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By

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ABSTRACT

DIFFUSION OF FLAVOR COMPONENTS IN CONCENTRATED MALTO-DEXTRIN SOLUTIONS

by

Edwin Mark Oosting

The diffusivities and the vapor-liquid equilibrium coefficients of the flavor components, 1-hexanol and 2-butanone, were measured in concentrated malto-dextrin solutions by newly developed techniques. Accurate determination of these parameters required complete material balances of the two phases and control of the water concentration in the measurement cell. The diffusivities of the flavor components through malto-dextrin solutions were correlated with water content using the Stokes-Einstein group, $D\mu/T$. The correlation took the form, $D\mu/T = K'' W^{\beta}$, where K" is an adjustable constant, W is the water weight fraction, and $\beta = -4$.

Measurements were also made of the vapor-liquid partition coefficients and the activity coefficients of 1-hexanol and 2-butanone in malto-dextrin solutions. The activity coefficients were shown to be strong functions of temperature and solids concentrations.

Viscosity data were obtained for the malto-dextrin solutions for use in correlating the diffusion coefficients.

The solution viscosities were shown to correlate with water content as $\mu = AW^{\beta}$, where A and B are temperature dependent constants.

To: Lynda, Kelli and Mark

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NOMENCLATURE

Symbol	Explanation	Units
English Letters:		
A	Slab surface area	cm^2
A	Constant in equation 25	cm^2/sec
A	Constant for equation 41	g/ml
A	Constant for equations 9, 42, and 107	unitless
A_D	Diffusant gas chromatograph peak area	unitless
A_{IS}	Internal standard gas chromatograph peak area	unitless
A_{STD}	Standard gas chromatograph peak area	unitless
A_2	Constant for equation 108	unitless
A_3	Constant for equation 109	unitless
A_4	Constant for equation 110	unitless
B	Constant in equation 25	$(g/ml)^{1/2}$
B	Constant for equation 41	g/ml
B	Constant for equations 9, 42, and 107	unitless
B_2	Constant for equation 108	unitless
B_3	Constant for equation 109	unitless
B_4	Constant for equation 110	unitless
Bi_{WO}	Biot Number for mass transfer	unitless
c	Concentration	g/ml

Symbol	Explanation	Units
English Letters:		
C	Constant for equations 9 and 43	unitless
C'	Constant in equation 16	unitless
C_i	Concentration of component i	g/ml
C_L	Liquid phase diffusant concentration	g/ml
C_{STD}	Standard concentration	g/ml
C_V	Vapor phase diffusant concentration	g/ml
C_W	Water concentration	g/ml
C_1	Concentration of component 1	g/ml
ΔC_1	Concentration difference of component 1 at t>0	g/ml
$\Delta C_1{}^0$	Concentration difference of component 1 at t=0	g/ml
C_2	Concentration of component 2	g/ml
ΔC_2	Concentration difference of component 2 at t>0	g/ml
$\Delta C_2{}^0$	Concentration difference of component 2 at t=0	g/ml
D	Constant for equations 4 and 44	unitless
D	Diffusivity	cm^2/sec
D_A	Diffusivity of component A	cm^2/sec
D_{AB}	Diffusivity of component A in component B	cm^2/sec
D_W	Diffusivity of water	cm^2/sec

Symbol	Explanation	Units
D_0	Frequency factor for diffusivity	cm^2/sec
D_{11}	Diffusivity of component 1 due to a concentration gradient in component 1	cm^2/sec
D_{11}^0	Diffusivity of component 1 in water	cm^2/sec
D_{12}	Diffusivity of component 1 due to a concentration gradient in component 2, cross diffusion coefficient	cm^2/sec
D_{21}	Diffusivity of component 2 due to a concentration gradient in component 1, cross diffusion coefficient	cm^2/sec
D_{22}	Diffusivity of component 2 due to a concentration gradient in component 2	cm^2/sec
E	Constant for equations 9 and 43	unitless
E_{DA}	Activation energy for diffusion of component A in water	Kcal/g mole
E_{DW}	Activation energy for self-diffusion of water	Kcal/g mole
E_{μ}	Activation energy for viscosity	Kcal/g mole
$E_{\mu W}$	Activation energy for viscosity of water	Kcal/g mole
F	Constant for equations 9 and 44	unitless
ΔH_B	Heat of vaporization of solvent	Kcal/g mole
ΔH_W	Heat of vaporization of water	Kcal/g mole
J_1	Flux of component 1	g/cm^2 sec

Symbol	Explanation	Units
English Letters (cont.):		
J_2	Flux of component 2	g/cm^2 sec
K	Boltzmann constant	g cm^2/sec^2 °K
K	Constant in equations 17, 24 and 100	unitless
K	Vapor-liquid equilibrium coefficient, concentration based	unitless
K'	Constant for equation 55	unitless
K"	Constant for equations 57 and 105	unitless
$\tilde{K}$	Vapor-liquid equilibrium coefficient, mole fraction based	unitless
k_A'	Gas phase mass transfer coefficient	cm/sec
K_B	Base ionization constant	unitless
k_C	Gas phase mass transfer coefficient	cm/sec
k_{eq}	Vapor-liquid concentration ratio at long time	unitless
k_L	Liquid phase mass transfer coefficient	cm/sec
K_L	Overall mass transfer coefficient	cm/sec
k_t	Vapor-liquid concentration ratio at short time	unitless
K_{WO}	Vapor-liquid equilibrium coefficient	unitless
l	Slab thickness	cm
M_B	Average molecular weight of solution	g/g mole

Symbol	Explanation	Units
English Letters (cont.):		
M_D	Diffusant molecular weight	g/g mole
M_S	Molecular weight of malto-dextrin	g/g mole
M_t	Mass of solute at time t	g
M_W	Molecular weight of water	g/g mole
M_∞	Mass of solute as t approaches infinity	g
N	Avogodro's Number	unitless
n	Running index	unitless
n_{DL}	Diffusant liquid molar concentration	g mole/ml
n_{DV}	Diffusant vapor molar concentration	g mole/ml
n_{SL}	Malto-dextrin liquid molar concentration	g mole/ml
n_{TL}	Total liquid molar concentration	g mole/ml
n_{TV}	Total vapor molar concentration	g mole/ml
n_{WL}	Water liquid molar concentration	g mole/ml
n_1	Number of carbon atoms in solute molecule	unitless
n_2	Number of carbon atoms in solvent molecule	unitless
P	Total absolute pressure	Torr
P^{sat}	Saturated vapor pressure	Torr
P_i^{sat}	Saturated vapor pressure of component i	Torr
q_n	Non-zero positive roots of equation 37	unitless

Symbol	Explanation	Units
English Letters (cont.):		
R	Ideal gas law constant	Kcal/g mole °K
R	Ideal gas law constant	ml Torr/g mole °K
r	Linear regression correlation coefficient	unitless
R_A	Molecular radius of component A	cm
R_S	Solution deflection reading	unitless
R_{STD}	Standard deflection reading	unitless
S	Solids weight fraction	unitless
S	Solubility	g/ml
S_T	Total solubility	g/ml
T	Absolute temperature	°K
t	Time or flow time	sec
T	Dimensionless time	unitless
t_W	Water flow time	sec
U	Percent uptake	unitless
V_A	Molar volume of component A	ml/g mole
V_B	Molar volume of component B	ml/g mole
V_L	Liquid volume	ml
V_S	Sample volume	ml
V_S	Solids volume	ml
V_{STD}	Standard volume	ml
V_V	Vapor volume	ml
V_W	Water volume	ml
W	Water weight fraction	unitless
W_D	Diffusant weight	g

Symbol	Explanation	Units
English Letters (cont.):		
W_{IS}	Internal standard weight	g
W_S	Sample weight	g
x	Distance	cm
x	Diffusant liquid phase mole fraction	unitless
x_i	Saturated liquid mole fraction of component i	unitless
X_B	Association parameter	unitless
y	Diffusant vapor phase mole fraction	unitless
Greek Letters:		
α	Vapor-liquid mass ratio	unitless
β	Cell constant	cm^{-2}
β	Constant for equation 55	unitless
β	Constant for equation 57	unitless
γ	Activity coefficient	unitless
γ_i	Activity coefficient of component i	unitless
γ_i^∞	Activity coefficient of component i at infinite dilution	unitless
γ_1^∞	Activity coefficient for solute at infinite dilution	unitless
γ_0	Activity coefficient of solute in water	unitless
μ	Viscosity	centipoise
μ_B	Viscosity of component B	centipoise
μ_R	Relative viscosity	unitless

Symbol	Explanation	Units
Greek Letters (cont.):		
μ_S	Viscosity of solution	centipoise
μ_{STD}	Viscosity of standard	centipoise
μ_W	Viscosity of water	centipoise
μ_0	Frequency factor for viscosity	centipoise
$[\mu]$	Intrinsic viscosity	unitless
ρ	Density	g/ml
σ_{CL}	Standard deviation of C_L	g/ml
σ_{CV}	Standard deviation of C_V	g/ml
σ_K	Standard deviation of K	unitless
ϕ	Solids volume fraction	unitless
Subscripts:		
STD	Standard solution	

INTRODUCTION

As the cost of energy rises, food storage systems requiring a minimum of energy are being sought. One of the oldest and most widely used methods of food preparation for storage is drying. Bomben, et al. (1973), estimated food concentration costs in dollars per 1000 Kg of water removed for liquid foods based on 7,500 hours per year at a water removal rate of 150 to 1000 Kg per hour. Freeze drying was the most expensive, costing between $150 and $200 per 1000 Kg of water removed. The least expensive were spray drying at $15 to $50 per 1000 Kg water, reverse osmosis at $10 to $15 per 1000 Kg water, freeze concentration at $8 to $15 per 1000 Kg water, and double effect evaporation with aroma recovery at $6 to $15 per 1000 Kg water. Reverse osmosis and double effect evaporation still require spray or freeze drying to make a dry product. Spray drying is a fairly inexpensive method of drying and is applicable to most liquid foods.

Perhaps the major disadvantage of spray drying as compared to freeze drying is the loss of volatile flavor components. Loss of flavors in the spray drying process can reduce the acceptability of the dried food. Flavor loss can be controlled if the basic mechanisms of spray drying are understood. The mass transfer of flavors from drying droplets depends on the basic physio-chemical characteristics of volatile flavor components in the food system.

In spray dryers, volatile loss occurs in two zones. Near the nozzle, the liquid spreads into an extremely thin, turbulent film. The thin film provides a very large surface area for mass transfer. Depending on drying conditions, much of the water and volatile flavor components can be lost from the film. Farther away from the nozzle, droplets are formed. Evaporation occurs on the surface of the droplets. A zone of low water concentration (dry zone) occurs near the surface. The diffusivity of flavors in this dry zone is less than the diffusivity of water, so water diffuses faster than the flavors as the droplet dries. The important parameter in the drying of food droplets is the diffusivity of volatile flavor components in food solutions over the water concentration experienced in spray drying.

Two approaches may be taken to analyze a spray dryer. One may run experiments with a given spray dryer and vary parameters that he thinks are important. Correlations can then be used to identify how flavor component characteristics will vary with spray dryer operating conditions. Numerous experiments must be performed in order to characterize the spray dryer. Another approach to the problem would be to measure the physical and chemical characteristics of the flavor components and the liquid food. Using these characteristics and the spray drying conditions, one could model the behavior of the flavor components and the liquid food material in a spray dryer. The model could be tested with a minimum number of spray drying experiments.

Numerous experiments have been performed to measure the retention of flavor components during spray drying. These experiments have done much to increase our qualitative understanding of spray drying. General mathematical models have not been proposed or solved for spray dryers mainly due to the lack of diffusion and equilibrium data for flavor components in food systems. Furthermore, there are few correlations which can be used to predict diffusivities and solubilities over the range of conditions experienced by the droplets.

Carbohydrate solutions have been used as surrogates for food liquids in spray drying experiments. The diffusivity and vapor-liquid equilibrium coefficient for various flavor components have been determined for sugar and malto-dextrin solutions, but these data were taken at room temperature and cannot be applied to spray dryer conditions. Also, no attempt has been made to correlate the data to a general correlation which could be extrapolated to higher temperatures or higher solids concentrations.

The purpose of this study is to acquire diffusion and equilibrium data for a common flavor component in a model food system. An attempt was to be made to correlate the data in a usable form. The ultimate goal of this research is to provide correlations to predict physical and chemical properties of the flavor-food system over the range of conditions experienced by a drying droplet in the spray dryer. These correlations are the tools necessary for a model of the flavor loss during spray drying.

LITERATURE REVIEW

Many experiments have been performed in the spray dryer in order to understand the mechanisms of flavor loss. Auxiliary experiments have been performed on slab drying to try to explain the phenomena observed in spray dryers. It is interesting to note how the theory and experiments have developed from simple experiments on the drying of single drops (Menting and Hoogstad, 1967) to measurements of the retention profile of acetates in spray drying sugar solutions (Kieckbusch and King, 1977).

Droplet Drying

In some of the earliest experiments, Menting and Hoogstad (1967) studied the retention of acetone, benzene, ethanol and ethyl acetate in a drying droplet of malto-dextrin solutions suspended on a wire in an air current. They used radioactive-labeled volatiles in their study. They observed the formation of a film on the drop surface which was permeable to water, but not acetone, benzene, ethanol or ethyl acetate. The film formed faster with higher initial solids concentration. Throughout the experiments, the drop temperature was constant, as measured by a thermocouple inside the drop.

Saravacos and Moyer (1968) observed that retention of volatile aroma compounds during vacuum drying of grape juice and pectin solutions was dependent on the relative volatility of the compounds and the beginning solids concentration of the solutions. The most volatile compounds exhibited the least retention. Percent retention was enhanced by starting with more concentrated fruit juices.

Slab Drying

In slab drying experiments with malto-dextrin solutions, Menting, et al. (1970b), observed that the retention of acetone was a function of the solids content of the initial solutions. Varying amounts of agar-agar were added to gel the solutions. They showed an increase from 0% to about 70% retention of acetone in solutions of 0 to 700 g/l initial dry matter. They also reported that loss of acetone from the drying slab stopped below a certain moisture content. The acetone content in the slab remained constant after the transition from a constant drying rate period to a falling rate period. The transition in drying modes was determined by the temperature in the malto-dextrin slab. An increase in the relative humidity of the drying air increased the time at which the constant rate period ended and when acetone loss ended. Using the concentration-dependent diffusion coefficients measured in a complimentary study (Menting, et al., 1970a), the observed loss of water and acetone was predicted.

Through some simple analyses, they determined that the value of the group $K_{WO}Bi_{WO}$ should be greater than 4 for the surface of a drying droplet to be in equilibrium with the drying air almost immediately after the onset of drying for dry air. K_{WO} is the vapor-liquid equilibrium coefficient of the flavor component for the solution to be dryed at the initial drying temperature. Bi_{WO} was the Biot Number for mass transfer and equaled k_A'/D_A where k_A' was the gas phase mass transfer coefficient. The value of 4 for $K_{WO}Bi_{WO}$ corresponded to immediate film formation at the drop surface. This also corresponded to the maximum retention of flavor components. Menting, et al. (1970b) also concluded that $K_{WO}Bi_{WO}$ was a function of the relative humidity of the drying air.

Thijssen (1971) concluded that retention of flavors from liquid foods was independent of their volatilities relative to water. Instead, the controlling factor was the diffusivity of the flavor component through the drying liquid. The rate of evaporation of flavor components could be described as molecular diffusion to the surface of the liquid with zero concentration at that surface. He stated that the reason for retention of flavors was their low diffusivity in the drying liquid as compared to the water diffusivity. The ratio D_A/D_W (relative diffusivity) decreased very rapidly with increasing solids content and increasing size of flavor component for acetone and alcohols in malto-dextrin solutions. Below a certain "critical water concentration," the relative diffusivity became small. The critical water concentration was defined as the water content where D_A/D_W becomes less than 0.01. Below this value of water concentration, the solution became nearly impermeable to flavor components. Thus, the conditions in spray drying that lead to rapid water loss at the surface and the formation of a high solids content skin or film gave the best retention of flavors.

Spray Drying

In spray drying experiments with alcohols in malto-dextrin solutions, the maximum retention was obtained for the combination of high solids content of the feed and high feed temperatures. Both of these cause rapid film formation. The film should retard flavor diffusion.

Rulkens and Thijssen (1972) have studied the effects of process variables on the retention of acetone and alcohols in spray drying aqueous solutions of malto-dextrin. They concluded that the retention of volatiles in malto-dextrin solutions was independent of the relative volatility (i.e., vapor-liquid equilibrium coefficient). Retention increased with increasing molecule size of the volatile. At the low concentrations of the volatiles studied, retention appeared to be independent of volatile concentration. Given a low enough viscosity to ensure proper atomization, retention increased strongly with increasing solids content. Thus, the maximum retention is obtained at high feed concentrations and high feed temperatures. They also concluded that retention increased with decreasing air temperatures, but was insensitive to air temperatures at low solids concentration.

A mathematical model for the concentration profiles of water and trace flavor component has been solved by Chandrasekaran and King (1972b). They used a ternary diffusion model for the fluxes in the slab. Data for the ternary diffusion coefficients was provided by a supplimentary work also by Chandrasekaran and King (1972a). The model was solved using the symmetrical Crank-Nicholsen implicit representation for a finite difference approximation. The model predicted a maximum in the concentration profile for the flavor component just below the drying surface, at long times. Qualitatively, the maximum was due to shrinkage of the slab as water diffused to the surface. As the slab shrinks, the concentration of the flavor component builds up close to the moving surface.

Drying experiments were performed on sucrose, fructose and orange juice containing 1.5% gelatin. These experiments gave flavor profiles qualitatively similar to the predicted profiles. The formation of a zone of high solids material (a skin or film) at the drying surface was responsible for the retention of the flavor component in the drying slab.

Kieckbusch and King (1977) have made major contributions to the understanding of spray dryer behavior. They studied the retention of volatile acetates at various distances from the atomizer for spray drying water and sucrose solutions. The observed retention of volatile components depends on whether the liquid or gas phase is controlling the volatile loss rate. They showed that a very large portion (60%) of the volatiles were lost within 2 cm of the atomizer, which corresponds to the film-disintegration zone for 40% sucrose solutions. They also observed that the retention of acetates in water was substantially less than in sucrose solutions. More striking was the observation that the order of retention in water was the reverse of that in sucrose solutions. This was explained as the overall mass transfer resistance

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Kk_C} \tag{1}$$

where K_L is the overall mass transfer coefficient, k_L and k_C are the individual liquid and gas phase coefficients, respectively, and K is the vapor-liquid equilibrium coefficient. For water, Kk_C is smaller than k_L and K_L is approximated by

$$K_L = Kk_C \ . \tag{2}$$

K increases with increasing molecular weight (Kieckbusch and King, 1979) and so K_L increases also. So, the retention should decrease with increasing molecular weight at low solids content. This was observed in the experiment.

Mass transfer in the liquid phase controls the overall mass transfer for solutions of 40% sucrose. That is, k_L is less than Kk_C and so K_L is represented by

$$K_L \doteq k_L \; . \qquad (3)$$

Now, k_L is proportional to the liquid diffusivity which is in turn proportional to the inverse of the molecular weight. So, K_L should decrease with increasing molecular weight and the retention whould increase with increasing molecular weight.

Further study of this system (Kieckbusch and King, 1980) demonstrates this hypothesis more. For 1% sucrose solutions, the retention is greatest for ethyl acetate and least for pentyl acetate. This indicates a gas-phase control of mass transfer because the vapor-liquid equilibrium coefficient is greatest for pentyl acetate. Thus, pentyl acetate is the most volatile and is retained the least. The diffusivity in the liquid phase should have some effect, but does not control the relative retentions in 1% sucrose solutions.

The trend is reversed for 40% sucrose solutions. Retention is greatest for pentyl acetate and least for ethyl acetate. This indicates liquid phase control of mass transport. The liquid diffusivity decreases with increasing molecular weight. So, pentyl acetate should have the lowest diffusivity and should have the highest retention.

Of particular interest is the retention of acetates in spray drying 20% sucrose solutions. The order of retention reverses at about 10 cm below the atomizer because the controlling phase for mass transfer changes. At distances of 0 to 10 cm, ethyl acetate has the highest retention, indicating gas phase mass transfer control. Beyond 10 cm, pentyl acetate has the maximum retention, indicating liquid phase mass transfer control. So, within one spray dryer, the mechanism may switch from gas to liquid phase mass transfer control. Indeed, Kieckbusch and King made the general conclusion that the gas phase controls during drop formation and the liquid phase controls once the drop is formed. This is reasonable since there is considerable turbulent mixing in the atomizer jet. But, once the drop has formed, viscous dissipation should reduce the mixing in the drop to zero.

These effects can also be explained by the formation of a film on the drying drop. Once a film of high solids content is formed on the drop, the mass transfer will be controlled by the film since the diffusivity is a very strong function of percent solids of the film (this work).

Kieckbusch and King (1980) also studied the effects of liquid feed temperature, air temperature, air flow rate, and sugar molecular weight on the retention of ethyl acetate. Malto-dextrin solutions exhibited a greater retention of ethyl acetate than sucrose and malto-dextrin solutions having the same kinematic viscosity. This is most likely due to structural binding of ethyl acetate to the malto-dextrin molecule. Malto-dextrin could form a helical structure in water solutions. During the drying process, ethyl acetate molecules could become trapped inside of the helix. Sucrose would not exhibit such binding effects.

A decrease in liquid feed temperature and an increase in air temperature both increased the retention. Since diffusivity is inversely proportional to feed temperature, the retention should increase at low feed temperatures. This argument cannot be used for the air temperatures, though. Instead, the increase in retention with increasing air temperatures may be attributed to the formation of a film at the higher air temperatures. Rulkens and Thijssen (1972) observed a reverse trend. They found that retention was decreased with increasing air temperatures. Their experiments were performed at considerably higher temperatures than those of Kieckbusch and King. A temperature range of 110° C to 220° C was used by Kieckbusch and King, while Rulkens and Thijssen used a range of 210° C to 290° C. In Rulkens and Thijssen's experiments, the reduced retention can be explained by bubbling of the malto-dextrin droplets at the higher temperatures.

