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Correlation Between the Solubility Parameter as a Measure of Sorbate/Polymer: Compatibility and Sorbate Equilibrium Solubility in a Two-Phase Aqueous/Polymer System

presented by

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<u>Master</u> degree in <u>Packaging</u>

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# CORRELATION BETWEEN THE SOLUBILITY PARAMETER AS A MEASURE OF SORBATE/POLYMER COMPATIBILITY AND SORBATE EQUILIBRIUM SOLUBILITY IN A TWO-PHASE AQUEOUS/POLYMER SYSTEM

By

Palarp Sailabada

# A THESIS

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

## MASTER OF SCIENCE

School of Packaging

### ABSTRACT

## CORRELATION BETWEEN THE SOLUBILITY PARAMETER AS A MEASURE OF SORBATE/POLYMER COMPATIBILITY AND SORBATE EQUILIBRIUM SOLUBILITY IN A TWO-PHASE AQUEOUS/POLYMER SYSTEM

By

### Palarp Sailabada

Partition coefficient (K) values of the aqueous/polymer systems were obtained using two experimental methods, TS/TD-GC and SPME-GC. The K values of limonene, ethyl acetate, methyl ethyl ketone and toluene in LDPE and in the water system were 200.85, 2.79, 0.54 and 95.46 respectively using TS/TD-GC. The K values of limonene, ethyl acetate, methyl ethyl ketone and toluene in LDPE and in the water system were 59.64, 1.09, 0.58 and 112.23 respectively using SPME-GC. The solubility parameter value was calculated using the solubility parameter program. The solubility parameter values determined for limonene, ethyl acetate, methyl ethyl ketone and toluene were 4.70, 13.37, 13.35 and 6.36  $(J/cm^3)^{1/2}$  respectively. When the solubility parameter values were less than or equal to 5, good solubility occurred. Therefore, a high degree of compatibility can be expected between sorbate and polymer. This was reflected in the high partition coefficient values. Finally, the correlation between the solubility parameter as a measure of sorbate/polymer compatibility and sorbate equilibrium solubility in a two-phase aqueous/polymer system was established using an exponential regression equation.

To my mom and dad and especially to Dr.Jack R. Giacin

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### INTRODUCTION

The solubility parameter ( $\delta$ ) was proposed in 1949 by Hilderbrand as a help explain the behavior of specific solvents (Van Krevelen, 1990). The solubility parameter ( $\delta$ ) is widely used to illustrate the mutual affinity of sorbate/polymer systems. Thus, it is an important characteristic which can be used to estimate the interaction or compatibility between product constituents and polymeric packaging systems. Normally, the solubility of a given sorbate in different polymers can be approximated by its chemical structure. Therefore, measurement of the solubility parameter is a method which can be used to indicate the probability of sorbate/polymer compatibility. Similar solubility parameters for two substances (i.e. sorbate/polymer system) indicate the compatibility of those substances. The solubility parameter can be used as a useful indicator of sorbate/polymer interaction to select a suitable package for a product, where quality is related to the retention of organic volatiles.

In considering the solubility parameter as a measure of sorbate/polymer compatibility, it is important to understand that this concept is not proposed as a substitute for actual storage stability or compatibility studies. It is a useful tool, which can result in the sound selection of polymeric package systems and may reduce the number of samples which need to be evaluated in long term stability studies.

In terms of practical utility, the results of this research have the following applications;

- Predict the compatibility of a product for a given packaging material.
- Aid in selecting the most suitable packaging material for a given package-product-environment system.
- Provide an alternative to accelerated storage studies for evaluating candidate-packaging systems.
- Reduce development time.

This study will focus on estimating the affinity of organic sorbates in a selected polymer, using three-dimensional (3-D) solubility parameters and to establish a correlation between the solubility parameters and equilibrium partition coefficient (K) for the sorbates in a two-phase, aqueous/polymer system.

## Chapter 1

# LITERATURE REVIEW

### 1.1 Solubility parameter

The solubility parameter provides a simple method of correlating and predicting the cohesive and adhesive properties of materials from knowledge of the properties of the components. For polymers, applications include finding compatible solvents for coating resins, predicting the swelling of cured elastomers by solvents, estimating solvent pressure in devolatilization and reactor equipment and predicting polymer-polymer; polymer-binary-solvent; random copolymer, and multicomponent solvent equilibria. Cohesive energy was the basis of the original definition by Hilderbrand and Scott for what is now called the solubility parameter (Du, et al 1996).

According to Hilderbrand (Van Krevelen, 1990), the enthalpy of mixing can be calculated by the following equation:

(i.e., polymer and sorbate, respectively)

$$\delta_{p}$$
 and  $\delta_{s}$  = solubility parameters of components

(i.e., polymer and sorbate, respectively).

From equation (1.1.1), the two components should be mutually soluble if  $\Delta H_m$  is equal or near to zero. This means that the solubility parameters of the

two components (i.e.  $\delta_p$  and  $\delta_s$ ) should be equal or close. Therefore, components with similar chemical structures and similar solubility parameters should easily dissolve in each other and exhibit a high propensity for sorbate/polymer interaction or compatibility. As large differences between solubility parameters of substances (i.e. sorbate/polymer) occur, lower solubility values are expected. However, in equation (1.1.1), it was assumed that there are no specific forces between the structural units of the substances involved, but only dispersive forces. If one of the substances involved contains strongly polar groups or hydrogen bonds,  $\Delta H_m$  may become higher than that calculated from equation (1.1.1) and solubility may not occur, even when the values of the solubility parameter are close or equal. On the other hand, if both substances involved contain intermolecular forces such as van der Waals forces, hydrogen bonding, or dipole interactions, solubility may be promoted, even if the solubility parameter values differ significantly (Van Krevelen, 1995).

A more specific treatment of the solubility concept was desired for situations where there is interaction between polymer and sorbate. The component group contribution methods of Hoy (Hoy, 1970) and of Hoftyzer and Van Krevelen (Hoftyzer, 1990) afford such a treatment and can be applied in cases to estimate the solubility parameters of sorbate/polymer systems. The component group contribution method provides the total solubility parameter ( $\delta_t$ ) as well as the dispersion ( $\delta_d$ ), polar ( $\delta_p$ ), and hydrogen bonding ( $\delta_h$ ) contributions to the solubility parameter. The total, or 3-dimensional (3-D) solubility parameter  $\delta_t$ , is described as the sum of these respective solubility parameter components.

$$\delta_{t} = \left(\delta_{d}^{2} + \delta_{p}^{2} + \delta_{h}^{2}\right)^{1/2}$$
(1.1.2)

An estimation of the solubility or compatibility of a sorbate molecule in a polymer, when dispersion, polar and hydrogen bonding contributions are considered, is shown in equation (1.1.3);

$$\overline{\Delta}\delta = \left[ \left( \delta_{d,p} - \delta_{d,s} \right)^2 + \left( \delta_{p,p} - \delta_{p,s} \right)^2 + \left( \delta_{h,p} - \delta_{h,s} \right)^2 \right]^{1/2}$$
(1.1.3)

where  $\delta_{d,p}$ ,  $\delta_{p,p}$ , and  $\delta_{h,p}$  are the dispersion, polar and hydrogen bonding solubility parameter values for the polymer and  $\delta_{d,s}$ ,  $\delta_{p,s}$ , and  $\delta_{h,s}$  are the dispersion, polar and hydrogen bonding solubility parameter values for the sorbate, respectively.

Thermodynamic considerations ler Bagley et al. (1971) to the conclusion that the effects of  $\delta_h$  and  $\delta_p$  show close similarity, whil the effect of  $\delta_h$  is of a quit different nature. Accordingly, they introduced the parameter  $\delta_v = \sqrt{\delta_d^2 + \delta_p^2}$ . This leads to a diagram in which  $\delta_v$  and  $\delta_h$  are plotted on the axes. Such a diagram is shown in figure 1.1 for the interaction between polystyrene and a number of solvents. A majority of the points for good solvents indeed fall in a single region of figure 1.1. The solubility region can approximately be delimited by a circle with a radious of about 5  $\delta$ -units. For extensive chemical activity or solubility of a sorbate molecule in a polymer matrix, the value  $\overline{\Delta}\delta$  should be less than or equal to 5 ( $\leq$  5) (Van Krevelen, 1990).





To facilitate determination of solubility parameter values and solution of equation (1.1.3) for  $\overline{\Delta}\delta$  values, a computer program was developed which has a data base of solubility parameter values and the associated  $\delta_{d,p}$ ,  $\delta_{p,p}$ , and  $\delta_{h,p}$  values for a series of commodity polymer structures, as well as group contribution tables (Hoy 1970) and (Hoftyzer and Van Krevelen 1990), which will

allow ready determination of the solubility parameter values for organic sorbates, given their molecular structure. The program also determines both associated  $\delta_{d,p}$ ,  $\delta_{p,p}$ , and  $\delta_{h,p}$  values and  $\delta_{d,s}$ ,  $\delta_{p,s}$ , and  $\delta_{h,s}$  values, as well as providing a value for  $\overline{\Delta}\delta$  as a prediction of sorbate/polymer affinity (Stephane, 1995).

# 1.2 Partition coefficient

Food/package interactions can be defined as chemical and/or physical reactions between a food, its package and the environment, which may change the composition, quality, or physical properties of the food and/or package. In general, food/package interactions can be divided into four types, which are (Hotchkiss, 1995):

- **Migration** can be defined as the transfer of package components to the product. This can result in safety concerns and flavor degradation.
- Scalping can be defined as the transfer of product components to the package. The transfer of desirable aromas from food to packaging can result in flavor alteration and/or loss of package performance.
- Egress permeation which is the transfer of product components through the package to the environment. Loss of aroma-flavor volatiles, CO<sub>2</sub>, or H<sub>2</sub>O can result in changes in food quality.
- Ingress permeation which is the transfer of environmental components through the package to the product. Ingress of O<sub>2</sub>, H<sub>2</sub>O, light or undesirable odors or toxicants can be detrimental.

The loss of volatile low molecular mass organic compounds from a food into polymeric packaging materials, based on a sorption mechanism is of major concern and continues to be a subject of study. Sorption, or the uptake of volatile components by the polymeric packaging material from food, may also result in increased permeability to other permeants, lower chemical and mechanical resistance of the packaging material, and/or affect the kinetics of the migration process (Giacin, 1995). The overall effect may result in the loss of aroma and flavor volatiles associated with product quality, as well as other volatile organic food components during package storage. In food product/package systems, the characterization of sorption behavior is necessary for quality control and prediction of change in product quality, as related to the loss of components associated with product shelflife. Sorption is measured as a function of sorbate concentration by a sorption equilibrium isotherm that can be described by Henry's Law or other mathematical models. For a specific value of concentration, the partition coefficient (K) is a practical way to describe the change in organic sorbate concentration, either in the food or packaging, from the moment that food product and packaging material are contacted, up to the moment they reach equilibrium (Giacin, 1995). Here, the partition coefficient is defined as the equilibrium concentration of sorbate in the polymer phase  $[C_p]$ divided by the equilibrium concentration of sorbate in the aqueous phase [C<sub>a</sub>]. For high solubility in the polymer phase,  $\Delta\delta$  should be less than 5 and therefore a significant high partition should be expected.

Gavara et al., 1995 applied three experimental techniques to determine the partition coefficient of toluene, d-limonene, and ethyl acetate between water and polystyrene. The authors found that gas chromatography (GC) was an excellent technique for determination of sorbate concentrations in the liquid phase, especially for sorbates with high K values. The dynamic thermal stripper/thermal desorption (DTS/TD) method was very useful for determination of sorbate concentrations in the polymer phase. The applicability of this technique was limited, however, by the retention capacity of the trap column and its selectivity (Gavara et al., 1995).

### 1.3 Solid Phase Microextraction

Solid Phase Microextraction (SPME) is a solvent-free sample preparation technique. The basic principle of this approach is to use a small amount of the extraction phase, usually less than 1  $\mu$ L. The SPME device consists of a 1 cm length of fused silica fiber, coated on the outer surface with a stationary phase and bonded to a stainless steel plunger, and a holder that looks like a modified microliter syringe (Figure 1.3.1) (Supelco, 1997).



Figure 1.3.1. Solid Phase Microextraction device

The fused silica fiber can be drawn into a hollow needle using the plunger on the fiber holder. Organic analytes are adsorbed onto the stationary phase coated fiber, and adsorption equilibrium is attained in 2 to 30 minutes. After sample adsorption, the fused silica fiber is drawn up into the needle, the needle withdrawn from the sample vial and injected directly into the gas chromatograph, where the sorbed analytes are thermally desorbed and delivered to a capillary column for analysis. This is shown in sequence in Figure 1.3.2.



Figure 1.3.2. Sequence of events showing extraction steps and desorption steps using SPME

The figure shows extraction and desorption (injection) steps necessary to perform an analysis using SPME. The fiber is inserted directly into a liquid sample with the subsequent absorption of most of the analyte molecules (small circles) from the solution (Alan et al., 1997).

For different structural characteristics of an analyte, the phase type or thickness of the fiber can be changed to enhance the stationary phase captive capacity of the analyte. SPME is a fast, inexpensive and solvent free technique that can be used to concentrate volatile, semi-volatile or non-volatile compounds from liquid samples or headspace. In the first process, the coated fiber is exposed to the sample, and the target analyte are extracted from the sample matrix into the coating. The fiber with concentrated analytes is then transferred

to an instrument where the analytes are thermally desorbed, separated and quantified by the detector. SPME can be used directly with any gas chromatograph or gas chromatograph-mass spectrometer system.

