.93
Diphenyloxide	1.65E-05	67.071	352726	236750	1.49
Isoamylacetate	1.65E-05	10.569	8343	5465	1.53
gamma-Undelactone	1.65E-05	42.887	3252157	1106000	2.94
Eugenol	1.65E-05	0.06719	2.42E+08	641333	377.74
Citronellol	1.65E-05	6.0552	556775	213000	2.61
Dimethylbenzyl-carbinol	1.65E-05	6.435	568325	658000	0.86
Menthol	1.65E-05	7.132	289508	669667	0.43
Phenylethylalcohol	1.65E-05	4.748	202730	597000	0.34
cis-3-Hexenol	1.65E-05	2.466	193244	95125	2.03
			Average :		30.21
			Stnd Dev:		100.33

Liquid phase molar volume: 38.8949

Tab

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Table 46 . UNIFAC Estimated Aroma K(L/G): 50% Ethanol at 25C

Aroma	K(L/G) x(i)	UNIFAC Act.Coef	UNIFAC K(L/G)	exp data K(L/G)	Ratio calc/exp
d-Limonene	1.28E-05	766.817	417	235	1.77
Diphenylmethane	1.28E-05	3486.90	7643	27350	0.28
Linalylacetate	1.28E-05	192.733	32475	16975	1.91
Camphor	1.28E-05	90.464	23409	23450	1.00
Diphenyloxide	1.28E-05	734.477	44037	24500	1.80
Isoamylacetate	1.28E-05	40.1733	3001	1175	2.55
gamma-Undelactone	1.28E-05	375.290	508100	930000	0.55
Eugenol	1.28E-05	0.45855	4.85E+07	812750	59.72
Citronellol	1.28E-05	42.636	108106	142667	0.76
Dimethylbenzyl-carbinol	1.28E-05	42.0415	118928	265750	0.45
Menthol	1.28E-05	49.5143	57011	119000	0.48
Phenylethylalcohol	1.28E-05	20.8507	63114	488333	0.13
cis-3-Hexenol	1.28E-05	7.8136	83381	34525	2.42
			Average :		5.68
			Stnd Dev:		15.62

Liquid phase molar volume: 28.4494

Tab

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Table 47. UNIFAC Estimated Aroma K(L/G): 35% Ethanol at 25C

Aroma	K(L/G) x(i)	UNIFAC Act. Coef	UNIFAC K(L/G)	exp data K(L/G)	Ratio calc/exp
d-Limonene	1.34E-05	3635.214	102.8	34.5	2.98
Diphenylmethane	1.34E-05	22153.86	1405.9	4155	0.34
Linalylacetate	1.34E-05	829.4075	8819.7	2300	3.83
Camphor	1.34E-05	317.0585	7806.2	5977	1.31
Diphenyloxide	1.34E-05	4019.404	9404.7	3468	2.71
Isoamylacetate	1.34E-05	108.4705	1298.9	377	3.45
gamma-Undelactone	1.34E-05	1824.682	1.22E+05	310000	0.39
Eugenol	1.34E-05	2.28084	1.14E+07	245000	46.55
Citronellol	1.34E-05	189.4024	28441.9	72500	0.39
Dimethylbenzyl-carbinol	1.34E-05	169.754	34424.0	95400	0.36
Menthol	1.34E-05	211.193	15621.7	21600	0.72
Phenylethylalcohol	1.34E-05	62.9745	24423.0	203000	0.12
cis-3-Hexenol	1.34E-05	19.4692	39110.0	12733	3.07
			Average :		5.09
			Stnd Dev:		12.04

Liquid phase molar volume: 24.34201

Table 48. UNIFAC Estimated n-Alkane K(L/G) at 25C

100% Ethanol: Experimental K(L/G) Comparisons with UNIFAC at 25C

n-alkane	Exp x(i)	Exp K(L/G)	Act. Coef UNIFAC	K(P/G) UNIFAC	Ratio UNIFAC/exp
Pentane	1.1E-04	79	6.06	102	1.30
Hexane	1.0E-04	200	7.75	270	1.35
Heptane	1.0E-04	531	9.70	714	1.34
Octane	1.1E-04	1457	11.95	1886	1.29
Nonane	1.0E-04	4860	14.53	4979	1.02
Decane	1.0E-04	17022	20.80	9767	0.57
Dodecane	1.0E-04	118229	24.80	91769	0.78
Tetradecan	1.0E-04	364940	34.29	634898	1.74
Hexadecane	1.0E-04	1522200	46.56	4412444	2.90
				Average :	1.37
				Stnd Dev:	0.63

Act. Coeff. = mole fraction activity coefficient
x(i) = mole fraction

Table 48. (cont.)

66% Ethanol: Experimental K(L/G) Comparisons with UNIFAC at 25C

n-alkane	Exp x(i)	Exp K(L/G)	Act. Coeff UNIFAC	K(P/G) UNIFAC	Ratio UNIFAC/exp
Pentane	4.0E-05	10	32.69	29	3.06
Hexane	2.4E-05	17	52.68	61	3.53
Heptane	1.6E-05	36	83.10	128	3.56
Octane	9.7E-06	200	129.04	269	1.34
Nonane	6.3E-06		197.91	563	
Decane	3.9E-06	417	300.47	1041	2.50
Dodecane	1.8E-05	1988	676.37	5180	2.61
Tetradecane	7.0E-07	7736	1486.12	22553	2.92
Hexadecane	3.1E-07	9550	3207.80	98613	10.33
				Average :	3.73
				Stnd Dev:	2.58

Act. Coeff. = mole fraction activity coefficient
x(i) = mole fraction

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Table 48. (cont.)

33% Ethanol: Experimental K(L/G) Comparisons with **UNIFAC** at 25C

n-alkane	Exp x(i)	Exp K(L/G)	Act. Coeff UNIFAC	K(P/G) UNIFAC	Ratio UNIFAC/exp
Pentane	4.0E-05	0.19	244	7.14	37.60
Hexane	2.4E-05	0.14	535	11.04	78.84
Heptane	1.6E-05	0.33	1149	17.01	51.54
Octane	9.7E-06	0.46	2426	26.23	57.01
Nonane	6.3E-06		5059	40.38	
Decane	3.9E-06	0.74	10446	54.90	74.19
Dodecane	1.8E-05	6.41	43488	147.71	23.04
Tetradecane	7.0E-07	14.65	176738	347.71	23.73
Hexadecane	3.1E-07	48.71	705465	822.16	16.88
				Average :	45.35
				Stnd Dev:	22.26

Act. Coeff. = mole fraction activity coefficient
x(i) = mole fraction

Tab

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Table 49. UNIFAC Estimated Aroma K(P/L): HDPE/100% Ethanol at 25C

Aroma	MW	UNIFAC a. Polymer	UNIFAC w(i) a.c. Polymer	Exp w(i) Polymer	UNIFAC x(i) a.c. Ethanol	Exp x(i) Ethanol
d-Limonene	136.24	0.00011	6.88	1.6E-05	18.31	2.9E-05
Diphenylmethane	168.23	0.00008	11.04	7.6E-06	20.51	3.2E-05
Linalylacetate	196.29	0.00010	23.71	4.6E-06	9.51	2.8E-05
Camphor	152.23	0.00002	8.23	2.8E-06	5.78	2.9E-05
Diphenyloxide	179.21	0.00021	14.02	1.5E-05	16.78	3.4E-05
Isoamylacetate	130.17	0.00004	17.54	2.3E-06	4.66	3.3E-05
gamma-Undelactone	184.28	0.00001	7.33	1.8E-06	9.00	3.0E-05
Eugenol	164.2	0.00018	264.08	7.1E-07	0.50	3.1E-05
Citronellol	156.27	0.00003	41.18	9.5E-07	1.71	3.0E-05
Dimethylbenzyl-carbinol	150.22	0.00005	56.13	9.5E-07	1.55	3.1E-05
Menthol	156.27	0.00014	32.69	4.4E-06	1.74	3.1E-05
Phenylethylalcohol	122.17	0.00010	71.91	1.4E-06	1.56	3.2E-05
cis-3-Hexenol	100.16	0.00004	63.98	7.1E-07	1.34	2.9E-05

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Table 49. (cont.)

Aroma	UNIFAC K(P/L)	Exp. K(P/L) (1)	cal/exp ratio	Exp. K(P/L) (2)	cal/exp ratio
d-Limonene	1.0952	0.2780	3.94	0.36	3.04
Diphenylmethane	0.6195	0.0992	6.25	0.24	2.58
Linalylacetate	0.1146	0.0549	2.09	0.065	1.76
Camphor	0.2589	0.0397	6.52	0.057	4.54
Diphenyloxide	0.3747	0.1483	2.53	0.16	2.34
Isoamylacetate	0.1146	0.0464	2.47		
gamma-Undelactone	0.3742	0.0267	14.01	0.035	10.69
Eugenol	0.0007	0.0181	0.04	0.024	0.03
Citronellol	0.0149	0.0168	0.89	0.016	0.93
Dimethylbenzylcarbinol	0.0103	0.0113	0.92	0.017	0.61
Menthol	0.0191	0.0225	0.85	0.019	1.01
Phenylethylalcohol	0.0099	0.0174	0.57	0.011	0.90
cis-3-Hexenol	0.0117	0.0139	0.84	0.014	0.84
		ave:	3.22		2.44
		std dev	3.71		2.77
		c.v.%	114.95		113.33

HDPE: density = .956, thickness = 100 micrometers
exp = experimental value
(1) = this work, CL = 70-105 ppm (w/v), average of HDPE and LDPE measurements across 10, 25 and 40C
(2) = Koszinowski and Piringer (1989), CL = 1500 ppm (w/v)
Blank spaces indicate missing values
MW = molecular weight
x(i) = mole fraction
w(i) = weight fraction
a = activity
a.c. = activity coefficient

Table 50. UNIFAC Estimated Aroma K(P/L): HDPE/75% Ethanol at 25c

Aroma	MW	UNIFAC w(i) a.c. Polymer	Exp w(i) Polymer	UNIFAC x(i) a.c. Ethanol	Exp x(i) Ethanol
d-Limonene	136.24	6.879	1.52E-04	85.816	1.65E-05
Diphenylmethane	168.23	11.035	4.86E-05	231.674	1.65E-05
Linalylacetate	196.29	23.706	4.58E-06	27.609	1.65E-05
Camphor	152.23	8.227	2.78E-06	17.185	1.65E-05
Diphenyloxide	179.21	14.008	1.50E-05	67.071	1.65E-05
Isoamylacetate	130.17	17.543	2.31E-06	10.569	1.65E-05
gamma-Undelactone	184.28	7.327	1.76E-06	42.887	1.65E-05
Eugenol	164.2	263.777	7.12E-07	0.067	1.65E-05
Citronellol	156.27	41.175	9.51E-07	6.055	1.65E-05
Dimethylbenzylcarbinol	150.22	56.116	9.51E-07	6.435	1.65E-05
Menthol	156.27	32.667	4.38E-06	7.132	1.65E-05
Phenylethylalcohol	122.17	71.902	1.45E-06	4.748	1.65E-05
cis-3-Hexenol	100.16	63.977	7.11E-07	2.466	1.65E-05

Table 50. (cont.)

Aroma	UNIFAC K(P/L)	Exp. K(P/L) (1)	calc./exp. ratio
d-Limonene	3.4048	1.8000	1.89
Diphenylmethane	4.6402	0.3387	13.70
Linalylacetate	0.2206	0.1471	1.50
Camphor	0.5102	0.0581	8.78
Diphenyloxide	0.9935	0.5258	1.89
Isoamylacetate	0.1721	0.1413	1.22
gamma-Undelactone	1.1811	0.0316	37.38
Eugenol	0.0001	0.0241	0.0024
Citronellol	0.0350		
Dimethylbenzyl-carbinol	0.0284	0.0228	1.24
Menthol	0.0519	0.0557	0.93
Phenylethylalcohol	0.0201	0.0160	1.26
cis-3-Hexenol	0.0143	0.0087	1.64
		ave:	5.95
		std dev	10.22
		c.v.%	171.72

HDPE: density = .956, thickness = 100 micrometers
Exp =experimental value this work, CL = 70-105 ppm (w/v)
average of HDPE and LDPE at 10,25 and 40C
Blank spaces indicate missing values
MW = molecular weight
x(i) = mole fraction
w(i) = weight fraction
a. c. = activity coefficient
calc.= UNIFAC calculated values

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Table 51. UNIFAC Estimated Aroma K(P/L): HDPE/50% Ethanol at 25C

Aroma	MW	UNIFAC w(i) a.c. Polymer	Exp w(i) Polymer	UNIFAC x(i) a.c. Ethanol	Exp x(i) Ethanol
d-Limonene	136.24	6.81	2.32E-03	766.82	1.28E-05
Diphenylmethane	168.23	10.98	5.15E-04	3486.90	1.28E-05
Linalylacetate	196.29	23.65	1.64E-04	192.73	1.28E-05
Camphor	152.23	8.50	4.41E-05	90.46	1.28E-05
Diphenyloxide	179.21	13.84	9.39E-04	734.48	1.28E-05
Isoamylacetate	130.17	17.54	4.06E-05	40.17	1.28E-05
gamma-Undelactone	184.28	7.33	2.49E-05	375.29	1.28E-05
Eugenol	164.2	262.65	1.71E+00	0.46	1.28E-05
Citronellol	156.27	41.17	4.23E-06	42.64	1.28E-05
Dimethylbenzyl-carbinol	150.22	56.11	4.23E-06	42.04	1.28E-05
Menthol	156.27	32.66	1.78E-05	49.51	1.28E-05
Phenylethylalcohol	122.17	71.87	6.44E-06	20.85	1.28E-05
cis-3-Hexenol	100.16	63.98	2.09E-06	7.81	1.28E-05

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calc.
a.c.

Table 49. (cont.)