Kieckbusch and King were able to predict the volatile loss very close to the nozzle using an expanding sheet, laminar flow model. Beyond the droplet formation distance, a solid sphere diffusion model was used. The expanding sheet model predicted volatile loss well, but the solid

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sphere diffusion model underpredicted the volatiles loss.

In a study on the vacuum spray desorption of carbon dioxide, oxygen, Freon 114, and butane from deionized water, sodium chloride solutions and freshly acidified sea water, Simpson and Lynn (1977) observed large losses of the gasses before droplet formation. The degree of stripping observed was much greater than that predicted by the solid sphere model. Instead, up to 90% of the gas was stripped in the thin sheet formed at the spray nozzle. The amount of stripping was predicted by an expanding sheet model for mass transfer developed by Hasson, et al. (1964). The model predicted the experimental observations very well. The reason for the high mass transfer rates from the water sheet is that before the sheet breaks into drops, it becomes very thin. The ratio of drop diameter to sheet thickness ranges from 10 to 50. Since the diffusional path length in the sheet is very small, a large quantity of gas is desorbed from the sheet.

A similar explanation might be used for the large loss of volatiles close to the spray nozzle in spray drying sucrose and malto-dextrin solutions (Kieckbusch and King, 1980).

Reineccius, et al. (1978) studied the retention of methyl ketones in spray drying of milk systems of different fat contents. The retention increased with molecular weight of the ketone. It was found that the retention was improved for fat contents of up to 21%. Above that value, the retention was reduced. Retention should be improved by the addition of some fat, since the ketones are soluble in fat. High fat contents, however, lead to a continuous fat phase which will serve as a path for diffusion out of the drying particle.

The spray drying literature discussed show some parallels. The primary observation to be made is that volatile retention is enhanced when a film of high solids impermeable to volatile flavors is formed on the drying droplet. This film acts as a barrier to larger flavor molecules through selective diffusion (Rulkens and Thijssen, 1972). The diffusivity of flavor molecules is substantially lower than the diffusivity of water in the film. The optimum conditions in spray drying liquid foods are the conditions at which the film is formed the most rapidly.

Large amounts of volatiles can be lost in the expanding liquid film at the spray nozzle. Volatile components can diffuse out of the film due to the short diffusional path length (Simpson and Lynn, 1977). Cracks can develop in the drying droplet which enhance the volatile loss rate (Rulkens and Thijssen, 1972). If the droplets are heated too much, the water may volatilize. Bubbling within the droplet may cause the skin to rupture, releasing much of the volatile flavor. There is a lack of information regarding the diffusivity and partition coefficients of volatile components in model foods.

If correlations can be developed which can predict the diffusivity and partition coefficient of flavor components in model foods, then mathematical models based on balances of heat, mass and momentum can be developed. In this fashion, the basic principles of spray drying may be more easily understood.

Vapor-Liquid Equilibrium Data

The vapor-liquid equilibrium coefficient is an important consideration in designing spray dryers. The vapor-liquid equilibrium may be defined in a number of ways. The convention used here is

$$K = \frac{C_V}{C_L} \tag{4}$$

where C_V and C_L are molar or mass concentration of the solute in the vapor and liquid phase, respectively. A more typical definition is

$$\tilde{K} = \frac{y}{x} \tag{5}$$

where x and y are the mole fraction of solute in the vapor and liquid phases. In the malto-dextrin system, the average molecular weight of the liquid phase is not well defined since the molecular weight of the malto-dextrin is not well defined. In these measurements, the vapor phase contained an unknown ratio of water and air. Therefore, the vapor-liquid equilibrium coefficient was based on Equation (4).

According to thermodynamic equilibrium, at low to moderate pressures, the mole fraction vapor-liquid equilibrium coefficient, $\tilde{K}$, is represented as

$$\tilde{K}_i = \gamma_i \frac{P_i^{\text{sat}}}{P} \tag{6}$$

where P_i^{sat} is the saturation vapor pressure of component i, γ_i is the activity coefficient for component i and P is the total pressure (Prausnitz, 1969). In partially soluble systems, the solubility of component i is related to the activity coefficient by

$$\gamma_i \doteq \frac{1}{x_i} \tag{7}$$

where x_i is the solubility of species i. Compounds with very low solubilities will have high activity coefficients and, therefore, high vapor-liquid equilibrium coefficients (Bomben, et al., 1973).

For very dilute flavors in food systems, the activity coefficient is often a constant with respect to the concentration of flavor component. At very low concentration of solute, the activity coefficient approaches a constant value, the activity coefficient at infinite dilution, γ_i^∞. That is,

$$\lim_{C_i \to 0} \gamma_i = \gamma_i^\infty \tag{8}$$

where C_i is the concentration of species i. So, γ_i^∞ is a good approximation to γ_i for flavor components at finite, small concentrations.

The activity coefficients at infinite dilution have been correlated for a number of organic compounds in water and other solvents by Pierotti, et al. (1959). The correlation is

$$\log \gamma_1^{\infty} = A + B\frac{n_1}{n_2} + \frac{C}{n_1} + D(n_1 - n_2)^2 + \frac{F}{n_2} \qquad (9)$$

where A - F are adjustable constants depending on the type of solute (component 1) and solvent (component 2), n_1 and n_2 are the number of carbon atoms in the solute and solvent, respectively. The constants A - F are given for a temperature range of 25° to 100° C. This correlation should be useful in predicting the vapor-liquid equilibrium coefficient of volatiles in water. Buttery, et al. (1971) used this correlation to calculate the vapor-liquid equilibrium coefficients of alkanals and 2-alkanones at 25° C. The calculated results were slightly higher than the experimental values.

The solubility of homologues tend to decrease with increasing chain length. Davis (1968) measured the solubility of C_5 - C_9 aldehydes in water at 25° C. He found that the solubility decreased from 22.00 g/l for pentanal to 0.11 for nonanal. The natural logarithm of the solubility was shown to be a linear function of the carbon chain length. Nishino and Nakamura (1978) measured the same trends for alcohols, amines and aliphatic acids. They also found that the solubilities demonstrated minima over the temperature range studied. Data presented by Stephen and Stephen (1963) show a minimum solubility for 1-hexanol at about 50° C and a minimum for 2-butanone at about 90° C. This has been explained in terms of an increase in partial molar enthalpy of the solute with a temperature increase which results from the breakdown of the water structure surrounding the nonpolar alkyl chain. Since the solubilities of alcohols, amines, ketones and aldehydes are not linear with temperature, it is expected that the corresponding activity coefficients are also non-linear with temperature.

Air-water vapor-liquid equilibrium coefficients at 25° C for aldehydes, ketones, and esters have been measured by Buttery, et al. (1965, 1969, and 1971). In all of his studies, Buttery measured the concentration of the volatile component in the vapor and liquid phases using a gas chromatograph. Liquid concentrations were well below the saturation levels, typically 5 - 200 ppm. The vapor-liquid equilibrium coefficient was shown to be a strong function of the carbon chain length. For each homologous series, the natural logarithm of the vapor-liquid equilibrium coefficient was a linear function of the number of carbon atoms in the carbon chain.

The activity coefficients for ethyl alcohol, n-hexanal and various esters in sucrose and d-fuctose solutions were measured by Chandrasekaran and King (1971 and 1972a). The amount of volatile component was measured in the vapor above a solution containing a known initial concentration of volatiles. The liquid-phase concentration of volatiles was not measured. The activity coefficient was calculated from the ratio of volatile concentration above the sugar solution to the volatile concentration above water. In all cases, the same amount of volatile component was added to the solution and allowed to equilibrate between the vapor and liquid phase. The activity coefficient in water was calculated from the correlation by Pierotti, et al. (1959).

Chandrasekaran and King also found that a plot of $\log \frac{\gamma}{\gamma_0}$ versus $\log C_W$ gave one straight line for the volatile components in fructose. In this case, γ and γ_0 are the activity coefficients for the volatile component in the sugar solution and water, respectively and C_W is the water concentration. The significant finding here is that all of the flavor components for one sugar fit a single, master curve. But, since the flavor component did not interact with the sugar, the value of the activity coefficient should be proportional to the water concentration.

Kieckbusch and King (1979 and 1980) measured the vapor-liquid equilibrium coefficients for a number of acetates in aqueous solutions of sucrose, maltose, dextran, dextrin, malto-dextrin, Brazil-Santos coffee extract, and commercial instant coffee over a temperature range of 25° to 40° C. They also measured the vapor-liquid equilibrium coefficients in mineral oil, peanut oil, and coffee oil. In their experiments, Kieckbusch and King added a known amount of acetate to a special thermostated bottle containing a known amount of water. For pure water solutions, samples of both the gas and liquid phases were analyzed with a gas chromatograph and the vapor-liquid equilibrium coefficient calculated. Only the vapor was sampled for solutions containing dissolved solids. The vapor-liquid equilibrium coefficient for the sugar solutions were calculated from the ratio of the concentration in the vapor above the sugar solutions to the vapor above water. In each case, the same amount of volatile was added to the solutions. The pressure in the bottles was atmospheric since a small sampling hole in the bottle cap was left open throughout the experiments. Some volatile component may have been lost, but this was ignored.

The results of these experiments showed that the vapor-liquid equilibrium coefficient in water increased with increasing molecular weight. This was true at all temperatures. The vapor-liquid equilibrium coefficient for pentyl acetate increased with increasing solids content in sucrose, maltose and dextran solutions, but decreased with increasing solids content in malto-dextrin, dextrin, commercial instant coffee and Brazil-Santos coffee extract solutions.

In this work, the vapor-liquid equilibrium coefficient was measured for 1-hexanol and 2-butanone. The concentration in the liquid and vapor phases were measured. It is important to measure both since some sorption may occur on the experimental apparatus that is not accounted for by a simple mass balance.

Diffusivity Measurements

A critical component of any mathematical model of a spray dryer is the diffusivity of water and flavor components in the model food system. Correlations for diffusivity must be developed which consider the effects of solids content of the solution, temperature, the type of flavor and the type of dissolved solids.

Diffusivity correlations in pure solvents. It is well known that diffusion, being a rate process, follows Arrhenius' Law:

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{10}$$

where the activation energy, E_D is a function of the water content of the malto-dextrin solution.

According to Stokes-Einstein theory, the group $\frac{D_{AB}\ \mu_A}{T}$ is a constant for a given solute B in a given solvent A. For large spherical particles (Bird, et al., 1960),

$$\frac{D_{AB}\ \mu_B}{T} = \frac{K}{4\pi\ R_A}\ . \tag{11}$$

If solvent and solute molecules are the same size and can be packed into a cubic lattice, R_A may be replaced by $\frac{1}{2}\left(\frac{V_A}{N}\right)^{1/3}$

resulting in

$$\frac{D_{AB}\ \mu_B}{T} = \frac{K}{2\pi}\left(\frac{N}{V_A}\right)^{1/3} . \tag{12}$$

Since the Stokes-Einstein Equation applies only to spherical molecules, numerous empirical correlations have been proposed. Wilke and Chang (1955) found that $\frac{D_{AB}\ \mu_B}{T}$ varies with the molecular weight of the solvent to the $\frac{1}{2}$ power and with the molar volume of the solute to the -0.6 power for pure solvents. That is,

$$\frac{D_{AB}\ \mu_B}{T} = 7.4 \times 10^{-8}\ \frac{\left(X_B\ \mu_B\right)^{1/2}}{V_A^{\ 0.6}} . \tag{13}$$

where X_B is an association parameter which is 2.6 for water, 1.9 for methanol, 1.6 for ethanol and 1 for unassociated solvents like benzene, ether, and heptane. Others have attempted to extend or refine the Wilke-Chang equation.

Othmer and Thakar (1953) based their correlation on Eyring rate theory. Viscosity and diffusivity vary as exponential functions of absolute temperature,

$$D = D_0\ \exp\left(\frac{E_D}{RT}\right) \tag{14}$$

$$\mu = \mu_0\ \exp\left(\frac{E_\mu}{RT}\right) . \tag{15}$$

Taking the logarithms and substituting for 1/RT yields

$$\log D = \frac{E_D}{E_\mu} \log \mu + C' . \tag{16}$$

For a number of materials at low concentration, $\frac{E_D}{E_\mu}$ was shown to be approximately equal to -1.1.

For solutes in water, Equation (16) becomes

$$\log D_A = \frac{E_{DA}}{E_{\mu W}} \log \mu_W + K \tag{17}$$

or

$$\log D_A = \frac{E_{DA}}{E_{DW}} \frac{E_{DW}}{E_{\mu W}} \log \mu_W + K \,. \tag{18}$$

Now,

$$\frac{E_{DW}}{E_{\mu W}} \doteq -1.1 \tag{19}$$

and the ratio of the activation energies is replaced by the latent heats of vaporization. The resulting empirical correlation becomes,

$$D_{AB} = \frac{1.4 \quad 10^{-4}}{\mu_W^{(1.1\ \Delta H_B/\Delta H_W)} \quad V_A^{0.6} \quad \mu_B} \tag{20}$$

Scheibel (1954) proposed an emperical correlation based on data for water and a number of other solvents.

$$\frac{D_{AB}\ \mu_B}{T} = 8.2 \times 10^{-8} \frac{\left(1 + \dfrac{3V_B}{V_A}\right)^{2/3}}{V_A^{\ 1/3}} \tag{21}$$

Sitaraman, et al. (1963) substituted the ratio of latent heats of vaporization for the Wilke-Chang association parameter X. They arrived at

$$D_{AB} = 5.4 \times 10^{-8} \left(\frac{M_B^{\ 1/2}}{\mu_B} \frac{\Delta H_B^{\ 1/3}}{\Delta H_A^{\ 0.3}} \frac{T}{V_A^{\ 0.5}} \right)^{0.93} \tag{22}$$

Reddy and Doraiswamy (1967) replaced the association parameter with $\frac{1}{V_B^{1/3}}$ resulting in

$$\frac{D_{AB}\ \mu_B}{T} = K \frac{M_B}{(V_A\ V_B)^{1/3}} \tag{23}$$

where

$$K = 1.0 \times 10^{-7} \text{ for } \frac{V_B}{V_A} \leqq 1.5 \tag{24a}$$

$$K = 8.5 \times 10^{-8} \text{ for } \frac{V_B}{V_A} > 1.5 \tag{24b}$$

No rational was given for the substitution of the association parameter with $\frac{1}{V_B^{1/3}}$.

Diffusivity measurements in malto-dextrin solutions. The first effort to measure the diffusion coefficient of volatile flavor compounds in malto-dextrin solutions was made by Menting, et al. (1970a). They measured the diffusivity of water, acetone and ethyl acetate over a wide range of solids content at 25° C. The water diffusivities were measured in drying experiments. The weight of a dish of malto-dextrin solution containing 1% agar-agar and benzoic acid was measured over a period of time. The air above the dish was maintained at a constant relative humidity. The diffusion coefficient was taken as an average of sorption and desorption experiments.

The diffusivities of acetone and ethyl acetate were measured in one of two ways. For solutions above 20% water, a small sample containing a small amount of agar-agar was placed inside a thermostated flask. It was assumed that the sample did not lose much water since the flask was small. A 10 ml mixture of acetone, ethyl acetate and benzene vapors was added to the flask. The concentration of flavor component in the vapor was measured from time to time by injecting 25 or 30 μl samples into a gas chromatograph. The diffusivity was calculated from the change in concentration in the vapor phase with time. The benzene was added as an internal standard for the vapor analysis. The concentration of benzene was assumed to be constant since it is not soluble to any appreciable extent in water. The solids content of the malto-dextrin solutions was not measured even though it would have been very easy to do so.

A radioactive tracer technique was used in malto-dextrin solutions containing less than 20% water. First, glass rods were coated with 50 wt-% malto-dextrin solutions of various thicknesses by drawing the rods out of the solution at a constant rate. The malto-dextrin was air dried at 80° C. Before use, the rods were placed in an enclosed container with a saturated salt solution at the desired relative humidity. They were then placed in a similar container with similar salt solution with a small amount of diffusant in the vapor. At selected times, the rods were removed and the malto-dextrin coating was dissolved in water. The resulting solution was analyzed with a scintillation detector for diffusant. The diffusivity was calculated from the change in the diffusant concentration in the liquid with time. The solids content was not measured in these solutions. It is important to measure the solids content to be sure the experiment works properly.

Menting found that the diffusivity was a strong function of the solids content. The diffusivity of acetone correlated with the water concentration, C_W as

$$D_A = A \exp\left(- \frac{B}{C_W^{1/2}}\right) . \tag{25}$$

Here A and B are arbitrary constants. No physical reason for correlating the data this way was given.

Benzene, carbon tetrachloride and camphor diffusivities were measured at 20.1% water content using the same procedure. Methane diffusivity at 20.1% water content was measured by a desorption experiment. Methane was introduced into a flask containing a thin layer of malto-dextrin solution. The system was allowed to come to equilibrium. The methane was removed from the vapor by flushing the flask with air. The vapor phase concentration of methane was measured as a function of time and the diffusion coefficient calculated. From these experiments, it was shown that log D was a linear function of the diffusant diameter.

Other workers have measured the diffusion coefficients of flavor analogs in food systems. The ternary diffusion coefficients of dilute ethanol, ethyl acetate, n-butyl acetate and n-hexanal were measured in solutions of sucrose, d-glucose and d-fructose by Chandrasekaran and

King (1972). A stirred diaphram cell was used since the sugar concentrations were fairly dilute. The initial concentration of sugar was slightly different across the cell. The initial concentration of organic diffusant was zero on one side of the cell and a small value on the other side. The equations for the flux of organic (component 1) and water (component 2) were

$$J_1 = D_{11} \nabla C_1 - D_{12} \nabla C_2 \tag{26a}$$

$$J_2 = D_{21} \nabla C_1 - D_{22} \nabla C_2 \tag{26b}$$

(Chandrasekaran and King, 1972a). The flux of the sugar (component 3) was not independent of the water and organic fluxes. The cell diaphram equation for a binary system was

$$\ln \left(\frac{\Delta C^0}{\Delta C}\right) = \beta D t \tag{27}$$

where ΔC^0 and ΔC were the concentration differences across the cell at time equal to zero and t, respectively, and β was the cell constant. The equations for a ternary system were reduced to

$$\frac{\Delta C_1}{\Delta C_1{}^0} = 1 - \left(D_{11} + \frac{\Delta C_2{}^0}{\Delta C_1{}^0} D_{12}\right) \beta t + \left[(D_{11}{}^2 + D_{12} D_{21}) + D_{12} (D_{11} + D_{22}) \frac{\Delta C_2{}^0}{\Delta C_1{}^0} \right] \frac{\beta^2 t^2}{2} + \cdots \tag{28}$$

and

$$\frac{\Delta C_2{}^0 - \Delta C_2}{\Delta C_1{}^0} = \left(D_{21} + D_{22} \frac{\Delta C_2{}^0}{\Delta C_1{}^0} \right) \beta \, t - \left[D_{21} \, (D_{11} + D_{22}) + \frac{\Delta C_2{}^0}{\Delta C_1{}^0} (D_{22}{}^2 + D_{12} \, D_{21}) \right] \frac{\beta^2 \, t^2}{2} + \cdots \qquad (29)$$

In order to use these equations, one could have used values of ΔC for two values of t, or one or more of the diffusion coefficients must have been known from previous experiments. Chandrasekaran and King used literature values for D_{22} in sugar solutions, but the literature values for D_{22} (the water diffusion coefficient in sugar solutions), which Chandrasekaran and King used in their work, were actually sugar diffusion coefficients. The data for D_{22} corresponded to diffusion coefficients for sucrose and d-glucose solutions presented by Henrion (1964a, b), English and Dole (1950), and Gladden and Dole (1952). According to Chandrasekaran and King, D_{22} in 0 wt % sugar, the self-diffusion coefficient of water, was approximately 6.0×10^{-6} cm^2/sec. Menting gave a value of 2.2×10^{-5} cm^2/sec for the water self-diffusion coefficient. Values for D_{22} in Chandrasekaran and King's paper were actually sugar diffusion coefficients which were significantly lower than water diffusion coefficients should have been. However, this did not invalidate their calculations. By inspecting equation 28, one sees that D_{22} appeared only in the quadratic terms. Thus, this error should not have introduced much error in the organic component diffusivities, D_{11}.

Chandrasekaran and King (1972a) made some rather interesting conclusions from their data. The ratio of the diffusivities of the organic components in a sugar solution to that in water (D_{11}/D_{11}^{o}) showed a logarithmic relationship with water concentration, C_W. That is, log D_{11}/D_{11}^{o} was approximately linear with log C_W or log W, where W was the water weight fraction. The significant observation was that the data for all organic components in all sugar solutions fit the same curve. The slope of the curve log D_{11}/D_{11}^{o} versus log W was about 3.4 at 298° K curve showed considerable scatter.

They also calculated the activation energy for diffusion (E_D) of ethanol and sucrose in sucrose solutions and the activation energy for the solution viscosity (E_μ) at various weight percent sucrose. The diffusion data that they claimed was for water, was actually for sucrose in a sucrose solution. They showed that E_D was approximately equal to E_μ (in absolute value) for sucrose at low concentrations. Above 20% sucrose, E_μ became greater than E_D.

Henrion (1964a) found that $D\mu/T$ for sucrose was a constant in dilute sucrose solutions from 25° to 75° C. Gladden and Dole (1952) also found that E_μ and E_D for glucose and sucrose became equal in very dilute solutions of glucose and sucrose. At increasing sugar concentrations, E_μ became significantly greater than E_D.

Since D and μ are exponential functions of their activation energies divided by absolute temperature, if E_D equals E_μ, the product Dμ should be constant with temperature and Dμ/T should be nearly constant with temperature.