The principle behind SPME is the partitioning of analytes between the sample matrix and the extraction medium (Zhang 1994). If a liquid polymeric coating is used, the amount of analyte absorbed by the coating at equilibrium is directly related to its concentration in the sample, as shown in equation 1.3.1.

n = 
$$\frac{K_{f_s} V_f C_0 V_s}{K_{f_s} V_f + V_s}$$
 (1.3.1)

where n is the mass of an analyte absorbed by the coating; V<sub>f</sub> and V<sub>s</sub> are the volumes of the coating and the sample, respectively;  $K_{f_i}$  is the partition coefficient of the analyte between the coating and the sample matrix; and C<sub>0</sub> is the initial concentration of the analyte in the sample. As equation 1.3.1 indicates, if V<sub>s</sub> is very large (V<sub>s</sub>>>K<sub>fs</sub> V<sub>f</sub>), the amount of analyte extracted by the fiber coating will not be related to the sample volume, as shown in equation 1.3.2.

$$n = K_{f_s} V_f C_0$$
 (1.3.2)

In SPME, equilibria are established among the concentrations of an analyte in the liquid or solid sample, in the headspace above the sample, and in the fused silica fiber phase. The amount of analyte absorbed by the fiber depends on the thickness of the stationary phase coating and the distribution constant for the analyte. Extraction time is determined by the time required to obtain precise extraction for the analyte with the highest distribution constant. Full equilibration is not necessary for high accuracy and precision with SPME,

but consistent sampling time and other sampling parameters are essential. Vial size, sample volume, and (for liquid samples) the depth the fiber is immersed into the sample are all important to keep consistent.

Two important steps in SPME are extraction of the analytes from the sample material, and desorbtion of them into an analytical instrument. A variety of sorbents have been used for SPME, since different groups of analytes can be extracted using different types of sorbents. The basic principle of "like dissolves like" applies for organic compounds. The coating can be selected based on the polarity and volatility characteristics of the analyte. One of the most useful coatings is polydimethylsiloxane (PDMS), which is very rugged and able to withstand injector temperatures up to 300 °C (Jnausz, 1999). PDMS is a non-polar liquid phase, so it extracts non-polar analytes very well. However, it can be applied to more polar compounds, particularly after optimizing extraction conditions. SPME can be used to analyze a wide range of compounds in various matrices through proper optimization or modification of SPME procedures.

Czerwinski et al. (1996) used a polydimethylsiloxane coated fiber system to determine the presence of myrcene, beta-pinene, limonene and menthol in four herbal remedies utilizing a headspace procedure, with GC-MS analysis. The detection limits were at the ppb level and 13 other compounds were identified. Shirey (1997) compared the extraction limits of different coated fiber phases for polar analytes in water samples. The results showed that carboxen/polydimethylsiloxane fiber had superior extraction capability as compared to the other coating phases, particularly, the more polar phases such

as Carbowax<sup>™</sup>/divinylbenzene and polyacrylate coating fibers. The author proposed that the small pores of carboxen/polydimethylsiloxane enables extraction of analytes at higher orders of magnitude than other coated fiber phases. Mersili (R&D magazine, 1999) evaluated the capabilities of SPME with respect to off-flavor in milk and concluded that SPME is not only significantly easier and faster to perform, but it has consistently demonstrated superior accuracy and precision without sacrifice in sensitivity.

## 1.4 Dynamic Thermal Stripper/Thermal Desorption (DTS/TD)

The dynamic thermal stripper unit is a sample preparation instrument designed to collect onto an adsorbent packed trap, a broad range of low to high molecular weight compounds that are present at the parts per billion to parts per million level. The thermal stripper system and the instrument parameters (i.e. carrier gas flow rate, temperature program and collection time), as well as the composition of the absorbent trap, are major factors contributing to the overall performance of sample collection (Dynatherm, TS manual, 1989).

The thermal desorption unit is an instrument used for direct thermal desorption of compounds from the sorbent tubes of the thermal stripper or a dynamic purge and trap system. The system is easily installed on virtually any gas chromatograph (GC), with a heated transfer line inserted into the column oven through an access hole or through one of the injectors. All zones of sample transport may be heated to a maximum of 250 °C to prevent condensation of higher molecular weight compounds. These features make the instrument ideal

for the analysis of sensitive environmental, food, flavor, and biological compounds. The sorbent tubes are generally packed with layers of different materials, so that a wide range of compounds having different molecular weight and polarities may be trapped onto an appropriate sorbent. Each sorbent layer protects the next increasingly active layer, and prevents a compound from being held so tenaciously that it cannot be desorbed quickly and completely during the trap and heat cycle, which is important to prevent degradation. Therefore, during sample collection, the gas flow enters the sorbent tube at the least active layer of sorbent material, and exits through the most tenacious layer (Dynatherm, TD manual, 1989).

The TS/TD system, interfaced with GC analysis has been used to determine the sorbate concentration in a polymer sample by trapping the total amount of sorbate from the polymer sample and quantitatively measuring the desorbing analytes with GC analysis. This method is acceptable in cases where the amount of sorbate in the polymer is relatively low (Gavara et al, 1996)

# Chapter 2

# MATERIALS AND METHODS

### **Materials**

2.1 Polymer

Low density polyethylene (LDPE) (thickness 1.19 mil, density 0.923 g/cm<sup>3</sup>) was used as the test material for all research herein.

### Methods

2.2 Determination of partition coefficient of sorbates in LDPE film and water

2.2.1 Solvents

The following solutions were used in this procedure;

Acetonitrile, CH<sub>3</sub>CN (HPLC Grade) from EM Industries, Inc. (Gibbstown,

NJ), molecular weight 41.05, density 0.78 g/mL at 25°C, boiling range 82.0  $\pm$  0.1

°C, purity 99.8 %

1,2-Dichlorobenxene,  $C_6H_4Cl_2$  (HPLC Grade) from Aldrich Chemical Company, Inc., molecular weight 147, density 1.306 g/mL at 25°C, boiling range 179-180 °C, purity 99.6 %

Dichloromethane, CH<sub>2</sub>Cl<sub>2</sub> (Analytical Reagent Grade) from Mallinckrodt, Inc. (Paris, KY), molecular weight 84.93, density 1.316 g/mL at 25°C, boiling range 40 °C, purity 99.9 %

Water, H<sub>2</sub>O (HPLC Grade) from J.T.Baker (Phillipsburg, NJ), molecular weight 18.0, density 1.000, boiling range 100 °C, purity 100%

Xylenes,  $C_6H_4(CH_3)_2$  (HPLC Grade) from EM Industries, Inc. (Gibbstown, NJ), molecular weight 41.05, density 0.78 g/mL at 25°C, boiling range 82.0  $\pm$  0.1 °C, purity 99.8 %

Methanol, CH<sub>3</sub>OH (HPLC Grade) from J.T. Baker (Phillipsburg, NJ), Molecular weight 32.04, Density 0.791 g/mL at 25°C, Boiling range 64.7 °C, Purity 100.0 %

2.2.2 Solutes

Ethyl acetate,  $CH_3COOC_2H_5$  (GLC Grade) from Aldrich Chemical Company, Inc., molecular weight 88.11, density 0.902 g/mL at 25°C, boiling range 76.5-77.5 °C, purity 99.8 %

Limonene, C<sub>10</sub>H<sub>16</sub> (GLC Grade) from Aldrich Chemical Company, Inc., molecular weight 136.24, density 0.840 g/mL at 25°C, boiling range 175.5-176 °F, purity 97 %

Methyl ethyl ketone, CH<sub>3</sub>COCH<sub>2</sub>CH<sub>3</sub> (Analytical Reagent Grade) from Mallinckrodt Specialty Chemical Co., molecular weight 72.11, density 0.803 g/mL at 25°C, boiling range 79.5-80.0 °C, purity 99.6 %

Toluene,  $C_6H_5CH_3$  (Analytical Reagent Grade) from J.T. Baker Chemical Co., molecular weight 92.14, density 0.865 g/mL at 25°C, boiling range 110.6 °C, purity 99.9 %

2.2.3 Instruments

Gas Chromatograph:

Hewlett Packard model 5890 A interfaced with HP 3395 integrator (Avondale, PA)

Gas Chromatography Column (Fused Silica Capillary Column):

SPB<sup>™</sup>5 (non-polar bounded stationary phase) 30 m long, 0.32 mm I.D.,

1.0 µm film thickness (Supelco Inc., Bellefonte, PA)

Syringes:

500 mL Gas-tight syringe (Hamilton Co., Reno, NV)

5 μl syringe (Hamilton Co., Reno, NV)

Separatory funnel

Vial and cap:

40 mL amber vial (Supelco Inc., Bellefonte, PA) open screw cap-teflon/silicon septa (Supelco Inc., Bellefonte, PA)

## Sample Preparation

Four sorbate solutions in water were obtained by separately mixing ethyl acetate, limonene, methyl ethyl ketone and toluene with water in a separatory funnel at room temperature (22±1°C) and allowing the solution to stand for 24 hours. Each of the aqueous, transparent phases was then separated as a primary aqueous sorbate solution. The concentrations of each sorbate solution were then determined by solvent extraction following the method of Gavara et al, 1995.



Figure 2.2.1. Sorption cell

Sorption cells for the determination of partition coefficient values consisted of 40 mL amber glass vials with an open-top screw cap-teflon/silicon septa closure. The LDPE film was cut into a round disk shape (OD 21.69 mm) with a cork borer. Approximately 30 film disks were weighed and then mounted onto a stainless steel wire, which was formed as a support stand threaded with glass beads to separate the film disks, so as to allow two-sided contact. The mounted film disks were then placed into the vial and it was filled with 40 mL of sorbate solution, as shown in figure 2.2.1. Three sorption cells were prepared with one blank cell (no film disks) per each sorption solution and the cells were stored at room temperature  $(22\pm1^{\circ}C)$  for 30 days. It was assumed that this storage time would allow the system to attain equilibrium (Harita and Tanaka 1989). During storage, the sorption cells were shaken by hand every 6-7 days (Baner, 1992). At the end of the storage time, the quantity of the sorbates in the aqueous phase was determined by a SPME method and the quantity of the sorbates sorbed by

the LDPE film determined using a TS/TD system interfaced with a gas chromatograph (GC). The equilibrium partition coefficient (K) was then determined by substitution into equation 2.2.1. The equilibrium partition coefficient K is defined as the equilibrium concentration of sorbate in the polymer phase  $[C_p]$  divided by the equilibrium concentration of sorbate in the aqueous phase  $[C_a]$ .

$$K = \frac{\left[C_{p}\right]}{\left[C_{a}\right]}$$
(2.2.1)

### 2.3 Determination of sorbates in polymer phase

2.3.1 Instruments

The following instruments were used in the above procedure;

Dynamic Thermal Stripper:

Dynatherm model 1000 thermal stripper unit (Dynatherm, Kelton PA)

20 mL sparging tube

Thermal Desorption:

Dynatherm 890/891 thermal desorption unit (Dynatherm, Kelton PA)

Carbotrap<sup>™</sup> 300 multi-bed thermal desorption tubes; 6 mm O.D. × 4 mm,

I.D. × 11.5 cm length (Supelco Inc., Bellefonte, PA)

Gas Chromatograph:

Hewlett Packard model 5890 A interfaced with HP 3395 integrator

(Avondale, PA)

Gas Chromatography Column (Fused Silica Capillary Column):

SPB<sup>™</sup>5 (non-polar bounded stationary phase) 30 m long, 0.32 mm I.D.,

1.0 μm film thickness (Supelco Inc., Bellefonte, PA) Syringes:

500 mL Gas-tight syringe (Hamilton Co., Reno, NV)

5 μl syringe (Hamilton Co., Reno, NV)

The dynamic thermal stripper model 1000 (Dynatherm., Kelton, PA) and thermal desorption model 890/891 (Dynatherm., Kelton, PA) interfaced with GC analysis were used to analyze the concentration of the sorbate in the polymer (LDPE) phase. After equilibrium, the polymer disks were immediately transferred into 20 mL sparging tubes, placed in the oven of a thermal stripper instrument and connected to sorption tubes containing Carbotrap<sup>™</sup> 300 (Supelco Inc., Bellefonte, PA) mounted outside the oven. The conditions used for the thermal stripper unit and thermal desorption are summarized in Table 2.3.1.