Aroma	UNIFAC K(P/L)	Exp. K(P/L) (1)	calc./exp. ratio
d-Limonene	22.477	32.353	0.69
Diphenylmethane	51.340	3.865	13.29
Linalylacetate	1.129	1.317	0.86
Camphor	1.901	0.534	3.56
Diphenyloxide	8.052	6.445	1.25
Isoamylacetate	0.479	0.416	1.15
gamma-Undelactone	7.561	0.160	47.28
Eugenol	0.0003	0.137	0.0021
Citronellol	0.180		
Dimethylbenzylcarbinol	0.136	0.113	1.20
Menthol	0.264	0.180	1.46
Phenylethylalcohol	0.065	0.121	0.54
cis-3-Hexenol	0.033	0.022	1.48
	Average:		6.06
	Stnd. Deviation:		12.89
	Coef. Variation		212.58

HDPE: density = .956, thickness = 100 micrometers
Exp = experimental value this work, CL = 70-105 ppm (w/v)
average of LDPE, HDPE and 10,25 and 40C
Blank spaces indicate missing values
MW = molecular weight
x(i) = mole fraction
calc. = UNIFAC estimated value
a.c. = activity coefficient

Table 52. UNIFAC Estimation Aroma K(P/L): HDPE/35% Ethanol at 25C

Aroma	MW	UNIFAC w(i) a.c. Polymer	Exp w(i) Polymer	UNIFAC x(i) a.c. Ethanol	Exp x(i) Ethanol
d-Limonene	136.24	6.51	1.22E-02	3635.21	1.34E-05
Diphenylmethane	168.23	10.85	1.65E-03	22153.9	1.34E-05
Linalylacetate	196.29	23.59	3.03E-04	829.41	1.34E-05
Camphor	152.23	8.22	1.14E-04	317.06	1.34E-05
Diphenyloxide	179.21	13.45	3.13E-03	4019.40	1.34E-05
Isoamylacetate	130.17	17.53	7.41E-05	108.47	1.34E-05
gamma-Undelactone	184.28	7.33	4.11E-05	1824.68	1.34E-05
Eugenol	164.2	263.13	1.15E-05	2.28	1.34E-05
Citronellol	156.27	41.02	5.12E-05	189.40	1.34E-05
Dimethylbenzyl-carbinol	150.22	55.88	5.12E-05	169.75	1.34E-05
Menthol	156.27	32.59	4.54E-05	211.19	1.34E-05
Phenylethylalcohol	122.17	71.90	2.53E-06	62.97	1.34E-05
cis-3-Hexenol	100.16	63.97	2.86E-06	19.47	1.34E-05

Table 52 (cont.)

Aroma	UNIFAC K(P/L)	Exp. K(P/L) (1)	calc./exp. ratio
d-Limonene	95.34	161.21	0.59
Diphenylmethane	282.51	8.99	31.41
Linalylacetate	4.17	3.14	1.33
Camphor	5.90	2.36	2.50
Diphenyloxide	38.82	27.64	1.40
Isoamylacetate	1.11	0.81	1.36
gamma-Undelactone	31.46	0.39	80.47
Eugenol	0.0012	0.11	0.0113
Citronellol	0.69		
Dimethylbenzyl-carbinol	0.47	0.58	0.82
Menthol	0.96	0.51	1.90
Phenylethylalcohol	0.17	0.16	1.03
cis-3-Hexenol	0.071	0.088	0.80
	Average:		10.30
	Stnd. Deviation:		22.74
	Coef. Variation		220.74

HDPE: density = .956, thickness = 100 micrometers
Exp =experimental value this work, CL = 70-105 ppm (w/v)
average of LDPE, HDPE and 10,25 and 40C measurements
Blank spaces indicate missing values
MW = molecular weight
x(i) = mole fraction
w(i) = weight fraction
act. coeff. = activity coefficient
calc = UNIFAC estimated value
a. = activity
a.c. = activity coefficient

Tab

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Table 53. **UNIFAC Estimated n-Alkane K(P/L) HDPE at 25C**

HDPE/100% Ethanol: UNIFAC Comparison with Experimental K(P/L) at 25C

n-Alkane	MW	UNIFAC (P/G) w(i) act coeff.	EXP (P/G) w(i)	UNIFAC (L/G) x(i) Act.Coeff.	(L/G) x(i)
Octane	114.22	10.358	5.57E-05	11.953	1.43E-05
Nonane	128.26	9.592	8.78E-05	14.5437	1.43E-05
Decane	142.276	9.0688	4.93E-05	17.518	1.43E-05
Dodecane	170.41	8.2912	7.90E-05	24.82	1.43E-05
Tetradecan	198.4	7.6257	1.52E-04	34.33	1.43E-05
Hexadecane	226.45	7.2236	3.07E-04	46.6359	1.43E-05
Octadecane	254.54	6.8781	9.51E-04	62.471	1.43E-05
Eicosane	282.56	6.58345	2.61E-03	82.7544	1.43E-05
Docosane	310.61	6.404	1.92E-03	108.624	1.43E-05

Table 53. (cont.)

HDPE/100% Ethanol: UNIFAC Comparison with Experimental K(P/L) at 25C

n-Alkane	UNIFAC K(P/L)	Exp. K(P/L)	Ratio calc/exp
Octane	0.57	1.38	0.410
Nonane	0.66	2.14	0.310
Decane	0.76	2.70	0.282
Dodecane	0.99	3.32	0.297
Tetradecan	1.27	5.99	0.212
Hexadecane	1.60	10.65	0.150
Octadecane	2.00	28.71	0.070
Eicosane	2.50	72.37	0.034
Docosane	3.06	48.49	0.063
		average:	0.203
		std. dev.:	0.124
		% std dev:	60.885

HDPE: density = .956, thickness = 100 micrometer
EXP = experimental measurement this work, CL = 17-40 ppm (w/v)
Act. Coeff. = activity coefficient
w(i) = weight fraction
x(i) = mole fraction
MW = molecular weight

Table 53. (cont.)

HDPE/75% Ethanol: UNIFAC Comparison with Experimental K(P/L) at 25C

n-Alkane	MW	UNIFAC (P/G) w(i) Act Coeff.	EXP (P/G) w(i)	EXP (L/G) x(i) Act.Coeff.	(L/G) x(i)
Octane	114.22	10.358	5.35E-05	65.377	4.50E-06
Nonane	128.26	9.592	8.39E-05	93.607	4.50E-06
Decane	142.276	9.06121	1.99E-04	132.676	4.50E-06
Dodecane	170.41	8.27875	3.76E-04	260.305	4.50E-06
Tetradecan	198.4	7.6093	6.15E-04	498.544	4.50E-06
Hexadecane	226.45	7.1794	1.72E-03	937.797	4.50E-06
Octadecane	254.54	6.7463	5.67E-03	1739.532	4.50E-06
Eicosane	282.56	6.1368	2.08E-02	3190.759	4.50E-06
Docosane	310.61	4.7148	9.04E-02	5799.508	4.50E-06

Table 53. (cont.)

HDPE/75% Ethanol: UNIFAC Comparison with Experimental K(P/L) at 25C

n-Alkane	UNIFAC K(P/L)	Exp. K(P/L)	Ratio calc/exp
Octane	2.05	2.558	0.80
Nonane	2.83	4.01	0.71
Decane	3.83		
Dodecane	6.86	9.813	0.70
Tetradecan	12.28	21.865	0.56
Hexadecane	21.45	53.711	0.40
Octadecane	37.67	154.72	0.24
Eicosane	68.42	529.3	0.13
Docosane	147.25	2259.5	0.07
		average:	0.45
		std. dev.:	0.26
		% std dev:	58.73

HDPE: density = .956, thickness = 100 micrometer
EXP = experimental measurement this work, CL = 19-42 ppm (w/v)
Blanks indicate missing values
Act. Coeff. = activity coefficient
w(i) = weight fraction
x(i) = mole fraction
MW = molecular weight

Table 53. (cont.)

HDPE/50% Ethanol: UNIFAC Comparison with Experimental K(P/L) at 25C

n-Alkane	MW	UNIFAC (P/G) w(i) Act Coeff.	EXP (P/G) w(i)	EXP (L/G) x(i) Act.Coeff.	(L/G) x(i)
Octane	114.22	10.2763	1.29E-03	487.9	1.42E-06
Nonane	128.26	9.4007	3.51E-03	858.62	1.42E-06
Decane	142.276	8.90341	3.37E-03	1495.8	1.42E-06
Dodecane	170.41	7.69139	1.52E-02	4433.8	1.42E-06
Tetradecan	198.4	6.22034	4.70E-02	12829.4	1.42E-06
Hexadecane	226.45	3.96917	1.67E-01	36459	1.42E-06
Octadecane	254.54	2.55433	3.39E-01	102174	1.42E-06
Eicosane	282.56	1.9455	8.67E-01	283145	1.42E-06
Docosane	310.61	1.4616	6.70E-01	777511	1.42E-06

Table 53. (cont.)

HDPE/50% Ethanol: UNIFAC Comparison with Experimental K(P/L) at 25C

n-Alkane	UNIFAC K(P/L)	Exp. K(P/L)	Ratio calc/exp
Octane	11.31	82.37	0.14
Nonane	19.37	232.82	0.08
Decane	32.12	414.94	
Dodecane	92.00	1453.8	0.06
Tetradecan	282.74	4359.2	0.06
Hexadecane	1103.22	13576	0.08
Octadecane	4274.04	34613	0.12
Eicosane	14008.70	403110	0.03
Docosane	46579.37	114920	0.41
		average:	0.12
		std. dev.:	0.11
		% std dev:	89.11

HDPE: density = .956, thickness = 100 micrometer
EXP = experimental measurement this work, CL = 8-16 ppm (w/v)
Blanks indicate missing values
Act. Coeff. = activity coefficient
w(i) = weight fraction
x(i) = mole fraction
MW = molecular weight

Appendix E

GCFEOS Estimations

Table 54

Aroma
d-Limone
Diphenyl
Linalyla
Camphor
Diphenyl
Isoamyla
gamma-Un
Eugenol
Citronel
Dimethyl
Menthol
Phenylet
cis-3-He
d-limone
Camphor
gamma-Un
Menthol

Act. Coe
W(i) = w
(c) = cy

Table 54. GCFEOS Estimated Aroma K(L/G): 100% Ethanol at 25C

Aroma	GCFEOS activity Ethanol	GCFEOS act.coef Ethanol	Exp (L/G) w(i)	GCFEOS K(L/G)	exp data	Ratio calc/exp
d-Limonene	0.00618	71.810	8.61E-05	730	15933	0.05
Diphenylmethane	0.000275	2.324	1.19E-04	1522436	527000	2.89
Linalylacetate	0.002257	19.030	1.19E-04	37420	317750	0.12
Camphor	0.000410	4.220	9.72E-05	73611	146750	0.50
Diphenyloxide	0.000626	4.955	1.27E-04	856467	570500	1.50
Isoamylacetate	0.000178	1.894	9.40E-05	10920	13366	0.82
gamma-Undelactone	0.000275	2.275	1.21E-04	1.0E+07		
Eugenol	0.000040	0.372	1.10E-04	8135033	738000	11.02
Citronellol	0.000045	0.449	1.01E-04	1466554	331000	4.43
Dimethylbenzyl-carbinol	0.000026	0.262	1.01E-04	2838978	641000	4.43
Menthol	0.000048	0.468	1.04E-04	862637	699000	1.23
Phenylethylalcohol	0.000017	0.205	8.36E-05	1171947	671667	1.74
cis-3-Hexenol	0.000033	0.521	6.37E-05	278801	135880	2.05
d-limonene (c)	0.000368	3.110	1.19E-04	16855	15933	1.06
Camphor (c)	0.000005	0.057	9.72E-05	5409094	146750	36.86
gamma-Undelactone(c)	0.000233	1.927	1.21E-04	1.2E+07		
Menthol (c)	0.000037	0.361	1.04E-04	1118940	699000	1.60
				Average :		2.57
				Stnd Dev:		2.92

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction
(c) = cyclic group parameters used

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Act.
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Table 55. GCFEOS Estimated Aroma K(L/G): 75% Ethanol at 25C

Aroma	GCFEOS activity Ethanol	GCFEOS act.coef Ethanol	Exp (L/G) w(i)	GCFEOS K(L/G)	exp data K(L/G)	Ratio calc/exp
d-Limonene	0.005174	60.121	8.61E-05	947	11257	0.08
Diphenylmethane	0.001634	13.777	1.19E-04	278915	241750	1.15
Linalylacetate	0.001187	10.007	1.19E-04	77297	132425	0.58
Camphor	0.002168	22.295	9.72E-05	15135	97125	0.16
Diphenyloxide	0.001061	8.387	1.27E-04	549579	236750	2.32
Isoamylacetate	0.000528	5.619	9.40E-05	3998	5465	0.73
gamma-Undelactone	0.001886	15.548	1.21E-04	1614383	1106000	1.46
Eugenol	0.000015	0.158	1.01E-04	2.1E+07	641333	32.37
Citronellol	0.000316	3.043	1.04E-04	235101	213000	1.10
Dimethylbenzyl-carbinol	0.000193	2.315	8.36E-05	348800	658000	0.53
Menthol	0.000342	5.375	6.37E-05	81520	669667	0.12
Phenylethylalcohol	0.000039	0.327	1.21E-04	800181	597000	1.34
cis-3-Hexenol	0.000062	0.721	8.61E-05	218738	95125	2.30
d-limonene (c)	0.000465	5.403	8.61E-05	10539	11257	0.94
Camphor (c)	0.001289	13.256	9.72E-05	25457	97125	0.26
gamma-Undelactone(c)	0.001225	10.099	1.21E-04	2485491	1106000	2.25
Menthol (c)	0.001393	21.875	6.37E-05	20032	669667	0.03
				Average :		3.40
				Stnd Dev:		8.39

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction
(c) = cyclic group parameters used
Liquid phase density: 0.85266