This could indicate that the mechanism for diffusion was the same as that of viscosity at low concentration of diffusant. At high dilution, solute molecules were far apart and could not interact with each other. They tended to diffuse the same way that solvent molecules flow. The resistance to flow (viscosity) is caused by shearing forces as solvent molecules slide past each other. At low concentrations, the resistance to solute diffusion should be caused by similar shearing forces between solute and solvent molecules. If the mechanism for diffusion and flow are the same, it is reasonable to expect their activation energies to be equal.

At higher solute concentrations the solute molecules had more opportunity to interact. They may diffuse in groups through the solvent. If they diffused in groups, the energy needed for each individual molecule to get through the solvent molecules (E_D) should have been less than the energy needed for individual solvent or solute molecules to slide past each other (E_μ). E_D for the group as a whole should have been greater than E_D for an individual molecule diffusing through the solvent. But, E_D for each individual molecule in the group should have been less than E_μ, since the solvent molecules would have resisted the group at its boundaries, but would not have interacted with each individual molecule in the group. The existance of such a group was reasonable since many organic molecules are known to hydrogen bond. Hydrogen bonding could have held the groups together as they diffused through the solvent.

Through the efforts of Menting, et al., and Chandrasekaran and King, a considerable amount of diffusion data has been obtained. None of the investigators have made an effort to develop a general correlation for diffusivity over a range of temperatures and solids content. It is important to be able to correlate the diffusivity with temperature and solids content so that a continuous function for diffusivity is available for use in mathematical models for spray dryers.

EXPERIMENTAL METHODS

Constant Temperature Bath

A constant temperature bath (figure 1) was used to keep the diffusion cell at a constant temperature. A temperature bath with a relatively large volume was needed to keep the temperature as constant as possible. A glass fish tank with a clear Plexiglass®[1] cover was used. The fish tank was 24 in. long, 12 in. wide, and 12 in. deep. The cover was made of a clear Plexiglass® sheet which was 3/8 in. thick. Plexiglass® was used because it is water resistant and transparent.

The cover was made in two parts, each measuring 12 in. by 12 in. One half was stationary on the bath. Holes were drilled into this half to accomodate the circulating water heater, heated syringe tubes, and a thermometer. The other half acted as a removable cover. Strips of Plexiglass® were glued along the bottom edges of both halves of the cover to keep them in place.

A Haake model E52 recirculating heater was used in the experiments. It provided temperature control to ± 0.1° C. The circulating pump on the heater was used to pump hot water to the syringe mantle as well as to

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[1] Registered Trademark, Rohm & Haas Co.

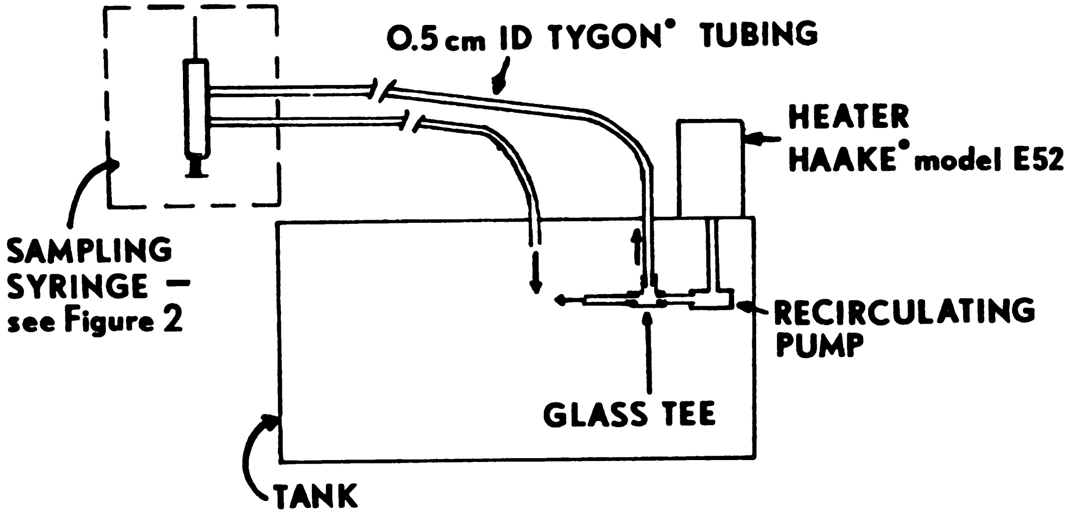

FIGURE 1. CONSTANT TEMPERATURE BATH

circulate the water in the bath. The Haake heater held the temperature to within 0.2° C at a bath temperature of 90° C with the bath cover removed for 15 minutes.

A Haake thermometer with 0.5° C graduations was used. Insulation on the sides of the bath was kept to a minimum amount. Three layers of aluminum foil and one layer of corrugated cardboard provided enough insulation.

Syringe

A Hamilton 1.0 ml gas sampling syringe (figure 2) was used to sample the vapor. The syringe performed very well when used in conjunction with a Plexiglass® heating mantle. The relative standard deviations of repetitive samplings was typically less than 1% of the mean. This type of glass syringe was rather fragile and care had to be taken to avoid physical and thermal shock to it.

Syringe Mantle

A Plexiglass® syringe mantle (figure 2) was fabricated to accomodate the 1.0 ml gas-tight syringe. The body of the mantle was made of a Plexiglass® tube which was 1 1/4 in. in diameter with 3/8 in. thick walls. The tube was cut to the length of the syringe body. The ends of the mantle were made of 3/8 in. flat Plexiglass®. A hole just large enough for the syringe needle to fit through was drilled in the bottom end piece. A hole large enough for the body of the syringe to pass through was drilled in the

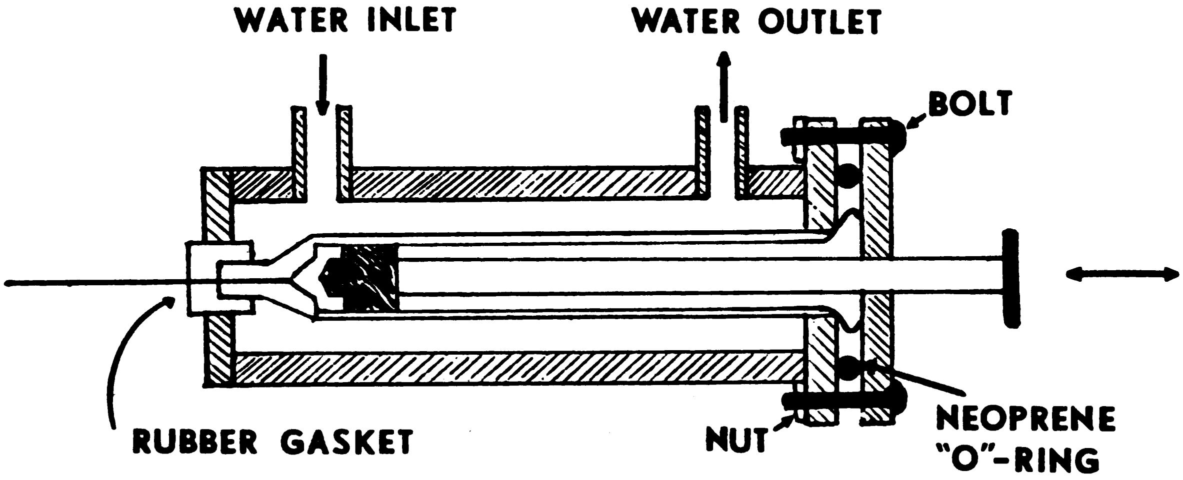

FIGURE 2. CROSS SECTIONAL VIEW OF HEATED GAS SAMPLING SYRINGE

top piece. The end pieces were glued to the body using cyano-acrylate glue. Two 3/8 in. holes were drilled near opposite ends of the mantle body. Into these holes were glued two pieces of copper tubing 1 in. long. The copper tubing acted as a connection for the water circulating tubing from the hot water bath.

Each syringe was held in its mantle by a back plate which was fastened to the top end plate by means of two 1 in. bolts and 1/8 in. diameter nuts. A hole large enough for the plunger to pass through was drilled in the back plate. The syringe was placed in the mantle resting on two rubber seals. One seal was a small round rubber disk through which the needle was pierced. This sealed the front end of the syringe. The second seal was a 1 in. rubber "O" ring. This second seal fit over the body of the syringe and sealed the back of the syringe. Over the back of the syringe, the back plate was fastened. The pressure of the back plate against the syringe pressed the seals against the front and back ends of the mantle, making the seal.

Diffusion Cells

During the diffusion experiments, it was desired to place an adequate number of diffusion cells into the water bath at any one time. The most reasonable approach to this requirement was to use relatively small containers as diffusion cells (figure 3). It was found that 125 ml

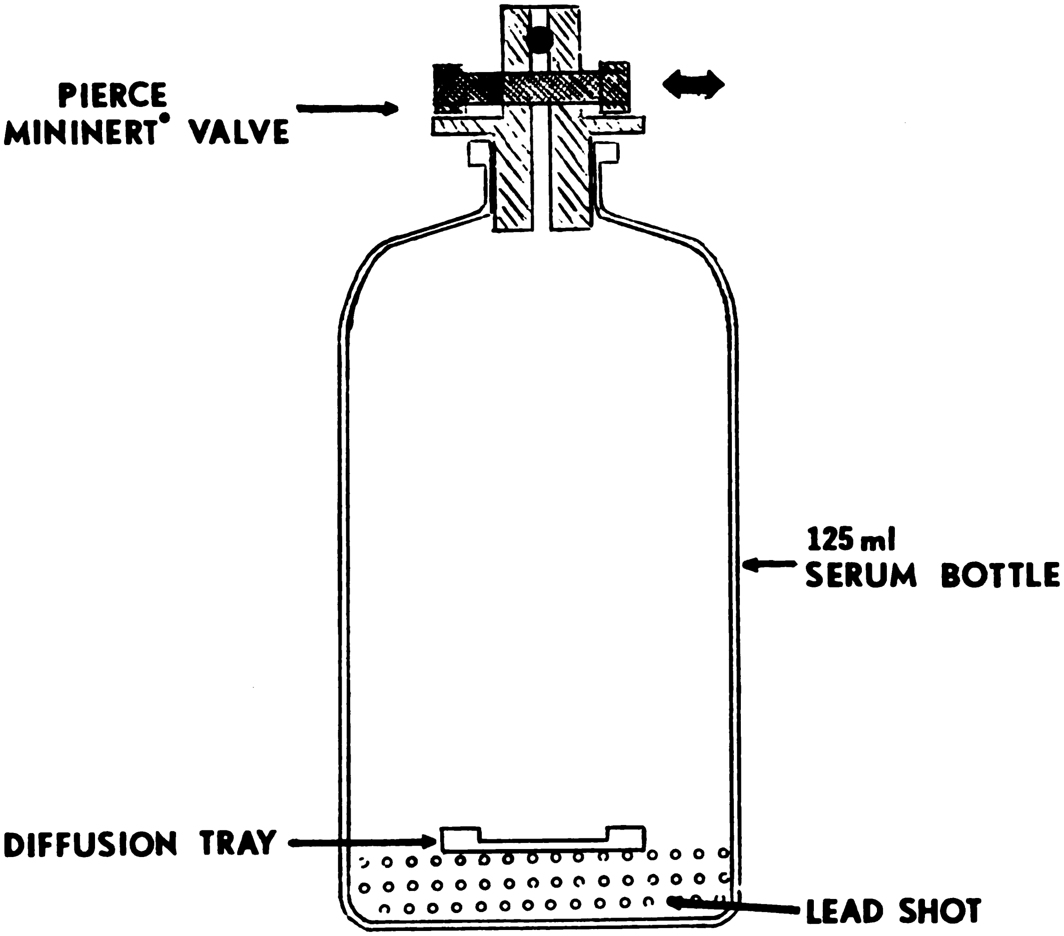

FIGURE 2. CROSS SECTIONAL VIEW OF DIFFUSION CELL

serum bottles worked well for this purpose.

It was necessary to sink the cells into the bath using some type of weight, so that the temperature was constant throughout the cell to prevent condensation of either diffusant or water on the cell walls. The external volume of each cell was 200 ml and its empty weight was 100 g, so, 100 g of 16 gauge lead shot was used to sink each cell. Lead shot was used because it is relatively inert to organic solvents and it is very dense. The lead shot also served as a good level platform upon which to place the diffusion trays. The shot was easily leveled in the bottom of the diffusion cells by shaking the cell.

A Pierce Mininert®[1] Valve was used to cap the diffusion cell. It provided a pressure tight seal up to at least 1.5 atmospheres. The body of the valve was made of Teflon®[2]. The pressure seal was made at the mouth of the cell by a system which consisted of two rubber rings encased inside the base of the valve on which pressure was exerted by a threaded ring. The ring was turned down on the rubber rings which caused the base of the valve to bulge, making the seal. The valve mechanism was a sliding cylinder which passed through the axis of the valve at right angles to it. When the valve was open, a needle could be inserted through the valve's axis into

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[1] Registered Trademark, Pierce Chemical Co.

[2] Registered Trademark, I. E. du Pont de Nemours & Co.

the diffusion cell. When the valve was closed, the hole in the sliding cylinder was no longer in line with the valve axis and a needle could not be pushed through it. To prevent gas from escaping around the needle when it was inserted, a small silicone septum was located above the sliding cylinder. So, to use the valve, one would slide the Teflon® cylinder to the open position and insert the syringe needle through the body of the valve.

Diffusion Trays

In order to reduce the time needed to perform the experiments, a thin layer of solution was used. Since some of the solutions were not very viscous, small Teflon® trays (figure 4) were made to contain the solutions during the experiment. Teflon® was chosen because of its inert characteristics. The outside dimensions of the trays were 1 1/8 in. long, 7/16 in. wide, and 1/8 or 7/32 in. thick. A pit 1.5 mm or 4.5 mm deep was machined into the middle of each tray. A small hole was drilled into one corner of each tray to provide a way to remove the trays from the diffusion cells. A small wire hook was used for this purpose. The hook was placed into the diffusion cell and through the small hole in the Teflon® tray. The hook was then used to place and position the trays in the diffusion cells and to remove the trays from the diffusion cells.

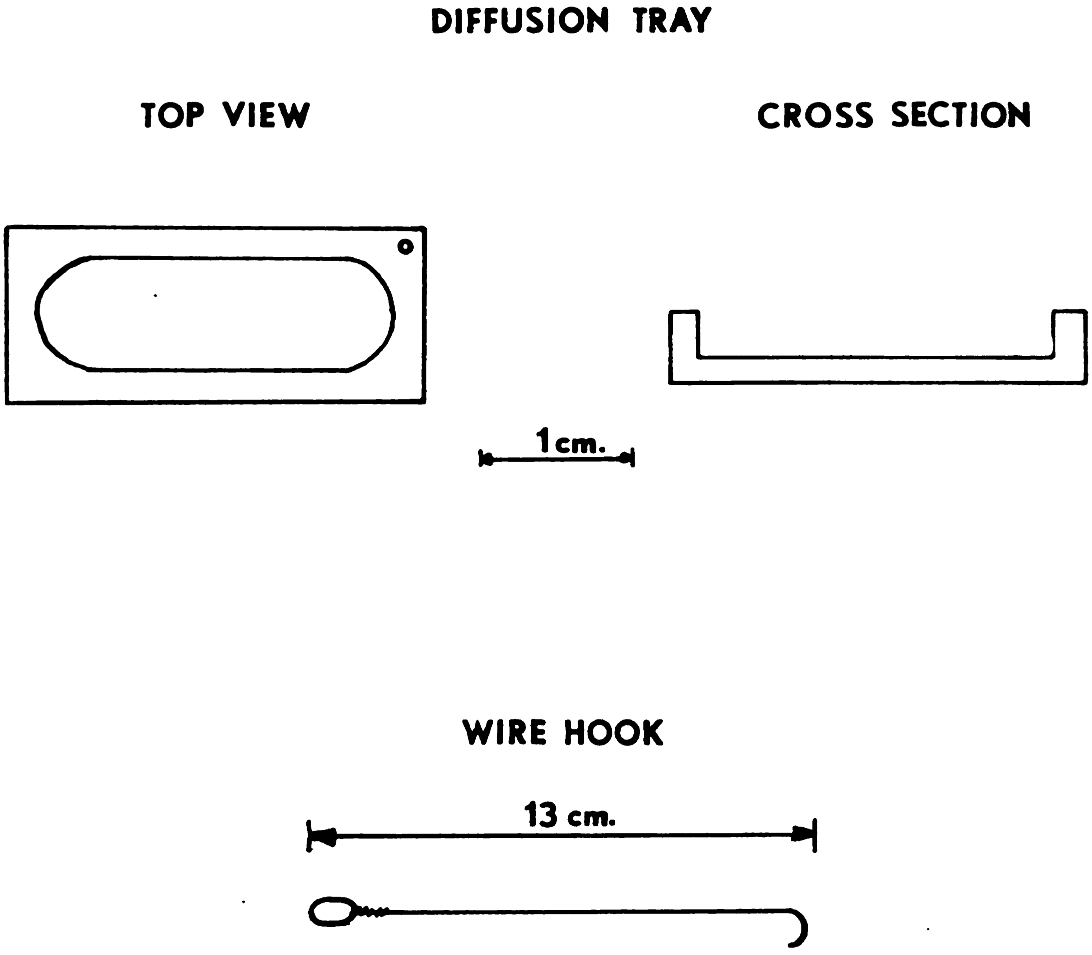

FIGURE 4. DIFFUSION TRAY AND WIRE HOOK

Manometer

A U-tube manometer was used to measure the pressure in the cells. It was made from 3/8 in. O.D. glass tubing. The glass tube was bent so that one side of the manometer tube was 38 cm tall and the other side was 72 cm tall. Triple distilled mercury was poured into the U-tube and a thin Tygon®[1] tube was attached to the short end. A 22 gauge, 3 in. long hypodermic syringe needle was affixed to the free end of this Tygon® tubing. A 40 cm ruler was placed behind the long tube with the graduation increasing up. In this way, the level of mercury in the long tube could be sighted through the tube. The long tube was left open to the atmosphere. The pressure in the diffusion cells was measured by inserting the manometer needle into the cell and observing the level in the U-tube.

Materials

Table 1 lists sources of the chemicals used in the experiments. The characteristics of the malto-dextrin, Fro-dex®[2] 10 are listed in table 2. The average molecular weight of the malto-dextrin was assumed to be 1641.2. Fro-dex® 10 has an average chain length of 10 sugar molecules according to the American Maize Products Company.

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[1] Registered Trademark, Norton, Inc.

[2] Registered Trademark, American Maize Products Co.

TABLE 1

CHEMICALS AND SOURCES

Chemical	Source
Fro-dex® 10 Malto-dextrin	American Maize Products Co.
2-Butanone	Mallinckrodt, Inc.
1-Hexanol	Aldrich Chemical Co, Inc.
1-Butanol	Mallinckrodt, Inc.
1-Pentanol	Mallinckrodt, Inc.

TABLE 2

CHEMICAL AND PHYSICAL DATA--
AMAIZO FRO-DEX® 10

Moisture	5.0%
Dextrose Equivalent	10
SO_2 (M.W.)	40 ppm
pH (1:1)	4.5
Weight per cu. ft.	30 lbs
Carbohydrate Composition (Approx. D.B.)	
Monosaccharides	1%
Disaccharides	4%
Trisaccharides	5%
Tetrasaccharides & Higher	90%

Experimental Procedure

Malto-dextrin solution preparation. Solutions of Fro-dex® 10 malto-dextrin in water were prepared on a weight basis with an accuracy of 1% absolute. About 12 g of the malto-dextrin was weighed into a 250 ml beaker to within 0.1 g on a top-loading digital balance. About 5 g of deionized water was added in excess of the desired weight percentage. This water was added so that upon heating, the malto-dextrin would completely dissolve before the desired weight percentage was obtained. This excess of water was especially important when preparing the 70 and 80 wt % solutions because they had a tendency to become very viscous as water evaporated from them, making them very difficult to stir.

After adding the water, the mixture was heated to 90° - 100° C on a hotplate, and was stirred continuously until the malto-dextrin completely dissolved. It was assumed that the malto-dextrin was in solution once the mixture was clear. The solution was stirred and periodically weighed on a top-loading balance until enough water was lost to increase the weight percentage to that desired. A stream of air was directed into the beaker of malto-dextrin solution while it was being heated to increase the evaporative water loss. When enough water was evaporated from the solution to make the desired weight percentage, it was allowed to cool to room temperature. The solution was weighed again and enough water was added to replace the water lost to evaporation during cooling. Then the solution was stirred and the beaker was covered with Parafilm®[1] wrap. The solution was stored in a refrigerator at 10° C until needed. Storing the solutions this way prevented infestation by mold for at least three months.

Solution density measurement. The density of malto-dextrin solutions was measured at varying temperature and weight percent solids using a glass pycnometer. Solutions of the malto-dextrin were prepared and placed in the pycnometer. Air bubbles were removed from the solutions by centrifuging the pycnometer at 2000 r.p.m. The more viscous 70 and 80 wt % solutions were heated to 60° C and then centrifuged to speed the displacement of trapped air. After the pycnometer had been filled with solution at room temperature, it was held in a 1000 ml beaker containing 600 ml of water. Clamps and a ring-stand were used to hold the pycnometer in the beaker so that the pycnometer was just covered with water. The beaker of water served as a constant temperature bath. An 8 cm long, Teflon® coated, magnetic stirring bar was placed in the beaker. The beaker rested on a stirring hotplate. A thermometer was held in the water by means of clamps and a ring-stand.

At the onset of the experiment, the pycnometer was clamped into place in the beaker and the hotplate was

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[1] Registered Trademark, American Can Co.

turned on. The beaker was heated at a rate of about 0.5° C per minute. As the desired temperature was approached, the heat setting on the hotplate was reduced. When the exact temperature was reached, the heat setting was adjusted carefully to obtain a constant bath temperature. The temperature was held for 20 minutes to insure thermal equilibrium within the pycnometer. After the 20 minute period, the pycnometer was removed from the water bath and allowed to cool to room temperature. The pycnometer was then weighed to within 0.01 mg. The pycnometer was opened with a pair of pliers and cleaned in hot water.