Table 2.3.1. Thermal and	flow rate conditions u	used for the thermal strippe	er.
--------------------------	------------------------	------------------------------	-----

	Preheat	Purge	Dry
He Flow rate, mL/min	50	100	50
Time, min	5	15	2
	Block	Oven	Tube
Temperature, °C	150	110	75

After stripping, the carbotrap sorption tube containing the trapped sorbate was transferred to the tube chamber of the thermal desorption unit. A transfer line connected the thermal desorption unit to the GC. The sorbate was thermally desorbed from the carbotrap matrix into the GC using the conditions shown in Tables 2.3.2 and 2.3.3 respectively.

|--|

Tube desorption chamber temperature, °C	370
Valve compartment temperature, °C	250
Transfer line temperature, °C	250
Tube preparation chamber temperature, °C	350
Desorption time, min	8
Preparation time, min	30
Desorption carrier gas flow rate at flow check port, mL/min	9
Preparation carrier gas flow at side port, mL/min	15

Table 2.3.3. Gas chromatographic thermal conditions, injection and retention times necessary to separate sorbates using the gas chromatograph procedure

Compound	Ethyl Acetate	Limonene	Methyl Ethyl Ketone	Toluene
Injection Temperature, °C	200	200	200	200
Initial Temperature, °C	100	60	50	40
Initial Time, min	9	1	2	5
Rate, ºC/min	10	10	10	10
Final Temperature, °C	220	200	200	200
Final Time, min	10	5	10	10
Detector Temperature, °C	250	250	250	250
Range	2	2	2	2
Retention Time, min	2.1	7.6	1.9	4.3

The concentration of sorbate in the polymer was calculated, and substituted into the following equation.

 $[C_p] = \frac{m_s}{m_p}$ 

(2.3.1)

where  $m_{s}$  is the mass of sorbate and  $m_{p}$  is the mass of polymer

Standard calibration curves for the TD and GC procedures were constructed for the analysis of sorbed levels of the respective sorbate from a series of standard solutions of known concentration. A 1 µl volume of standard solution of sorbate of known concentration was directly injected into the carbotrap<sup>™</sup> 300 tube. The sorption tube was then inserted into the heating chamber of the thermal desorption unit, which was directly interfaced to the column of the gas chromatograph, where the sorbates were separated. The optimized conditions for the TD and GC procedures are shown in Table 2.3.2 and 2.3.3 respectively. The standard calibration curves of sorbates by thermal desorption are shown in Appendix B.

## 2.4 Determination of sorbates in liquid (aqueous) phase

2.4.1 Instruments

The following instruments were used in the above analysis;

Gas Chromatograph:

Hewlett Packard model 5890 A interfaced with HP 3395 integrator

(Avondale, PA)

Gas Chromatography Column (Fused Silica Capillary Column):

SPB<sup>™</sup>5 (non-polar bounded stationary phase) 30 m long, 0.32 mm l.D.,

1.0 µm film thickness (Supelco Inc., Bellefonte, PA)

Solid Phase Microextraction device

100 µm Polydimethylsiloxane (PDMS) fiber (Supelco Inc., Bellefonte, PA)

SPME manual injection syringe (Supelco Inc., Bellefonte, PA)

Determination of sorbate concentration levels in the aqueous phase was carried out by solvent extraction and SPME with GC analysis. Sorbate concentrations in the blank cell were evaluated and used as the initial sorbate concentration. Concentrations of ethyl acetate, methyl ethyl ketone, and toluene in the primary aqueous standard solution were determined by a one-step extraction of the sorbate from the aqueous solution with dichlorobenzene, followed by analysis using GC. A similar procedure was employed, for limonene, in the primary aqueous standard solutions using dichloromethane as the extracting solvent. The conditions for the analysis of sorbates by GC are shown in table 2.4.1.

Compound	Ethyl Acetate	Limonene	Methyl Ethyl Ketone	Toluene
Injection Temperature, °C	200	200	200	200
Initial oven Temperature, °C	100	60	50	40
Initial Time, min	9	1	2	5
Rate, °C/min	5	7	5	10
Final Temperature, °C	220	200	200	200
Final Time, min	10	5	10	10
Detector Temperature, °C	250	250	250	250
Range	2	2	2	2
Retention Time	1.7	7.6	2.0	4.3
Solvent	acetonitrile	acetonitrile	xyle <b>ne</b>	acetonitrile

Table 2.4.1. Gas chromatograph conditions used to separate sorbates

The SPME-GC procedure was used to determine the sorbate concentration in the liquid (aqueous) phase of the polymer-aqueous phase distribution system. After storing the filled sorption cell for 30 days, the sorbate
solution was extracted using SPME and then directly injected into the GC. The extraction time for each sorbate was obtained from the time required to achieve precise extraction of the sorbate with the highest distribution constant. The extraction time for ethyl acetate, limonene, and methyl ethyl ketone was found to be 4 minutes and for toluene were 10 minutes. The standard calibration curves of known series dilutions of the sorbates concentration were constructed, as shown in Appendix C.

#### Chapter 3

#### **RESULTS AND DISCUSSION**

Partition coefficient values of aqueous/polymer systems were obtained by using two experimental methods, TS/TD-GC and SPME-GC. The solubility parameter values were determined using a solubility parameter program. A correlation between partition coefficient values and solubility parameter values was established.

# 3.1 <u>Determination of the partition coefficient of several aqueous/polymer systems</u> using the TS/TD-GC method

The partition coefficient of sorbates between LDPE film and water were determined by measuring the sorbate concentration in polymer and the remaining sorbate concentration in the aqueous phase. The partition coefficient values (K) are reported as a ratio of the concentration of sorbate in the polymer phase  $[C_p]$  divided by the concentration of sorbate in the aqueous phase  $[C_a]$ . Results for three sample systems and one blank control (no film disks-sorption cell) were determined (Appendix D) and the results are summarized in Table 3.1.1, 3.1.2, 3.1.3, and 3.1.4 for limonene, ethyl acetate, methyl ethyl ketone and toluene respectively.

-	4.58 × 10 <sup>-6</sup>	•
5.12 × 10-4	3.32 × 10 <sup>-6</sup>	154.18
6.68 × 10-4	3.22 × 10 <sup>-6</sup>	207.42
7.81 × 10-4	3.24 × 10 <sup>-6</sup>	240.96
•	•	200.85
-	•	43.76
	5.12 × 10 <sup>-4</sup> 6.68 × 10 <sup>-4</sup> 7.81 × 10 <sup>-4</sup> -	$5.12 \times 10^{-4} \qquad 3.32 \times 10^{-6} \\ 6.68 \times 10^{-4} \qquad 3.22 \times 10^{-6} \\ 7.81 \times 10^{-4} \qquad 3.24 \times 10^{-6} \\ - \qquad -$

### Table 3.1.1. Partition coefficient values for limonene in a LDPE film and water

## system

\* TS/TD-GC method

Table 3.1.2. Partition coefficient values for ethyl acetate in a LDPE film and water

### system

Sample	C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
Blank	-	6.16 × 10 <sup>-5</sup>	•
1	2.22 × 10-4	6.11 × 10 <sup>-5</sup>	3.64
2	1.42 × 10-4	6.14 × 10 <sup>-5</sup>	2.31
3	1.48 × 10 <del>-</del> 4	6.11 × 10 <sup>-5</sup>	2.42
Average	-	-	2.79
Standard deviation	-	-	0.74
tTOTO CO method			

\* TS/TD-GC method

## Table 3.1.3. Partition coefficient values for methyl ethyl ketone in a LDPE film

## and water system

Sample	C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
Blank	•	3.64 × 10 <sup>-5</sup>	-
1	1.95 × 10⁻⁵	3.61 × 10 <sup>-5</sup>	0.54
2	2.65 × 10⁻⁵	3.61 × 10 <sup>-5</sup>	0.73
3	1.30 × 10 <sup>-5</sup>	3.62 × 10 <sup>-5</sup>	0.36
Average	•	-	0.54
Standard deviation	•	-	0.19
* TS/TD-GC method			

C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
•	7.17 × 10 <sup>-6</sup>	•
3.65 × 10-4	4.08 × 10⁻ <sup>6</sup>	89.40
4.33 × 10-4	4.08 × 10 <sup>-6</sup>	106.10
4.48 × 10-4	4.08 × 10 <sup>-6</sup>	90.88
•	•	95.46
-	-	9.24
	C <sub>p</sub> (wt/wt) - 3.65 × 10 <sup>-4</sup> 4.33 × 10 <sup>-4</sup> 4.48 × 10 <sup>-4</sup> -	$\begin{array}{c ccc} C_{p} (\text{wt/wt}) & C_{a} (\text{wt/wt}) \\ \hline & - & 7.17 \times 10^{-6} \\ \hline & 3.65 \times 10^{-4} & 4.08 \times 10^{-6} \\ \hline & 4.33 \times 10^{-4} & 4.08 \times 10^{-6} \\ \hline & 4.48 \times 10^{-4} & 4.08 \times 10^{-6} \\ \hline & - & - $

Table 3.1.4. Partition coefficient values for toluene in a LDPE film and water

\* TS/TD-GC method

system

The partition coefficient (K), average partition coefficient (Kavg) and

standard deviation ( $\sigma$ ) for the above sorbates were calculated and are

summarized in Table 3.1.5.

			_		_	-		*
Tahla 3 1 5	Partition	coefficient	values	of the	Janneonie/	nolv	mor e	vetome
	1 artition	coefficient	values		aqueous	poiy	11101 0	Jacoma

Sample	Limonene	Ethyl acetate	Methyl ethyl ketone	Toluene
1	154.18	3.64	0.54	89.40
2	207.42	2.30	0.73	106.10
3	240.96	2.42	0.36	90.88
Kavg	200.85	2.79	0.54	95.46
σ	43.76	0.74	0.19	9.24

\* TS/TD-GC method

 $K_{avg}$  values of limonene and toluene were 200.85 and 95.46 respectively. These values indicate a high preference for limonene and toluene to dissolve in the LDPE rather than in the water. The  $K_{avg}$  values of ethyl acetate and methyl ethyl ketone were 2.79 and 0.54, which implies that ethyl acetate and methyl ethyl ketone were more likely to dissolve in water than in LDPE.

# 3.2 Determination of the Partition coefficient of several aqueous/polymer systems using the SPME-GC method

Sorbate concentration levels in the aqueous and in the polymer phase were determined using the SPME-GC method. The partition coefficient values of sorbate in a LDPE and water system were calculated (Appendix E) and summarized in Table 3.2.1, 3.2.2, 3.2.3 and 3.2.4 for limonene, ethyl acetate, methyl ethyl ketone and toluene respectively.

Table 3.2.1. Partition coefficient values for limonene in a LDPE film and water system

Sample	C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
Blank		4.58 × 10 <sup>-6</sup>	-
1	1.90 × 10-4	3.32 × 10⁻ <sup>6</sup>	57.14
2	1.99 × 10-4	3.22 × 10⁻ <sup>6</sup>	61.93
3	1.94 × 10⁴	3.24 × 10⁻ <sup>6</sup>	59.85
Average	•	-	59.64
Standard deviation		-	2.40
* SPME-GC method			

SPME-GC method

#### system

Sample	C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
Blank		6.16 × 10 <sup>-5</sup>	-
1	8.76 × 10 <sup>-5</sup>	6.11 × 10 <sup>-5</sup>	1.43
2	3.41 × 10⁻⁵	6.14 × 10 <sup>-5</sup>	0.55
3	7.75 × 10 <sup>-5</sup>	6.11 × 10⁻⁵	1.27
Average	-	-	1.09
Standard deviation	•	-	0.47
* SPME-GC method		····	

,

Sample	C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
Blank	-	3.64 × 10 <sup>-5</sup>	
1	2.33 × 10 <sup>-5</sup>	3.61 × 10 <sup>-5</sup>	0.38
2	4.15 × 10⁻⁵	3.61 × 10 <sup>-5</sup>	0.68
3	4.05 × 10 <sup>-5</sup>	3.62 × 10 <sup>-5</sup>	0.66
Average	•	 	0.58
Standard deviation	•		0.17
		· · · · · · · · · · · · · · · · · · ·	

Table 3.2.3. Partition coefficient values for methyl ethyl ketone in a LDPE film

and water system

\* SPME-GC method

#### Table 3.2.4. Partition coefficient values for toluene in a LDPE film and water

	*
system	

Sample	C <sub>p</sub> (wt/wt)	C <sub>a</sub> (wt/wt)	K
Blank	•	7.17 × 10 <sup>-6</sup>	•
1	4.58 × 10-4	<b>4.08</b> × 10 <sup>−6</sup>	112.17
2	4.58 × 10⁴	<b>4.08</b> × 10 <sup>-6</sup>	112.28
3	4.58 × 10-4	4.08 × 10 <sup>-6</sup>	112.23
Average	-	•	112.23
Standard deviation	•	-	0.05
tophie oo attack			

\* SPME-GC method

The K,  $K_{\text{avg}}$  and standard deviation  $(\sigma)$  for the above sorbates were

calculated and are summarized in Table 3.2.5

Table 3.2.5. Partition coefficient values of the aqueous/polymer systems

Sample	Limonene	Ethyl acetate	Methyl ethyl ketone	Toluene
1	57.14	1.43	0.38	112.17
2	61.93	0.55	0.68	112.28
3	59.85	1.27	0.66	112.23
Kavg	59.64	1.09	0.58	112.23
σ	2.70	0.47	0.17	0.05

\* SPME-GC method

 $K_{avg}$  values of limonene and toluene were 59.64 and 112.23 respectively. These values indicate a high preference for limonene and toluene to dissolve in the LDPE rather than in water. The  $K_{avg}$  of ethyl acetate and methyl ethyl ketone are 1.09 and 0.58, which implies that these two sorbates are more likely to dissolve in water rather than in LDPE.

The results from the two experimental methods are summarized in Table 3.2.6.