Table 5

Aroma

d-Limo

Diphen

Linaly

Campho

Diphen

Isoamy

gamma-

Eugen

Citro

Dimet

Menth

Pheny

cis-

d-li

Camp

gamma

Ment

Act.
W(i)
(c) =
Liqui

Table 56. GCFEOS Estimated Aroma K(L/G): 50% Ethanol at 25C

Aroma	GCFEOS activity Ethanol	GCFEOS act.coef Ethanol	Exp (L/G) w(i)	GCFEOS K(L/G)	exp data K(L/G)	Ratio calc/exp
d-Limonene	0.05565	646.64	8.61E-05	94.0	235	0.400
Diphenylmethane	0.02192	184.82	1.19E-04	22205	27350	0.812
Linalylacetate	0.01161	97.88	1.19E-04	8440	16975	0.497
Camphor	0.0313	321.88	9.72E-05	1120	23450	0.048
Diphenyloxide	0.00403	31.86	1.27E-04	154527	24500	6.307
Isoamylacetate	0.006249	66.49	9.40E-05	361	1175	0.307
gamma-Undelactone	0.08103	668.01	1.21E-04	40130	930000	0.043
Eugenol	0.000020	0.20	1.01E-04	1.8E+07	812750	21.635
Citronellol	0.006852	65.95	1.04E-04	11587	142667	0.081
Dimethylbenzyl-carbinol	0.00238	28.49	8.36E-05	30270	265750	0.114
Menthol	0.01206	189.38	6.37E-05	2471	119000	0.021
Phenylethylalcohol	0.000168	1.39	1.21E-04	201128	488333	0.412
cis-3-Hexenol	0.000149	1.74	8.61E-05	96941	34525	2.808
d-limonene (c)	0.007806	90.70	8.61E-05	670	235	2.853
Camphor (c)	0.01826	187.78	9.72E-05	1919	23450	0.082
gamma-Undelactone(c)	0.05194	428.19	1.21E-04	62605	930000	0.067
Menthol (c)	0.08207	1288.79	6.37E-05	363	119000	0.003
				Average :		2.58
				Stnd Dev:		5.76

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction
(c) = cyclic group parameters used
Liquid phase density: 0.91

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Table 57. GCFEOS Estimated Aroma K(L/G): 35% Ethanol at 25C

Aroma	GCFEOS activity Ethanol	GCFEOS act.coef Ethanol	Exp (L/G) w(i)	GCFEOS K(L/G)	exp data K(L/G)	Ratio calc/exp
d-Limonene	0.3316	3853.13	8.61E-05	16.3	34.5	0.473
Diphenylmethane	0.1331	1122.26	1.19E-04	3777.9	4155	0.909
Linalylacetate	0.07545	636.06	1.19E-04	1341.7	2300	0.583
Camphor	0.1957	2012.55	9.72E-05	185.0	5977	0.031
Diphenyloxide	0.01104	87.27	1.27E-04	58274.6	3468	16.804
Isoamylacetate	0.0436	463.88	9.40E-05	53.4	377	0.142
gamma-Undelactone	1.42	1.2E+04	1.21E-04	2.37E+03	310000	0.008
Eugenol	0.000029	0.30	1.01E-04	1.22E+07	245000	49.969
Citronellol	0.06196	596.34	1.04E-04	1323.8	72500	0.018
Dimethylbenzylcarbinol	0.0164	196.29	8.36E-05	4538.3	95400	0.048
Menthol	0.1486	2333.54	6.37E-05	207.2	21600	0.010
Phenylethylalcohol	0.000536	4.42	1.21E-04	6.52E+04	203000	0.321
cis-3-Hexenol	0.000321	3.74	8.61E-05	46543.3	12733	3.655
d-limonene (c)	0.06742	783.41	8.61E-05	80.2	34.5	2.325
Camphor (c)	0.1105	1136.36	9.72E-05	327.6	5977	0.055
gamma-Undelactone(c)	0.8912	7347.07	1.21E-04	3.77E+03	310000	0.012
Menthol (c)	0.9781	1.5E+04	6.37E-05	31.48	21600	0.001
				Average :		5.61
				Stnd Dev:		13.54

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction
(c) = cyclic group parameters used
Liquid phase density: 0.94076

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Ment

Phen

cis-

d-lin

Camph

gamma

Menth

Act. C
W(i) =
(c) = c
Liquid

Table 58. GCFEOS Estimated Aroma K(L/G): 100% Water at 25C

Aroma	GCFEOS activity Ethanol	GCFEOS act.coeff. Ethanol	Exp (L/G) w(i)	GCFEOS K(L/G)
d-Limonene	9.735	486750.00	2.00E-05	0.1
Diphenylmethane	2.721	136050.00	2.00E-05	33.1
Linalylacetate	2.75	137500.00	2.00E-05	6.6
Camphor	4.3	215000.00	2.00E-05	1.8
Diphenyloxide	0.0285	1425.00	2.00E-05	3785.4
Isoamylacetate	2.624	131200.00	2.00E-05	0.2
gamma-Undelactone	838.7	4.19E+07	2.00E-05	7.00E-01
Eugenol	0.0002303	11.52	2.00E-05	3.34E+05
Citronellol	4.553	227650.00	2.00E-05	3.7
Dimethylbenzyl-carbinol	0.6285	31425.00	2.00E-05	30.1
Menthol	29.63	1481500.0	2.00E-05	0.3
Phenylethylalcohol	0.002604	130.20	2.00E-05	2.35E+03
cis-3-Hexenol	0.0004894	24.47	2.00E-05	7545.8
d-limonene (c)	6.101	305050.00	2.00E-05	0.2
Camphor (c)	2.096	104800.00	2.00E-05	3.8
gamma-Undelactone (c	701.3	3.5E+07	2.00E-05	8.38E-01
Menthol (c)	22.4	1.12E+06	2.00E-05	0.46

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction
(c) = cyclic group parameters used
Liquid phase density: 0.9978

Table 59. GCFEOS Estimated n-Alkane K(L/G) at 25C

100% Ethanol: Experimental K(L/G) Comparisons with GCFEOS at 25C

n-alkane	Exp x(i)	Exp K(L/G)	Act.Coeff GCFEOS	K(P/G) GCFEOS	Ratio GCFEOS/EXP
Pentane	1.1E-04	79	6.33	62	0.79
Hexane	1.0E-04	200	6.16	182	0.91
Heptane	1.0E-04	531	6.15	517	0.97
Octane	1.1E-04	1457	6.27	1450	1.00
Nonane	1.0E-04	4860	6.46	4021	0.83
Decane	1.0E-04	17022	6.73	9775	0.57
Dodecane	1.0E-04	118229	7.44	82694	0.70
Tetradecan	1.0E-04	364940	8.37	603995	1.66
Hexadecane	1.0E-04	1522200	9.53	4388380	2.88
Octadecane			10.93	2.67E+07	
Eicosane			12.61	2.23E+08	
Docosane			14.61	1.76E+09	
				Average:	1.15
				Standard Deviation:	0.68

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction

Table 59. (cont.)

66% Ethanol: Experimental K(L/G) **Comparisons with** GCFEOS at 25C

n-alkane	Exp x(i)	Exp K(L/G)	Act.Coeff. GCFEOS	K(P/G) GCFEOS	Ratio GCFEOS/EXP
Pentane	4.0E-05	10	101.5	4.3	0.45
Hexane	2.4E-05	17	159.4	7.8	0.45
Heptane	1.6E-05	36	257.6	13.7	0.38
Octane	9.7E-06	200	423.8	23.8	0.12
Nonane	6.3E-06		706.5	40.9	
Decane	3.9E-06	417	1189	61.5	0.15
Dodecane	1.8E-05	1988	3433	199	0.10
Tetradecane	7.0E-07	7736	10080	558	0.07
Hexadecane	3.1E-07	9550	29960	1551	0.16
Octadecane			89760	3615	
Eicosane			270500	11570	
Docosane			818400	35006	
				Average:	0.24
				Standard Deviation:	0.15

Act. Coeff. = **weight** fraction activity coefficient
w(i) = **weight** fraction

Table 59. (cont.)

33% Ethanol: Experimental K(L/G) Comparisons with GCFEOS at 25C

n-alkane	Exp x(i)	Exp K(L/G)	Act.Coeff. GCFEOS	K(P/G) GCFEOS	Ratio GCFEOS/EXP
Pentane	4.0E-05	0.19	6126	0.078	0.41
Hexane	2.4E-05	0.14	18250	0.074	0.53
Heptane	1.6E-05	0.33	55910	0.069	0.21
Octane	9.7E-06	0.46	174500	0.063	0.14
Nonane	6.3E-06		551400	0.057	
Decane	3.9E-06	0.74	1759000	0.045	0.061
Dodecane	1.8E-05	6.41	18270000	0.041	0.006
Tetradecane	7.0E-07	14.65	1.93E+08	0.032	0.002
Hexadecane	3.1E-07	48.71	2.06E+09	0.024	0.001
Octadecane			2.22E+10	0.016	
Eicosane			2.41E+11	0.012	
Docosane			2.62E+12	0.010	
				Average:	0.17
				Standard Deviation:	0.19

Act. Coeff. = weight fraction activity coefficient
w(i) = weight fraction

Table 60 . GCFEOS Estimated Aroma K(P/L): HDPE/100% Ethanol at 25C

Aroma	GCFEOS a. Polymer	GCFEOS a.c. Polymer	Exp w(i) Polymer	GCFEOS a. Ethanol	GCFEOS a.c. Ethanol	Exp w(i) Ethanol
d-Limonene	0.000289	18.08	1.60E-05	0.00618	71.81	8.61E-05
Diphenylmethane	0.000476	63.12	7.55E-06	0.00027	2.32	1.19E-04
Linalylacetate	0.000062	13.68	4.58E-06	0.00225	19.03	1.19E-04
Camphor	0.000432	155.48	2.78E-06	0.00041	4.22	9.72E-05
Diphenyloxide	0.000153	10.23	1.50E-05	0.00062	4.95	1.27E-04
Isoamylacetate	0.000015	6.86	2.31E-06	0.00017	1.89	9.40E-05
gamma-Undelactone	0.000021	12.04	1.76E-06	0.00027	2.27	1.21E-04
Eugenol	0.000056	78.86	7.12E-07	0.00004	0.37	1.10E-04
Citronellol	0.000010	10.61	9.51E-07	0.00004	0.45	1.01E-04
Dimethylbenzyl-carbinol			9.51E-07	0.00002	0.26	1.01E-04
Menthol	0.000252	57.60	4.38E-06	0.00004	0.47	1.04E-04
Phenylethylalcohol	0.000087	60.77	1.45E-06	0.00001	0.21	8.36E-05
cis-3-Hexenol	0.000011	16.59	7.11E-07	0.00003	0.52	6.37E-05
d-Limonene (c)			1.60E-05	0.00036	3.11	1.19E-04
Camphor (c)	0.000015	5.66	2.78E-06	0.00000	0.06	9.72E-05
gamma-Undelactone (c)	0.000014	8.28	1.76E-06	0.00023	1.93	1.21E-04
Menthol (c)	0.000142	32.45	4.38E-06	0.00003	0.36	1.04E-04

Table 60 (cont.)

Aroma	GCFEOS K(P/L)	Exp. K(P/L) (1)	calc./exp ratio	Exp. K(P/L) (2)	calc./exp. ratio
d-Limonene	4.8346	0.2780	17.39	0.36	13.43
Diphenylmethane	0.0448	0.0992	0.45	0.24	0.19
Linalylacetate	1.6932	0.0549	30.84	0.065	26.05
Camphor	0.0330	0.0397	0.83	0.057	0.58
Diphenyloxide	0.5893	0.1483	3.97	0.16	3.68
Isoamylacetate	0.3357	0.0464	7.24		
gamma-Undelactone	0.2300	0.0267	8.61	0.035	6.57
Eugenol	0.0057	0.0181	0.32	0.024	0.24
Citronellol	0.0515	0.0168	3.07	0.016	3.22
Dimethylbenzyl-carbinol		0.0113		0.017	
Menthol	0.0099	0.0225	0.44	0.019	0.52
Phenylethylalcohol	0.0041	0.0174	0.24	0.011	0.37
cis-3-Hexenol	0.0382	0.0139	2.75	0.014	2.73
d-Limonene (c)		0.278		0.36	
Camphor (c)	0.0124	0.0397	0.31	0.057	0.22
gamma-Undelactone (c)	0.2835	0.0267	10.62	0.035	8.10
Menthol (c)	0.0222	0.0225	0.99	0.019	1.17
		ave:	6.35		5.23
		std dev	8.81		7.59
		c.v.%	138.80		144.90

HDPE: density = .956, thickness = 100 micrometer
blank spaces indicate either a missing value or model's inability to estimate an activity coefficient
w(i) = weight fraction
exp = experimental measurement
(1) = this work
(2) = Koszinowski and Piringer (1989)
(c) = cyclic group contribution parameters used
a. = activity
a.c. = activity coefficient

Table 61 . GCFEOS Estimated Aroma K(P/L): HDPE/75% Ethanol at 25C

Aroma	GCFEOS a. Polymer	GCFEOS a.c. Polymer	Exp w(i) Polymer	GCFEOS a. Ethanol	GCFEOS a.c. Ethanol	Exp w(i) Ethanol
d-Limonene	0.00273	18.06	1.52E-04	0.00517	60.12	8.61E-05
Diphenylmethane	0.00306	63.10	4.86E-05	0.00163	13.78	1.19E-04
Linalylacetate	0.00032	13.68	2.39E-05	0.00118	10.01	1.19E-04
Camphor	0.00098	156.13	6.28E-06	0.00216	22.30	9.72E-05
Diphenyloxide	0.00074	10.23	7.25E-05	0.00106	8.39	1.27E-04
Isoamylacetate	0.00005	6.87	7.39E-06	0.00052	5.62	9.40E-05
gamma-Undelactone	0.00004	12.04	3.89E-06	0.00188	15.55	1.21E-04
Eugenol	0.00032	78.84	4.14E-06	0.00001	0.16	1.01E-04
Citronellol	0.00003	10.61	3.72E-06	0.00031	3.04	1.04E-04
Dimethylbenzyl-carbinol			3.72E-06	0.00019	2.31	8.36E-05
Menthol	0.00076	57.57	1.34E-05	0.00034	5.38	6.37E-05
Phenylethylalcohol	0.00012	60.78	2.02E-06	0.00003	0.33	1.21E-04
cis-3-Hexenol	0.00003	16.59	2.34E-06	0.00006	0.72	8.61E-05
d-Limonene (c)			1.52E-04	0.00046	5.40	8.61E-05
Camphor (c)	0.00035	56.58	6.28E-06	0.00128	13.26	9.72E-05
gamma-Undelactone (c)	0.00003	8.28	3.89E-06	0.00122	10.10	1.21E-04
Menthol (c)	0.00043	32.44	1.34E-05	0.00139	21.88	6.37E-05

Table 61 (cont.)