The weight of the pycnometer was determined when it was empty and dry. The volume was calibrated with boiled, deionized water at the temperatures used in the experiment. The deionized water was boiled to remove dissolved carbon dioxide.

Viscosity measurements. The viscosity of 30, 50 and 65 wt % solids solutions were measured at 60°, 75° and 90° C. An Ostwald-Fenske viscometer was used for the 30 and 50 wt % solids solutions. A Ferranti Couette viscometer of the coaxial cylinder type was used for the 65 wt % solids solution. The procedures are similar to those discussed by Collins, et al. (1973). The Ostwald-Fenske viscometer was clamped to a ring-stand and immersed in the constant temperature bath. Into the viscometer was pipetted 10 ml of the solution. Ten minutes were allowed for the contents of the viscometer to reach the bath temperature. Using a rubber pipette bulb, the solution was drawn up past the upper mark above the capillary and released. The flow time between marks was measured to .001 minutes with a timer. The flow times for water and 30 and 50 wt % solutions were measured. the viscosity of the malto-dextrin solutions was calculated by taking the ratios of flow times for water and the malto-dextrin solutions. That is,

$$\mu = \frac{t}{t_W} \mu_W \ . \tag{30}$$

For the 65 wt % solids solution, the Couette viscometer was used. A 250 ml beaker containing about 150 ml of the solution was clamped to a ring-stand and placed in the constant temperature water bath so that the water level was higher than the solution level. The viscometer was clamped above the beaker on the ring-stand so that the cylinders were immersed in the solution. The deflection meter needle was zeroed. The motor was turned on and the deflection reading was taken over a period of at least five minutes. The readings showed no change over the five minute period. The deflection reading represented the torque applied to the inner cylinder while the outer cylinder was rotating. This was repeated until three consecutive readings agreed. The deflection reading is proportional to the viscosity of the liquid being tested. Pure glycerine was used to calibrate the viscometer. The deflection reading was taken for glycerin at 38° C using the same rotation speed and the same set of cylinders. According to Ferranti, the resistance spring in the viscometer gives a linear displacement with applied force (Users Manual), the readings of the standard and the unknown solutions can be ratioed to give the ratio of the standard and unknown viscosities. That is,

$$\mu_S = \frac{R_S}{R_{Std}} \mu_{Std} \ . \tag{31}$$

Where R is the deflection reading.

Attempts were made to measure the viscosities of malto-dextrin solutions with concentrations greater than 65 wt % using a Weissenberger Rheogoniometer. However, the evaporation rate from the edge of a cone and plate assembly was so rapid that the solutions solidified before measurements could be obtained.

Diffusion Experiment

The diffusion coefficient and the vapor-liquid equilibrium coefficient were measured in aqueous malto-dextrin solutions containing 30, 50, 70 and 80 wt % solids and water. The vapor-liquid equilibrium coefficient was measured for 15 wt % solids solutions, also. The experiments were performed at 60°, 75° and 90° C.

Concentrated malto-dextrin solutions. For solutions containing 30, 50, 70 and 80 wt % solids, the experiments were performed using Teflon® diffusion trays inside the diffusion cells. The diffusion trays were filled with malto-dextrin solution and the trays were placed in the cells.

The solutions were placed in the diffusion trays and diffusion cells in one of two ways, depending on their percent solids. The low-percent solids solutions (30 and 50 wt %) were pipetted into a diffusion tray already placed in a diffusion cell. A small wire hook was used to place the diffusion trays in their cells. The trays had to be tipped to place them in the diffusion cell, therefore, low percent solids solutions were pipetted directly into the diffusion cells using a disposable pipette because they were not viscous enough to stay in the diffusion tray when it was tipped. High percent solids solutions (70 and 80 wt % solids) were pressed into the diffusion trays with a metal spatula. The diffusion tray was then placed into a diffusion cell with the small wire hook.

In the experiments, samples were of two types. Steady state samples were the samples with which the vapor-liquid equilibrium coefficient was measured. They were exposed to the diffusant until equilibrium was approached. Unsteady state samples were exposed to the diffusant for a short period. The diffusion coefficient was measured with the unsteady state samples.

In order to maintain the malto-dextrin solutions at a constant weight percent during the experiment, deionized water was injected into the diffusion cells before placing them into the temperature bath. A 250 µl and a 50 µl syringe were used to inject the water. Table 3 gives the amounts of water added to the diffusion cells. For a given percent solids, the same amount was added at all temperatures. These amounts of water were determined from a simple experiment and trial-and-error. The simple experiment consisted of injecting varying amounts of water into diffusion cells containing a given percent solids solution and measuring the change in percent solids after about 24 hours. A rough estimate of the required amount of water was calculated. It was also noted if a skin was formed in the 24-hour period. Formation of a skin on the solution was an indication of drying. The percent solids measured during the diffusion runs showed that the amounts of water added to the cells were reasonably close to the amounts needed.

After the water was added to each of the sample cells, they were placed in the constant temperature bath for a period of time called the "conditioning period." Diffusant was added to the steady state sample cells before the conditioning period and to the unsteady state sample cells after the conditioning period. During the conditioning period, vapor-liquid equilibrium with respect to diffusant was approached in the steady state sample cells. Vapor-liquid equilibrium with respect to water was approached in all of the sample cells during this period. Regardless of the experiment temperature, each

TABLE 3

VOLUME OF WATER ADDED TO DIFFUSION CELLS

Wt % Solids	μl Water
30	160
50	100
70	50
80	30

set of samples were conditioned for 24 hours at 90° C. This was the total conditioning period for 90° C samples. The 75° C samples were conditioned at 75° C for another 48 hours after the initial 90° C conditioning. The 60° C samples conditioned at 90° C for 24 hours, 75° C for another 24 hours and, finally, for 72 hours at 60° C. So, the 90° samples received a total of 24 hours of conditioning, the 75° C samples received a total of 72 hours of conditioning and the 60° C samples received a total of 120 hours of conditioning.

The approximate diffusivity of diffusant was determined in early experiments. With these approximate values, an approximate run time was determined for each experimental condition using the solution to the unsteady state equation. Run times were targeted at 20% approach to steady state. Enough diffusant was added to both the steady state and unsteady state sample cells to bring the partial pressure of diffusant up to one-half of its vapor pressure. Table 4 gives the amounts of diffusant added at each temperature. Gaseous diffusants could easily be used in this experimental apparatus. A gas tight syringe could be used to inject the diffusant into the cell.

The head space of the diffusion cell was sampled using a 1 ml Hamilton gas tight syringe. The syringe was heated to the water bath temperature inside a Plexiglass® mantle as described earlier. The syringe

TABLE 4

AMOUNTS OF DIFFUSANT ADDED TO DIFFUSION CELLS

Temperature	Volume of Liquid Diffusant (μl)	
	1-Hexanol	2-Butanone
60° C	4.6	30
75° C	10.1	100
90° C	20.8	200

was cleaned by aspiration of water and methanol through the needle. The contents of the syringe was evacuated using an aspirator before each sample injection. Prior to sampling the vapor, the pressure inside the cell was measured using a manometer. The syringe needle was plunged through the cell valve into the body of the cell. About 0.5 ml of the vapor was drawn into the syringe and expelled back into the cell. This was done to fill the small void volume of the syringe with the vapor in the cell. Then 1.0 ml of the vapor was drawn into the syringe. The syringe needle was drawn out of the cell and the sample was quickly injected onto the gas chromatograph column. The needle was kept in the injection port for ten seconds to prevent loss of vapor through the port. Immediately after removing the syringe, the valve on the cell was closed. This process was repeated at least three times and the results of the best two injections were averaged.

Aqueous solutions of the diffusant were used as standards. Standard curves of peak area versus weight injected were linear in their entire range. The gas chromatograph column and conditions are tabulated in table 5 for the vapor and liquid samples. A Hewlet-Packard 5840A gas chromatograph with a flame ionization detector was used.

After the vapor had been analyzed, the cell was removed from the water bath and liquid samples were taken.

TABLE 5

GAS CHROMATOGRAPH COLUMN AND CONDITIONS

	Liquid Samples	Vapor Samples
Column	5% Carbowax 20 M	5% SP 2100
Column Temp.	115° C	110° C
Detector Temp.	400° C	400° C
Nitrogen Flow	60 ml/min.	40 ml/min.
Injector Temp	140° C	130° C
Carrier Gas	N_2	N_2

The time that the cell was removed from the bath was recorded as the end of the experiment. The valve was removed from the diffusion cell and the cell was flushed for about two seconds with clean air. Air flushing was necessary to remove the diffusant and water vapor from the cells so that they did not condense on the liquid samples. The liquid sample was then removed from the Teflon® trays. Half of the sample was used to determine the percent solids and half was used to determine the concentration of diffusant. Samples were taken in one of two ways. Less viscous 30 and 50 wt % solids solutions were sampled with a disposable pipette when the diffusion trays were inside the cells. Solutions of 70 and 80 wt % solids were sampled after the diffusion trays were removed from the cells. A spatula was used to scrape the solution out of the tray.

The liquid sample for the percent solids determination was weighed to within 0.01 mg into a preweighed aluminum dish. The weight of the sample was recorded. The sample was dried at 110° C for 48 hours. The sample was allowed to cool to room temperature in a dessicator and then weighed. The dry weight of the sample and dish were recorded. Prior to their use, the aluminum dishes were dried at 110° C for at least 24 hours to remove any volatiles absorbed on the dish surface.

The portion of the liquid sample for the concentration determination was weighed into a preweighed 6 ml serum bottle. A small amount of internal standard was added to the vial and the vial was weighed again. Internal standards for 1-hexanol and 2-butanone were 1-butanol and 1-pentanol, respectively. The weights of the vial, the vial plus sample, and the vial with sample and internal standard were recorded to within 0.01 mg. The vial was filled to the top with deionized water. A silicone rubber septum with a Teflon® coating on one side and an aluminum crimp cap was used to cover the vial. The septum was placed with the Teflon® side toward the solution in the vial. The aluminum cap was placed over the septum and crimped down. The septa were used to prevent volatile loss prior to the liquid analysis.

Concentrated liquid standards containing a known ratio of diffusant to internal standard were prepared. The approximate amount of malto-dextrin that was contained in the samples was weighed into the standard serum vial. Two drops of the concentrated standard solution containing a known weight ratio of diffusant to internal standard were pipetted into the vial. The vial was filled to the top with deionized water and a septum was crimped on the top of the vial.

Liquid samples of 3 µl were injected onto a gas chromatograph column. At least three duplicate injections were done for each sample. The gas chromatograph column and conditions are listed in table 5. Since there was some malto-dextrin in the sample, the glass wool in the injector end of the column was changed before each set of samples. Also, the detector was kept at 400° C (its maximum temperature) during the runs to prevent fouling of the detector by volatile components of the malto-dextrin.

Dilute malto-dextrin solutions. The diffusion coefficient of 2-butanone and 1-hexanol was measured in water. The vapor-liquid equilibrium coefficient of each was measured in water and 15 wt % solids solution. Water or 15 wt % malto-dextrin solution was placed in 2 ml screw-top vials in the diffusion cells. Wire loops were attached to the neck of the vials so that they could be removed from the cells without spilling the contents. The vials were placed in the very bottom of the diffusion cells and lead shot was banked up against the vials to keep them vertical. After the vials had been positioned inside the cells, 1.4 ml of the liquid was placed in each of them. To maintain the humidity in the cell, 200 µl of deionized water was added to the vapor space. The gas sampling procedure was the same as that used for the concentrated solutions. Before the conditioning period of 24 hours, diffusant was added directly to the steady state sample vials. Diffusant was added directly to the sample vials to ensure fast equilibrium in the steady state samples. After the conditioning period, diffusant was injected into the unsteady state sample cells. Care was taken not to get any diffusant in the unsteady state vials. The diffusant was dropped onto the lead shot at the bottom of each diffusion cell containing unsteady state samples. The beginning of the experiment was recorded as the time at which the diffusant was injected into the cell. At the end of the experiment, after the gas had been sampled, the valve was removed from the cell and the sample vial was quickly removed and capped.

After the samples had cooled to room temperature, they were directly injected onto a gas chromatograph column. Triplicate 3 µl injections were used. A standard of known concentration was injected with the same syringe used to inject the samples. The same syringe was used to insure accurate volume reproduction. All other details of the analysis follow the procedure for concentrated malto-dextrin solutions.

Effects of pH on Coefficients

Solutions of constant pH were prepared by adding 1.0 ml of a pH buffer solution to 20 g of 50 % wt solids malto-dextrin solution. Phosphate buffer solutions were used (Weast, 1975). For the pH 6.0 and 8.0 stock solutions, 2.4 g and 0.2 g of monobasic sodium phosphate was weighed into a 100 ml beaker. To this, 50 ml of deionized water was added. The pH was adjusted to 6.0 and 8.0 with a saturated solution of dibasic sodium phosphate. This solution was diluted to 100 ml in a volumetric flask.

These 50 wt % solutions were run at 90° C in the same way that all of the other solutions were. The diffusivities and equilibrium coefficient of the pH 6 and 9 solutions were compared to that of the unbuffered solution. The pH of the unbuffered solution was 4.3.

Calculation of the Diffusion Coefficients

The diffusivities of 1-hexanol and 2-butanone were measured by performing an unsteady state experiment. A quasi-steady state experiment using a fritted diffusion cell was impossible to do here because the viscosity of the high solids malto-dextrin solutions were extremely large. It would be impossible to stir a malto-dextrin solution at a solids content of 80%. The only option left was to do an unsteady state experiment using diffusant in the vapor phase.

In these experiments, a small amount of liquid diffusant was added to the cell. It was assumed that the liquid diffusant evaporated and mixed very rapidly. The vapor phase was not mixed since the diffusivity of gasses is at least 1,000 times the diffusivity of the liquid. The physical situation in the experiments may be described as diffusion from a stirred solution of limited volume. Crank (1975) discusses the solution of this diffusion problem. The diffusion equation is

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (32)$$

where c is the diffusant concentration, t is time, x is distance and D is the diffusivity. The initial condition is

$$c = 0,\ 0 < x < 1,\ t = 0 \tag{33}$$

where l is the slab thickness. The boundary conditions are

$$\frac{\partial c}{\partial x} = 0,\ 1 = 0,\ t > 0 \tag{34}$$

and

$$\frac{KV_V}{A}\frac{\partial c}{\partial t} = -D\frac{\partial c}{\partial t,}\ x = 1,\ t > 0 \tag{35}$$

where V_V is the vapor volume, K is the vapor-liquid equilibrium coefficient and A is the slab surface area. This means that the concentration at the slab surface changes with time.

The solution to this equation is most easily obtained using the Laplace transform. In the form M_t/M_∞, where M_t and M_∞ are the mass of solute in the slab at time t and at infinity, the solution is

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha\ (1 + \alpha)}{1 + \alpha + \alpha q_n{}^2} \exp\ (-Dq_n{}^2/1^2) \tag{36}$$

where q_n is the non-zero positive root of

$$\tan q_n - \alpha q_n \tag{37}$$

where

$$\alpha = K\frac{V_V}{V_L}\ . \tag{38}$$

This form is good for all values of t, but is very difficult to solve numerically. A simpler form is

$$\frac{M_t}{M_\infty} = (1 + \alpha) \left[1 - \exp\ (T/\alpha^2)\ \mathrm{erfc}\ (\ T/\alpha^2)^{1/2}\right] \tag{39}$$

where $T = Dt/l^2$. This solution works well for small values of T. The solution behavior is shown in figure 5. The numbers on the graph represent the percent uptake, U. U is represented by

$$U = \frac{100}{1 + \alpha}\ . \tag{40}$$

Notice that $M_t/\ M_\infty$ is a linear function of $T^{1/2}$ for 0% uptake. The linearity in the curve decreases with increasing percent uptake. Notice also the extremely rapid change in M_t/M_∞ for 99% uptake. For systems that have small vapor-liquid equilibrium coefficients, the diffusant is absorbed rapidly.

D can be calculated in an iterative fashion using equation 39. Values of M_t/M_∞ and α are substituted and values of T are guessed until the correct value is found.

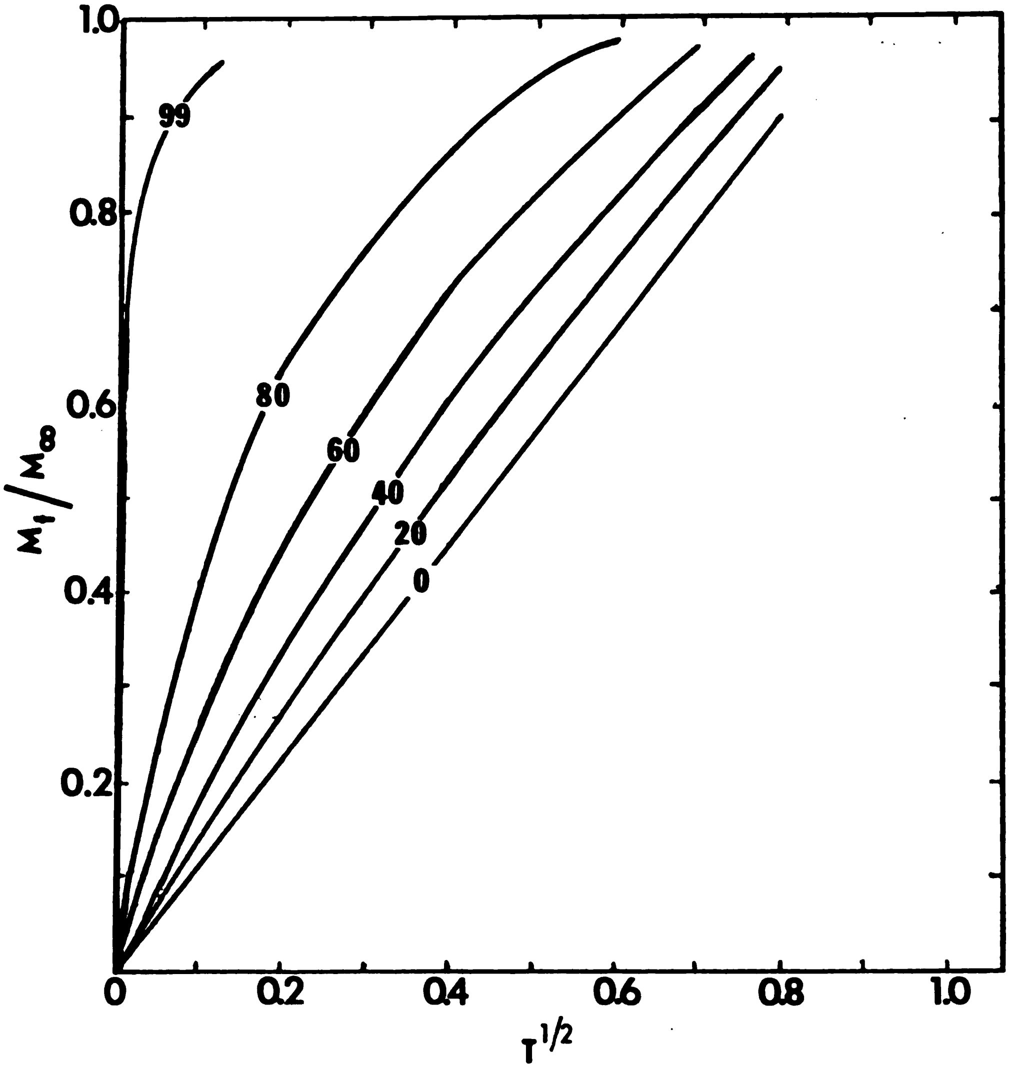

FIGURE 5. UPTAKE BY A SLAB FROM A STIRRED SOLUTION OF LIMITED VOLUME

RESULTS AND DISCUSSION

Solution Density

The density of the malto-dextrin solutions was measured over the range of experimental conditions used in the diffusion experiments. The density (table 6 and figure 6) was linear with S and fit the form

$$\rho = A + BS. \tag{41}$$

Table 7 gives A, B and the correlation coefficient, r, calculated for the data. Table 8 gives the density extrapolated from equation 41 at 0 and 100 wt % solids and the density of water (Weast, 1975). Since the extrapolated values are approximately 3% below the actual values of water density, the solutions are nearly ideal.