Table 3.2.6. Partition coefficient values of aqueous/polymer systems using theTS/TD and SPME method

	Limonene	Ethyl acetate	Methyl ethyl ketone	Toluene
K (TS/TD)	200.85	2.79	0.54	95.46
K (SPME)	59.64	1.09	0.58	112.23
Kavg	130.25	1.94	0.56	103.85
σ	99.85	1.20	0.03	11.86

The partition coefficient values of the aqueous/polymer systems showed a similar trend for both TS/TD-GC and SPME-GC. Experimental error may have cause the difference in the K values of limonene between the two methods. The  $K_{avg}$  of limonene and toluene were 130.25 and 103.85 respectively. The high partition coefficients observed with limonene and toluene indicate that these two sorbates are more likely to be absorbed by LDPE rather than water. Conversely, ethyl acetate and methyl ethyl ketone were highly absorbed by water rather than LDPE due to the low partition coefficients. The  $K_{avg}$  of ethyl acetate and methyl ethyl ketone were 1.94 and 0.56 respectively. These results can be expected from the similarity of chemical structures and characteristics of the sorbates, polymer and water. Ethyl acetate and methyl ethyl ketone are more polar than

limonene and toluene, and water is more polar than LDPE. SPME is a fast, easy and solvent free method. Because it is a single-step method, the error from loss of sorbate during analysis is minimized. To obtain accurate results with this method there should be a large difference between initial concentration and final concentration of the sorbate. The extraction time is also an important variable affecting precision. The constancy of results is obtained by optimizing the extraction time. The TS/TD method is a good technique for determining sorbate concentration in the polymer. In this technique the total amount of sorbate stripped from the polymer must be quantitatively sorbed by the trap. If a very large quantity of sorbate is present, an overloading of the trap can occur, resulting in sorbate loss and underestimation of the sorbate concentration in the polymer (Gavara, 1996).

# 3.3 <u>Determination of the solubility parameter values of aqueous/polymer systems</u> using the solubility parameter values

The solubility parameter is an important characteristic which can be used to estimate the interaction or compatibility between product constituents and polymeric packaging systems. To determine the three-dimensional solubility parameter values, including the total solubility parameter ( $\delta_t$ ), as well as dispersion ( $\delta_d$ ), polar ( $\delta_p$ ), and hydrogen bonding ( $\delta_h$ ) parameters, a software program was written in excel (Example shown in appendix A). The equations used for the calculation are based on Van Krevelen and Hoftyzer's method (Van Krevelen, 1990) and Hoy's method (Van Krevelen, 1990). The program can be used to calculate solubility parameter values and therefore predict the

compatibility between sorbates and polymers, without spending a considerable amount of time on preliminary laboratory tests. Moreover, a database, containing solubility parameter values for a series of sorbates and polymers, has been created for easy reference (Appendix A).

According to Hilderbrand (Van Krevelen 1990), the cohesive energy may be divided into three parts, corresponding to the three types of interacting forces

$$E_{coh} = E_d + E_p + E_h$$
 (3.3.1)  
where  $E_d$ ,  $E_p$ , and  $E_h$  are contributors of dispersion forces, and polar forces and  
hydrogen bonds, respectively. For many liquids and amorphous polymers, the  
solubility parameter, as defined, corresponds to the total cohesive energy, which  
is dependent on the interaction between polar groups and hydrogen bonding.  
Thus, the corresponding equation for the solubility parameter is shown in the  
following equation 3.3.2

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$
 (3.3.2)

where  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  contribute dispersion forces, polar forces and hydrogen bonds to the solubility parameter, respectively.

The method of Van Kreven and Hoftyzer predicted the solubility parameter components from group contributions, using the following equations: (Van Krevelen 1990)

$$\delta_{d} = \frac{\sum F_{di}}{V} \qquad (3.3.3)$$

$$\delta_{p} = \frac{\sqrt{\sum F_{pi}^{2}}}{V} \qquad (3.3.4)$$

$$\delta_{h} = \frac{\sqrt{\sum E_{hi}}}{V} \qquad (3.3.5)$$

The group contributions  $F_{di}$ ,  $F_{pi}$ , and  $E_{hi}$  for a number of structural groups are given in Table A.1 (Appendix A)

The polar component is still further reduced, if two identical polar groups are present in a symmetrical position. To take this effect into account, the value of  $\delta_p$ , calculated using equation (3.3.4) must be multiplied by a symmetry factor of 0.5 for one plane of symmetry, 0.25 for two planes of symmetry, and 0 for more planes of symmetry (Van Krevelen, 1990).

The F-method is not applicable to the calculation of  $\delta_h$ . It has already been stated by Hansen (Van Krevelen, 1990) that the hydrogen bonding energy (E<sub>hi</sub>) per structural group is approximately constant. This leads to the form of equation 3.3.5. For molecules with several planes of symmetry,  $\delta_h = 0$  (Van Krevelen, 1990).

3.3.2 The method of Hoy (Van Krevelen, 1990) differs from the method of Hoftyzer and Van Krevelen in many ways. Table A.2. and Table A.3.(Appendix A) shows equations incremental and values used in the method of Hoy. It contains four additive molar functions, a number of auxiliary equations, and the final expressions for  $\delta_{t(total)}$  and the components of  $\delta$ .

 $F_T$  is the molar attraction function,  $F_P$  its polar component; V is the molar volume of the solvent molecule or the structure unit of the polymer.  $\Delta_T$  is the Lynderson correction factor for non-ideality, used in the auxiliary equations.

Of the quantities shown in the auxiliary equations, the significance is the following:  $\alpha$  is the molecular aggregation number, which describes the association of the molecules; and  $\overline{n}$  is the number of repeating units per effective chain segment of the polymer (Van Krevelen, 1990).

The results of the two algorithmic methods for estimation of the solubility parameter and its components (Hoftyzer-Van Krevelen and Hoy) are of the same order in accuracy ( $\pm 10\%$ ). Thus, the safest way to estimate is to apply both methods, taking the average of the results. The full equation which is used to determine the solubility of a polymer in an organic liquid is:

$$\overline{\Delta}\delta = \left[ \left( \delta_{d,p} - \delta_{d,s} \right)^2 + \left( \delta_{p,p} - \delta_{p,s} \right)^2 + \left( \delta_{h,p} - \delta_{h,s} \right)^2 \right]^{1/2}$$
(3.3.6)

For good solubility  $\overline{\Delta}\delta$  must be smaller than 5 ( $\leq$  5) (Van Krevelen, 1990).

The solubility parameter program was used to calculate the threedimensional (3-D) solubility parameter values of sorbates in LDPE as shown in Table 3.3.1. In Table 3.3.2 the solubility parameters of the sorbates/LDPE system are presented. The structural details of the sorbates and polymer material are shown in Appendix F.

The solubility of a given polymer in various solvents is largely determined by its chemical structure. Besides the chemical structure, also the physical state of a polymer is important for its solubility properties. Crystalline polymers are

relatively insoluble and often dissolve only at temperatures slightly below their melting points (Van krevelen, 1990).

Table 3.3.1. Three-dimensional (3-D) solubility parameters of LDPE and sorbates calculated using the solubility parameter program

Sorbates/Polymer	delta total (\deltat)	delta dispersive ( $\delta_d$ )	delta polar (δ <sub>p</sub> )	delta hydrogen (\deltah)
	(J/cm <sup>3</sup> ) <sup>1/2</sup>			
LDPE (1)	18.01	18.01	0.00	0.00
	17.74	17.74	0.00	0.00
limonene <sup>(1)</sup>	18.31	15.84	5.77	7.13
limonene <sup>(2)</sup>	16.40	16.40	0.00	0.00
ethyl acetate (1)	21.77	14.22	9.19	13.68
ethyl acetate (2)	18.22	15.34	5.01	8.46
methyl ethyl ketone (1)	22.26	14.11	9.47	14.39
methyl ethyl ketone (2)	18.45	15.63	8.60	4.73
toluene <sup>(1)</sup>	20.68	16.85	8.16	8.78
toluene (2)	17.44	17.41	1.04	0.00
water	48.00	13.30	31.30	34.20

\* (1) Hoy method

(2) Van Krevelen and Hoftyzer method

### Table 3.3.2. Solubility parameter values of the sorbate/LDPE systems

Sorbates	$\Delta\delta$ between LDPE (J/cm <sup>3</sup> ) <sup>1/2</sup>	$\Delta\delta$ between water (J/cm <sup>3</sup> ) <sup>1/2</sup>
Limonene <sup>(1)</sup>	9.43	37.30
Limonene <sup>(2)</sup>	1.34	46.46
Ethyl acetate (1)	16.91	30.18
Ethyl acetate (2)	10.12	36.85
Methyl ethyl ketone (1)	17.66	29.49
Methyl ethyl ketone (2)	10.03	37.28
Toluene <sup>(1)</sup>	12.05	34.58
Toluene <sup>(2)</sup>	1.09	45.85

\* (1) Hoy method

(2) Van Krevelen and Hoftyzer method

3.4 Correlation between the solubility parameters using Hoy method and partition

coefficient (K) of the sorbates in a two-phase, aqueous/polymer system

The partition coefficients (K) and solubility parameter values ( $\Delta\delta$ ) of aqueous/polymer systems are summarized in Table 3.4.

Table 3.4. Partition coefficients and solubility parameters using Hoy method of

the	aqueous	/polyme	er systems
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	Limonene	Ethyl acetate	Methyl ethyl ketone	Toluene
K <sup>(1)</sup>	200.85	2.79	0.54	95.46
K <sup>(2)</sup>	59.64	1.09	0.58	112.23
K <sup>(3)</sup>	130.25	1.94	0.56	103.85
Δδ (J/cm <sup>3</sup> ) <sup>1/2</sup>	9.43	16.91	17.66	12.05

\* (1) K average using TS/TD-GC method

(2) K average using SPME-GC method

(3) K average from TS/TD and SPME method

The solubility parameter value of limonene was 9.43 (J/cm<sup>3</sup>)<sup>1/2</sup>. This indicates that there is a chemical similarity between limonene and LDPE. Therefore, a high partition coefficient should be expected and the K<sub>avg</sub> of limonene/LDPE was 130.25. For toluene a similar trend was observed. Toluene had a solubility parameter value of 12.05 (J/cm<sup>3</sup>)<sup>1/2</sup>. Therefore, a substantial amount of toluene was expected to be sorbed by LDPE, which was reflected in a K<sub>avg</sub> of 103.85. Conversely, the solubility parameter values of ethyl acetate and methyl ethyl ketone were 16.91 (J/cm<sup>3</sup>)<sup>1/2</sup> and 17.66 (J/cm<sup>3</sup>)<sup>1/2</sup> respectively, which implies chemical difference between both ethyl acetate and methyl ketone, and LDPE. The low partition coefficient is expected. The K<sub>avg</sub> of ethyl acetate/LDPE and methyl ethyl ketone/LDPE were 1.94 and 0.96 respectively.

From the results generated, a correlation between the partition coefficients of an aqueous/polymer system from the TS/TD-GC and the SPME-GC methods,

and solubility parameter values can be established. The correlation was determined using exponential regression as shown in Figure 3.4.



Figure 3.4. Correlation between partition coefficients using the TS/TD-GC and SPME-GC method and solubility parameters using Hoy method

3.5 <u>Correlation between the solubility parameters using Hoftyzer and Van</u> <u>Krevelen method and partition coefficient (K) of the sorbates in a two-phase,</u> <u>aqueous/polymer system</u>

The partition coefficients (K) and solubility parameter values ( $\Delta\delta$ ) of aqueous/polymer systems are summarized in Table 3.5.

Table 3.5. Partition coefficients and solubility parameters using Hoftyzer and Van

	Limonene	Ethyl acetate	Methyl ethyl ketone	Toluene
K <sup>(1)</sup>	200.85	2.79	0.54	95.46
K <sup>(2)</sup>	59.64	1.09	0.58	112.23
K <sup>(3)</sup>	130.25	1.94	0.56	103.85
Δδ (J/cm <sup>3</sup> ) <sup>1/2</sup>	1.34	10.12	10.03	1.09

Krevelen method of the aqueous/polymer systems

\* (1) K average using TS/TD-GC method

(2) K average using SPME-GC method

(3) K average from TS/TD and SPME method

The solubility parameter values between limonene and toluene and LDPE are 1.34 and 1.09 respectively. This indicates high compatibility between both limonene and toluene and LDPE. Therefore, the partition coefficient values of limonene and toluene are 13.025 and 103.85 respectively. On the other hand, solubility parameter values of ethyl acetate and methyl ethyl ketone are 10.12 and 10.13 respectively. This effect low partition coefficient values of 1.94 and 0.96 for ethyl acetate and methyl ethyl ketone respectively.

From the data, a correlation between partition coefficient values and solubility parameter values using Hoftyzer and Van Krevelen method can be established as shown in figure 3.5.