Aroma	GCFEOS K(P/L)	Exp. K(P/L) (1)	calc./exp. ratio
d-Limonene	3.7323	1.8000	2.07
Diphenylmethane	0.2448	0.3387	0.72
Linalylacetate	0.8202	0.1471	5.58
Camphor	0.1601	0.0581	2.76
Diphenyloxide	0.9195	0.5258	1.75
Isoamylacetate	0.9174	0.1413	6.49
gamma-Undelactone	1.4479	0.0316	45.82
Eugenol	0.0023	0.0241	0.09
Citronellol	0.3215		
Dimethylbenzyl-carbinol		0.0228	
Menthol	0.1047	0.0557	1.88
Phenylethylalcohol	0.0060	0.0160	0.38
cis-3-Hexenol	0.0487	0.0087	5.60
d-Limonene (c)		1.8	
Camphor (c)	0.2627	0.0581	4.52
gamma-Undelactone (c)	1.3681	0.0316	43.29
Menthol (c)	0.7560	0.0557	13.57
		ave:	6.75
		std dev	13.18
		c.v.%	195.07

HDPE: density = .956, thickness = 100 micrometer
blank spaces indicate either a missing value or model's inability to estimate a activity coefficient
75% Ethanol/Water (w/w) density = .85266
Exp =experimental value this work, CL = 70-105 ppm (w/v)
(c) = cyclic group contribution parameters used
w(i) = weight fraction
Exp =experimental value this work, CL = 70-105 ppm (w/v) average of HDPE and LDPE at 10,25 and 40C
calc.= GCFEOS calculated values

Table 62. GCFEOS Estimated Aroma K(P/L): HDPE/50% Ethanol at 25C

Aroma	GCFEOS a. Polymer	GCFEOS a.c. Polymer	Exp w(i) Polymer	GCFEOS a. Ethanol	GCFEOS a.c. Ethanol	Exp w(i) Ethanol
d-Limonene	0.04137	17.83	2.32E-03	0.05565	646.64	8.61E-05
Diphenylmethane	0.03235	62.87	5.15E-04	0.02192	184.82	1.19E-04
Linalylacetate	0.002248	13.67	1.64E-04	0.01161	97.88	1.19E-04
Camphor	0.006883	156.07	4.41E-05	0.03130	321.88	9.72E-05
Diphenyloxide	0.009575	10.20	9.39E-04	0.00403	31.86	1.27E-04
Isoamylacetate	0.000278	6.86	4.06E-05	0.00625	66.49	9.40E-05
gamma-Undelactone	0.000299	12.04	2.49E-05	0.08103	668.01	1.21E-04
Eugenol	0.001345	78.86	1.71E-05	0.00002	0.20	1.01E-04
Citronellol	0.000044	10.61	4.23E-06	0.00685	65.95	1.04E-04
Dimethylbenzyl-carbinol			4.23E-06	0.00238	28.49	8.36E-05
Menthol	0.001023	57.55	1.78E-05	0.01206	189.38	6.37E-05
Phenylethylalcohol	0.00039	60.75	6.44E-06	0.00017	1.39	1.21E-04
cis-3-Hexenol	0.000034	16.59	2.09E-06	0.00015	1.74	8.61E-05
d-Limonene (c)			2.32E-03	0.00781	90.70	8.61E-05
Camphor (c)	0.002492	56.51	4.41E-05	0.01826	187.78	9.72E-05
gamma-Undelactone (c)	0.000205	8.28	2.49E-05	0.05194	428.19	1.21E-04
Menthol (c)	0.000576	32.44	1.78E-05	0.08207	1288.8	6.37E-05

Table 62 (cont.)

Aroma	GCFEOS K(P/L)	Exp. K(P/L) (1)	calc./exp. ratio
d-Limonene	38.078	32.353	1.18
Diphenylmethane	3.086	3.865	0.80
Linalylacetate	7.519	1.317	5.71
Camphor	2.165	0.534	4.05
Diphenyloxide	3.280	6.445	0.51
Isoamylacetate	10.169	0.416	24.47
gamma-Undelactone	58.250	0.160	364.29
Eugenol	0.0027	0.137	0.019
Citronellol	6.525		
Dimethylbenzyl-carbinol		0.113	
Menthol	3.455	0.180	19.16
Phenylethylalcohol	0.024	0.121	0.20
cis-3-Hexenol	0.110	0.022	4.91
d-Limonene (c)		32.353	
Camphor (c)	3.489	0.534	6.53
gamma-Undelactone (c)	54.319	0.160	339.71
Menthol (c)	41.709	0.180	231.33
	Average:		38.66
	Stnd. Deviation:		103.27
	Coef. Variation		267.10

HDPE: density = .956, thickness = 100 micrometer
blank spaces indicate either a missing value or model's inability to estimate a activity coefficient
50% Ethanol/Water (w/w) density = .91063
Exp = experimental value this work, CL = 70-105 ppm (w/v) average of LDPE, HDPE and 10,25 and 40C
(c) = cyclic group contribution parameters used
w(i) = weight fraction
calc = GCFEOS estimated value
a. = activity
a.c. = activity coefficient

Tab

Aro

d-L

Dip

Lin

Cam

Dip

Isoa

gamm

Euge

Citr

Dime

Ment

Phen

cis-

d-Li

Camp

gamm

Ment

Table 63. GCFEOS Estimation Aroma K(P/L): HDPE/35% Ethanol at 25C

Aroma	GCFEOS a. Polymer	GCFEOS a.c. Polymer	Exp w(i) Polymer	GCFEOS a. Ethanol	GCFEOS a.c. Ethanol	Exp w(i) Ethanol
d-Limonene	0.2052	16.85	1.22E-02	0.3316	3853.1	8.61E-05
Diphenylmethane	0.1031	62.36	1.65E-03	0.1331	1122.3	1.19E-04
Linalylacetate	0.00414	13.66	3.03E-04	0.07545	636.1	1.19E-04
Camphor	0.01779	155.96	1.14E-04	0.1957	2012.5	9.72E-05
Diphenyloxide	0.03161	10.12	3.13E-03	0.01104	87.3	1.27E-04
Isoamylacetate	0.00050	6.86	7.41E-05	0.0436	463.9	9.40E-05
gamma-Undelactone	0.00049	12.04	4.11E-05	1.42	11707	1.21E-04
Eugenol	0.00090	78.86	1.15E-05	0.00002	0.296	1.01E-04
Citronellol	0.00054	10.61	5.12E-05	0.06196	596.3	1.04E-04
Dimethylbenzyl-carbinol			5.12E-05	0.0164	196.3	8.36E-05
Menthol	0.00261	57.50	4.54E-05	0.1486	2333.5	6.37E-05
Phenylethylalcohol	0.00015	60.73	2.53E-06	0.00053	4.42	1.21E-04
cis-3-Hexenol	0.00004	16.59	2.86E-06	0.00032	3.74	8.61E-05
d-Limonene (c)			1.22E-02	0.06742	783.4	8.61E-05
Camphor (c)	0.00645	56.54	1.14E-04	0.1105	1136.4	9.72E-05
gamma-Undelactone (c)	0.00033	8.27	4.11E-05	0.8912	7347.1	1.21E-04
Menthol (c)	0.00147	32.448	4.54E-05	0.9781	15360	6.37E-05

Table 63. (cont.)

Aroma	GCFEOS K(P/L)	Exp. K(P/L) (1)	calc./exp. ratio
d-Limonene	232.41	161.21	1.44
Diphenylmethane	18.29	8.99	2.03
Linalylacetate	47.32	3.14	15.05
Camphor	13.11	2.36	5.56
Diphenyloxide	8.77	27.64	0.32
Isoamylacetate	68.68	0.81	84.50
gamma-Undelactone	988.41	0.39	2528.55
Eugenol	0.0038	0.11	0.035
Citronellol	57.13		
Dimethylbenzyl-carbinol		0.58	
Menthol	41.24	0.51	81.34
Phenylethylalcohol	0.074	0.16	0.46
cis-3-Hexenol	0.23	0.088	2.60
d-Limonene (c)		161.21	
Camphor (c)	20.42	2.36	8.66
gamma-Undelactone (c)	902.28	0.39	2308.22
Menthol (c)	481.02	0.51	948.76
	Average:		247.4
	Stnd. Deviation		722.0
	Coef. Variation		291.8

HDPE: density = .956, thickness = 100 micrometer
blank spaces indicate either a missing value or model's inability to estimate a activity coefficient
35% Ethanol/Water (w/w) density = .94076
Exp =experimental value this work, CL = 70-105 ppm (w/v) average of LDPE, HDPE and 10,25 and 40C measurements
(c) = cyclic group contribution parameters used
w(i) = weight fraction
calc = GCFEOS estimated value
a. = activity
a.c. = activity coefficient

Table 64. GCFEOS Estimated n-Alkane K(P/L): HDPE at 25C

HDPE/100% Ethanol: Comparison of Experimental with GCFEOS K(P/L) at 25C

n-Alkane	MW	GCFEOS (P/G) Act.Coeff. w(i)	EXP (P/G) w(i)	GCFEOS (L/G) activity	GCEOS (L/G) Act.Coeff. w(i)	EXP (L/G) w(i)
Octane	114.22	4.7125404	5.57E-05	0.0001213	6.2700299	1.93E-05
Nonane	128.26	4.4648345	8.78E-05	0.0001251	6.4664530	1.93E-05
Decane	142.276	4.2739207	4.93E-05	0.0001302	6.7300734	1.93E-05
Dodecane	170.41	3.9896176	7.90E-05	0.000144	7.4433991	1.93E-05
Tetradecan	198.4	3.7949589	1.52E-04	0.000162	8.3738240	1.93E-05
Hexadecane	226.45	3.6412830	3.07E-04	0.0001843	9.5265171	1.93E-05
Octadecane	254.54	3.5250926	9.51E-04	0.0002115	10.932492	1.93E-05
Eicosane	282.56	3.4260429	2.61E-03	0.000244	12.612426	1.93E-05
Docosane	310.61	3.3573441	1.92E-03	0.0002827	14.612839	1.93E-05

HDPE/1

HDPE: de
EXP = ex
Act. Coe
P = pol
L = Liq
G = Gas
w(i) =
MW = mol

Table 64. (cont.)

HDPE/100% Ethanol: Comparison of Experimental with GCFEOS K(P/L) at 25C

n-Alkane	GCFEOS K(P/L)	Exp. K(P/L)	Ratio calc/exp
Octane	1.62	1.38	1.17
Nonane	1.76	2.14	0.82
Decane	1.92	2.70	0.71
Dodecane	2.27	3.32	0.68
Tetradecan	2.69	5.99	0.45
Hexadecane	3.19	10.65	0.30
Octadecane	3.78	28.71	0.13
Eicosane	4.48	72.37	0.06
Docosane	5.30	48.49	0.11
		average:	0.49
		std. dev.:	0.36
		% std dev:	72.64

HDPE: density = .956, thickness = 100 micometer
EXP = experimental value
Act. Coeff. = molecular fraction activity coefficient
P = polymer
L = Liquid
G = Gas
w(i) = weight fraction
MW = molecular weight

Table 64. (cont.)

HDPE/75% Ethanol: Comparison of Experimental with GCFEOS K(P/L) at 25C

n-Alkane	MW	GCFEOS (P/G) Act.Coeff. w(i)	EXP (P/G) w(i)	GCFEOS (L/G) activity w(i)	GCFEOS (L/G) Act.Coeff. w(i)	w(i) Fraction (P/L)
Octane	114.22	4.7110928	5.35E-05	0.002361	122.03883	1.93E-05
Nonane	128.26	4.4656907	8.39E-05	0.003439	177.76008	1.93E-05
Decane	142.276	4.2729790	1.99E-04	0.005055	261.29027	1.93E-05
Dodecane	170.41	3.9878182	3.76E-04	0.01116	576.85448	1.93E-05
Tetradecane	198.4	3.7865855	6.15E-04	0.02499	1291.7198	1.93E-05
Hexadecane	226.45	3.6332613	1.72E-03	0.05671	2931.3098	1.93E-05
Octadecane	254.54	3.4990824	5.67E-03	0.1297	6704.1243	1.93E-05
Eicosane	282.56	3.3330131	2.08E-02	0.2984	15424.137	1.93E-05
Docosane	310.61	2.9549402	9.04E-02	0.6893	35629.551	1.93E-05

Appendix F

UNIFAC Program Listing and Data Input.

GCFEOS Data Input and Output

Table 64. (cont.)

HDPE/75% Ethanol: Comparison of Experimental with GCFEOS K(P/L) at 25C

n-Alkane	GCFEOS K(P/L)	Exp. K(P/L)	Ratio calc/exp
Octane	29.04	2.558	11.35
Nonane	44.63	4.01	11.13
Decane	68.56		
Dodecane	162.19	9.813	16.53
Tetradecan	382.47	21.865	17.49
Hexadecane	904.58	53.711	16.84
Octadecane	2148.18	154.72	13.88
Eicosane	5188.55	529.3	9.80
Docosane	13518.97	2259.5	5.98
		average:	12.88
		std. dev.:	3.77
		% std dev:	29.28

HDPE: density = .956, thickness = 100 micometer
EXP = experimental value
Act. Coeff. = molecular fraction activity coefficient
P = polymer
L = Liquid
G = Gas
w(i) = weight fraction
MW = molecular weight

Table 64. (cont.)

HDPE/50% Ethanol: Comparison of Experimental with GCFEOS K(P/L) at 25C

n-Alkane	MW	GCFEOS (P/G) Act.Coeff. w(i)	EXP (P/G) w(i)	GCFEOS (L/G) activity w(i)	GCFEOS (L/G) Act.Coeff. w(i)	w(i) Fraction (P/L)
Octane	114.22	4.6989720	1.29E-03	0.05561	7147.5392	7.78E-06
Nonane	128.26	4.4323616	3.51E-03	0.124	15937.688	7.78E-06
Decane	142.276	4.2458239	3.37E-03	0.2818	36219.683	7.78E-06
Dodecane	170.41	3.8776850	1.52E-02	1.485	190866.67	7.78E-06
Tetradecane	198.4	3.4942577	4.70E-02	7.943	1020911.7	7.78E-06
Hexadecane	226.45	2.7966557	1.67E-01	43.04	5531920.3	7.78E-06
Octadecane	254.54	2.1536019	3.39E-01	235.1	30217343.	7.78E-06
Eicosane	282.56	1.1455788	8.67E-01	1291	165931904	7.78E-06
Docosane	310.61	1.4178080	6.70E-01	7124	915645926	7.78E-06

Table 64. (cont.)