Viscosity Correlations

The viscosity of malto-dextrin solutions was measured so that the group $\frac{D\mu}{T}$ could be calculated from the diffusion data. Table 9 and figure 7 give the viscosity in centipoise for various percent solids and temperatures. The values of viscosity at 0 wt % are for water (Bennet and Meyers, 1974). The viscosity was a dramatic function of solids content, increasing over three orders of magnitude from 0 wt % solids (water) to 63 wt % solids. Temperature

TABLE 6

MALTO-DEXTRIN SOLUTION DENSITY (g/ml)

Wt % Solids	Temperature (° C)		
	60°	75°	90°
30.9	1.119	1.110	1.099
47.0	1.202	1.193	1.181
67.5	1.317	1.307	1.296

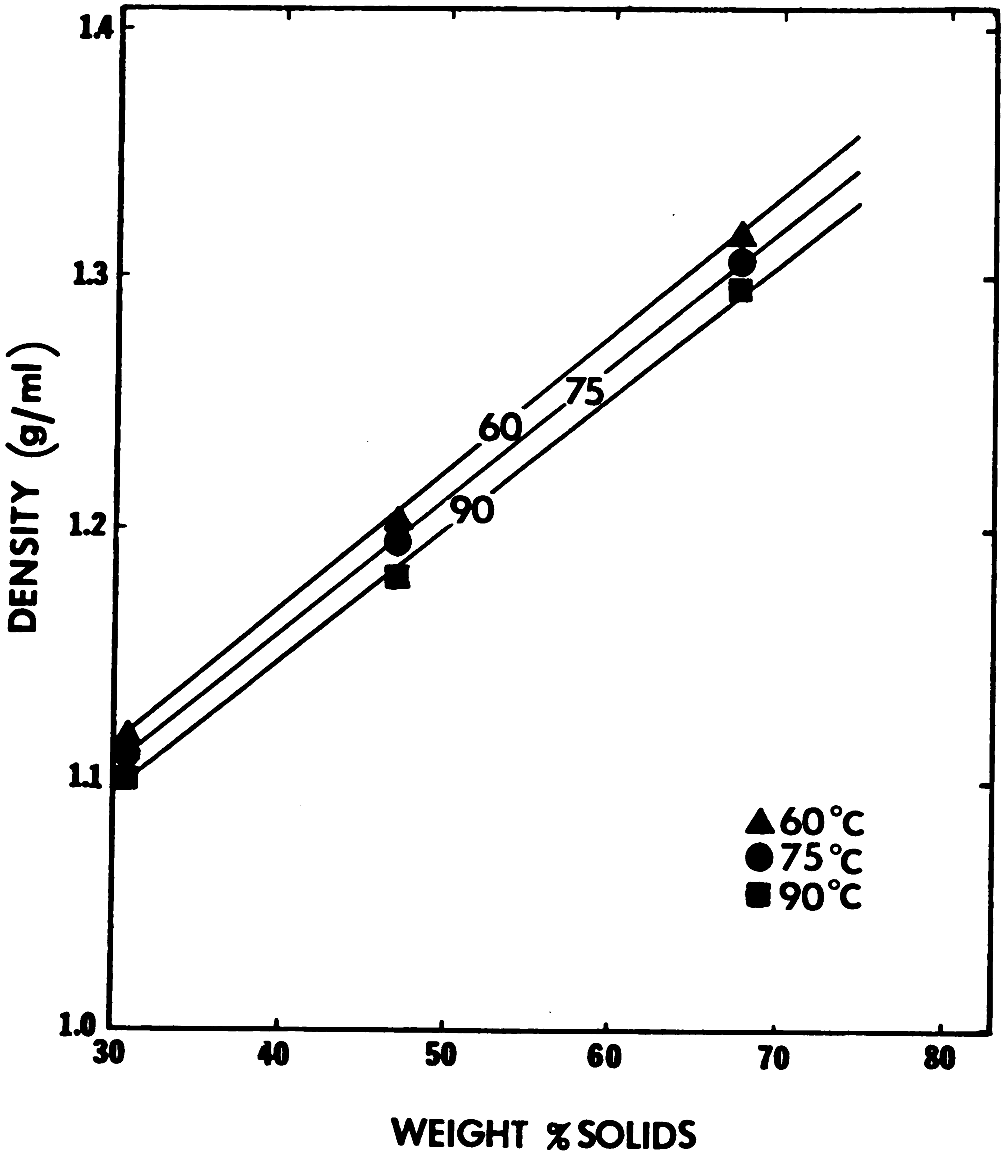

FIGURE 6. DENSITY vs. WEIGHT PERCENT SOLIDS

TABLE 7

CONSTANTS FOR THE DENSITY CORRELATION, EQUATION 26

Temperature (° C)	A	B	r
60°	0.9503	0.5414	0.9998
75°	0.9420	0.5390	0.9998
90°	0.9309	0.5388	0.9996

TABLE 8

EXTRAPOLATED VALUES OF WATER AND MALTO-DEXTRIN DENSITY AND ACTUAL VALUES OF WATER DENSITY

	Density (g/ml)		
Temp. (° C)	Water (Actual)	Water (Extrapolated)	Malto-dextrin (Extrapolated)
60°	0.9832	0.9503	0.4917
75°	0.9749	0.9420	0.4810
90°	0.9653	0.9309	0.4697

TABLE 9

VISCOSITY OF MALTO-DEXTRIN SOLUTIONS (cp)

Wt % Solids	Temperature (° C)		
	60°	75°	90°
0	0.4688	0.3799	0.3165
31.1	6.15	4.18	3.03
47.2	43.46	26.68	16.69
63.2	757	359	197

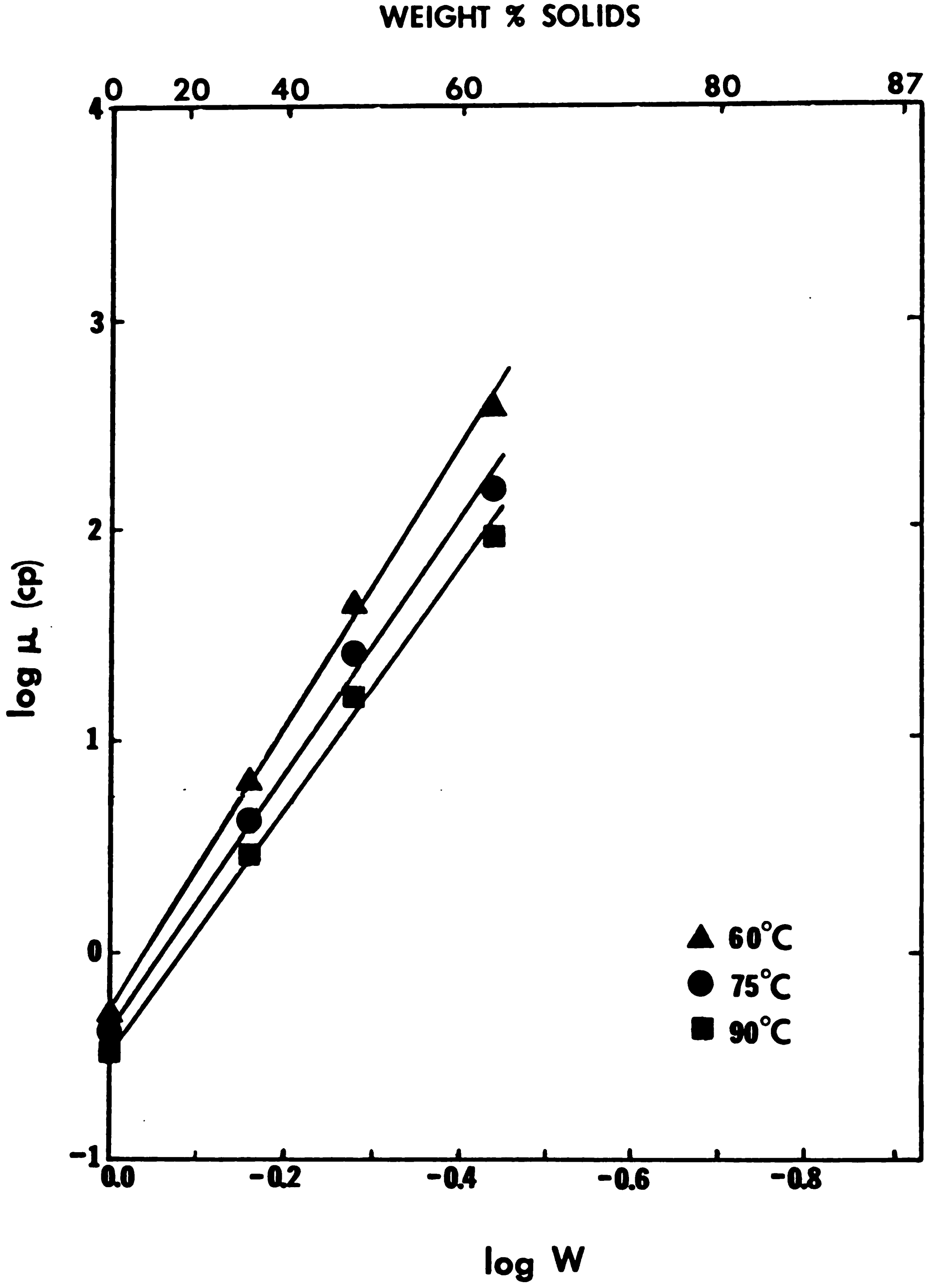

FIGURE 7. LOG μ vs. LOG W FOR MALTO-DEXTRIN SOLUTIONS

also had a marked effect on the viscosity.

Since the viscosity was to be used to calculate $\frac{D\mu}{T}$ at a number of values of percent solids, a correlation for viscosity was desired as a function of both temperature and solution concentration. It was also desired to extrapolate the viscosity above 63.2 wt % solids because of the rapid increase in viscosity with increasing solids content. Numerous equations were fit to the data with varying success (see appendix III).

The simplest correlation that gave good agreement was

$$\log \mu = A + B \log W \ . \tag{42}$$

This form showed the best correlation coefficients. Table 10 gives the constants and the correlation coefficients. Since the constants A and B are based on the log of the viscosity, they should be a linear function of $\frac{1}{T}$. That is,

$$A = C + \frac{E}{T} \tag{43}$$

$$B = D + \frac{F}{T} \ . \tag{44}$$

Linear regression analysis of A and B versus $\frac{1}{T}$ gave

$$A = -2.325 + \frac{651.8}{T} \ , \ r = 1 \tag{45}$$

and

$$B = 4.162 - \frac{3844}{T} \ , \ r = -0.9994 \ . \tag{46}$$

The total correlation became

$$\log \mu = -2.325 + 4.162 \log W + \frac{1}{T} (651.9 - 3844 \log W) \ . \tag{47}$$

TABLE 10

CONSTANTS FOR EQUATION 42

Temperature (° C)	A	B	r
60°	-0.3681	-7.3834	-0.9994
75°	-0.4523	-6.8584	-0.9996
90°	-0.5297	-6.4313	-0.9995

Viscosity data for sucrose and dextrose (Stephen and Stephen, 1963) were correlated to the same form,

$$\log \mu = C + D \log W + \frac{1}{T} (E + F \log W) \quad . \tag{48}$$

The constants C, D, E, and F, and the maximum correlation coefficient are given in table 11. C and D are fairly constant for the sugars studied. E and F show a decreasing trend with increasing molecular weight. E is the activation energy for the viscosity of water. E should be a constant. So, the only parameter which shows a significant variation with the molecular weight of the solute is F. F represents the magnitude of the effect of W on the activation energy. Since W is less than 1, a decrease in W (increase in percent solids) will cause an increase in the viscosity activation energy. For malto-dextrin,

$$E_\mu = 652 - 3844 \log W \tag{49}$$

an increase in percent solids causes an increase in the viscosity activation energy. Since equation 48 worked well for sucrose over a very wide temperature range, it was assumed to be generally valid.

Vapor-Liquid Equilibrium Coefficients

The vapor-liquid equilibrium coefficient, K, was calculated from the experimental results. K is defined as

$$K = \frac{C_V}{C_L} \tag{50}$$

where C_V and C_L are the concentration diffusants in the

TABLE 11

CONSTANTS FOR EQUATION 48

Compound	Molecular Weight (g/mole)	Temperature Range (° C)	Maximum r	C	D	E	F
Dextrose	180	25° - 50°	0.997	-2.74	3.71	790	-2511
Sucrose	342.3	15° - 85°	0.992	-2.48	4.14	703	-2109
Malto-dextrin	1621.4	60° - 90°	0.999	-2.32	4.16	652	-3844

vapor and liquid phases, respectively (see figures 8 and 9).

Assuming an ideal gas in the vapor phase, a low diffusant concentration in the liquid phase, and an average molecular weight of the malto-dextrin (M_S), the activity coefficient, γ, was calculated from the partition coefficient,

$$\gamma = K \frac{RT\rho}{P^{sat}} \left(\frac{S}{M_S} + \frac{1 - S}{M_W} \right) . \tag{51}$$

See appendix II for the derivation of this equation. The results of these calculations of γ are presented in figures 10 and 11.

The 1-hexanol vapor-liquid equilibrium coefficient was a steadily increasing function of temperature as one would expect since P^{sat} is also an increasing function of temperature. The striking feature of the vapor-liquid equilibrium coefficient is the minima in the curves with respect to percent solids. Kieckbusch and King (1979) have demonstrated that K decreases for pentyl acetate in malto-dextrin from 0 to 50 wt % solids. Their measurements were made at 25° C. For 1-hexanol at 60°, 75° and 90° C, K showed this trend. K can be written as

$$K = \frac{\gamma P^{sat}}{RT\rho \left(\frac{S}{M_S} + \frac{1 - S}{M_W} \right)} . \tag{52}$$

The strong minimum in K versus S for 1-hexanol was due to the combination of the rapid decrease in γ and the non-linearity of the denominator of equation 52. K was a non-linear function of S for 2-butanone as well but