Figure 3.5. Correlation between average of partition coefficients using the TS/TD-GC and SPME-GC method and solubility parameters using Hoftyzer and Van Krevelen method

#### Chapter 4

#### SUMMARY AND CONCLUSION

The partition coefficient (K) is defined as the equilibrium concentration of sorbate in the polymer phase [C<sub>p</sub>] divided by the equilibrium concentration of sorbate in the aqueous phase  $[C_a]$ . The partition coefficient results of aqueous/polymer systems were generated using two experimental methods, TS/TD-GC and SPME-GC. The TS/TD methodology, which includes GC analysis, was used to directly determine the sorbate concentration in the polymer. In this technique the total amount of sorbate stripped from the polymer sample must be quantitatively sorbed by the trap (Gavara, et al., 1995). The K values of limonene, ethyl acetate, methyl ethyl ketone and toluene using TS/TD-GC system were 200.85, 2.79, 0.54 and 95.46 respectively. The SPME method is a newer technique and can be used to determine sorbate concentration in the aqueous phase. It is a relatively easy and fast way compared to the solvent extraction analysis. The K values of limonene, ethyl acetate, methyl ethyl ketone and toluene using SPME-GC system were 59.64, 1.09, 0.58 and 112.23 respectively. The partition coefficient values from the two experimental methods had a high degree of correlation. The solubility parameter value can be used to estimate the solubility of a sorbate in a polymer, and is a good indicator of the chemical compatibility between a sorbate and a polymer. The solubility parameter values using Hoy method for limonene, ethyl acetate, methyl ethyl ketone and toluene were 9.43, 16.91, 17.66 and 12.05  $(J/cm^3)^{1/2}$  respectively.

The solubility parameter values using Hoftyzer and Van Krevelen method are 1.34, 10.12, 10.03 and 1.09 (J/cm<sup>3</sup>)<sup>1/2</sup> for limonene, ethyl acetate, methyl ethyl ketone and toluene respectively.

Values of  $\Delta\delta$  determined using the solubility parameter program and K values from two experimental methods for each sorbate were compared. Chemical similarity between sorbate and polymer was found, when the solubility parameter value was equal or less than 5 and thus, a high partition was achieved as indicated by a high value for the partition coefficient. On the other hand, low solubility was found with a low partition coefficient value. In this research a correlation between partition coefficient values and solubility parameter values for the compatibility of sorbates/polymer system was established. An exponential regression was used to determine the correlation between solubility parameter values is a useful indicator of a sorbate/polymer system. It can be used to help select the most suitable packaging material for a given package-product-environment system. Also it provides an alternative to accelerated storage studies for evaluating candidate-packaging systems.

APPENDICES

## APPENDIX A

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6	Groups	Group	bi-	tri-	tetra-	(J.cm <sup>3</sup> ) <sup>1/2</sup> /mol	(J.cm <sup>3</sup> ) <sup>1/2</sup> /	mol
7	-снз	1	0	0	0	303.5	Û	
8	-CH2-	1	0	0	0	269	0	
9	>CH-	1	0	0	0	176	0	
10	>C<	0	0	0	0	0	0	
11	=CH2	0	0	0	0	0	0	
12	=CH-	0	0	0	0	0	0	
13	=C<	0	0	0	0	0	0	
14	CH aromatic	0	0	0	0	0	0	
15	C aromatic	0	0	0	0	0	0	
16	-HC=0	0	0	0	0	0	0	
17	>C=0	0	0	0	0	0	0	
18	-COOH	0	0	0	0	0	0	
19	-000-	1	0	0	0	640	528	
20	-00-0-00-	0	0	0	0	0	0	
21	-CN (3Bonds)	0	0	0	0	0	0	
22	-N=C=0	0	0	0	0	0	0	
23	HCON<	0	0	0	0	0	0	
24	-CONH2	0	0	0	0	0	0	لتر.
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Figure A.1 Example of solubility parameter program of Hoy method

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84			Cali	culation va	ues	Group	contributions <b>\</b>
85	Structural	Number of	Fai	F <sub>Pi</sub>	E <sub>N</sub>	Fai	F <sub>Pi</sub>
86	Group	Group	J.cm <sup>3</sup> ) <sup>1/2</sup> /mi	l.cm <sup>3</sup> ) <sup>1/2</sup> /m	J/mol	(J.cm <sup>3</sup> ) <sup>1/2</sup> /mol	(J.cm <sup>3</sup> ) <sup>1/2</sup> /mol
87	-CH3	0	Û	0	0	420	0
88	-CH2-	2	540	0	0	270	0
89	>CH-	0	0	0	0	80	0
90	>C<	0	0	0	0	-70	O
91	=CH2	0	0	0	0	400	0
92	=CH-	0	0	0	0	200	0
93	=C<	0	0	0	0	70	0
94	$\langle \rangle$	0	0	0	0	1620	0
55	<b>N</b>	U	U	U	U	1430	110
90	ġ-	U	U	U	U	12/0	110
9/	-r A	U	U	U	U	22U 450	550
90 00	-VI Dr		U N	U N	U	400 550	330
33 100	-DI -CN		U N	U N	U N	330 130	1100
101	-0H	n o	n	n	n	-30 210	500
102	-0-	0	n l	n N	0 0	100	400
103	-COH-	Õ	Ō	Ō	Ō	470	800
104	-00-	Ū	Ō	Ō	Ō	290	770
105	-COOH	0	0	0	0	530	420 -1
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# Figure A.2 Example of solubility parameter program of Hoftyzer and Van

Krevelen method

Table A.1. Solubility parameter component group contributions (Method Hoftyzer-

Structural	F <sub>di</sub>	F <sub>pi</sub>	E <sub>hi</sub>
Group	(J.cm <sup>3</sup> ) <sup>1/2</sup> /mol	(J.cm <sup>3</sup> ) <sup>1/2</sup> /mol	J/mol
-CH <sub>3</sub>	420	0	0
-CH <sub>2</sub> -	270	0	0
>CH-	80	0	0
>C<	-70	0	0
=CH <sub>2</sub>	400	0	0
=CH-	200	0	0
=C<	70	0	0
Ю	1620	0	0
- <b>O</b>	1430	110	0
-0-	1270	110	0
-F	220	-	-
-Cl	450	550	400
-Br	550	-	-
-CN	430	1100	2500
-OH	210	500	20000
-0-	100	400	3000
-COH-	470	800	4500
-CO-	290	770	2000
-COOH	530	420	10000
-C00-	390	490	7000
HCOO-	530	-	-
-NH <sub>2</sub>	280	-	8400
-NH-	160	210	3100
-N<	20	800	5000
-NO <sub>2</sub>	500	1070	1500
-S-	440	-	-
-PO4-	740	1890	13000
Ring	190	-	-

Van Krevelen) (Van Krevelen 1990)

Formulae	Low-molecular Liquids (Solvents)	Amorphous Polymers
Additive	$F_t = \Sigma N_i F_{ti}$	$F_t = \Sigma N_i F_{t,i}$
Molar	$F_p = \Sigma N_i F_{p,i}$	$F_p = \Sigma N_i F_{p,i}$
functions	$V = \Sigma N_i V_i$	$V = \Sigma N_i V_i$
	$\Delta_{\rm T} = \Sigma N_i \Delta_{\rm T,i}$	$\Delta^{(P)}_{T,i} = \Sigma N_i \Delta^{(P)}_{T,i}$
Auxiliary	$Log \alpha = 3.39 \left(\frac{T_b}{T_{cr}}\right) - 0.1585 - logV$	$\alpha^{(P)} = \frac{777\Delta_T^{(P)}}{V}$
equations	$T_b$ = boiling point; $T_{cr}$ = critical temp.	
	$\left(\frac{T_{b}}{T_{cr}}\right) = 0.567 + \Delta_{T} - (\Delta_{T})^2$	$\overline{n} = \frac{0.5}{\Delta_T^{(P)}}$
	(Lynderson equation)	
Expressions for $\delta$ and $\delta$ -components	$\delta_t = \frac{F_t + B}{V}  B = 277$	$\delta_t = \frac{F_t + B/\overline{n}}{V}$
	$\delta_{p} = \delta_{l} \left( \frac{1}{\alpha} \frac{F_{p}}{F_{t} + B} \right)^{1/2}$	$\delta_{p} = \delta_{t} \left( \frac{1}{\alpha} \frac{F_{p}}{F_{t} + B/\overline{n}} \right)^{1/2}$
(Note that $F_1$ must be combined with a Base	$\delta_{h} = \delta_{l} \left( \frac{\alpha - 1}{\alpha} \right)^{1/2}$	$\delta_{h} = \delta_{t} \left( \frac{\alpha^{(P)} - 1}{\alpha^{(P)}} \right)^{1/2}$
value; B for liquids and B/ $\overline{\mathbf{n}}$ for polymers	$\delta_{d} = \left( \delta_{t}^{2} - \delta_{p}^{2} - \delta_{h}^{2} \right)^{1/2}$	$\delta_{d} = \left(\delta_{t}^{2} - \delta_{p}^{2} - \delta_{h}^{2}\right)^{1/2}$

Table A.2. The equations to be used in Hoy's system for estimation of thesolubility parameter and its components (Van Krevelen, 1990).

I

Groups	Fu	$F_{p,i}$	Vi	Δτ,*	Δ <sup>(P)</sup> <sub>Τ,i</sub>	Groups	Fu	Fpj	Vi	`ز⊤∆	Δ <sup>(P)</sup> <sub>Τ,i</sub>
	(J.cm <sup>3</sup> )	) <sup>1/2</sup> /mol	cm <sup>3</sup> /mol	-	-		(J.cm <sup>3</sup> )	) <sup>1/2</sup> /moł	cm <sup>3</sup> /mol	-	-
-CH <sub>3</sub>	303.5	0	21.55	0.023	0.022	-OH (H-bond)	485	485	10.65	0.082	0.034
-CH <sub>2</sub> -	269	0	15.55	0.02	0.02	-OH (Prim.)	675	675	12 <b>.4</b> 5	0.082	0.049
>CH-	176	0	9.56	0.012	0.013	-OH (Sec.)	591	591	12.45	0.082	0.049
>C<	65.5	0	3.56	0	0.04	-OH (Tert.)	500	500	12.45	0.082	0.049
=CH <sub>2</sub>	259	67	19.17	0.018	0.019	-OH (Phenolic)	350	350	12.45	0.031	0.006
=CH-	249	59.5	13.18	0.018	0.0185	-O- (Ether)	235	216	6.45	0.021	0.018
=C<	173	63	7.18	0	0.013	-O- (Acetal)	236	102	6.45	0.018	0.018
CH aromatic	241	62.5	13.42	0.011	0.018	-O- (Epoxide)	361	156	6.45	0.027	0.027
C aromatic	201	65	7.42	0.011	0.015	-NH <sub>2</sub>	464	464	17	0.031	0.035
-HC=O	600	532	23.3	0.048	0.045	-NH-	368	368	11	0.031	0.0275
>C=0	538	525	17.3	0.04	0.04	>N-	125	125	12.6	0.014	0.009
-COOH	565	415	26.1	0.039	0.039	-S-	428	428	18	0.015	0.032
-000-	640	528	23.7	0.047	0.05	-F	845	73.5	11.2	0.018	0.006
-00-0-00-	1160	1160	41.0	0.086	0.086	-Cl (Prim.)	419.5	307	19.5	0.017	0.031
-C≡N	725	725	23.1	0.06	0.054	-CI (Sec.)	426	315	19.5	0.017	0.032
-N=C=O	736	8.2	25.9	0.054	0.054	-CI (Aromatic)	330	81.5	19.5	0.017	0.025
HCON<	1020	725	35.8	0.062	0.055	<cl<sub>2 (Twinned)</cl<sub>	705	572	39	0.034	0.052
-CONH <sub>2</sub>	1200	900	34.3	0.071	0.084	-Br (Aliphatic)	528	123	25.3	0.01	0.039
-CONH-	1131	895	28.3	0.054	0.073	-Br (Aromatic)	422	100	25.3	0.01	0.031
-OCONH-	1265	890	34.8	0.078	0.094		- 4				
Configurations	Fu	Fpi	Vi	<b>Δ</b> τ,	Δ <sup>(P)</sup> <sub>Τ,i</sub>	Configurations	Fu	F <sub>p,i</sub>	Vi	Δτ, <sup>*</sup>	Δ <sup>(P)</sup> <sub>Τ,i</sub>
Base value (B)	277	-	-	-	-	Conjugation isomerism	47.5	-19.8	-	0	0.0035
Ring size						cis	-14.6	-14.6	-	0	-0.001
(non-aromatic)						trans	-27.6	-27.6	-	0	-0.002
4-membered	159	203	-	0	0.012	Aromatic					
						substitution					
5-membered	43	85	-	0	0.003	otho	20.2	-13.3	-	0	0.0015
6-membered	-48	61	-	0	- 0.0035	meta	13.5	-24.3	-	0	0.001
7-membered	92	0	-	0	0.007	para	83	-34	-	0	0.006

Table A.3. Values of increments in Hoy's system for the molar attraction function

\* For bi-, tri- and tetra-valent groups in saturated rings the  $\Delta$ T-values must be multiplied by a factor 2/3.