HDPE/50% Ethanol: Comparison of Experimental with GCFEOS K(P/L) at 25C

n-Alkane	GCFEOS K(P/L)	Exp. K(P/L)	Ratio calc/exp
Octane	1596.88	82.37	19.39
Nonane	3774.93	232.82	16.21
Decane	8955.73	414.94	
Dodecane	51674.45	1453.8	35.54
Tetradecan	3.07E+05	4359.2	70.36
Hexadecane	2.08E+06	13576	152.96
Octadecane	1.47E+07	34613	425.57
Eicosane	1.52E+08	403110	377.22
Docosane	6.78E+08	114920	5899.74
		average:	874.63
		std. dev.:	1905.28
		% std dev:	217.84

HDPE: density = .956, thickness = 100 micometer
EXP = experimental value
Act. Coeff. = molecular fraction activity coefficient
P = polymer
L = Liquid
G = Gas
w(i) = weight fraction
MW = molecular weight

Input for UNIFACWB.BAS Program

This is a BASIC program for binary polymer solutions. It contains the Oishi and Prausnitz (1978) free volume correction and calculates weight fraction activity coefficients. The program calculates weight fractions from the initial liquid phase concentration and the experimental polymer/liquid partition coefficient. The program was originally written to compare UNIFAC estimations with experimental values so polymer/liquid partition coefficients may need to be estimated if experimental data is not available.

Sequential file format with individual data separated by commas. First column is always the line number.

First line:
1,number of calculations to be made

Second line:
2,temperature in °C

Lines 3-7: input for one binary mixture.
3,number of components (always 2),liquid phase concentration,$K_{P/L}$

4, solute name,solute density,solute molecular weight,number of different group-contribution groups for solute

5,group number,frequency group appears in
        molecule,0,0,0,0,0,0,0,0,0,0,0,0
        note: up to eight different groups may be entered,
              where no groups are needed a zero is used.

6,polymer name,polymer density,polymer monomer molecular weight, number of different group-contributions for solute.

7,group number,frequency of group,0,0,0,0,0,0,0,0,0,0,0,0

The sequence from 3-7 are repeated for subsequent binary solutions.

The End-of-File is indicated by the last two lines:
eof
0,0,0,0,0,0,0,0,0,0,0,0,0,0,0

Example of Input:

UNIFAC and GCFEOS Group Contribution Group Numbers

Group	UNIFAC	GCFEOS	Group	UNIFAC	GCFEOS	Group	UNIFAC	GCFEOS
CH3	1	1	CHNH	34	-	Cl(C=C)	70	-
CH2	2	2	CH3N	35	-	ACF	71	-
CH	3	3	CH2N	36	-	DMF-1	72	-
C	4	4	ACHNH2	37	-	DMF-2	73	-
c-CH2	-	5	C5H5N	38	-	CF3	74	-
CH2=CH	5	15	C5H4N	39	-	CF2	75	-
CH=CH	6	16	C5H3N	40	-	CF	76	-
CH2=C	7	17	CH3CN	41	-	SiH3	78	-
C=C	9	-	CH2CN	42	-	SiH2	79	-
ACH	10	6	COOH	43	-	SiH	80	-
AC	11	7	HCOOH	44	-	Si	81	-
ACCH3	12	-	CH2CL	45	19	SiH2O	82	-
ACCH2	13	-	CHCL	46	20	SiHO	83	-
ACCH	14	-	CCL	47	-	SiO	84	-
OH	15	13	CH2CL2	48	21	NMP	85	-
CH3OH	16	14	CHCL2	49	22			
H2O	17	26	CCL2	50	-			
ACOH	18	-	CHCL3	51	23			
CH3CO	19	-	CCL3	52	24			
CH2CO	20	-	CCL4	53	25			
CHO	21	11	ACCL	54	-			
CH3COO	22	-	CH3NO2	55	-			
CH2COO	23	-	CH2NO2	56	-			
HCOO	24	-	CHNO2	57	-			
C=O	-	8	ACNO2	58	-			
COO	77	9	CS2	59	-			
CH3O	25	-	CH3SH	60	-			
CH2O	26	10	CH2SH	61	-			
CH-O	27	-	furfural	62	-			
CH2OCH2	-	12	(CH2OH)2	63	-			
FCH2O	28	-	I	64	-			
CH3NH2	29	-	Br	65	-			
CH2NH2	30	-	CH~C	66	-			
CHNH2	31	-	C~C	67	-			
CH3NH	32	-	Me2SO	68	-			
CH2NH	33	-	ACRY	69	-			