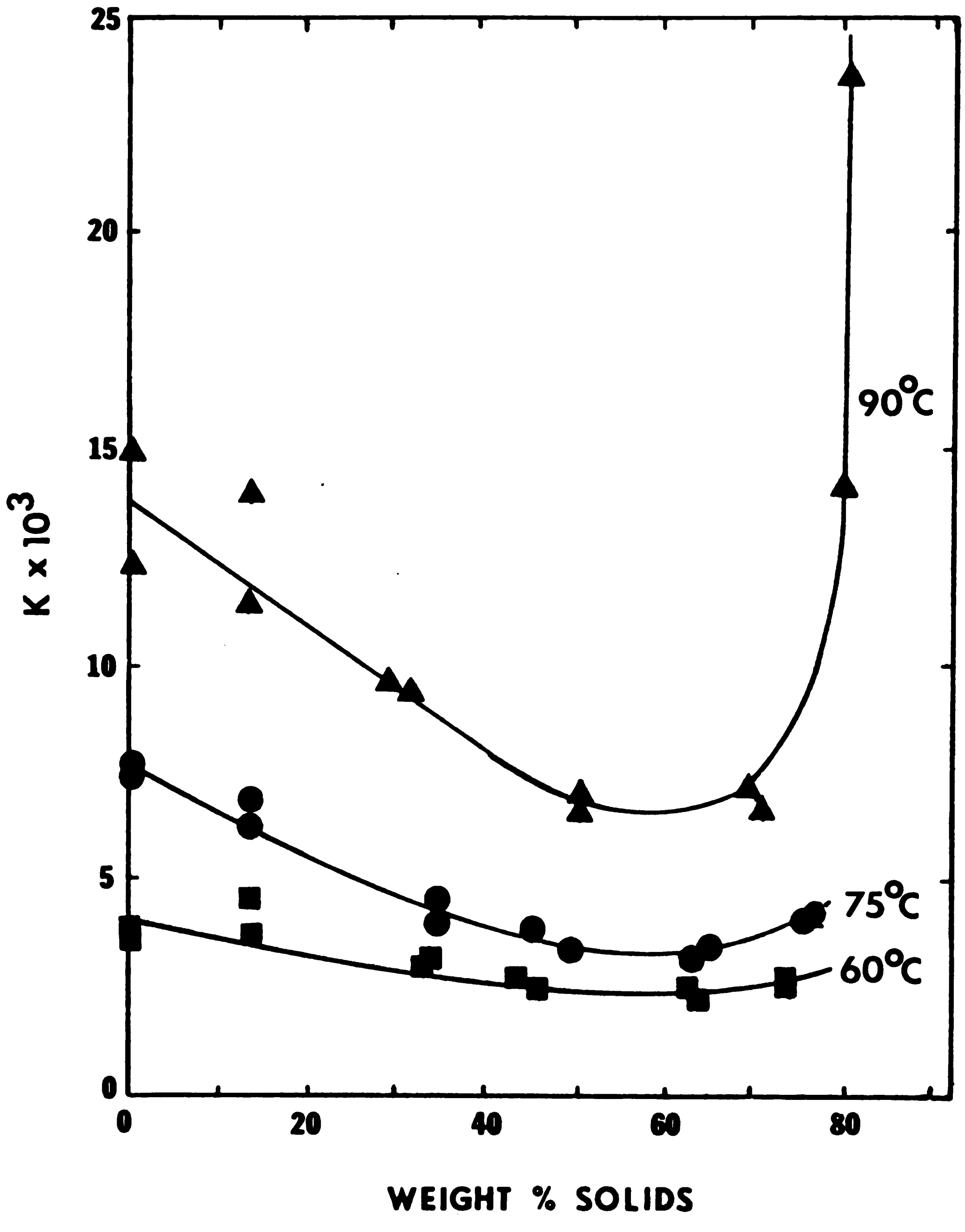

FIGURE 8. VAPOR-LIQUID EQUILIBRIUM COEFFICIENT vs. WEIGHT PERCENT SOLIDS FOR 1-HEXANOL IN MALTO-DEXTRIN SOLUTIONS

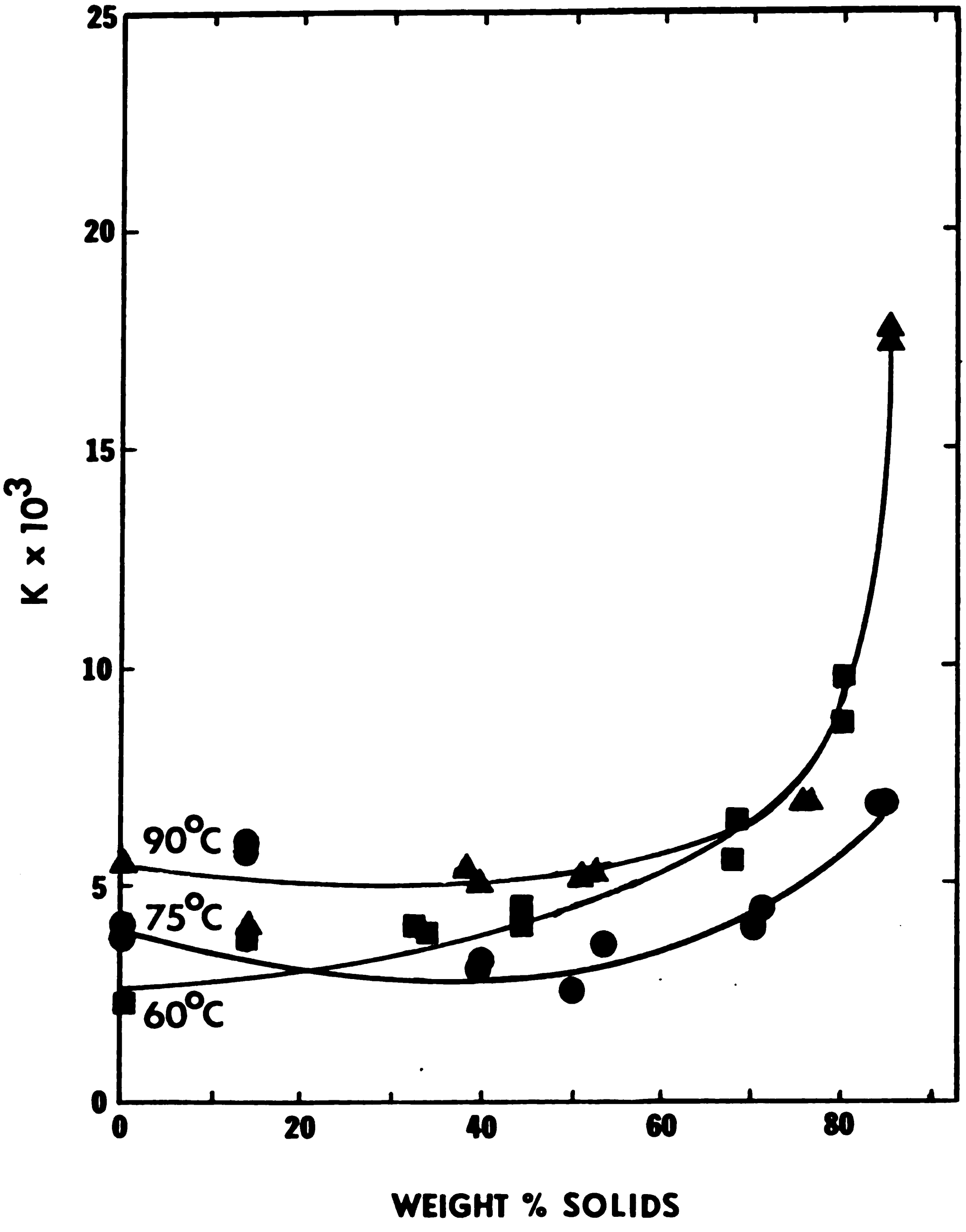

FIGURE 9. VAPOR-LIQUID EQUILIBRIUM COEFFICIENT vs. WEIGHT PERCENT SOLIDS FOR 2-BUTANONE IN MALTO-DEXTRIN SOLUTIONS

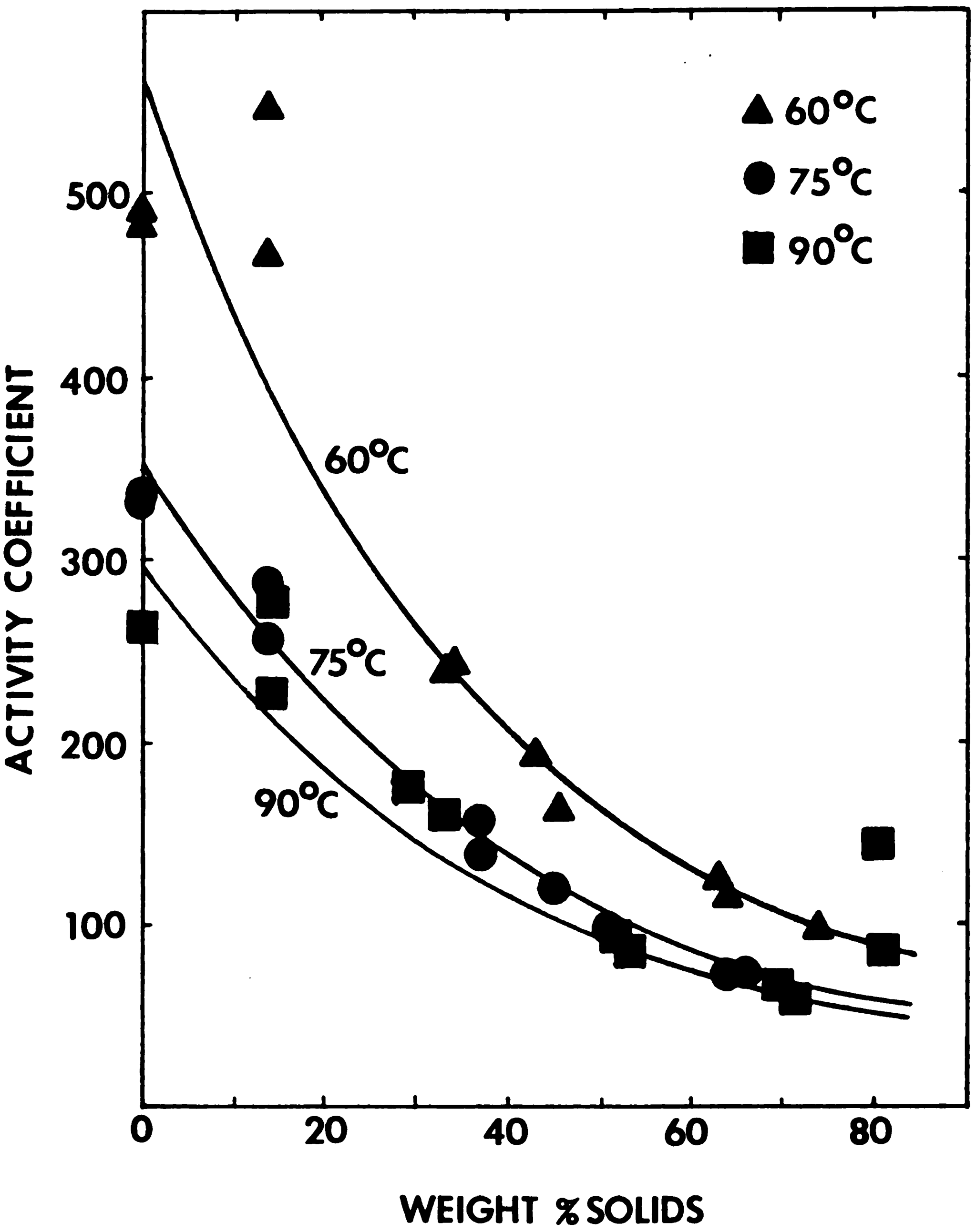

FIGURE 10. ACTIVITY COEFFICIENT vs. WEIGHT PERCENT SOLIDS FOR 1-HEXANOL IN MALTO-DEXTRIN SOLUTIONS

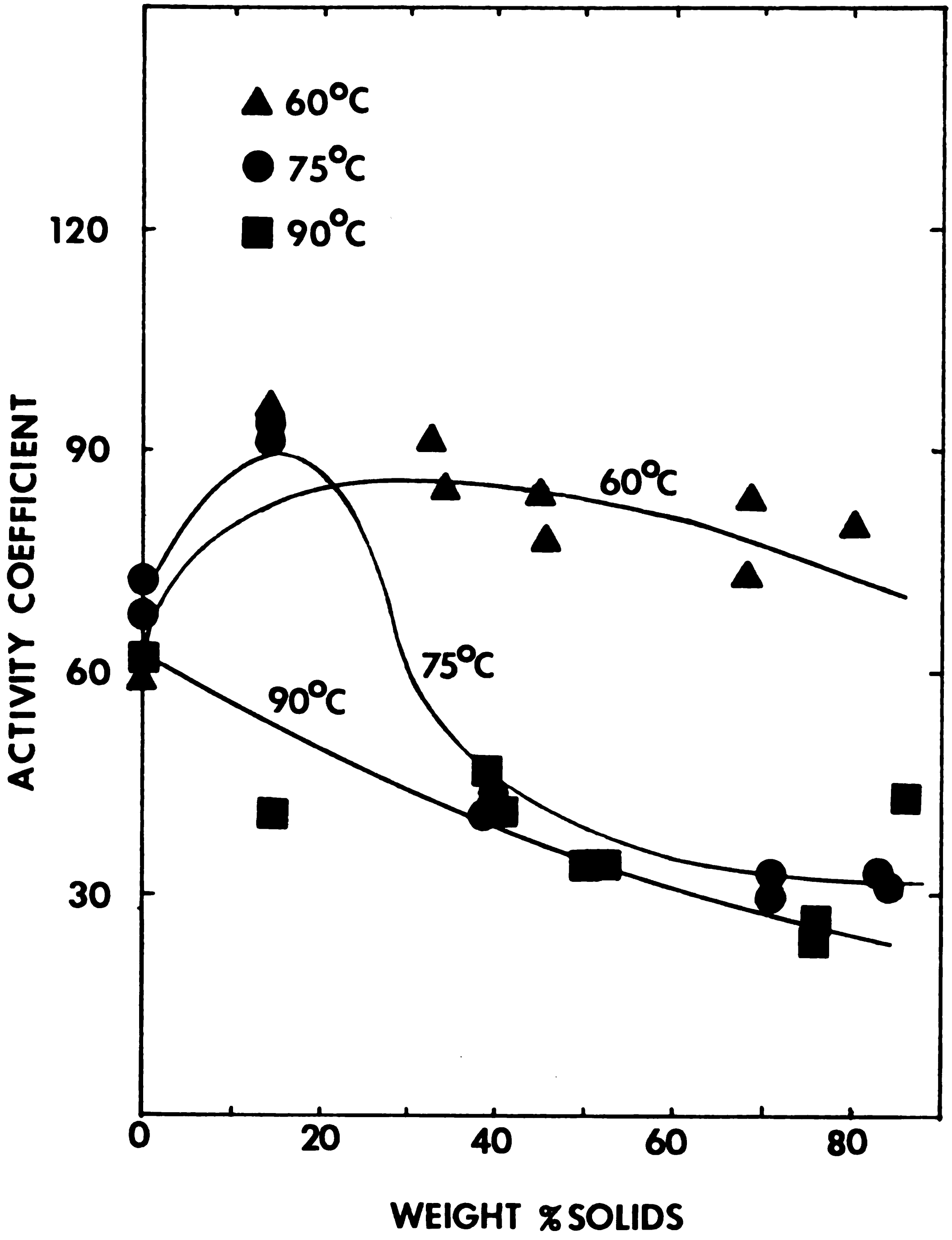

FIGURE 11. ACTIVITY COEFFICIENT vs. WEIGHT PERCENT SOLIDS FOR 2-BUTANONE IN MALTO-DEXTRIN SOLUTIONS

not show a minimum. The general trends in the activity coefficient for 2-butanone agreed with this. For the most part, γ for 2-butanone was relatively constant compared with γ for 1-hexanol. That was why K showed, at most, a very weak minimum for 2-butanone.

The activity coefficient at 0 wt % solids was calculated from other sources. Table 12 gives values of γ^{∞} for 1-hexanol and 2-butanone calculated from the Pierotti correlation (equation 9). Table 13 gives γ for saturated solutions of 1-hexanol and 2-butanone in water (equation 7) calculated from solubility data. The Pierotti correlation best approximated the data presented here. Most of the data for 1-hexanol was in the range of γ^{∞} at 50° and 100° C, calculated from the Pierotti correlation. The data for 2-butanone fell slightly above the expected values calculated from the Pierotti correlation at 50° and 100° C. The general trends in γ with respect to temperature were predicted by the Pierotti correlation with the exception of 2-butanone at 90° C.

The activity coefficients calculated from solubility data did not predict the absolute values of γ, but did predict the general trends in the data with the exception of 2-butanone at 90° C. According to solubility data and the Pierotti correlation, γ for 2-butanone should show a general increasing trend from 60° to 90° C, but γ at 90° C was between γ for 75° and 60° C. This discrepancy might have been due to experimental error or, more likely,

TABLE 12

ACTIVITY COEFFICIENT CALCULATED FROM THE PIEROTTI CORRELATION

Temp. (° C)	Activity Coefficient, γ	
	1-Hexanol	2-Butanone
50°	613.8	36.9
100°	319.9	41.1

TABLE 13

ACTIVITY COEFFICIENTS CALCULATED FROM SOLUBILITY DATA

Temp. (° C)	1-Hexanol		2-Butanone	
	Solubility (wt. %)	γ	Solubility (wt. %)	γ
30°	0.545	1100	21.9	15.3
50°	0.515	1160	17.5	19.9
70°	0.565	1060	16.2	21.7
90°	0.68	880	16.1	21.8
110°	0.89	670	17.7	19.6

Source: Stephen and Stephen, 1963

was a true representation of the behavior of γ.

The activity coefficient calculated from the solubility data showed a maximum at 90° C. Since the solubility of 2-butanone was significantly greater than the concentrations of 2-butanone used in this study, the activity coefficients calculated from solubility data cannot be directly compared with the data presented here. What the data did show is that there was a maximum in γ as a function of temperature and that the maximum occured at 90° C for high 2-butanone concentrations (solubility data) and at 75° C at low concentrations (this work).

The behavior of γ as a function of S showed some interesting results. The activity coefficient was a much stronger function of S for 1-hexanol than for 2-butanone. Since γ was inversely proportional to solubility, a decrease in γ should be interpreted as an increase in solubility or affinity of the solute to the solution. Therefore, the strong decrease in γ versus S in the 1-hexanol data should be interpreted as a strong affinity of 1-hexanol molecules to malto-dextrin molecules. Since γ was a much stronger decreasing function of solids content for 1-hexanol than for 2-butanone, 1-hexanol molecules had a much higher affinity toward malto-dextrin than did 2-butanone. The stronger affinity of 1-hexanol toward malto-dextrin as compared with 2-butanone was most likely due to hydrogen bonding. The alcohol should have hydrogen bonded to the malto-dextrin due to the hydroxyl group present. The ketone should have shown less hydrogen bonding with the malto-dextrin molecules since it does not have a hydroxyl group.

For 2-butanone, the maximum in γ as a function of temperature disappeared as the solids content increased. The maximum disappeared at about 20 wt % solids (figure 11). The disappearance of the maximum in γ indicated basic differences in attractive forces between 2-butanone and water, and between 2-butanone and malto-dextrin. The maximum in γ in water solutions has been explained as the formation and subsequent breakdown of ice-like structures of water formed around the non-polar part of the solute molecule as the temperature rises (Nishino and Nakamura, 1978). As the solids content increased, the maximum in γ disappeared. This indicates that the attraction of 2-butanone to malto-dextrin was not a result of structural changes similar to those exhibited by water. Whatever attraction there was between 2-butanone and malto-dextrin, was probably due to very weak hydrogen bonding.

Diffusion Coefficients

The diffusivity of 1-hexanol and 2-butanone in malto-dextrin solutions was a strong function of the solids content. Figures 12 and 13 show the log of the diffusivity versus the percent solids of the malto-dextrin solution. One should notice two trends in the diffusivity.

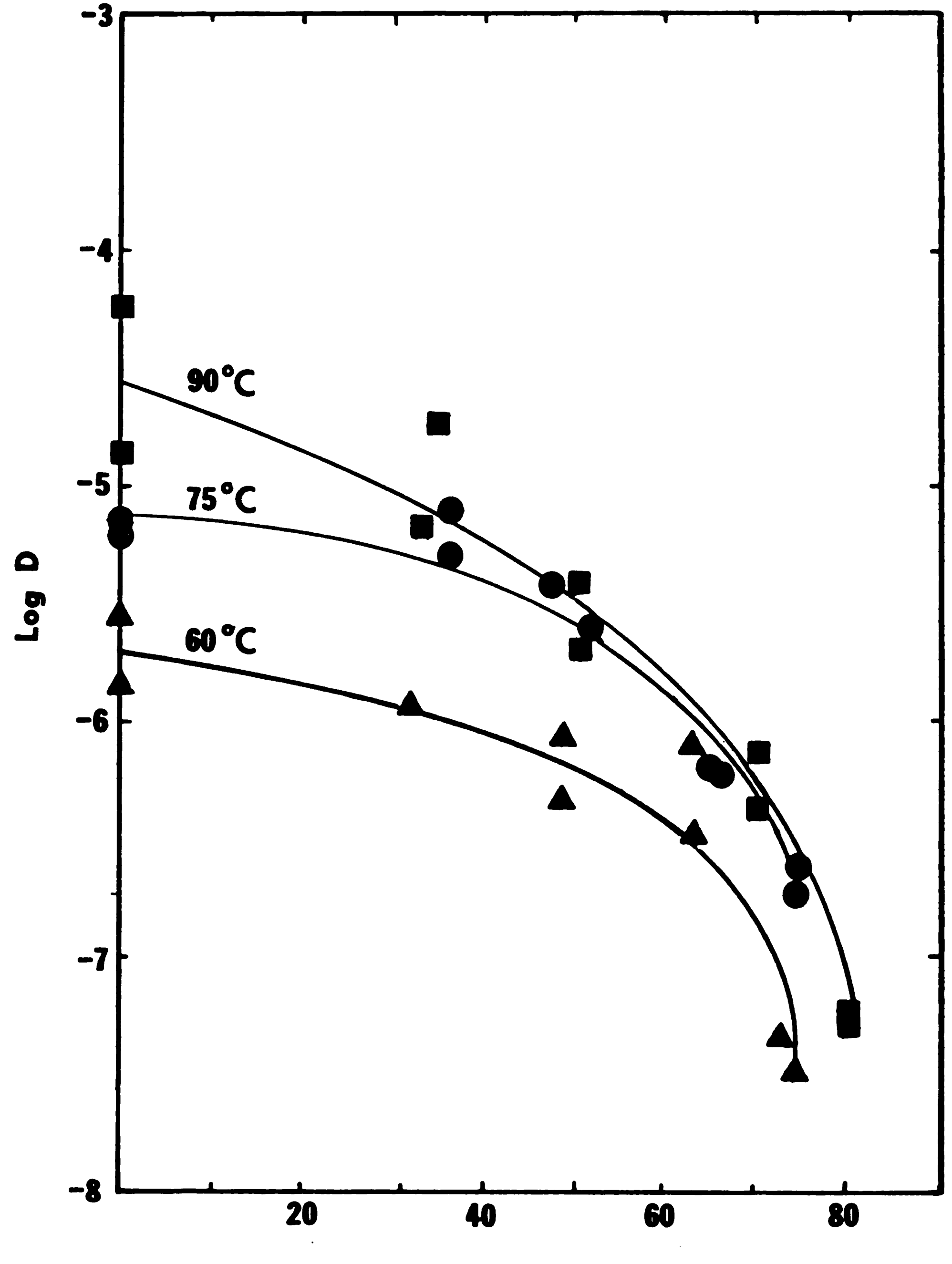

FIGURE 12. LOG D vs. WEIGHT PERCENT SOLIDS FOR 1-HEXANOL IN MALTO-DEXTRIN SOLUTIONS

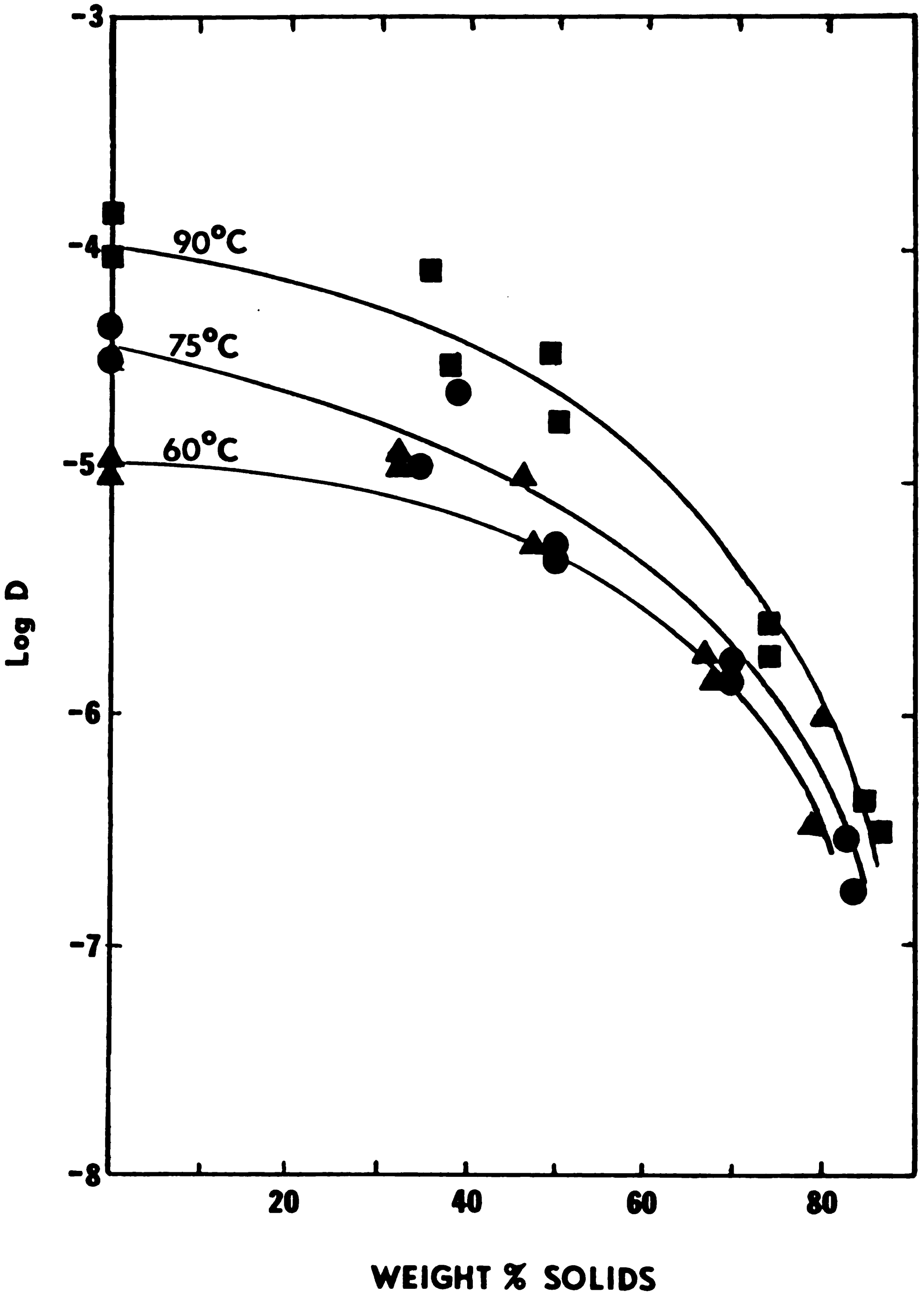

FIGURE 13. LOG D vs. WEIGHT PERCENT SOLIDS FOR 2-BUTANONE IN MALTO-DEXTRIN SOLUTIONS

First, the diffusivity decreased by several orders of magnitude from 0 to 80 wt % solids. Second, one should notice that the diffusivity decreased significantly with decreasing temperature.

Figures 14 and 15 show log $\frac{D\mu}{T}$ versus log W where W is the water weight fraction. The values of $\frac{D\mu}{T}$ were calculated from the diffusivity data and the malto-dextrin solution viscosity data. Notice that the data gave a straight line when plotted in this fashion. There was considerable scatter in the data, though.

Correlations for diffusivities of organic components from the literature were tried as a first evaluation of the data (equations 11 to 24). However, they did not work well to predict $\frac{D\mu}{T}$ of organic solutes in malto-dextrin solutions. M_B, which was used in the literature correlations, was assumed to be the average molecular weight of the solution,

$$M_B = \frac{M_W \, M_S}{M_W + (M_S - M_W) \, W} \tag{53}$$

where M_W is the molecular weight of water and M_S is the average molecular weight of the malto-dextrin. The correlations showed a slight decrease in log $\frac{D\mu}{T}$ below W = 1. The data showed a slope of about 4 times that of the correlations.