## Table A.4. Database of the solubility parameter values of sorbates from the

### solubility parameter program

Sorbates	(δ <sub>t</sub> ) (J/cm <sup>3</sup> ) <sup>1/2</sup>	(δ₀) (J/cm <sup>3</sup> ) <sup>1/2</sup>	(δ <sub>p</sub> ) (J/cm <sup>3</sup> ) <sup>1/2</sup>	(δ <sub>h</sub> ) (J/cm <sup>3</sup> ) <sup>1/2</sup>
Hydrocarbons		<b></b>		••
hexane (1)	14.8-14.9	14.80	0.00	0.00
hexane (2)	18.61	15.75	0.00	9.92
hexane (3)	14.71	14.71	0.00	0.00
hexane (4)	16.66	15.23	0.00	4.96
heptane (1)	15.20	15.20	0.00	0.00
heptane (2)	18.44	15.80	0.00	9.52
heptane (3)	14.95	14.95	0.00	0.00
heptane (4)	16.70	15.37	0.00	4.76
octane (1)	15.60	15.60	0.00	0.00
octane (2)	18.31	15.79	0.00	9.27
octane (3)	15.14	15.14	0.00	0.00
octane (4)	16.73	15.47	0.00	4.64
cyclohexane (1)	16.70	16.70	0.00	0.00
cyclohexane (2)	19.75	15.75	2.91	11.56
cyclohexane (3)	16.75	16.75	0.00	0.00
cyclohexane (4)	18.25	16.25	1.46	5.78
benzene (1)	18.5-18.8	17.6-18.5	1.00	2.00
benzene (2)	21.40	16.92	8.93	9.58
benzene (3)	18.27	18.23	1.24	0.00
benzene (4)	19.84	17.58	5.08	4.79
methylbenzene (toluene) (1)	18.30	17.70	1.40	2.00
methylbenzene (toluene) (2)	20.68	16.85	8.16	8.78
methylbenzene (toluene) (3)	17.44	17.41	1.04	0.00
methylbenzene (toluene) (4)	19.06	17.13	4.60	4.39
1,2-dimethylbenzene (o-xylene) (1)	18.40	16.8-17.6	1.00	1.00
1,2-dimethylbenzene (o-xylene) (2)	20.34	16.92	7.42	8.51
1,2-dimethylbenzene (o-xylene) (3)	19.09	19.07	0.91	0.00
1,2-dimethylbenzene (o-xylene) (4)	19.71	17.99	4.17	4.25
1,3-dimethylbenzene (m-xylene) (1)	18.00	16.7-17.4	1.00	1.00

Table A.4. (Cont'd)

1,3-dimethylbenzene (m-xylene) (2)	20.28	16.91	7.30	8.48
1,3-dimethylbenzene (m-xylene) (3)	18.74	18.72	0.90	0.00
1,3-dimethylbenzene (m-xylene) (4)	19.51	17.81	4.10	4.24
1,4-dimethylbenzene (p-xylene) (1)	17. <del>9</del> -18.0	16.6-17.3	1.00	1.00
1,4-dimethylbenzene (p-xylene) (2)	20.90	17.52	7.31	8.74
1,4-dimethylbenzene (p-xylene) (3)	18.68	18.65	0.89	0.00
1,4-dimethylbenzene (p-xylene) (4)	19.79	18.09	4.10	4.37
ethylbenzene (1)	17.9-18.0	16.7-17.8	0.60	1.40
ethylbenzene (2)	20.21	16.90	7.58	8.08
ethylbenzene (3)	18.89	18.87	0.90	0.00
ethylbenzene (4)	19.55	17.88	4.24	4.04
ethenylbenzene (styrene) (1)	18.0/19.0	16.8-18.6	1.00	4.10
ethenylbenzene (styrene) (2)	20.50	16.49	9.01	8.20
ethenylbenzene (styrene) (3)	19.36	19.33	0.96	0.00
ethenylbenzene (styrene) (4)	19.93	17.91	4.98	4.10
Hydrocarbon <mark>s, ha</mark> log	inated			
dichloromethane (methylene chloride) (1)	19.90	17.4-18.2	6.40	6.10
dichloromethane (methylene chloride) (2)	22.93	12.96	11.89	14.72
dichloromethane (methylene chloride) (3)	22.38	18.40	12.23	3.55
dichloromethane (methylene chloride) (4)	22.66	15.68	12.06	9.13
trichlorometh <b>ane</b> (chloroform) (1)	18.9-19.0	17.7-18.1	3.10	5.70
trichloromethane (chloroform) (2)	23.18	12.81	14.37	12.91
trichloromethane (chloroform) (3)	21.92	17.95	11.96	3.88

Table A.4. (Cont'd)

trichloromethane (chloroform) (4)	22.55	15.38	13.16	8.40
tetrachloromethane (carbon tetrachloride) (1)	17.70	16.1-17.7	0.00	0.00
tetrachloromethane (carbon tetrachloride) (2)	21.49	11.32	15.52	9.64
tetrachloromethane (carbon tetrachloride) (3)	21.64	17.94	11.40	4.07
tetrachloromethane (carbon tetrachloride) (4)	21.56	14.63	13.46	6.85
<b>chloroethane (ethyl chloride) (1)</b>	17.40	16.30	-	-
<b>chloroethane (ethyl chloride) (2)</b>	22.54	14.96	8.57	14.51
chloroethane (ethyl chloride) (3)	17.42	15.55	7.50	2.34
chloroethane (ethyl chloride) (4)	19.98	15.26	8.04	8.42
1,2-dicloroethane (ethylene chloride) (1)	20.0-20.1	17.4-18.8	5.30	4.10
1,2-dicloroethane (ethylene chloride) (2)	23.69	15.21	11.77	13.82
1,2-dicloroethane (ethylene chloride) (3)	21.03	18.29	9.88	3.19
1,2-dicloroethane (ethylene chloride) (4)	22.36	16.75	10.83	8.50
1,1-dicloroethane (ethylidene chloride) (1)	18.30	16.80	-	-
1,1-dicloroethane (ethylidene chloride) (2)	20.85	13.43	10.77	11.75
1,1-dicloroethan <del>e</del> (ethylidene chloride) (3)	19.25	16.61	9.23	3.08
1,1-dicloroethane (ethylidene chloride) (4)	20.05	15.02	10.00	7.42
1,1,2-trichloroethane (1)	19.7-20.8	18.30	-	-
1,1,2-trichloroethane (2)	22.08	13.77	13.12	11.23
1,1,2-trichloroethane (3)	21.38	18.39	10.30	3.60
1,1,2-trichloroethane (4)	21.73	16.08	11.71	7.42
1,1,1-trichloroethane (1)	17.50	16.6-16.9	4.30	2.00
1,1,1-trichloroethane (2)	22.78	14.52	14.05	10.52
1,1,1-trichloroethane (3)	19.66	16.88	9.46	3.45

## Table A.4. (Cont'd)

1,1,1-trichloroethane (4)	21.22	15.70	11.76	6.99
1,1,2,2-trichloroethane (1)	19.9-20.2	18.70	-	-
1,1,2,2-trichloroethane (2)	20.99	12.54	14.18	9.08
1,1,2,2-trichloroethane (3)	21.78	18.68	10.48	3.91
1,1,2,2-trichloroethane (4)	21.39	15.61	12.33	6.49
1-chloropropane (n-propylchloride) (1)	17.40	15.90	-	-
1-chloropropane (n-propylchloride) (2)	21.32	15.41	7.69	12.57
1-chloropropane (n-propylchloride) (3)	17.28	15.98	6.23	2.13
1-chloropropane (n-propylchloride) (4)	19.30	15.69	6.96	7.35
1-chlorobutane (n-butyl chloride) (1)	17.30	16.1-16.3	5.50	2.10
1-chlorobutane (n-butyl chloride) (2)	20.60	15.68	7.09	11.33
1-chlorobutane (n-butyl chloride) (3)	16.99	16.04	5.25	1.95
1-chlorobutane (n-butyl chloride) (4)	18.80	15.86	6.17	6.64
chlorobenzene (1)	19.5-19.6	18.8-19.0	4.30	2.10
chlorobenzene (2)	21.41	17.18	9.34	8.73
chlorobenzene (3)	19.40	18.49	5.52	1.98
chlorobenzene (4)	20.40	17.83	7.43	5.36
bromobenzene (1)	21.70	20.50	5.50	4.10
bromobenzene (2)	21.09	17.85	9.67	5.70
bromobenzene (3)	18.93	18.90	1.05	0.00
bromobenzene (4)	20.01	18.38	5.36	2.85
1,1,2 trichloro-1,2,2- trifluoroethane (freon113) (1)	14.80	14.50	1.60	0.00
1,1,2 trichloro-1,2,2- trifluoroethane (freon113) (2)	41.06	30.65	18.73	19.89
1,1,2 trichloro-1,2,2- trifluoroethane (freon113) (3)	17.80	15.61	7.95	3.16
1,1,2 trichloro-1,2,2- trifluoroethane (freon113) (4)	29.43	23.13	13.34	11.53

Table A.4. (Cont'd)

Ethers				
ethoxyethane (diethyl ether) (1)	15.2-15.6	14.40	2.90	5.10
ethoxyethane (diethyl ether) (2)	20.55	15.02	5.82	12.76
ethoxyethane (diethyl ether) (3)	15.72	14.26	3.85	5.38
ethoxyethane (diethyl ether) (4)	18.13	14.64	4.83	9.07
1-propoxypropane (dipropyl ether) (1)	14.10	-	-	-
1-propoxypropane (dipropyl ether) (2)	19.64	15.32	5.06	11.20
1-propoxypropane (dipropyl ether) (3)	15.54	14.55	2.88	4.65
1-propoxypropane (dipropyl ether) (4)	17.59	14.93	3.97	7.93
2-isopropoxypropane (diisopropyl ether) (1)	14.40	13.70	-	-
2-isopropoxypropane (diisopropyl ether) (2)	18.59	14.87	5.06	9.95
2-isopropoxypropane (diisopropyl ether) (3)	14.81	13.79	2.84	4.62
2-isopropoxypropane (diisopropyl ether) (4)	16.70	14.33	3.95	7.28
1-butoxybutane (dibutyl ehter) (1)	14.5-15.9	15.20	-	-
1-butoxybutane (dibutyl ehter) (2)	19.13	15.37	4.50	10.47
1-butoxybutane (dibutyl ehter) (3)	15.87	15.12	2.36	4.21
1-butoxybutane (dibutyl ehter) (4)	17.50	15.24	3.43	7.34
dimethoxymethane (methylal) (1)	17.40	15.10	1.80	8.60
dimethoxymethane (methylal) (2)	26.21	16.99	7.59	18.45
dimethoxymethane (methylal) (3)	18.03	14.74	6.36	8.22
dimethoxymethane (methylal) (4)	22.12	15.86	6.98	13.34

Table A.4. (Cont'd)

methoxybenzene (anisole) (1)	19.5/20.3	17.80	4.10	6.80
methoxybenzene (anisole) (2)	22.90	17.31	9.39	11.68
methoxybenzene (anisole) (3)	22.75	21.81	3.82	5.25
methoxybenzene (anisole) (4)	22.83	19.56	6.60	8.47
2,2'-dichlorodiethyl ether (1)	21.1-21.2	17.2-18.3	9.00	3.10
2,2'-dichlorodiethyl ether (2)	22.67	15.27	11.13	12.52
2,2'-dichlorodiethyl ether (3)	20.10	17.77	7.47	5.70
2,2'-dichlorodiethyl ether (4)	21.38	16.52	9.30	9.11
1-chloro-2,3-epoxypropane (epichlorohydrin) (1)	21.90	19.00	10.20	3.70
1-chloro-2,3-epoxypropane (epichlorohydrin) (2)	26.60	16.85	10.02	17.97
1-chloro-2,3-epoxypropane (epichlorohydrin) (3)	18.47	14.92	8.67	6.58
1-chloro-2,3-epoxypropane (epichlorohydrin) (4)	22.53	15.89	9.35	12.28
Esters				
ethyl formate (1)	18.70	15.50	7.20	7.60
ethyl formate (2)	22.38	14.13	9.11	14.78
ethyl formate (3)	19.59	15.22	5.24	11.17
ethyl formate (4)	20.99	14.67	7.17	12.97
propyl formate (1)	19.60	15.00	-	-
propyl formate (2)	21.38	14.60	8.35	13.20
propyl formate (3)	18.79	15.24	4.30	10.11
propyl formate (4)	20.08	14.92	6.32	11.66
methyl acetate (1)	18.70	15.50	7.20	7.60
methyl acetate (2)	22.81	13.75	10.01	15.21
methyl acetate (3)	19.16	15.51	6.18	9.39
methyl acetate (4)	20.98	14.63	8.09	12.30
ethyl acetate (1)	18.60	15.20	5.30	9.20
ethyl acetate (2)	21.77	14.22	9.19	13.68
ethyl acetate (3)	18.22	15.34	5.01	8.46
ethyl acetate (4)	20.00	14.78	7.10	11.07
propyl acetate (1)	17.9-18.0	15.60	-	-
propyl acetate (2)	21.06	14.53	8.52	12.65