- group is not available
c = cyclic
A = Aromatic group
For description of groups see Sandler (1989) for UNIFAC and
Chen et al. (1990) for GCFEOS.

```
10 '****************************************************************
20 '*                      UNIFACWB.BAS                            *
30 '*IMPORTANT: PROGRAM CAN BE USED ONLY FOR BINARY POLYMER SOLNS.*
40 '*     VAPOR-LIQUID ACTIVITY COEFFICIENTS ESTIMATED BY THE      *
50 '*              UNIFAC GROUP CONTRIBUTION METHOD                *
60 '*                      Fith Revision                           *
70 '*                                                              *
80 '*                                                              *
90 '*               PROGRAM  REVISED 19 April 1992                 *
100 '*                PROGRAMMED BY A.L. BANER                     *
110 '*      PROGRAM USES THE OISHI & PRAUSNITZ POLYMER FREE        *
120 '*                 VOLUME CORRECTION FACTOR                    *
130 '*    PROGRAM USES WEIGHT FRACTIONS OF POLYMER AND SOLUTE      *
140 '*     USES MONOMER OF POLYMER AS DESCRIPTION OF POLYMER       *
150 '*                                                             *
160 '* Uses calculation algorithms from Sandler (1989) UNIFAC      *
170 '**************************************************************
180 CLS
190 PRINT TAB(12);"************************************************************"
200 PRINT TAB(12);"*                       UNIFACWB.BAS                      *"
210 PRINT TAB(12);"*IMPORTANT: THIS PROGRAM IS FOR BINARY POLYMER SOLNS. ONLY*"
220 PRINT TAB(12);"*           Programmed by L. BANER 19 April 1992          *"
230 PRINT TAB(12);"* CALCULATES WEIGHT FRACTION ACTIVITY COEFFICIENTS USING  *"
240 PRINT TAB(12);"*         THE UNIFAC GROUP CONTRIBUTION METHOD            *"
250 PRINT TAB(12);"*      With the Oishi and Prausnitz Free Volume Correction *"
260 PRINT TAB(12);"*            for solutions containing polymers            *"
270 PRINT TAB(12);"*                                                          *"
280 PRINT TAB(12);"*This program requires a user supplied data file and      *"
290 PRINT TAB(12);"*UNIFAC group contribution parameters in a separate file  *"
300 PRINT TAB(12);"*The program calculates weight and mole fraction from     *"
310 PRINT TAB(12);"*user supplied liquid concentrations and approx.  K(P/L)  *"
320 PRINT TAB(12);"************************************************************"
330 PRINT: PRINT : PRINT "Loading data....."
340 DEFINT I-K,M-N
350 OPTION BASE 1
360 DIM IARM(100),ANM(100),ANMX(100),LGC(10),LNG(10,10),LNGM(100),ILS(10),G(10)
370 DIM A(44,44),R(85),Q(85),N1(85),N2(85),IAR(10,10),AN(10,10),P(21),XX(21)
380 DIM N2$(85),N1$(85),C$(10),X(10),R1(10),Q1(10),TH(10),PH(10),L(10),L2(10)
390 DIM CTH(10,10),CTHM(100),D2(20),LG(10),Y(100),GAM(2,21),YY(2,21),PVAP(2)
400 DIM H$(17),AA(2),BB(2),CC(2),AMS1(100),AMS2(100),UMW(85),REDVOL(100)
410 DIM ACTIVEFV(10), COEFFFV(10), LNFV(10),WMOLAR(10),DEN(10),WM(10),COEFF(10)
420 DIM XMOLAR(10), W(10), WCOEFF(10), FRACT(10)
430 OPEN "I",#1,"c:\baSICA\UFNRQM.DTA"
440 FOR I=1 TO 85
450 INPUT #1,N1$(I),N1(I),N2$(I),N2(I),R(I),Q(I),UMW(I)
460 NEXT I
470 CLOSE #1
480 OPEN "I",#1,"C:\basica\UNFA44.DTA"
490 FOR I=1 TO 44
500 FOR JJ=1 TO 11
510 J=1+4*(JJ-1)
520 INPUT #1, A(I,J), A(I,J+1), A(I,J+2), A(I,J+3)
530 NEXT JJ
540 NEXT I
550 CLOSE #1
560 PRINT "UNIFAC Parameters are Loaded"
570 '----------------------------------------------------------------------
580 'Subrountines to call DATA Files
590 'First load the number of calculations in the file: NOCALC
600 'Then load temperature: TC in degrees C
610 '----------------------------------------------------------------------
620 NCALC = 1
630 INPUT "Enter Data File to be used: FILE$: "; FILE$
640 INPUT "Result File to be used: 'NAME'.RES: "; RESULT$
```

```
650 OPEN "I",3,FILE$
660 OPEN "O",2,RESULT$
670    INPUT #3,N$,NOCALC
680    INPUT #3,N$,TC
690 ' Load Parameters from Data File and then calculate each result
700 '   N$ = file line #, IMX = # of components in this mixture, CL = concentrati
on (g/ml) of liquid phase, EXPK = estimated polymer/liquid partition coefficient
710    INPUT #3,N$,IMX,CL,EXPK
720    IF N$ = "eof" THEN GOTO 920
730 ' C$ = name of compound, DEN = density, WMOLAR = molecular weight, ILS = num
ber of different UNIFAC group contribution groups
740    INPUT #3,N$,C$(1),DEN(1),WMOLAR(1),ILS(1)
750 ' IAR(I,J) = group contribution group number, AN(I,J) = # of groups needed
760    INPUT #3,N$,IAR(1,1),AN(1,1),IAR(1,2),AN(1,2),IAR(1,3),AN(1,3),IAR(1,4),A
N(1,4),IAR(1,5),AN(1,5),IAR(1,6),AN(1,6),IAR(1,7),AN(1,7),IAR(1,8),AN(1,8)
770    INPUT #3,N$,C$(2),DEN(2),WMOLAR(2),ILS(2)
780    INPUT #3,N$,IAR(2,1),AN(2,1),IAR(2,2),AN(2,2),IAR(2,3),AN(2,3),IAR(2,4),A
N(2,4),IAR(2,5),AN(2,5),IAR(2,6),AN(2,6),IAR(2,7),AN(2,7),IAR(2,8),AN(2,8)
790 ITEMP = 0: IAPFLG = 0: ICONC = 0: IRTRN = 0: ILST=0: ILST1=0
800 '---------------Call temperature subroutine---------------
810 GOSUB 1460
820 '--------Call groups present subroutine -------------------
830 GOSUB 960
840 '-----------Begin Calculations------------------------
850 '------Subroutine calculating mole weight and weight fraction---
860 GOSUB 3400
870 '------Subroutine to normalize weight fraction------------------
880 GOSUB 1240
890 '---Calculate the coefficients !-------------------------------
900 GOSUB 1530
910 GOTO 690
920 CLOSE 2
930 CLOSE 3
940 END
950 CLS
960 CLS : PRINT : PRINT TAB(20);"UNIFAC ESTIMATION OF ACTIVITY COEFFICIENTS"
970 PRINT TAB(20);"==========================================" : PRINT
980 PRINT TAB(34);"COMPONENT DATA"
990 PRINT TAB(34);"--------------"
1000 PRINT TAB(48);"Molecular Subgroups"
1010 PRINT TAB(42);"--------------------------------"
1020 PRINT TAB(9);"Component No.       Name         Number   Description   Frequ
ency"
1030 PRINT TAB(9);"-------------   ------------     ------   -----------   -----
----"
1040 L1$="             ##         \          \       ##      \      \        ###
"
1050 L2$="                                           ##      \      \        ###
"
1060 FOR I=1 TO IMX : JMX = ILS(I)
1070 PRINT USING L1$; I,C$(I),IAR(I,1),N2$(IAR(I,1)),AN(I,1)
1080 IF JMX = 1 THEN 1120
1090 FOR J=2 TO JMX
1100 PRINT USING L2$; IAR(I,J),N2$(IAR(I,J)),AN(I,J)
1110 NEXT J
1120 PRINT
1130 X(I)=1/IMX
1140 XMOLAR(I) = 1
1150 NEXT I
1160 PRINT: PRINT "Press any key to continue."
1170 IF INKEY$="" GOTO 1170
1180 PRINT: PRINT "Checking for availability of interaction parameters."
1190 PRINT "This may take several seconds if many groups are present."
1200 IRTRN = 2
```

```
1210 GOSUB 2920
1220 GOTO 1580
1230 '--------------Normalize weight fractions------------------------
1240 ICONC = 1
1250 SUMX=0
1260 FOR I=1 TO IMX
1270 X(I) = W(I)
1280 IF X(I)>1 THEN PRINT "!!! INPUT ERROR !!!" : GOTO 1270
1290 IF X(I)<0 THEN PRINT "!!! INPUT ERROR !!!" : GOTO 1270
1300 IF X(I)=0 THEN X(I)=.0000001
1310 SUMX=SUMX+X(I) : NEXT I
1320 IF SUMX<.999999 THEN GOTO 1350
1330 IF SUMX>1.000001 THEN GOTO 1350
1340 GOTO 1360
1350 PRINT "WEIGHT FRACTIONS DO NOT SUM TO 1, BEING NORMALIZED"
1360 FOR I=1 TO IMX: X(I)=X(I)/SUMX: NEXT I
1370 PRINT : PRINT : PRINT TAB(30);"COMPONENT CONCENTRATIONS" : PRINT TAB(30);"-
-----------------------"
1380 PRINT TAB(22);"No         Name            WEIGHT Fraction"
1390 PRINT TAB(22);"--     ------------        -------------"
1400 L1$="                     ##     \          \           #.#####"
1410 FOR I=1 TO IMX
1420 PRINT USING L1$ ; I,C$(I),X(I)
1430 NEXT I
1440 GOSUB 2920
1450 RETURN
1460 'TEMP> -------------------TEMPERATURE ENTRY --------------------
1470 FOR IQ = 1 TO 10: NNSE$=INKEY$: NEXT IQ
1480 ITEMP = 1
1490 ILST = 0: ILST1 = 0: IPVAP = 0
1500 PRINT : PRINT "Temperature = ";TC;" deg C"
1510 TK=TC + 273.15
1520 RETURN
1530 'COEFF>
1540  FOR IQ = 1 TO 10: NNSE$=INKEY$: NEXT IQ
1550 ' UNIFAC CALCULATION -------------------------------------------
1560 ' COMBINATORIAL
1570 IRTRN = 0
1580 R2 = 0: Q2 = 0
1590 FOR I=1 TO IMX
1600 R1(I)=0 : Q1(I)=0
1610 FOR J=1 TO ILS(I)
1620 R1(I)=R1(I)+R(IAR(I,J))*AN(I,J)
1630 Q1(I)=Q1(I)+Q(IAR(I,J))*AN(I,J)
1640 NEXT J
1650 R2=R2+X(I)*R1(I)/WMOLAR(I)
1660 Q2=Q2+X(I)*Q1(I)/WMOLAR(I)
1670 NEXT I
1680 L1=0
1690 FOR I=1 TO IMX
1700 PH(I)=R1(I)*X(I)/(R2*WMOLAR(I))
1710 TH(I)=Q1(I)*X(I)/(Q2*WMOLAR(I))
1720 NEXT I
1730 FOR I=1 TO IMX
1740 LGC(I)=LOG(PH(I))+1-PH(I)+5*Q1(I)*(LOG(TH(I)/PH(I))-1+(PH(I)/TH(I)))
1750 NEXT I
1760 ' RESIDUAL CALCULATION -----------------------------------------
1770 FOR I = 1 TO IMX
1780 SUMQ = 0
1790 FOR J = 1 TO ILS(I)
1800 D2(J) = AN(I,J)*Q(IAR(I,J))
1810 SUMQ = SUMQ + D2(J)
1820 NEXT J
1830 FOR J = 1 TO ILS(I)
```

```
1840 CTH(I,J) = D2(J)/SUMQ
1850 NEXT J
1860 NEXT I
1870 SUMQ = 0
1880 FOR K=1 TO KMAX
1890 D2(K) = ANMX(K)*Q(IARM(K))
1900 SUMQ = SUMQ + D2(K)
1910 NEXT K
1920 FOR K = 1 TO KMAX
1930 CTHM(K) = D2(K)/SUMQ
1940 NEXT K
1950 'GAMMA RESIDUAL FOR EACH GROUP IN EACH MOLECULE ----------------
1960 IAFLG = 0
1970 FOR I = 1 TO IMX
1980 FOR K = 1 TO ILS(I)
1990 KK = N1(IAR(I,K))
2000 SUM1 = 0: SUM2 = 0
2010 FOR M = 1 TO ILS(I)
2020 MM=N1(IAR(I,M))
2030 SUM3 = 0
2040 FOR N = 1 TO ILS(I)
2050 NN=N1(IAR(I,N))
2060 SUM3 = SUM3 + CTH(I,N)*EXP(-A(NN,MM)/TK)
2070 NEXT N
2080 SUM2 = SUM2 + CTH(I,M)*(EXP(-A(KK,MM)/TK))/SUM3
2090 SUM1 = SUM1 + CTH(I,M)*EXP(-A(MM,KK)/TK)
2100 NEXT M
2110 LNG(I,K) = Q(IAR(I,K))*(1-LOG(SUM1)-SUM2)
2120 NEXT K
2130 NEXT I
2140 'GAMMA RESIDUAL FOR EACH GROUP IN MIXTURE ----------------------
2150 FOR K = 1 TO KMAX
2160 SUM1 = 0: SUM2 = 0
2170 KK = N1(IARM(K))
2180 FOR M = 1 TO KMAX
2190 MM = N1(IARM(M))
2200 SUM3 = 0
2210 FOR N = 1 TO KMAX
2220 NN = N1(IARM(N))
2230 SUM3 = SUM3 + CTHM(N)*EXP(-A(NN,MM)/TK)
2240 NEXT N
2250 SUM2 = SUM2 + CTHM(M)*(EXP(-A(KK,MM)/TK))/SUM3
2260 IF MM=KK GOTO 2350
2270 IF A(MM,KK) <> 0 GOTO 2350
2280 IF MM=7 AND KK=31 GOTO 2350
2290 IF MM=31 AND KK=7 GOTO 2350
2300 IF MM=22 AND KK=23 GOTO 2350
2310 IF MM=23 AND KK=22 GOTO 2350
2320 IF IAPFLG = 1 GOTO 2350
2330 IAFLG = IAFLG + 1
2340 AMS1(IAFLG) = N2(IARM(M)): AMS2(IAFLG) = N2(IARM(K))
2350 SUM1 = SUM1 + CTHM(M)*EXP(-A(MM,KK)/TK)
2360 NEXT M
2370 LNGM(K) = Q(IARM(K))*(1-LOG(SUM1)-SUM2)
2380 NEXT K
2390 'GAMMA RESIDUAL FOR EACH MOLECULE
2400 GOSUB 3110
2410 FOR I = 1 TO IMX
2420 SUM = 0
2430 FOR J = 1 TO ILS(I)
2440 FOR K = 1 TO KMAX
2450 IF IARM(K) = IAR(I,J) THEN 2470
2460 NEXT K
2470 SUM = SUM + AN(I,J) * (LNGM(K) - LNG(I,J))
```

```
2480 ' SUM = LN RESIDUAL ACTIVITY COEFF.
2490 NEXT J
2500 LG(I)=SUM + LGC(I) + LNFV(I)
2510 ' THE ACTIVITY IS THEN = G(I)
2520 G(I) = EXP(LG(I))
2530 NEXT I
2540 FOR I = 1 TO IMX
2550   WCOEFF(I) = G(I) / X(I)
2560   COEFF(I) = G(I)/XMOLAR(I)
2570    NEXT I
2580 IF IAPFLG > 0 THEN GOTO 2730
2590 IAPFLG = 1
2600 IF IAFLG > 0 THEN GOTO 2630
2610 PRINT: PRINT "All interaction parameters are available."
2620 GOTO 2730
2630 CLS: PRINT "Interaction parameters unavailable (and set to zero) for the"
2640 PRINT "following pairs of groups:": PRINT
2650 FOR IAFLAG = 1 TO IAFLG
2660 IF AMS1(IAFLAG) < AMS2(IAFLAG) GOTO 2680
2670 PRINT "     ",N2$(AMS1(IAFLAG))," with ",N2$(AMS2(IAFLAG))
2680 NEXT IAFLAG
2690 PRINT: PRINT "Press any key to continue":
2700 FOR IQ = 1 TO 10: NNSE$ = INKEY$: NEXT IQ
2710 IF INKEY$="" THEN GOTO 2710
2720 CLS
2730 IF IRTRN = 2 THEN GOTO 840
2740 PRINT : PRINT : PRINT TAB(27);"COMPONENT ACTIVITY COEFFICIENTS"
2750 PRINT TAB(27);"---------------------------------"
2760 L1$="            & +###.## &"
2770 PRINT : PRINT USING L1$ ; "Temperature:",TC,"Deg C" : PRINT TAB(13);"------
--------------------"
2780 PRINT TAB(5);"No   Name    WEIGHT Fraction       Activity    X(I)
Wt. COEFF"
2790 PRINT TAB(5);"--------------------------------------------------------------
-------"
2800 L1$="  ##  \          \ #.######## #######.####### #.####### #######.######
#"
2810 FOR I=1 TO IMX
2820 PRINT USING L1$ ; I,C$(I),X(I),G(I),XMOLAR(I),WCOEFF(I)
2830 NEXT I
2840 FOR I=1 TO IMX
2850 WRITE #2,NCALC,I,C$(I),X(I),G(I),WCOEFF(I),XMOLAR(I),COEFF(I)
2860 NEXT I
2870 NCALC = NCALC + 1
2880 INPUT "Hit Return to Continue";R
2890 RETURN
2900 '----------------------------------------------------------------------
2910 'COMPUTATION OF GROUP MOLE FRACTIONS>
2920 FOR J = 1 TO ILS(1)
2930 IARM(J) = IAR(1,J): ANM(J) = AN(1,J): ANMX(J) = X(1)*AN(1,J)
2940 NEXT J
2950 KMAX = ILS(1)
2960 FOR I = 2 TO IMX
2970 FOR J = 1 TO ILS(I)
2980 FOR K = 1 TO KMAX
2990 IF IARM(K) = IAR(I,J) THEN 3010
3000 GOTO 3030
3010 ANM(K) = ANM(K) + AN(I,J)
3020 ANMX(K) = ANMX(K) + X(I)*AN(I,J): GOTO 3080
3030 NEXT K
3040 KMAX=KMAX + 1
3050 IARM(KMAX) = IAR(I,J)
3060 ANM(KMAX) = AN(I,J)
3070 ANMX(KMAX) = X(I)*AN(I,J)
```

```
3080 NEXT J
3090 NEXT I
3100 RETURN
3110 '-------------------SUBROUTINE ------------------------------
3120 ' OISHI AND PRAUSNITZ POLYMER FREE VOLUME CORRECTION
3130 ' FREE VOLUME CORRECTION IN TERMS OF MOLAR VOLUMES
3140 ' POLYMER MOLAR VOLUME IS TAKEN AS THAT OF THE MONOMER UNIT
3150 ' MOLAR VOLUMES OF COMPONENTS MUST BE ENTERED
3160 ' -----------------------------------------------------------
3170 REDMIX = 0
3180 C = 1.1
3190 FOR I = 1 TO IMX
3200 '  IMX = NUMBER OF COMPONENTS IN MIXTURE
3210 '  COMPONENT 1 IS ALWAYS THE SOLUTE
3220 '  COMPONENT 2 IS ALWAYS THE POLYMER
3230    B = 1.28
3240 '  B AND C COME FROM OISHI AND PRAUSNITZ (1987)
3250   REDVOL(I) = WMOLAR(I)/ (15.17 * B * R1(I)*DEN(I))
3260    REDMIX = REDMIX + ((X(I)/DEN(I)) / (15.17 * B * R2))
3270 NEXT
3280 ' NOW CALCULATE FV ACTIVITY COEFFICIENT CONTRIBUTION
3290 FOR I = 1 TO IMX
3300 POW = 1/3
3310 STEP1 = LOG(((REDVOL(I)^(POW)) - 1 ) / ( (REDMIX^(POW)) - 1 ))
3320 STEP2 = 3 * C * STEP1
3330 STEP3 = ( REDVOL(I) / REDMIX ) - 1
3340 STEP4 = 1 - ((1 / REDVOL(I))^POW)
3350 STEP6 = C * STEP3 / STEP4
3360 ACTIVEFV(I) = EXP(STEP2 - STEP6)
3370 LNFV(I) = LOG(ACTIVEFV(I))
3380 NEXT
3390 RETURN
3400 '---------------------SUBROUTINE-------------------------------------
3410 '        CALCULATE WEIGHT FRACTION FROM EXPK AND CL
3420 '  CALCULATE MOLAR FRACTION FROM Kexp AND CL --FOR POLYMER SOLNS. ONLY
3430 ' -------------------------------------------------------------------
3440 CP = EXPK * CL
3450 BW = CP / DEN(2)
3460 W(1) = BW / (BW + 1)
3470 W(2) = 1 - W(1)
3480 BM1 = BW / WMOLAR(1)
3490 BM2 = DEN(2) / WMOLAR(2)
3500 XMOLAR(1) = BM1 / (BM1 + BM2)
3510 XMOLAR(2) = 1 - XMOLAR(1)
3520 RETURN
```

```
1,13
2,25
3,2,67.562e-6,2.145
4,d-Limonene,.8411,136.24,5
5,1,2,2,3,3,1,7,1,8,1,0,0,0,0,0,0
6,HDPE,.956,28.0514,1
7,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
8,2,93.128e-6,.4988
9,Diphenylmethane,1.0008,168.23,3
10,10,10,11,1,13,1,0,0,0,0,0,0,0,0,0
11,HDPE,.956,28.0514,1
12,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
13,2,94.692e-6,.2418
14,Linalylacetate,.895,196.29,5
15,1,3,2,2,4,1,5,1,22,1,0,0,0,0,0,0
16,HDPE,.956,28.0514,1
17,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
18,2,76.34e-6,.0787
19,Camphor,.9935,152.23,5
20,1,3,2,2,3,1,4,2,20,1,0,0,0,0,0,0
21,HDPE,.956,28.0514,1
22,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
23,2,99.34e-6,.6978
24,Diphenyloxide,1.0706,170.21,3
25,10,10,11,1,27,1,0,0,0,0,0,0,0,0,0
26,HDPE,.956,28.0514,1
27,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
28,2,73.788e-6,.09573
29,Isoamylacetate,.867,130.17,4
30,1,2,2,2,3,1,22,1,0,0,0,0,0,0,0,0
31,HDPE,.956,28.0514,1
32,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
33,2,95.252e-6,.03907
34,gamma-undelactone,.949,184.28,4
35,1,1,2,7,23,1,3,1,0,0,0,0,0,0,0,0
36,HDPE,.956,28.0514,1
37,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
38,2,86.088e-6,.04592
39,Eugenol,1.0664,164.2,6
40,5,1,10,3,11,1,13,1,18,1,25,1,0,0,0,0
41,HDPE,.956,28.0514,1
42,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
43,2,79.044e-6,.045
44,Citronellol,.855,156.27,5
45,1,3,2,4,3,1,8,1,15,1,0,0,0,0,0,0
46,HDPE,.956,28.0514,1
47,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
48,2,79.044e-6,.045
49,DBC,.9783,150.22,5
50,1,2,4,1,10,5,13,1,15,1,0,0,0,0,0,0
51,HDPE,.956,28.0514,1
52,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
53,2,81.58e-6,.1566
54,Menthol,.9,156.27,4
55,1,3,2,3,3,4,15,1,0,0,0,0,0,0,0,0
56,HDPE,.956,28.0514,1
57,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
58,2,65.594e-6,.0294
59,PEA,1.01502,122.17,4
60,2,1,10,5,13,1,15,1,0,0,0,0,0,0,0,0
61,HDPE,.956,28.0514,1
62,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
63,2,49.991e-6,.0447
64,cis-3-Hexenol,.8453,100.16,4
65,1,1,2,3,6,1,15,1,0,0,0,0,0,0,0,0
66,HDPE,.956,28.0514,1
67,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0
eof
69,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
```

Output for UNIFACWB.BAS

Use DOS command to print file to printer:

```
C> type 'filen.ame'>prn
```

Output for each line referring to example printed below:

mixture number, substance number, name of substance, weight fraction, activity, weight fraction activity coefficient, mole fraction, mole fraction activity coefficient.