Most of the emperical correlations for $\frac{D\mu}{T}$ have the general form

$$\frac{D\mu}{T} = K M_B{}^{1/2} \quad . \tag{54}$$

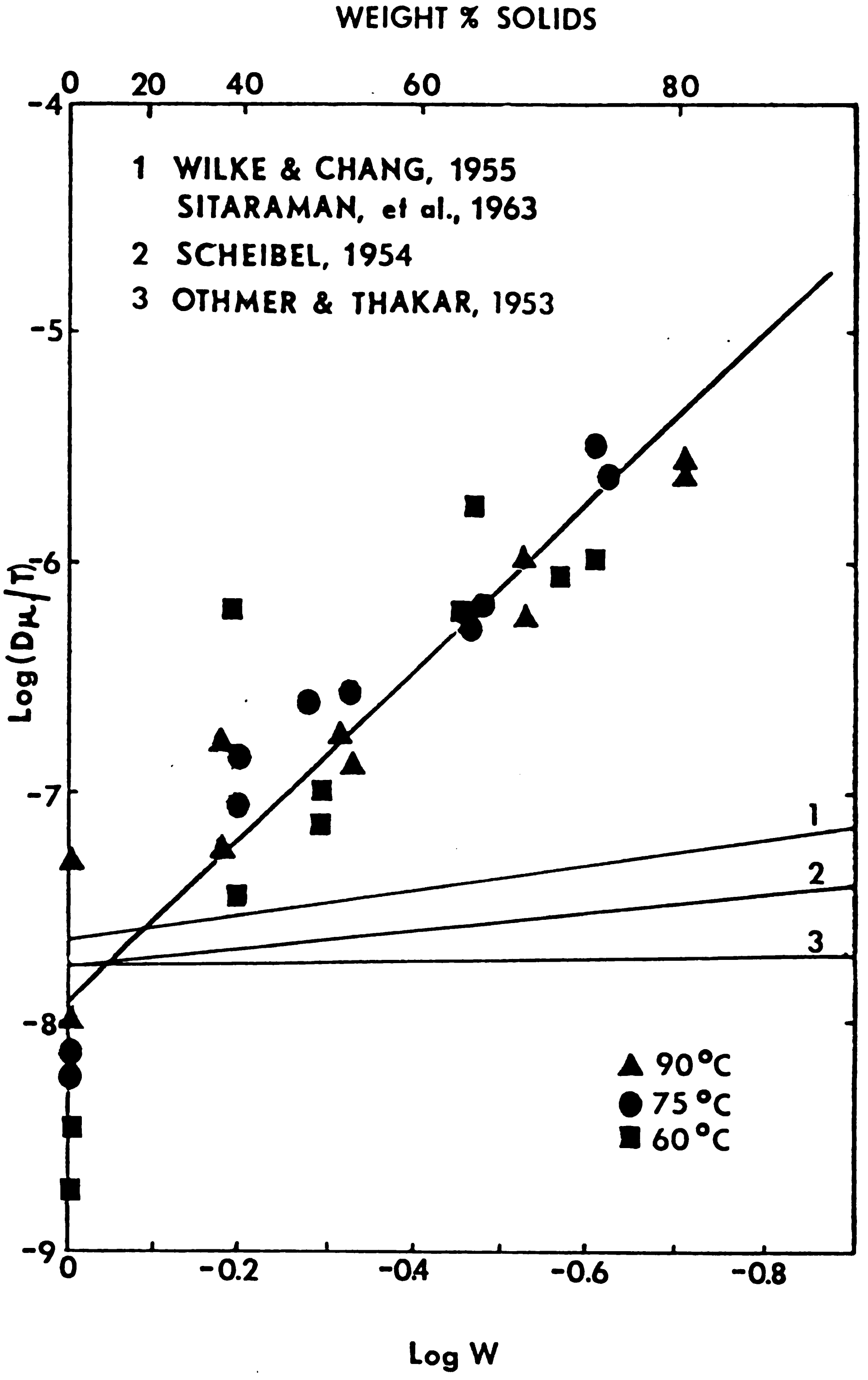

FIGURE 14. LOG (Dμ/T) vs. LOG W FOR 1-HEXANOL IN MALTO-DEXTRIN SOLUTIONS

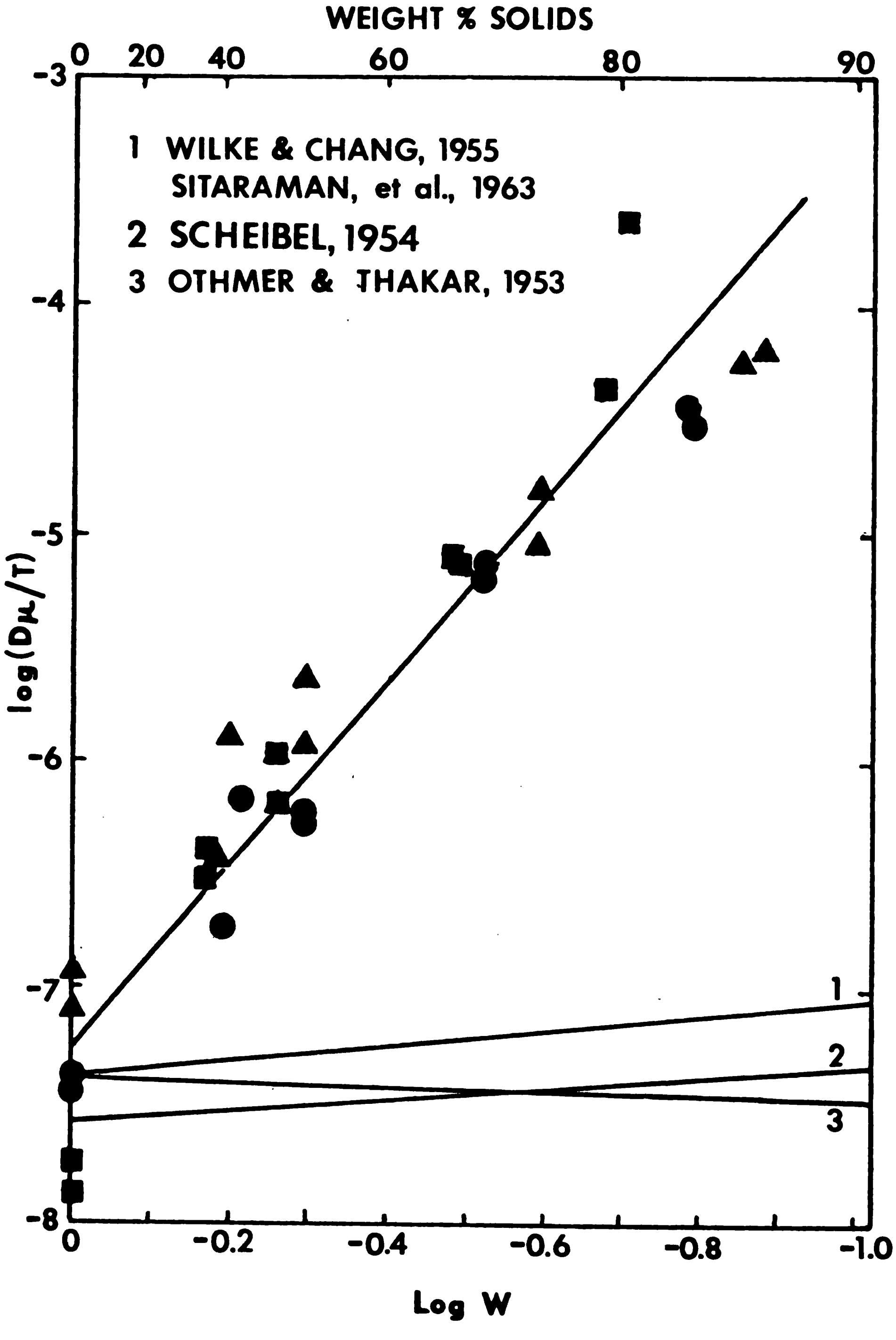

FIGURE 15. LOG (Dμ/T) vs. LOG W FOR 2-BUTANONE IN MALTO-DEXTRIN SOLUTIONS

It would be reasonable to assume that a correlation for $\frac{D\mu}{T}$ in malto-dextrin solutions should have a similar form. That is,

$$\frac{D\mu}{T} = K' \, M_B^{-\beta} \tag{55}$$

where $\beta < 0$. For high values of W,

$$M_B \doteq \frac{M_W}{W} \tag{56}$$

so,

$$\frac{D\mu}{T} = K'' \, W^{\beta} \tag{57}$$

or

$$\log \frac{D\mu}{T} = \log K'' + \beta \log W \quad . \tag{58}$$

Linear regression analysis was done on the data at each temperature and for all of the data combined. Table 14 shows the results of those regression analyses.

Log $\frac{D\mu}{T}$ correlated better for individual temperatures than for all the temperatures, but, given the poor correlation coefficients (r in table 14), it was not reasonable to draw any conclusions with respect to trends in K" and β with temperature. Given the scatter in the data (see figure 14 and 15), one could only conclude that K" and β are relatively constant with respect to temperature. This conclusion is consistant with literature correlations for $\frac{D\mu}{T}$. The literature correlations discussed earlier were all independent of temperature.

Given $\frac{D\mu}{T}$ does not vary with temperature, one may also conclude that the activation energy for diffusion, E_D is

TABLE 14

CONSTANTS FOR EQUATION 57

Compound	Temp. (° C)	Log K"	β	r
1-Hexanol	60°	-8.23	-4.41	-0.895
	75°	-7.95	-4.16	-0.979
	90°	-7.57	-2.87	-0.962
	All Temp.	-7.89	-3.70	-0.919
2-Butanone	60°	-7.58	-5.23	-0.984
	75°	-7.31	-3.79	-0.989
	90°	-6.86	-3.25	-0.982
	All Temp.	-7.73	-3.96	-0.961

equal to the negative of the activation energy for viscosity, E_μ. Chandrasekaran and King (1972a) made a similar conclusion for ethanol in sucrose solutions. They found that E_D for ethanol was equal to E_μ for sucrose solutions from 0 to 70 wt % sucrose between 25° and 35° C. E_D for sucrose in these solutions was substantially lower than E_D for ethanol and E_μ. At low sucrose concentrations, E_D for sucrose approached E_μ and E_D for dilute ethanol.

Othmer and Thaker (1953) obtained a range of values for E_D/E_μ of -1.07 to -1.15 for water, calcium chloride, phenol, mannitol and sucrose over a temperature range of 10° to 50° C. The significance of this conclusion is that the activation energy for diffusivity may be obtained from simple viscosity measurements. Viscosity is very easily measured over a wide range of temperatures and solids content. The diffusivity, however, is, at best, difficult to measure. With one series of diffusion experiments at one temperature and viscosity measurements over the temperature range and percent solids content, one could generate a complete set of diffusivity values if the dependence of $\frac{D\mu}{T}$ on solids content were known.

Other workers have not tried to correlate their data in this manner. The viscosity of malto-dextrin must be known to use the data of Menting, et al. (1970a), but it can be estimated from equation 47. The malto-dextrin viscosity was estimated at 21.5° C and values for $\frac{D\mu}{T}$ for the data from Menting, et al., for water, acetone, ethyl acetate, benzene, camphor, and carbon tetrachloride were calculated. Figure 16 shows the results of these calculations. The intercept for each compound at log W = 0 is different due to differing molecular volumes. One may see a general trend in all of the data. For high water contents, the slope of the log $\frac{D\mu}{T}$ versus log W curve has a slope of approximately -4 for ethyl acetate, acetone, benzene and carbontetrachloride. At higher solids content (low values of W), the curves level off.

In work involving unsteady state diffusion in aqueous solutions of malto-dextrin, it is very important to measure the final water content after the diffusion experiment has been performed. Since Menting, et al., did not measure the final moisture content in their experiments, there is reason to believe that their diffusion data at the high solids content may not be accurate.

In all of Menting's work, the water content of the final sample was assumed, not measured. For water contents above 30 wt % water, samples were equilibrated in a flask containing a large amount of malto-dextrin solution at the desired weight percent water for 15 hours. The sample was placed in the 200 ml glass flask, and the diffusion run was made. It was assumed that the moisture content did not change due to the small volume of the flask. This is probably a reasonable assumption since the vapor pressure of water at 21.5° C is quite low. The

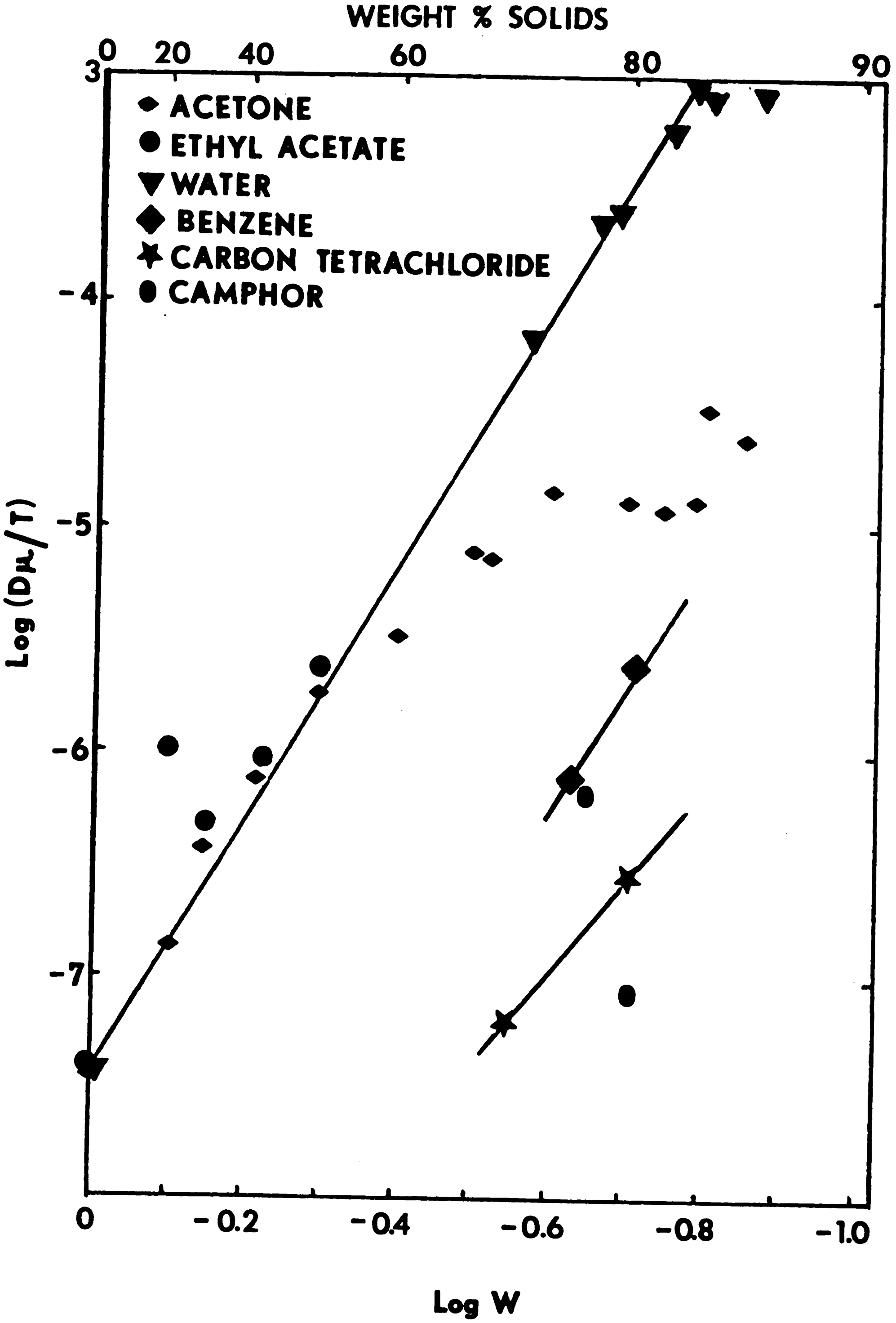

FIGURE 16. LOG (Dμ/T) vs. LOG W FOR MENTING'S DATA

change in the concentration of diffusant with time in the vapor phase was measured.

For water contents below 30%, the change in the concentration of the diffusant with time in the liquid phase was measured. Due to the extremely low concentration of diffusant in the liquid phase, the diffusant concentration was measured with a radioactive tracer technique. Glass bars were coated with 50 wt % solids malto-dextrin by drawing them out of the solution at a constant velocity. These rods were air blown dry at 80° C. In order to obtain the desired percent solids for the experiment, the malto-dextrin coated rods were placed in a closed container with a constant humidity salt solution.

The experiment was carried out in another chamber similar to the first, except that 1% radioactive labled acetone or other diffusant was added to the constant humidity salt solution. Rods were removed periodically and the concentration of diffusant was measured. The diffusivity was calculated from the initial slope of the curve of M_t/M_∞ versus $t^{1/2}$. This experimental method is excellent and should produce very good results. The question that should concern anyone performing such experiments is whether the assumptions made are correct. Menting assumed values of the weight percent solids in this experiment. He assumed that the solutions come to equilibrium above the constant humidity solutions, but he did not measure the percent solids in any of his experiments after the experiment had been completed. In the present work, the solids content of every solution was measured and, in fact, it was found necessary for determining accurate data.

According to the trends in log $\frac{D\mu}{T}$ in Menting's data (figure 16), the diffusion coefficients measured for ethyl acetate and acetone were low below moisture content of 30 wt %. One might look at it another way. Perhaps the assumed water content of the malto-dextrin solutions was significantly higher than the actual water content in the experiment. If the malto-dextrin coated bars were not equilibrated long enough with the constant humidity solutions, the water content could have been significantly lower than the assumed value. In the present work, the solids content of every solution was measured.

Examination of the trends in $\frac{D\mu}{T}$ for Menting's data indicate that there may have been some discrepancy between the assumed solids content and the actual solids content. This might explain why log $\frac{D\mu}{T}$ is not linear with log W below a water content of 30 wt % water. The data for water diffusivity are linear to a water content of about 10 wt % water. The data presented here for 1-hexanol and 2-butanone indicate that log $\frac{D\mu}{T}$ is approximately linear to a water content of 20 wt % water. The data also indicate that the slope of the log $\frac{D\mu}{T}$ versus log W line is -4 for all of the diffusion data in malto-dextrin solutions so far. This is an important result, since a considerable amount of diffusion data can be approximated if this holds for all diffusants in malto-dextrin.

Chandrasekaran and King (1972a) showed similar trends in their data for diffusion of various dilute organics in sugar solutions. All of their data for ethanol, ethyl acetate, n-butyl acetate and n-hexanal in solutions of d-fructose, d-glucose, sucrose and a mixture of the three correlate to one master plot at 25° C. When the data is plotted as log D_{11}/D_{11}^{0} versus log W, the data all lie on the same line. D_{11} and D_{11}^{0} are the diffusivity of the dilute organic in sugar solution and in water, respectively. At 35° C, data were collected for ethanol and ethyl acetate in sucrose solution. These higher temperature data show the same behavior as the 25° C data, except there was less variation.

The slope of the log D_{11}/D_{11}^{0} versus log W curve should have the same slope as the log D_{11} versus log W curve. The viscosity correlates in a similar fashion. The slope of log μ versus log W curve is known. The sum of the slopes of the log D versus log W curve and log μ versus log W curve should give the slope of the log $\frac{D\mu}{T}$ curve, β. Table 15 gives the values of β curves for sugar solutions for data from Chandrasekaran and King (1972a). Notice that β is nearly constant. Also, β is considerably larger for malto-dextrin solutions than

TABLE 15

VALUES FOR β FOR DIFFUSANTS IN SIMPLE SUGAR SOLUTIONS

Temperature (° C)	β
25°	-0.9
35°	-1.2

(Chandrasekaran and King, 1972)

for simple sugar solutions. This is probably due to the greater dependence of viscosity on solids content in the malto-dextrin solutions than in simple sugar solutions.

From the experiments performed here and elsewhere, the following conclusions can be made. First, $\frac{D\mu}{T}$ is nearly constant with respect to temperature for dilute diffusants in sugar and malto-dextrin solutions. Second, the slope of the log $\frac{D\mu}{T}$ versus log W curve is a constant depending on the type of dissolved solid. For malto-dextrin solutions, it is approximately equal to -4. For sugar solutions, it is about -1.

pH Effects

The effect of pH on the equilibrium coefficient, K, the diffusivity of 1-hexanol in 50 wt % solids solutions at 90° C was studied. A pH range of 4.3 to 8 was considered. The unbuffered solution had a pH of 4.3. Other solutions were buffered at pH6 and pH8. Outside of this range, the malto-dextrin breaks down.

Figure 17 shows the variation in diffusivity and partition coefficient with pH. The diffusivity is nearly constant from a pH of 4 to 8. The equilibrium coefficient increases a small amount over the range. The decrease in equilibrium coefficient with decreasing pH must be attributed to association with water. Since there is no effect of pH on the diffusivity, the association of 1-hexanol with the malto-dextrin solutions is not pH

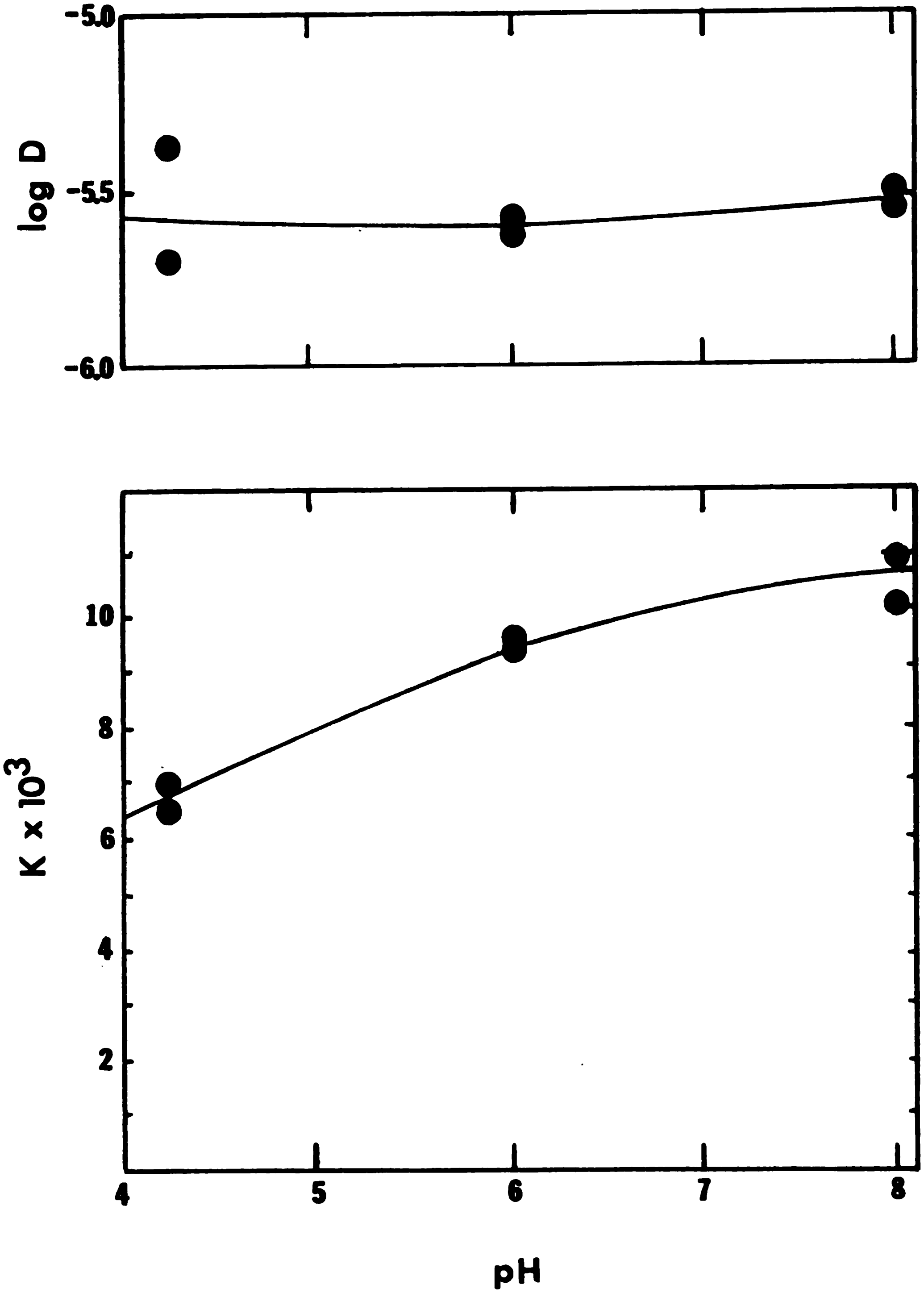

FIGURE 17. EFFECTS OF pH ON LOG D AND K FOR 1-HEXANOL

dependent. So, association with water must be pH dependent. This would indicate that 1-hexanol becomes more soluble in acidic solutions.