Table A.4. (Cont'd)

propyl acetate (3)	17.75	15.37	4.26	7.80
propyl acetate (4)	19.41	14.95	6.39	10.22
isopropyl acetate (1)	17.2-17.6	14.4-14.9	4.50	8.20
isopropyl acetate (2)	20.46	14.25	8.52	11.96
isopropyl acetate (3)	17.21	14.79	4.19	7.74
isopropyl acetate (4)	18.83	14.52	6.36	9.85
butyl acetate (1)	17.3-17.4	15.70	3.70	6.40
butyl acetate (2)	20.55	14.71	7.96	11.93
butyl acetate (3)	17.52	15.49	3.72	7.29
butyl acetate (4)	19.03	15.10	5.84	9.61
isobutyl acetate (1)	17.0/172	15.10	3.70	7.60
isobutyl acetate (2)	20.83	14.74	8.19	12.22
isobutyl acetate (3)	16.08	13.87	3.67	7.24
isobutyl acetate (4)	18.45	14.31	5.93	9.73
amyl acetate (1)	17.10	15.30	3.10	7.00
amyl acetate (2)	20.16	14.82	7.48	11.43
amyl acetate (3)	17.29	15.53	3.29	6.86
amyl acetate (4)	18.72	15.17	5.39	9.15
isoamyl acetate (1)	17.00	15.30	3.10	7.00
isoamyl acetate (2)	19.70	14.63	7.49	10.86
isoamyl acetate (3)	16.91	15.12	3.26	6.83
isoamyl acetate (4)	18.30	14.87	5.38	8.84
ethyl lactate (1)	20.5/21.6	16.00	7.60	12.50
ethyl lactate (2)	24.53	12.56	11.07	17.93
ethyl lactate (3)	22.74	15.62	6.11	15.35
ethyl lactate (4)	23.63	14.09	8.59	16.64
butyl lacetate (1)	19.2/19.8	15.70	6.60	10.20
butyl lacetate (2)	22.87	13.05	9.81	16.02
butyl lacetate (3)	20.94	15.43	4.64	13.37
butyl lacetate (4)	21.90	14.24	7.22	14.69
2-ethoxyethyl acetate (cellosolve acetate) (1)	19.70	15.90	4.70	10.60
2-ethoxyethyl acetate (cellosolve acetate) (2)	22.45	15.13	8.83	14.05
2-ethoxyethyl acetate (cellosolve acetate) (3)	18.53	15.76	4.66	8.58
2-ethoxyethyl acetate (cellosolve acetate) (4)	20.49	15.44	6.74	11.31

Table A.4. (Cont'd)

diethylene glycol, monothyl ether, acetate (carbitol acetate) (1)	17.4/19.3	16.20	-	-
diethylene glycol, monothyl ether, acetate (carbitol acetate) (2)	21.21	14.11	8.97	13.04
diethylene glycol, monothyl ether, acetate (carbitol acetate) (3)	18.61	15.92	4.29	8.63
diethylene glycol, monothyl ether, acetate (carbitol acetate) (4)	19.91	15.02	6.63	10.84
Ketones and aldehyde	<b>3</b> S	<b>.</b>		
2-propanone (acetone) (1)	20.0-20.5	15.50	10.40	7.00
2-propanone (acetone) (2)	23.54	13.55	10.37	16.22
2-propanone (acetone) (3)	19.36	15.41	10.50	5.22
2-propanone (acetone) (4)	21.45	14.48	10.43	10.72
2-butanone (methyl ethyl ketone) (1)	19.00	15.90	9.00	5.10
2-butanone (methyl ethyl ketone) (2)	22.26	14.11	9.47	14.39
2-butanone (methyl ethyl ketone) (3)	18.45	15.63	8.60	4.73
2-butanone (methyl ethyl ketone) (4)	20.36	14.87	9.03	9.56
3-pentanone (diethyl ketone) (1)	18.0/18.1	15.70	-	-
3-pentanone (diethyl ketone) (2)	21.42	14.46	8.75	13.17
3-pentanone (diethyl ketone) (3)	17.96	15.82	7.30	4.35
3-pentanone (diethyl ketone) (4)	19.69	15.14	8.02	8.76
2-pentanone (methyl propyl ketone) (1)	18.30	15.80	-	-
2-pentanone (methyl propyl ketone) (2)	21.42	14.46	8.75	13.17
2-pentanone (methyl propyl ketone) (3)	17.87	15.74	7.26	4.34
2-pentanone (methyl propyl ketone) (4)	19.65	15.10	8.00	8.75

Table A.4. (Cont'd)

2-hexanone (methyl butyl ketone) (1)	17.4/17.7	15.90	-	-
2-hexanone (methyl butyl ketone) (2)	20.82	14.68	8.15	12.32
2-hexanone (methyl butyl ketone) (3)	17.31	15.65	6.21	4.02
2-hexanone (methyl butyl ketone) (4)	19.07	15.16	7.18	8.17
4-methyl-2-pentanone (mehtyl isobutyl ketone) (1)	17.2/17.5	15.30	6.10	4.10
4-methyl-2-pentanone (mehtyl isobutyl ketone) (2)	20.27	14.43	8.15	11.68
4-methyl-2-pentanone (mehtyl isobutyl ketone) (3)	16.90	15.21	6.17	4.00
4-methyl-2-pentanone (mehtyl isobutyl ketone) (4)	18.58	14.82	7.16	7.84
2,6-dimetyl-4-heptanone (diisobutl ketone) (1)	16.0/16.7	15.90	3.70	4.10
2,6-dimetyl-4-heptanone (diisobutl ketone) (2)	18.99	14.61	6.84	10.02
2,6-dimetyl-4-heptanone (diisobutl ketone) (3)	16.10	15.13	4.36	3.37
2,6-dimetyl-4-heptanone (diisobutl ketone) (4)	17.55	14.87	5.60	6.69
4-methyl-3-penten-2-one (mesity oxide) (1)	18.4/18.8	16.30	7.20	6.10
4-methyl-3-penten-2-one (mesity oxide) (2)	20.99	14.59	9.59	11.65
4-methyl-3-penten-2-one (mesity oxide) (3)	17.70	15.84	6.70	4.17
4-methyl-3-penten-2-one (mesity oxide) (4)	19.34	15.21	8.14	7.91
methyl penyl ketone (acetophenone) (1)	19.80	17.5-18.5	8.60	3.70
methyl penyl ketone (acetophenone) (2)	22.27	15.54	11.59	10.96
methyl penyl ketone (acetophenone) (3)	19.88	18.28	6.64	4.13
methyl penyl ketone (acetophenone) (4)	21.07	16.91	9.12	7.55
ethanal (acetaldehyde) (1)	20.20	14.70	8.00	11.30
ethanal (acetaldehyde) (2)	26.32	12.80	11.59	19.86

Table	A.4.	(Cont'd)

ethanal (acetaldehyde) (3)	23.08	15.82	14.22	8.94
ethanal (acetaldehyde) (4)	24.70	14.31	12.91	14.40
butanal (butyraldehyde) (1)	17.10	14.70	5.30	7.00
butanal (butyraldehyde) (2)	22.63	14.13	9.46	14.93
butanal (butyraldehyde) (3)	19.89	16.20	9.07	7.14
butanal (butyraldehyde) (4)	21.26	15.17	9.26	11.03
benxenecarbonal (benzaldehyde) (1)	19.2-21.3	18.2-18.7	8.60	5.30
benxenecarbonal (benzaldehyde) (2)	23.34	15.30	12.45	12.47
benxenecarbonal (benzaldehyde) (3)	21.49	18.80	7.99	6.67
benxenecarbonal (benzaldehyde) (4)	22.41	17.05	10.22	9.57
Alcohols	·····	······································	· · · · · · · · · · · · · · · · · · ·	
methanol (1)	29.2-29.7	15.20	12.30	22.30
methanol (2)	33.09	12.17	11.13	28.69
methanol (3)	29.83	15.57	12.36	22.23
methanol (4)	31.46	13.87	11.74	25.46
ethanol (1)	26.0-26.5	15.80	8.80	19.50
ethanol (2)	27.95	12.74	9.63	22.93
ethanol (3)	25.56	15.41	8.56	18.51
ethanol (4)	26.75	14.08	9.10	20.72
1-propanol (1)	24.4-24.5	15.90	6.80	17.40
1-propanol (2)	25.33	13.15	8.66	19.84
1-propanol (3)	23.07	15.19	6.49	16.11
1-propanol (3)	23.61	15.65	6.69	16.36
1-propanol (4)	24.00	14.66	7.28	17.44
2-propanol (isopropyl alcohol) (1)	23.60	15.80	6.10	16.40
2-propanol (isopropyl alcohol) (2)	24.40	12.74	8.62	18.94
2-propanol (isopropyl alcohol) (3)	22.84	14.76	6.53	16.16
2-propanol (isopropyl alcohol) (4)	23.62	13.75	7.58	17.55
1-butanol (1)	23.1/23.3	16.00	5.70	15.80
1-butanol (2)	23.75	13.44	7.94	17.90
1-butanol (3)	22.27	15.74	5.46	14.78
Table A.4. (Cont'd)

1-butanol (4)	23.01	14.59	6.70	16.34
2-methyl-1-propanol	22 90	15 20	5 70	16.00
(isobutyl alcohol) (1)		10.20	0.70	
2-methyl-1-propanol	23.00	13.12	7.92	17.16
(isobutyl alcohol) (2)				
2-methyl-1-propanol	21.78	15.13	5.40	14.70
2-methyl-1-propanol				· · · · · · · · · · · · · · · · · · ·
(isobutyl alcohol) (4)	22.39	14.12	6.66	15.93
2-butanol	00.00	45.00		
(secbutyl alcohol) (1)	22.20	15.80	-	-
2-butanol	23.00	13 12	7 92	17 16
(secbutyl alcohol) (2)	20.00	10.12	1.02	
2-butanol	21.92	15.26	5.45	14.77
(SecDutyl alconol) (3)	····			
(sec -hutvl alcohol) (4)	22.46	14.19	6.69	15.96
1-pentanol (amvl alcohol) (1)	21.70	16.00	4.50	13.90
1-pentanol (amyl alcohol) (2)	22.69	13.64	7.38	16.56
1-pentanol (amyl alcohol) (3)	21.34	15.79	4.62	13.59
1-pentanol (amyl alcohol) (4)	22.01	14.72	6.00	15.07
cyclohexanol (1)	22.4-23.3	17.40	4.10	13.50
cyclohexanol (2)	22.82	13.52	7.68	16.70
cyclohexanol (3)	22.89	17.58	4.80	13.86
cyclohexanol (4)	22.85	15.55	6.24	15.28
phenol (1)	24.10	18.00	5.90	14.90
phenol (2)	25.45	14.12	11.48	17.79
phenol (3)	24.71	18.68	5.83	15.09
phenol (4)	25.08	16.40	8.66	16.44
3-methylphenol	22 70	18 1-19 4	5,10	12.90
(m-cresol) (1)				
3-methylphenol	24.28	14.38	10.41	16.55
(M-cresol) (2)			· · · · · · · · · · · · · · · · · · ·	
o-meuryiphenoi (m-crosol) (3)	23.35	18.17	4.90	13.83
3-methylphenol				
(m-cresol) (4)	23.81	16.28	7.65	15.19
phenyl methanol	23.80	18.40	630	13 70
(benzyl alcohol) (1)	20.00	10.40	0.00	10.70
phenyl methanol	24.20	14.34	10.61	16.35
(benzyl alcohol) (2)				

Table A.4. (Cont'd)

phenyl methanol (benzyl alcohol) (3)	23.73	18.55	4.97	13.94
phenyl methanol (benzyl alcohol) (4)	23.96	16.44	7.79	15.14
1,2-ethanediol (ethylene glycol) (1)	29.1-33.4	16.90	11.10	26.00
1,2-ethanediol (ethylene glycol) (2)	34.06	11.21	12.22	29.76
1,2-ethanediol (ethylene glycol) (3)	34.18	17.15	12.63	26.73
1,2-ethanediol (ethylene glycol) (3)	34.33	17.26	12.71	26.82
1,2-ethanediol (ethylene glycol) (4)	34.19	15.21	12.52	27.77
1,2-propanediol (propylene glycol) (1)	30.30	16.90	9.40	23.30
1,2-propanediol (propylene glycol) (2)	29.36	11.28	10.97	24.79
1,2-propanedioł (propylene glycol) (3)	30.08	16.26	9.66	23.38
1,2-propanedioł (propylene glycol) (4)	29.72	13.77	10.32	24.09
1,3-butanediol (butylene glycol) (1)	29.00	16.60	10.00	21.50
1,3-butanediol (butylene glycol) (2)	27.12	11.68	10.11	22.29
1,3-butanediol (butylene glycol) (3)	27.81	16.28	7.89	21.12
1,3-butanediol (butylene glycol) (4)	27.46	13.98	9.00	21.70
1,2,3-propanetiol (glycerol) (1)	33.8-43.2	17.30	12.10	29.30
1,2,3-propanetiol (glycerol) (2)	33.69	10.24	12.40	29.60
1,2,3-propanetiol (glycerol) (3)	35.41	17.10	11.85	28.65
1,2,3-propanetiol (glycerol) (4)	34.55	13.67	12.13	29.13
2-methoxyethanol (methyl cellosolve) (1)	24.70	16.20	9.20	16.40
2-methoxyethanol (methyl cellosolve) (2)	26.37	13.53	9.26	20.66

Table A.4. (Cont'd)