Note that the polymer mole fraction activity coefficient is calculated based on the molecular weight of the polymer monomer unit.

Example of Output:

```
1,1,"d-Limonene",1.515675E-04,1.042706E-03,6.879483,3.264748E-05,31.93833
1,2,"HDPE",.9998484,1.000004,1.000156,.9999673,1.000037
2,1,"Diphenylmethane",4.858786E-05,5.361864E-04,11.0354,8.474974E-06,63.26703
2,2,"HDPE",.9999514,.9999992,1.000048,.9999916,1.000008
3,1,"Linalylacetate",2.394977E-05,5.677464E-04,23.70572,3.580211E-06,158.579
3,2,"HDPE",.9999761,.9999986,1.000023,.9999964,1.000002
4,1,"Camphor",6.284436E-06,5.170386E-05,8.227288,1.211337E-06,42.68332
4,2,"HDPE",.9999938,.9999993,1.000006,.9999988,1.000001
5,1,"Diphenyloxide",7.250463E-05,1.01564E-03,14.00794,1.249981E-05,81.25248
5,2,"HDPE",.9999275,1,1.000073,.9999875,1.000013
6,1,"Isoamylacetate",7.388779E-06,1.296232E-04,17.54325,1.665562E-06,77.8255
6,2,"HDPE",.9999926,1,1.000007,.9999983,1.000002
7,1,"gamma-undelactone",3.892763E-06,2.852403E-05,7.327452,6.198374E-07,46.01857
7,2,"HDPE",.9999961,.9999954,.9999992,.9999994,.9999959
8,1,"Eugenol",4.135089E-06,1.090739E-03,263.7765,7.389411E-07,1476.084
8,2,"HDPE",.9999959,1.000002,1.000006,.9999993,1.000002
9,1,"Citronellol",3.720677E-06,1.531983E-04,41.17486,6.986253E-07,219.2854
9,2,"HDPE",.9999963,1.000002,1.000006,.9999993,1.000003
10,1,"DBC",3.720677E-06,2.087912E-04,56.11645,7.267618E-07,287.2897
10,2,"HDPE",.9999963,1.000004,1.000007,.9999993,1.000004
11,1,"Menthol",1.336324E-05,4.365413E-04,32.66732,2.509213E-06,173.9754
11,2,"HDPE",.9999866,1.000004,1.000018,.9999975,1.000007
12,1,"PEA",2.017217E-06,1.45041E-04,71.90154,4.844908E-07,299.3681
12,2,"HDPE",.999998,1.000004,1.000006,.9999995,1.000004
13,1,"cis-3-Hexenol",2.33744E-06,1.495415E-04,63.97661,6.84768E-07,218.3827
13,2,"HDPE",.9999977,1.000004,1.000006,.9999993,1.000004
```

Input for UNIFACBX.BAS

This is a BASIC program is for solutions not containing polymers. The program requires only the mole fractions and group contribution parameter numbers of the mixture's components.

Sequential file format with individual data separated by commas. First column is always the line number.

First line:
1,number of calculations to be made

Second line:
2,temperature in °C

Lines 3: input for a mixture (minimum of two substances).
3,number of components (2 up to 10)

repeat the inputs in line 4 and 5 for each component of the mixture.

4,solute name,mole fraction, number of different group-contribution groups for solute

```
5,group number,frequency group appears in
        molecule,0,0,0,0,0,0,0,0,0,0,0,0
        note: up to eight different groups may be entered,
              where no groups are needed a zero is used.
```

For each mixture start with the number of components on a separate line followed by the contents of lines 4 and 5 on subsequent lines.

The End-of-File is indicated by the last two lines:

```
eof
0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
```

Example of Input:

```
1,
2,25
3,3
4,d-Limonene,1.6446e-5,5
5,1,2,2,3,3,1,7,1,8,1,0,0,0,0,0,0
6,ETOH,.539889,3
7,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
8,H2O,.460094,1
9,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
10,3
11,Diphenylmethane,1.6446e-5,3
10,10,10,11,1,13,1,0,0,0,0,0,0,0,0,0,0
13,ETOH,.539889,3
14,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
15,H2O,.460094,1
16,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
17,3
18,Linalylacetate,1.6446e-5,5
19,1,3,2,2,4,1,5,1,22,1,0,0,0,0,0,0
20,ETOH,.539889,3
22,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
23,H2O,.460094,1
24,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
25,3
25,Camphor,1.6446e-5,5
26,1,3,2,2,3,1,4,2,20,1,0,0,0,0,0,0
27,ETOH,.539889,3
28,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
29,H2O,.460094,1
30,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
31,3
32,Diphenyloxide,1.6446e-5,3
33,10,10,11,1,27,1,0,0,0,0,0,0,0,0,0,0
34,ETOH,.539889,3
35,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
36,H2O,.460094,1
37,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
38,3
39,Isoamylacetate,1.6446e-5,4
40,1,2,2,2,3,1,22,1,0,0,0,0,0,0,0,0
41,ETOH,.539889,3
42,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
43,H2O,.460094,1
44,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
45,3
46,gamma-undelactone,1.6446e-5,4
47,1,1,2,7,23,1,3,1,0,0,0,0,0,0,0,0
48,ETOH,.539889,3
49,1,1,2,1,15,1,0,0,0,0,0,0,0,0,0,0
50,H2O,.460094,1
51,17,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0
eof
  ,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
```

```
10 '***************************************************************
20 '*                      UNIFACBX.BAS                           *
30 '*                                                             *
40 '*     VAPOR-LIQUID ACTIVITY COEFFICIENTS ESTIMATED BY THE     *
50 '*              UNIFAC GROUP CONTRIBUTION METHOD               *
60 '*                  UNIFAC  Fifth Revision                     *
70 '*                                                             *
80 '*                                                             *
90 '*            PROGRAM LAST REVISED 19 April 1992               *
100 '*               PROGRAMMED BY A.L. BANER                     *
110 '*                                                            *
120 '*                                                            *
130 '*   Requires user supplied mole fractions, files containing  *
140 '*       UNIFAC parameters and data and result files          *
150 '*   Uses algorithims from Sandler (1989) UNIFAC interactive  *
160 '*                  Basic program                             *
170 '**************************************************************
180 CLS
190 PRINT TAB(12);"***********************************************************"
200 PRINT TAB(12);"*                     UNIFACBX.BAS                        *"
210 PRINT TAB(12);"*                                                         *"
220 PRINT TAB(12);"*      Programmed by L. BANER 9 APRIL 1992                *"
230 PRINT TAB(12);"*  VAPOR-LIQUID ACTIVITY COEFFICIENTS ESTIMATED BY THE    *"
240 PRINT TAB(12);"*       FROM UNIFAC GROUP CONTRIBUTION METHOD             *"
250 PRINT TAB(12);"*            Revision 5 UNIFAC Parameters                 *"
260 PRINT TAB(12);"*                                                         *"
270 PRINT TAB(12);"*  Requires user supplied mole fractions for components   *"
280 PRINT TAB(12);"*    files containing UNIFAC parameters and data and      *"
290 PRINT TAB(12);"*                   result files.                         *"
300 PRINT TAB(12);"*                                                         *"
310 PRINT TAB(12);"*                                                         *"
320 PRINT TAB(12);"***********************************************************"
330 PRINT: PRINT : PRINT "Loading data....."
340 DEFINT I-K,M-N
350 OPTION BASE 1
360 DIM IARM(100),ANM(100),ANMX(100),LGC(10),LNG(10,10),LNGM(100),ILS(10),G(10)
370 DIM A(44,44),R(85),Q(85),N1(85),N2(85),IAR(10,10),AN(10,10),P(21),XX(21)
380 DIM N2$(85),N1$(85),C$(10),X(10),R1(10),Q1(10),TH(10),PH(10),L(10),L2(10)
390 DIM CTH(10,10),CTHM(100),D2(20),LG(10),Y(100),GAM(2,21),YY(2,21),PVAP(2)
400 DIM H$(17),AA(2),BB(2),CC(2),AMS1(100),AMS2(100),UMW(85),REDVOL(100)
410 DIM ACTIVEFV(10), COEFFFV(10), LNFV(10),WMOLAR(10),DEN(10),WM(10),COEFF(10)
420 DIM XMOLAR(10), W(10), WCOEFF(10), FRACT(10)
430 OPEN "I",#1,"c:\baSICA\UFNRQM.DTA"
440 FOR I=1 TO 85
450 INPUT #1,N1$(I),N1(I),N2$(I),N2(I),R(I),Q(I),UMW(I)
460 NEXT I
470 CLOSE #1
480 OPEN "I",#1,"C:\basica\UNFA44.DTA"
490 FOR I=1 TO 44
500 FOR JJ=1 TO 11
510 J=1+4*(JJ-1)
520 INPUT #1, A(I,J), A(I,J+1), A(I,J+2), A(I,J+3)
530 NEXT JJ
540 NEXT I
550 CLOSE #1
560 PRINT "UNIFAC Parameters are Loaded"
570 '--------------------------------------------------------------------------
580 'Subrountines to call DATA Files
590 'First load the number of calculations in the file: NOCALC
600 'Then load temperature: TC in degrees C
610 ' IMX = # of components in a mixture, ILS = # of different groups
620 '  X = mole fraction, IAR = UNIFAC group number, AN = frequency of group
630 '--------------------------------------------------------------------------
640 NCALC = 1
```

```
650 INPUT "Enter Data File to be used: FILE$: "; FILE$
660 INPUT "Result File to be used: 'NAME'.RES: "; RESULT$
670 OPEN "I",3,FILE$
680 OPEN "O",2,RESULT$
690    INPUT #3,N$,NOCALC
700    INPUT #3,N$,TC
710 ' Load Parameters from Data File and then calculate each result
720    INPUT #3,N$,IMX
730    IF N$ = "eof" THEN GOTO 890
740 FOR I=1 TO IMX
750    INPUT #3,N$,C$(I),X(I),ILS(I)
760    INPUT #3,N$,IAR(I,1),AN(I,1),IAR(I,2),AN(I,2),IAR(I,3),AN(I,3),IAR(I,4),A
N(I,4),IAR(I,5),AN(I,5),IAR(I,6),AN(I,6),IAR(I,7),AN(I,7),IAR(I,8),AN(I,8)
770 NEXT I
780 ITEMP = 0: IAPFLG = 0: ICONC = 0: IRTRN = 0: ILST=0: ILST1=0
790 '---------------Call temperature subroutine---------------
800 GOSUB 1410
810 '--------Call groups present subroutine -------------------
820 GOSUB 930
830 '-----------Begin Calculations------------------------
840 '------Subroutine to normalize weight fraction------------------
850 GOSUB 1190
860 '---Calculate the coefficients !-------------------------------
870 GOSUB 1480
880 GOTO 710
890 CLOSE 2
900 CLOSE 3
910 END
920 CLS
930 CLS : PRINT : PRINT TAB(20);"UNIFAC ESTIMATION OF ACTIVITY COEFFICIENTS"
940 PRINT TAB(20);"==========================================" : PRINT
950 PRINT TAB(34);"COMPONENT DATA"
960 PRINT TAB(34);"--------------"
970 PRINT TAB(48);"Molecular Subgroups"
980 PRINT TAB(42);"--------------------------------"
990 PRINT TAB(9);"Component No.       Name         Number   Description   Freque
ncy"
1000 PRINT TAB(9);"-------------   ------------     ------   -----------   -----
----"
1010 L1$="             ##         \          \       ##      \      \        ###
"
1020 L2$="                                           ##      \      \        ###
"
1030 FOR I=1 TO IMX : JMX = ILS(I)
1040 PRINT USING L1$; I,C$(I),IAR(I,1),N2$(IAR(I,1)),AN(I,1)
1050 IF JMX = 1 THEN 1090
1060 FOR J=2 TO JMX
1070 PRINT USING L2$; IAR(I,J),N2$(IAR(I,J)),AN(I,J)
1080 NEXT J
1090 PRINT
1100 NEXT I
1110 PRINT: PRINT "Press any key to continue."
1120 IF INKEY$="" GOTO 1120
1130 PRINT: PRINT "Checking for availability of interaction parameters."
1140 PRINT "This may take several seconds if many groups are present."
1150 IRTRN = 2
1160 GOSUB 2870
1170 GOTO 1530
1180 '--------------Normalize weight fractions-----------------------
1190 ICONC = 1
1200 SUMX=0
1210 FOR I=1 TO IMX
1220 'continue
1230 IF X(I)>1 THEN PRINT "!!! INPUT ERROR !!!" : GOTO 1220
```

```
1240 IF X(I)<0 THEN PRINT "!!! INPUT ERROR !!!" : GOTO 1220
1250 IF X(I)=0 THEN X(I)=.0000001
1260 SUMX=SUMX+X(I) : NEXT I
1270 IF SUMX<.999999 THEN GOTO 1300
1280 IF SUMX>1.000001 THEN GOTO 1300
1290 GOTO 1310
1300 PRINT "MOLE FRACTIONS DO NOT SUM TO 1, BEING NORMALIZED"
1310 FOR I=1 TO IMX: X(I)=X(I)/SUMX: NEXT I
1320 PRINT : PRINT : PRINT TAB(30);"COMPONENT CONCENTRATIONS" : PRINT TAB(30);"-
-----------------------"
1330 PRINT TAB(22);"No         Name            Mole Fraction"
1340 PRINT TAB(22);"--     --------------      -------------"
1350 L1$="                     ##     \          \           #.#####"
1360 FOR I=1 TO IMX
1370 PRINT USING L1$ ; I,C$(I),X(I)
1380 NEXT I
1390 GOSUB 2870
1400 RETURN
1410 'TEMP> -----------------TEMPERATURE ENTRY --------------------
1420 FOR IQ = 1 TO 10: NNSE$=INKEY$: NEXT IQ
1430 ITEMP = 1
1440 ILST = 0: ILST1 = 0: IPVAP = 0
1450 PRINT : PRINT "Temperature = ";TC;" deg C"
1460 TK=TC + 273.15
1470 RETURN
1480 'COEFF>
1490  FOR IQ = 1 TO 10: NNSE$=INKEY$: NEXT IQ
1500 ' UNIFAC CALCULATION -------------------------------------------
1510 ' COMBINATORIAL
1520 IRTRN = 0
1530 R2 = 0: Q2 = 0
1540 FOR I=1 TO IMX
1550 R1(I)=0 : Q1(I)=0
1560 FOR J=1 TO ILS(I)
1570 R1(I)=R1(I)+R(IAR(I,J))*AN(I,J)
1580 Q1(I)=Q1(I)+Q(IAR(I,J))*AN(I,J)
1590 NEXT J
1600 R2=R2+X(I)*R1(I)
1610 Q2=Q2+X(I)*Q1(I)
1620 NEXT I
1630 L1=0
1640 FOR I=1 TO IMX
1650 PH(I)=R1(I)*X(I)/R2
1660 TH(I)=Q1(I)*X(I)/Q2
1670 L(I) = 5*(R1(I)-Q1(I))-(R1(I)-1)
1680 L1 = L1+X(I)*L(I)
1690 NEXT I
1700 FOR I=1 TO IMX
1710 LGC(I)=LOG(PH(I)/X(I))+5*Q1(I)*LOG(TH(I)/PH(I))+L(I)-(PH(I)/X(I))*L1
1720 NEXT I
1730 ' RESIDUAL CALCULATION -----------------------------------------
1740 FOR I = 1 TO IMX
1750 SUMQ = 0
1760 FOR J = 1 TO ILS(I)
1770 D2(J) = AN(I,J)*Q(IAR(I,J))
1780 SUMQ = SUMQ + D2(J)
1790 NEXT J
1800 FOR J = 1 TO ILS(I)
1810 CTH(I,J) = D2(J)/SUMQ
1820 NEXT J
1830 NEXT I
1840 SUMQ = 0
1850 FOR K=1 TO KMAX
1860 D2(K) = ANMX(K)*Q(IARM(K))
```

```
1870 SUMQ = SUMQ + D2(K)
1880 NEXT K
1890 FOR K = 1 TO KMAX
1900 CTHM(K) = D2(K)/SUMQ
1910 NEXT K
1920 'GAMMA RESIDUAL FOR EACH GROUP IN EACH MOLECULE ----------------
1930 IAFLG = 0
1940 FOR I = 1 TO IMX
1950 FOR K = 1 TO ILS(I)
1960 KK = N1(IAR(I,K))
1970 SUM1 = 0: SUM2 = 0
1980 FOR M = 1 TO ILS(I)
1990 MM=N1(IAR(I,M))
2000 SUM3 = 0
2010 FOR N = 1 TO ILS(I)
2020 NN=N1(IAR(I,N))
2030 SUM3 = SUM3 + CTH(I,N)*EXP(-A(NN,MM)/TK)
2040 NEXT N
2050 SUM2 = SUM2 + CTH(I,M)*(EXP(-A(KK,MM)/TK))/SUM3
2060 SUM1 = SUM1 + CTH(I,M)*EXP(-A(MM,KK)/TK)
2070 NEXT M
2080 LNG(I,K) = Q(IAR(I,K))*(1-LOG(SUM1)-SUM2)
2090 NEXT K
2100 NEXT I
2110 'GAMMA RESIDUAL FOR EACH GROUP IN MIXTURE ----------------------
2120 FOR K = 1 TO KMAX
2130 SUM1 = 0: SUM2 = 0
2140 KK = N1(IARM(K))
2150 FOR M = 1 TO KMAX
2160 MM = N1(IARM(M))
2170 SUM3 = 0
2180 FOR N = 1 TO KMAX
2190 NN = N1(IARM(N))
2200 SUM3 = SUM3 + CTHM(N)*EXP(-A(NN,MM)/TK)
2210 NEXT N
2220 SUM2 = SUM2 + CTHM(M)*(EXP(-A(KK,MM)/TK))/SUM3
2230 IF MM=KK GOTO 2320
2240 IF A(MM,KK) <> 0 GOTO 2320
2250 IF MM=7 AND KK=31 GOTO 2320
2260 IF MM=31 AND KK=7 GOTO 2320
2270 IF MM=22 AND KK=23 GOTO 2320
2280 IF MM=23 AND KK=22 GOTO 2320
2290 IF IAPFLG = 1 GOTO 2320
2300 IAFLG = IAFLG + 1
2310 AMS1(IAFLG) = N2(IARM(M)): AMS2(IAFLG) = N2(IARM(K))
2320 SUM1 = SUM1 + CTHM(M)*EXP(-A(MM,KK)/TK)
2330 NEXT M
2340 LNGM(K) = Q(IARM(K))*(1-LOG(SUM1)-SUM2)
2350 NEXT K
2360 'GAMMA RESIDUAL FOR EACH MOLECULE
2370 FOR I = 1 TO IMX
2380 SUM = 0
2390 FOR J = 1 TO ILS(I)
2400 FOR K = 1 TO KMAX
2410 IF IARM(K) = IAR(I,J) THEN 2430
2420 NEXT K
2430 SUM = SUM + AN(I,J) * (LNGM(K) - LNG(I,J))
2440 ' SUM = LN RESIDUAL ACTIVITY COEFF.
2450 NEXT J
2460 LG(I)=SUM + LGC(I)
2470 ' THE ACTIVITY IS THEN = coeff(I)
2480 COEFF(I) = EXP(LG(I))
2490 NEXT I
2500 FOR I = 1 TO IMX
```

```
2510   G(I) = COEFF(I) / X(I)
2520     NEXT I
2530 IF IAPFLG > 0 THEN GOTO 2680
2540 IAPFLG = 1
2550 IF IAFLG > 0 THEN GOTO 2580
2560 PRINT: PRINT "All interaction parameters are available."
2570 GOTO 2680
2580 CLS: PRINT "Interaction parameters unavailable (and set to zero) for the"
2590 PRINT "following pairs of groups:": PRINT
2600 FOR IAFLAG = 1 TO IAFLG
2610 IF AMS1(IAFLAG) < AMS2(IAFLAG) GOTO 2630
2620 PRINT "       ",N2$(AMS1(IAFLAG))," with ",N2$(AMS2(IAFLAG))
2630 NEXT IAFLAG
2640 PRINT: PRINT "Press any key to continue":
2650 FOR IQ = 1 TO 10: NNSE$ = INKEY$: NEXT IQ
2660 IF INKEY$="" THEN GOTO 2660
2670 CLS
2680 IF IRTRN = 2 THEN GOTO 830
2690 PRINT : PRINT : PRINT TAB(27);"COMPONENT ACTIVITY COEFFICIENTS"
2700 PRINT TAB(27);"-------------------------------"
2710 L1$="             & +###.## &"
2720 PRINT : PRINT USING L1$ ; "Temperature:",TC,"Deg C" : PRINT TAB(13);"------
--------------------"
2730 PRINT TAB(5);"No   Name           Activity    X(I)      Act.Coeff"
2740 PRINT TAB(5);"-------------------------------------------------------------
-------"
2750 L1$="  ##  \           \ #######.####### #.####### #######.#######"
2760 FOR I=1 TO IMX
2770 PRINT USING L1$ ; I,C$(I),G(I),X(I),COEFF(I)
2780 NEXT I
2790 FOR I=1 TO IMX
2800 WRITE #2,NCALC,I,C$(I),G(I),X(I),COEFF(I)
2810 NEXT I
2820 NCALC = NCALC + 1
2830 INPUT "Hit Return to Continue";R
2840 RETURN
2850 '-----------------------------------------------------------------------
2860 'COMPUTATION OF GROUP MOLE FRACTIONS>
2870 FOR J = 1 TO ILS(1)
2880 IARM(J) = IAR(1,J): ANM(J) = AN(1,J): ANMX(J) = X(1)*AN(1,J)
2890 NEXT J
2900 KMAX = ILS(1)
2910 FOR I = 2 TO IMX
2920 FOR J = 1 TO ILS(I)
2930 FOR K = 1 TO KMAX
2940 IF IARM(K) = IAR(I,J) THEN 2960
2950 GOTO 2980
2960 ANM(K) = ANM(K) + AN(I,J)
2970 ANMX(K) = ANMX(K) + X(I)*AN(I,J): GOTO 3030
2980 NEXT K
2990 KMAX=KMAX + 1
3000 IARM(KMAX) = IAR(I,J)
3010 ANM(KMAX) = AN(I,J)
3020 ANMX(KMAX) = X(I)*AN(I,J)
3030 NEXT J
3040 NEXT I
3050 RETURN
```