2-methoxyethanol (methyl cellosolve) (3)	24.86	16.12	8.13	17.09	
2-methoxyethanol (methyl cellosolve) (4)	25.62	14.82	8.69	18.87	
2-ethoxyehtanol (ethyl cellosolve) (1)	24.30	16.10	9.20	14.30	
2-ethoxyehtanol (ethyl cellosolve) (2)	24.71	13.09	9.24	18.81	
2-ethoxyehtanol (ethyl cellosolve) (3)	23.10	15.89	6.61	15.41	
2-ethoxyehtanol (ethyl cellosolve) (4)	23.90	14.49	7.92	17.11	
2-butoxyethanol (butyl cellosolve) (1)	21.00	15.90	6.40	12.10	
2-butoxyethanol (butyl cellosolve) (2)	23.81	14.24	7.81	17.41	
2-butoxyethanol (butyl cellosolve) (3)	21.27	15.89	4.89	13.26	
2-butoxyethanol (butyl cellosolve) (4)	22.54	15.07	6.35	15.33	
4-hydroxy-4-methyl-2- pentanone (diacetone alcohol) (1)	18.8-20.8	15.7	8.20	10.90	
4-hydroxy-4-methyl-2- pentanone (diacetone alcohol) (2)	22.78	12.38	10.04	16.28	
4-hydroxy-4-methyl-2- pentanone (diacetone alcohol) (3)	21.98	15.83	7.41	13.33	
4-hydroxy-4-methyl-2- pentanone (diacetone alcohol) (4)	22.38	14.10	8.73	14.80	
Acids					
formic acid (1)	24.9-25.0	14.3-15.3	11.90	16.60	
formic acid (2)	40.12	9.59	16.46	35.30	
formic acid (3)	39.99	18.02	25.00	25.48	
formic acid (4)	40.06	13.81	20.73	30.39	
acetic acid (1)	18.8-21.4	14.5-16.6	8.00	13.50	
acetic acid (2)	24.04	13.39	10.09	17.23	
acetic acid (3)	22.45	16.60	7.34	13.22	
acetic acid (4)	23.24	14.99	8.71	15.22	

Table A.4. (Cont'd)

butyric acid (1)	18.8-23.1	14.9-16.3	4.10	10.60
butyric acid (2)	21.38	14.60	8.35	13.20
butyric acid (3)	19.82	16.22	4.57	10.43
butyric acid	20.60	15.41	6.46	11.82
acetic acid, anhydride (1)	21.3-22.2	15.4-16.0	11.10	9.60
acetic acid, anhydride (2)	24.30	11.88	13.61	16.26
acetic acid, anhydride (3)	22.02	16.11	12.30	8.61
acetic acid, anhydride (4)	23.16	13.99	12.95	12.44
Nitrogen compounds		• • • • • • • • • • • • • • • • • • •	▲	<b>.</b>
1-aminopropane (propylamine) (1)	19.70	17.00	4.90	8.60
1-aminopropane (propylamine) (2)	22.72	14.49	9.33	14.80
1-aminopropa <b>ne</b> (propylamine) (3)	18.16	15.08	0.00	10.11
1-aminopropane (propylamine) (4)	20.44	14.79	4.67	12.46
diethylamine (1)	16.30	14.90	2.30	6.10
diethylamine (2)	21.01	14.64	7.45	13.10
diethylamine (3)	15.99	14.89	2.03	5.47
diethylamine (4)	18.50	14.76	4.74	9.29
aminobenzene (aniline) (1)	22.6-24.2	19.50	5.10	10.20
aminobenzene (aniline) (2)	23.46	15.76	12.65	11.91
aminobenzene (aniline) (3)	21.12	18.77	1.21	9.60
aminobenzene (aniline) (4)	22.29	17.26	6.93	10.76
2-aminoethanol (ethanolamine) (1)	31.70	17.10	15.60	21.30
2-aminoethanol (ethanolamine) (2)	30.03	11.96	12.90	24.33
2-aminoethanol (ethanolamine) (3)	28.94	17.17	8.33	21.76
2-aminoethanol (ethanolamine) (4)	29.48	14.56	10.62	23.04
nitromethane (1)	25.1-26.0	15.8-16.4	18.80	5.10
nitromethane (2)	24.98	11.86	11.26	18.89
nitromethane (3)	26.65	17.03	19.81	5.27
nitromethane (4)	25.82	14.45	15.53	12.08
nitroethane (1)	22.70	16.0-16.6	15.60	4.50
nitroethane (2)	23.08	12.81	10.14	16.30

Table A.4. (Cont'd)

nitroethane (3)	22.89	16.68	14.99	4.58	
nitroethane (4)	22.98	14.74	12.57	10.44	
nitrobenzene (1)	20.5-21.9	17.6-19.9	12.30	4.10	
nitrobenzene (2)	22.78	14.60	12.17	12.55	
nitrobenzene (3)	21.95	18.88	10.52	3.83	
nitrobenzene (4)	22.36	16.74	11.35	8.19	
ethanenitrile (acetonitrile) (1)	24.1-24.5	15.4-16.2	18.00	6.10	
ethanenitrile (acetonitrile) (2)	29.24	12.27	13.71	22.72	
ethanenitrile (acetonitrile) (3)	27.40	16.21	20.98	6.91	
ethanenitrile (acetonitrile) (4)	28.32	14.24	17.35	14.81	
methanamide (formamide) (1)	36.70	17.20	26.20	19.00	
methanamide (formamide) (2)	33.28	10.22	17.37	26.48	
methanamide (formamide) (3)	32.97	18.88	20.14	18.02	
methanamide (formamide) (4)	33.12	14.55	18.76	22.25	
dimethylformamide (1)	24.90	17.40	13.70	11.30	
dimethylformamide (2)	24.13	14.68	11.51	15.31	
dimethylformamide (3)	21.33	14.30	12.17	10.11	
dimethylformamide (4)	22.73	14.49	11.84	12.71	
dimethylacetamide (1)	22.1/22.8	16.80	11.50	10.20	
dimethylacetamide (2)	21.24	16.78	1.10	12.98	
dimethylacetamide (3)	22.62	16.77	11.42	10.01	
dimethylacetamide (4)	21.93	16.77	6.26	11.49	
1,1,3,3-tetramethylurea (1)	21.70	16.80	8.20	11.10	
1,1,3,3-tetramethylurea (2)	18.86	15.34	3.76	10.30	
1,1,3,3-tetramethylurea (3)	25.80	19.10	11.42	13.05	
1,1,3,3-tetramethylurea (4)	22.33	17.22	7.59	11.67	
Sulpher compounds					
dimethyl sulphide (1)	18.40	17.60	-	-	
dimethyl sulphide (2)	21.47	13.96	9.72	13.10	
dimethyl sulphide (3)	17.43	17.43	0.00	0.00	
dimethyl sulphide (4)	19.45	15.70	4.86	6.55	
diethyl sulphide (1)	17.30	16.0-16.9	3.10	2.10	
diethyl sulphide (2)	20.07	15.02	8.24	10.44	
diethyl sulphide (3)	16.89	16.89	0.00	0.00	

Tab	le /	4.4.	(Con	ťd)
			( : :	

diethyl sulphide (4)	18.48	15.96	4.12	5.22
water (1)	47.9-48.1	12.3-14.3	31.30	34.20
Polymer				
Polyethylene (2)	18.01	18.01	0.00	0.00
Polyethylene (3)	17.74	17.74	0.00	0.00
Polyehtylene (4)	17.88	17.88	0.00	0.00
Polypropylene (2)	16.69	16.69	0.00	0.00
Polypropylene (3)	15.55	15.55	0.00	0.00
Polypropylene (4)	16.12	16.12	0.00	0.00
Polystyrene (2)	20.83	17.82	7.58	7.70
Polystyrene (3)	17.99	17.95	1.11	0.00
Polystyrene (4)	19.41	17.88	4.34	3.85
Polyvinyl Chloride (2)	20.33	15.44	11.26	6.95
Polyvinyl Chloride (3)	21.72	17.73	12.19	2.98
Polyvinyl Chloride (4)	21.03	16.58	11.72	4.96
Polyvinylidene Dichloride (2)	18.96	10.74	11.16	10.93
Polyvinylidene Dichloride (3)	23.35	18.82	13.31	3.70
Polyvinylidene Dichloride (4)	21.15	14.78	12.24	7.31
Polyvinyl Alcohol (2)	28.79	14.89	16.34	18.45
Polyvinyl Alcohol (3)	32.12	16.00	14.29	23.90
Polyvinyl Alcohol (4)	30.45	15.44	15.31	21.18
Polyethylene Terephthalate (2)	24.50	15.62	13.87	12.81
Polyethylene Terephthalate (3)	21.34	17.99	6.96	9.13
Polyethylene Terephthalate (4)	22.92	16.80	10.42	10.97
Nylon 6 (2)	22.10	15.70	12.31	9.51
Nylon 6 (3)	20.11	17.24	7.64	6.99
Nylon 6 (4)	21.10	16.47	9.98	8.25

- (1) Van Krevelen, 1990
   (2) Hoy method
   (3) Hoftyzer and Van Krevelen method
   (4) Average values

#### APPENDIX B

### STANDARD CALIBRATION CURVE FOR THERMAL DESORPTION

Table B.1. Calibration data for ethyl acetate in acetonitrile with 1  $\mu$ l injection volume by TD-GC

Solution concentration	Total Quantity	Area Response
(ppm)	(g)	(AU)
0	0	0
10	9.02E-09	114351
20	1.80E-08	257164
40	3.61E-08	558258
60	5.41E-08	762270



Figure B.1. Standard calibration curve of ethyl acetate in acetonitrile by TD-GC

Solution concentration	Total Quantity	Area Response
(ppm)	(g)	(AU)
0	0	0
6	5.04E-09	194602
10	8.40E-09	296995
20	1.68E-08	514685
40	3.36E-08	971624

Table B.2. Calibration data for limonene in acetonitrile with 1  $\mu$ l injection volume by TD-GC



Figure B.2. Standard calibration curve of limonene in acetonitrile by TD-GC

Table B.3. Calibration data for methyl ethyl ketone in xylene with 1  $\mu$ l injection volume by TD-GC

Solution concentration	Total Quantity	Area Response
(ppm)	(g)	(AU)
0	0	0
10	8.03E-09	211129
20	1.61E-08	309065
40	3.21E-08	477840
100	8.03E-08	1180606



Figure B.3. Standard calibration curve of methyl ethyl ketone in xylene by TD-GC

Solution concentration	Total Quantity	Area Response
(ppm)	(g)	(AU)
0	0	0
10	8.70E-09	280378
20	1.74E-08	548962
40	3.48E-08	910359
60	5.22E-08	1353807

Table B.4. Calibration data for toluene in acetonitrile with 1  $\mu l$  injection volume by TD-GC



Figure B.4. Standard calibration curve of toluene in acetonitrile by TD-GC

#### **APPENDIX C**

#### STANDARD CALIBRATION CURVE FOR SOLID PHASE MICROEXTRACTION

Total Quantity	Area Response
(g)	(AU)
0	0
9.02E-09	253222
1.80E-08	384728
3.61E-08	580711
5.41E-08	774359



Figure C.1. Standard calibration curve of ethyl acetate in water by SPME-GC

Total Quantity	Area Response	
(g)	(AU)	
0	0	
3.11E-09	172709	
6.22E-09	286079	
1.24E-08	638591	
1.40E-08	715777	

Table C.2. Calibration data for limonene in water by SPME-GC



Figure C.2. Standard calibration curve of limonene in water by SPME-GC

Total Quantity		
(9)	(A0)	
9.035.06	25024	
	129107	
2 215-05	130107	
	670007	
0.032-05	0/090/	

Table C.3. Calibration data for methyl ethyl ketone in water by SPME-GC



Figure B.3. Standard calibration curve of methyl ethyl ketone in water by SPME-GC

Total Quantity (g)	Area Response (AU)	
0	0	
1.91E-06	909858	
3.83E-06	1829625	
7.66E-06	3441474	
9.57E-06	4478939	

Table C.4. Calibration data for toluene in water by SPME-GC



Table C.4. Standard calibration curve of toluene in water by SPME-GC

## APPENDIX D

# CALCULATION FOR THE PARTITION COEFFICIENT BY TS/TD-GC METHOD

Concentration of sorbate in polymer  $[C_p]$  was calculated by the following equation;

$$[C_p] = \frac{m_a}{m_p}$$

Where  $m_{e}$  is mass of sorbate in polymer and  $m_{p}$  is the mass of polymer disks respectively.

### APPENDIX E

## CALCULATION FOR THE PARTITION COEFFICIENT BY TS/TD-GC METHOD

Concentration of sorbate in polymer  $[C_p]$  was calculated by the following equation;

$$[C_p] = \frac{(C_{a,i} - C_{a,f})m_a}{m_p}$$

Where  $C_{a,i}$  is initial concentration of sorbate in the aqueous phase  $C_{a,f}$  is final concentration of sorbate in the aqueous phase  $m_a$  is mass of water contained in the vial  $m_p$  is mass of the polymer disks

## APPENDIX F

# STRUCTURE AND DETAILS OF SORBATES AND POLYMER

# Table F. Structure and details of sorbates and polymer

	Structure	Molecular weight	Density (g/cm <sup>3</sup> )
LDPE	R-CH <sub>2</sub> -CH <sub>2</sub> -R	28.1	0.923
Limonene	CH <sub>3</sub> CH <sub>3</sub> -C=CH <sub>2</sub> H	136.24	0.840
Ethyl acetate	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>3</sub> II O	88.10	0.901
Methyl ethyl ketone	CH <sub>3</sub> CCH <sub>2</sub> CH <sub>3</sub> II O	72.10	0.805
Toluene	CH3	92.13	0.867

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