Output for UNIFACBX.BAS

Use DOS command to print file to printer:

```
C> type ’filen.ame’>prn
```

Output for each line referring to example printed below:

mixture number, substance number, name of substance, activity, mole fraction, mole fraction activity coefficient.

Example of Output:

```
1,1,"d-Limonene",5218034,1.644601E-05,85.81583
1,2,"ETOH",2.154905,.5398893,1.16341
1,3,"H2O",3.375311,.4600943,1.552961
2,1,"Diphenylmethane",1.408694E+07,1.644601E-05,231.674
2,2,"ETOH",2.154873,.5398893,1.163393
2,3,"H2O",3.375364,.4600943,1.552985
3,1,"Linalylacetate",1678738,1.644601E-05,27.60854
3,2,"ETOH",2.154917,.5398893,1.163417
3,3,"H2O",3.375284,.4600943,1.552949
4,1,"Camphor",1044960,1.644601E-05,17.18542
4,2,"ETOH",2.154933,.5398893,1.163425
4,3,"H2O",3.375264,.4600943,1.55294
5,1,"Diphenyloxide",4078233,1.644601E-05,67.07066
5,2,"ETOH",2.154897,.5398893,1.163406
5,3,"H2O",3.375324,.4600943,1.552967
6,1,"Isoamylacetate",642620,1.644601E-05,10.56853
6,2,"ETOH",2.15494,.5398893,1.163429
6,3,"H2O",3.375237,.4600943,1.552927
7,1,"gamma-undelactone",2607757,1.644601E-05,42.88719
7,2,"ETOH",2.154906,.5398893,1.163411
7,3,"H2O",3.375309,.4600943,1.55296
8,1,"Eugenol",4086.047,1.644601E-05,6.719916E-02
8,2,"ETOH",2.154942,.5398893,1.16343
8,3,"H2O",3.375246,.4600943,1.552931
9,1,"Citronellol",368187.8,1.644601E-05,6.05522
9,2,"ETOH",2.154916,.5398893,1.163416
9,3,"H2O",3.375281,.4600943,1.552947
10,1,"DBC",391298.4,1.644601E-05,6.435297
10,2,"ETOH",2.154918,.5398893,1.163417
10,3,"H2O",3.375282,.4600943,1.552948
11,1,"Menthol",433659.4,1.644601E-05,7.131966
11,2,"ETOH",2.154917,.5398893,1.163417
11,3,"H2O",3.375284,.4600943,1.552949
12,1,"PEA",288710.9,1.644601E-05,4.748142
12,2,"ETOH",2.154936,.5398893,1.163427
12,3,"H2O",3.37525,.4600943,1.552933
13,1,"cis-3-Hexenol",149914.9,1.644601E-05,2.465502
13,2,"ETOH",2.154953,.5398893,1.163436
13,3,"H2O",3.37522,.4600943,1.552919
```

Input for GCEOS1.FOR

GCEOS1.FOR is the program POLGEOS (March 5, 1991) in FORTRAN from Fei Chen (Instituttet for Kemiteknik, Technical University Denmark, Lyngby, Denmark) adapted for use with WATFOR77 FORTRAN Compiler.

Input file name is always "INDAT".

Lines are not numbered, each line is considered a separate line of input. A space separates data in a line.

First Line: the number of mixtures to be calculated.

Subsequent Lines: Required inputs for mixture. Example shown for binary mixture.

name of system (a text string)

number of components in mixture (maximum 5)

Component #1: # of repeat units making up molecule (for polymers); the group contribution number; frequency of group contribution; etc. up to 7 different group contribution groups.

Component #2: same input as #1

...Add one line for each additional mixture component...

temperature in K

weight fraction component number 1, weight fraction component number 2, etc.

...Repeat above pattern for second mixture starting with name of system to weight fractions. See input example below:

GCFEOS Output

Output of GCEOS1.FOR is always the file named 'LDDAT'.

The file can be printed using the DOS command:

```
C> type lddat>prn
```

or simply viewed on the screen with the type command. It is recommended that the result be viewed on the screen since the output is so large and only a small fraction of the output is necessary.

```
 5
  WATER-PS
 2
 1 26  1  0  0  0  0  0  0  0  0  0  0  0  0
154 2  1  3  1  6  5  7  1  0  0  0  0  0  0
 4.5100E+02
 0.0001E+00 0.9999E+00
  WATER-PS
 2
 1 26  1  0  0  0  0  0  0  0  0  0  0  0  0
1154 2  1  3  1  6  5  7  1  0  0  0  0  0  0
 4.5600E+02
 0.1000E-07 0.9999E+00
  HEXANE-PIB
 2
 1  1  2  2  4  0  0  0  0  0  0  0  0  0  0
946 1  2  2  1  4  1  0  0  0  0  0  0  0  0
 4.2315E+02
 0.1000E-07 0.9999E+00
  CYCLOHEXANE-PIB
 2
 1  5  6  0  0  0  0  0  0  0  0  0  0  0  0
946 1  2  2  1  4  1  0  0  0  0  0  0  0  0
 4.2315E+02
 0.1000E-07 0.9999E+00
  BENZENE-PIB
 2
 1  6  6  0  0  0  0  0  0  0  0  0  0  0  0
946 1  2  2  1  4  1  0  0  0  0  0  0  0  0
 3.2315E+02
 0.1000E-07 0.9999E+00
```

Appendix G

Aqueous Ethanol and Mole Fractions at 25°C

Table 63. Aqueous Ethanol Concentrations and Mole Fractions at 25C

% (w/w) Aqueous Ethanol	Ethanol Mole Fraction	Water Mole Fraction
100	1.000	0.000
90	0.779	0.221
80	0.610	0.380
75	0.540	0.460
70	0.477	0.523
66	0.432	0.568
60	0.370	0.630
50	0.281	0.719
40	0.207	0.793
35	0.174	0.826
33	0.162	0.838
30	0.144	0.856
20	0.115	0.885
10	0.089	0.911
0	0.000	1.000

with solute mole concentration sum(x) = 1E-4

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