Alcohols are slightly basic compared to water (Morrison and Boyd, 1973). They have the ability to accept a proton.

$$ROH + H^+ \rightarrow ROH_2^+ \tag{59}$$

This reaction has the equilibrium constant K_B. The equilibrium expression is

$$\frac{[ROH_2^+]}{[ROH]\ [H^+]} = K_B \tag{60}$$

where [ ] denotes concentration. Rearranging, we get

$$[ROH_2^+] = K_B\ [ROH]\ [H^+] \tag{61}$$

The solubility in neutral solution is a constant, S, equal to the concentration of unprotonated alcohol, [ROH]. The concentration of the protonated alcohol is

$$[ROH_2^+] = K_B\ S\ [H^+] \tag{62}$$

The total solubility of the alcohol, S_T, is

$$S_T = S + [ROH_2^+]\ . \tag{63}$$

Substituting,

$$S_T = S\ (1 + K_B[H^+])\ . \tag{64}$$

So, the total solubility increases with increasing hydronium ion concentration or with decreasing pH. This gives the observed result that K decreases with decreasing pH.

CONCLUSIONS

1. The vapor-liquid equilibrium and activity coefficients for 1-hexanol and 2-butanone in aqueous malto-dextrin solutions are a strong function of temperature.

2. The diffusivity of flavor components in aqueous malto-dextrin solutions can be correlated using the Stokes-Einstein group. Log $(D\mu/T)$ was shown to be a linear function of log W for 1-hexanol and 2-butanone at 60° to 90° C (this study) and for acetone and ethyl acetate and water at 21.5° C (Menting, et al., 1970a). The slope of the log $(D\mu/T)$ versus log W line was about -4 for all of the diffusion data in the literature to date.

3. The diffusion coefficient is not affected by pH. The vapor-liquid equilibrium of 1-hexanol is dependent on pH. The solubility is increased at low pH due to increased ionization of alcohol.

4. The viscosity of aqueous sucrose, glucose and malto-dextrin solutions was correlated with the water weight fraction (W). The log μ was a linear function of log W. The activation energy of viscosity, E_μ was also shown to be a linear function of log W.

5. The density of aqueous malto-dextrin solutions was a linear function of weight percent solids.

RECOMMENDATIONS

1. The experimental methods developed here should be used on other food systems like solutions of simple sugars, milk solids and coffee.

2. The diffusivity of flavor components of widely varying molecular weight in malto-dextrin in the 60° to 90° C range should be measured to test the validity of the Stokes-Einstein group correlation.

3. The diffusivity and vapor-liquid equilibrium of water in malto-dextrin solutions in the 60° to 90° C range should be measured.

4. Models for spray dryers should be developed and the correlations for diffusivity and the vapor-liquid equilibrium data should be used to predict flavor retention in malto-dextrin. The calculated model could then be compared with actual spray drying data.

APPENDICES

APPENDIX I

RAW DATA AND CALCULATED RESULTS

The following tables (tables 16 through 20) give raw data and calculated results for the diffusion experiments performed in this study. Data for the standards is presented in tables 30 and 31. The relative standard deviation ($\sigma/\bar{x}$) and standard deviation (σ) values in the tables are for the data in the columns to their immediate left. Samples A and B were steady state samples and samples C and D were unsteady state samples in all of the tables.

The calculated results were calculated using the equations in Appendix II. See the nomenclature section (page xi) for definitions of the variables used in the tables.

TABLE 16

HIGH SOLIDS DATA FOR 2-BUTANONE AT 60° C

Sample Number	P (atm)	$A_D \times 10^{-7}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^4$ (g/ml)	A_D/A_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^3$ (g/ml)	$k \times 10^2$	$\sigma \times 10^2$	S	t (sec)
30A	1.184	3.203	0.04	1.639	0.0456	0.50	0.1271	0.12714	4.203	3.901	0.02	0.340	245,820
30B	1.180	3.213	0.11	1.639	0.6004	0.15	0.1550	0.15496	3.989	4.109	0.08	0.325	246,699
30C	1.163	3.796	0.28	1.404	0.1364	0.38	0.4637	0.46372	2.926	4.799	0.02	0.320	5,627
30D	1.158	3.475	0.10	1.280	0.1376	1.08	0.3696	0.36956	3.862	3.314	0.04	0.323	10,357
50A	1.164	3.629	0.56	1.826	0.0457	0.80	0.1220	0.12198	4.452	4.102	0.04	0.456	248,220
50B	1.157	3.613	0.00	1.807	0.0589	0.66	0.1566	0.15769	4.084	4.424	0.03	0.452	249,180
50C	1.180	3.793	0.11	1.423	0.0665	1.59	0.3988	0.39877	1.734	8.209	0.13	0.470	6,383
50D	1.183	3.666	0.04	1.379	0.1278	1.52	0.4818	0.48183	2.999	4.600	0.07	0.456	11,246
70A	1.137	3.832	0.11	1.883	0.0392	1.60	0.1766	0.17655	2.800	6.726	0.11	0.685	235,220
70B	1.145	3.853	1.45	1.407	0.0442	0.70	0.1635	0.16345	3.247	5.874	0.05	0.681	236,243
70C	1.203	4.037	1.45	1.545	0.0281	0.26	0.1601	0.16014	2.252	6.860	0.10	0.668	7,549
70D	1.208	4.043	1.26	1.554	0.0437	0.28	0.1703	0.17034	3.077	5.049	0.10	0.674	12,049
80A	1.141	3.900	1.40	1.924	0.0176	5.92	0.2050	0.20503	1.163	16.540	1.00	0.798	238,440
80B	1.203	3.930	0.02	2.044	0.0296	0.17	0.1769	0.17692	2.168	9.428	0.02	0.798	239,400
80C	1.203	4.168	0.54	1.595	0.0044	0.14	0.1921	0.19214	0.288	55.420	0.31	0.803	9,004
80D	1.204	4.155	0.60	1.591	0.0091	1.27	0.1911	0.19109	0.588	27.050	0.38	0.793	12,666

TABLE 17

HIGH SOLIDS DATA FOR 2-BUTANONE AT 75° C

Sample Number	P (atm)	$A_D \times 10^{-8}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^6$ (g/ml)	A_D/A_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^3$ (g/ml)	$k \times 10^2$	$\sigma \times 10^2$	S	t (sec)
30A	1.305	1.683	2.56	6.259	0.1400	0.11	0.0952	0.01331	19.790	3.162	0.58	0.381	263,400
30B	1.309	1.647	1.33	6.146	0.1585	0.61	0.1115	0.01247	18.060	3.403	0.05	0.398	268,980
30C	1.146	1.516	0.24	4.953	0.6107	0.64	0.3156	0.01140	2.240	22.110	0.01	0.391	1,140
30D	1.257	1.839	0.19	6.589	0.1866	0.12	0.2595	0.01355	9.707	6.788	0.05	0.351	2,769
50A	1.254	1.770	2.20	6.327	0.1731	0.02	0.1108	0.01383	23.080	2.742	0.06	0.501	269,220
50B	1.239	1.788	0.12	6.315	0.1521	0.03	0.1249	0.01234	16.360	3.860	0.01	0.546	269,460
50C	1.307	1.851	2.41	6.896	0.1816	0.33	0.3706	0.01304	6.839	10.080	0.25	0.507	1.880
50D	1.249	1.777	1.23	6.327	0.2085	0.81	0.3981	0.01405	7.866	8.043	0.12	0.504	3,489
70A	1.112	1.780	2.01	5.461	0.1219	0.23	0.1536	0.01274	11.850	4.759	0.10	0.721	269,790
70B	1.239	1.721	3.20	6.076	0.1494	0.39	0.1585	0.01283	14.160	4.291	0.14	0.718	270,060
70C	1.303	1.912	2.21	7.100	0.0797	0.66	0.1443	0.01288	8.277	8.578	0.20	0.702	2,540
70D	1.262	1.360	0.11	4.891	0.0781	1.37	0.1565	0.01241	7.207	6.786	0.09	0.701	5,100
80A	1.237	1.767	1.22	6.229	0.0919	0.48	0.1788	0.01360	8.566	7.272	0.10	0.831	270,315
80B	1.238	1.765	0.40	6.453	0.1172	2.17	0.1982	0.01224	8.877	7.269	0.16	0.836	270,555
80C	1.296	1.839	0.62	6.792	0.0180	1.68	0.1843	0.01523	1.853	36.660	0.66	0.828	4,698
80D	1.300	1.755	0.48	6.502	0.0360	0.21	0.1813	0.01316	3.188	20.400	0.11	0.820	8,267

TABLE 18

HIGH SOLIDS DATA FOR 2-BUTANONE AT 90° C

Sample Number	P (atm)	$A_D \times 10^{-8}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^4$ (g/ml)	A_D/A_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^2$ (g/ml)	$k \times 10^2$	$\sigma \times 10^2$	S	t (sec)
30A	1.420	1.968	1.53	6.266	0.0955	0.54	0.0968	0.01225	1.269	4.939	0.08	0.397	75,780
30B	1.392	1.940	0.04	6.054	0.0845	1.35	0.1008	0.01278	1.115	5.430	0.07	0.397	76,080
30C	1.392	1.953	0.25	6.094	0.4608	0.07	0.3806	0.00981	1.224	4.978	0.05	0.360	1,692
30D	1.392	1.998	0.07	6.236	0.3324	0.39	0.3046	0.00980	1.092	5.710	0.02	0.341	3,556
50A	1.400	2.054	0.58	6.447	0.0871	1.55	0.0892	0.01253	1.354	4.763	0.08	0.512	76,350
50B	1.392	2.046	1.24	6.386	0.0625	1.72	0.0735	0.01385	1.308	4.884	0.10	0.520	76,620
50C	1.392	1.798	3.34	5.611	0.1412	0.05	0.2984	0.02207	1.150	4.877	0.16	0.504	4,207
50D	1.392	1.847	0.42	5.763	0.2450	0.66	0.3948	0.01249	1.855	6.744	0.05	0.506	4,712
70A	1.364	2.050	0.90	6.270	0.0937	3.65	0.1471	0.01258	1.985	6.365	0.24	0.764	76,920
70B	1.383	2.060	0.97	6.387	0.1044	0.04	0.1517	0.01188	1.003	6.371	0.06	0.757	77,280
70C	1.405	1.761	0.08	5.548	0.0522	0.22	0.1839	0.01218	0.422	13.160	0.03	0.742	2,294
70D	1.404	1.263	1.47	3.975	0.0719	1.07	0.1437	0.01077	0.657	6.054	0.11	0.741	4,694
80A	1.379	2.093	0.54	6.472	0.0421	0.32	0.1768	0.01230	0.374	17.290	0.11	0.861	77,580
80B	1.353	2.110	0.48	6.401	0.0426	0.26	0.1881	0.01288	0.373	17.180	0.09	0.861	77,940
80C	1.418	2.144	0.13	6.817	0.0088	0.32	0.1818	0.02365	0.078	87.260	0.30	0.866	2,850
80D	1.418	2.015	0.91	6.407	0.0140	0.64	0.2005	0.01234	0.110	58.190	0.65	0.853	5,117

TABLE 19

HIGH SOLIDS DATA FOR 1-HEXANOL AT 60° C

Sample Number	P (atm)	$\dot{A}_D \times 10^{-6}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^6$ (g/ml)	A_D/A_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^3$ (g/ml)	$k \times 10^3$	$\sigma \times 10^8$	S	t (sec)
30A	1.078	4.430	1.32	7.866	0.0388	0.29	0.1654	0.01352	2.523	3.118	0.042	0.343	418,000
30B	1.097	4.561	0.19	8.247	0.0858	1.32	0.3526	0.01412	2.720	3.032	0.040	0.334	418,000
30C	1.099	5.087	0.93	9.209	0.0888	0.34	0.4210	0.01306	2.169	4.244	0.042	0.339	2.779
30D	1.113	5.472	13.40	10.040	0.0432	1.29	0.3676	0.01226	1.152	8.716	1.173	0.353	5.570
50A	1.101	5.907	0.43	10.720	0.0553	2.82	0.1606	0.01400	3.987	2.689	0.077	0.427	418,000
50B	1.116	5.875	2.07	10.800	0.0542	2.89	0.1346	0.01331	4.493	2.404	0.085	0.457	418,000
50C	1.086	4.905	0.62	8.770	0.0214	3.38	0.2973	0.01391	0.852	10.290	0.354	0.490	3,532
50D	1.028	6.975	5.78	11.810	0.0439	6.11	0.3839	0.01281	1.246	9.483	0.798	0.488	6,253
70A	1.113	5.919	0.38	10.860	0.0624	2.47	0.1588	0.01217	4.325	2.510	0.063	0.632	418,000
70B	1.120	5.741	0.37	10.590	0.0575	3.42	0.1455	0.01290	4.617	2.294	0.079	0.636	418,000
70C	1.108	5.833	1.67	10.650	0.0342	0.21	0.1561	0.01221	2.427	4.387	0.074	0.639	4,330
70D	1.116	7.053	0.06	12.970	0.0403	1.50	0.1625	0.01425	3.205	4.046	0.061	0.633	12,707
80A	1.109	5.668	1.10	10.360	0.0592	0.80	0.1709	0.01207	3.954	2.620	0.032	0.741	418,000
80B	1.108	5.716	0.40	10.430	0.0540	0.50	0.1569	0.01250	4.065	2.567	0.020	0.737	418,000
80C	1.109	6.892	0.41	12.600	0.0144	0.64	0.1869	0.01261	0.916	13.750	0.105	0.730	6,882
80D	1.116	6.505	0.93	11.960	0.0145	0.38	0.1908	0.01319	0.957	12.500	0.126	0.754	13,618

TABLE 20

HIGH SOLIDS DATA FOR 1-HEXANOL AT 75° C

Sample Number	P (atm)	$A_D \times 10^{-6}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^5$ (g/ml)	A_D/A_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^3$ (g/ml)	$k \times 10^3$	$\sigma \times 10^3$	S	t (sec)
30A	1.162	8.433	0.15	1.551	0.0863	0.07	0.3012	0.01398	3.384	4.584	0.008	0.372	165,600
30B	1.213	8.725	3.13	1.675	0.1312	2.47	0.3679	0.01357	4.095	4.091	0.163	0.375	165,600
30C	1.214	9.364	0.00	1.800	0.0208	4.87	0.1927	0.01319	1.193	15.090	0.735	0.359	1,480
30D	1.213	9.281	0.17	1.782	0.0661	0.09	0.3341	0.01310	2.178	8.182	0.016	0.357	4,217
50A	1.203	10.600	2.94	2.018	0.0438	0.40	0.0898	0.01300	5.917	3.410	0.101	0.506	165,600
50B	1.184	11.040	2.94	2.069	0.0598	1.53	0.1319	0.01350	5.373	3.851	0.128	0.452	165,600
50C	1.184	9.105	2.56	1.707	0.0896	1.67	0.4124	0.01328	1.849	9.231	0.204	0.456	2,174
50D	1.184	9.841	1.28	1.845	0.0647	1.39	0.4151	0.01261	2.456	7.510	0.196	0.515	4,860
70A	1.114	9.048	1.78	1.596	0.0591	0.89	0.1519	0.01223	4.573	3.491	0.069	0.662	165,600
70B	1.208	9.963	0.95	1.905	0.0610	0.98	0.1566	0.01571	5.829	3.268	0.045	0.641	165,600
70C	1.193	9.675	4.96	1.927	0.0301	5.03	0.1533	0.01258	2.354	8.186	0.578	0.647	3,083
70D	1.207	10.202	0.95	1.848	0.0393	1.79	0.1627	0.01323	3.035	6.088	0.123	0.643	6,556
80A	1.199	10.036	0.76	1.904	0.0543	2.45	0.1577	0.01337	4.603	4.137	0.106	0.758	165,600
80B	1.193	10.024	4.68	1.894	0.0622	1.49	0.1862	0.01320	4.419	4.285	0.210	0.764	165,600
80C	1.207	10.653	5.83	2.035	0.0188	4.32	0.1626	0.01399	1.613	12.61	0.915	0.754	5,958
80D	1.146	11.550	2.57	2.096	0.0238	1.45	0.1589	0.01362	2.027	10.340	0.305	0.750	10,905

TABLE 21

HIGH SOLIDS DATA FOR 1-HEXANOL AT 90° C

Sample Number	P (atm)	$A_D \times 10^{-7}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^5$ (g/ml)	A_D/A_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^3$ (g/ml)	$k \times 10^3$	$\sigma \times 10^3$	S	t (sec)
30A	1.339	1.650	0.77	3.973	0.1557	0.75	0.3772	0.01368	4.229	9.394	0.101	0.331	57,600
30B	1.325	1.622	0.12	3.863	0.1861	0.56	0.4570	0.01325	3.049	9.783	0.056	0.284	57,600
30C	1.345	1.844	1.68	4.457	0.0544	0.12	0.4242	0.01245	1.191	37.430	0.630	0.322	1,056
30D	1.332	1.726	1.31	4.131	0.1149	0.38	0.3243	0.01227	3.246	12.730	0.174	0.325	4,003
50A	1.336	1.646	4.73	3.951	0.0532	0.39	0.1045	0.01467	6.102	6.476	0.307	0.517	57,600
50B	1.330	1.675	2.62	4.005	0.0558	0.18	0.1040	0.01311	5.740	6.978	0.183	0.514	57,600
50C	1.330	1.807	5.24	4.321	0.0476	1.28	0.3212	0.01207	1.454	29.710	1.603	0.516	1,852
50D	1.328	1.934	1.61	4.615	0.1054	0.31	0.3906	0.01289	2.812	16.410	0.269	0.495	5,518
70A	1.329	1.814	0.78	4.333	0.0559	1.46	0.1200	0.01548	6.409	6.762	0.112	0.713	57,600
70B	1.333	1.730	1.02	4.144	0.0814	1.04	0.1479	0.01180	5.722	7.241	0.105	0.694	57,600
70C	1.316	1.746	1.66	4.129	0.0234	1.44	0.1203	0.01229	2.109	19.577	0.430	0.696	2,848
70D	1.321	2.115	8.12	5.051	0.0459	0.28	0.1469	0.01117	3.071	16.350	1.329	0.691	6,638
80A	1.279	1.996	0.92	4.589	0.0319	1.93	0.1707	0.00952	1.929	23.790	0.925	0.816	57,600
80B	1.305	1.667	0.51	3.911	0.0356	0.49	0.1784	0.01493	2.754	14.200	0.707	0.815	57,600
80C	1.288	1.939	2.59	4.489	0.0064	1.46	0.1620	0.01417	0.518	86.620	2.580	0.806	5,085
80D	1.316	2.066	0.48	4.887	0.0111	14.80	0.1706	0.01080	0.649	75.250	11.140	0.806	7,754

TABLE 22

LOW SOLIDS DATA FOR 2-BUTANONE

Temp. (° C)	Sample Number	P (atm)	$A_D \times 10^{-7}$ (vapor)	$\sigma/\bar{x}$ (%)	$C_V \times 10^{6}$ (g/ml)	$A_D \times 10^{-6}$ (liquid)	$\sigma/\bar{x}$ (%)	$C_L \times 10^{3}$ (g/ml)	$k \times 10^{2}$	$\sigma \times 10^{2}$	S	Time (sec)
60°	WA	1.125	3.263	0.02	1.363	8.112	0.56	6.310	2.160	0.012	0	81,000
	WB	1.117	3.205	0.24	1.348	8.078	0.95	6.283	2.146	0.021	0	81,000
	WC	1.020	6.120	0.72	2.318	2.553	2.30	1.985	11.670	0.281	0	4,473
	WD	1.111	4.508	0.33	1.859	2.753	0.62	2.141	8.682	0.020	0	6,928
	15A	1.117	3.612	0.18	1.498	5.193	1.14	4.037	3.712	0.043	0.140	81,000
	15B	1.108	3.950	0.24	1.477	5.212	3.60	3.984	3.707	0.134	0.140	81,000
75°	WA	1.208	10.525	0.47	5.577	14.845	1.00	13.250	4.211	0.047	0	55,800
	WB	1.199	10.450	0.41	5.495	15.705	2.66	14.010	3.922	0.106	0	55,800
	WC	1.259	12.190	0.70	6.733	3.663	0.85	3.268	20.600	0.194	0	2,032
	WD	1.225	12.610	0.22	6.776	5.476	0.12	4.886	13.870	0.035	0	3,198
	15A	1.212	11.100	1.66	5.901	11.540	0.25	10.300	5.731	0.096	0.138	55,800
	15B	1.175	10.955	1.10	5.647	10.595	4.47	9.453	5.945	0.275	0.138	55,800
90°	WA	1.099	16.731	9.36	5.755	14.625	1.11	10.490	5.487	0.052	0	43,200
	WB	-	-	-	-	-	-	-	-	-	-	-
	WC	1.404	18.070	9.74	7.935	3.840	0.45	2.754	28.810	0.050	0	818
	WD	1.445	17.305	0.04	7.821	5.354	0.63	3.840	20.370	0.013	0	982
	15A	1.388	15.725	5.00	6.829	24.220	18.45	17.370	3.931	0.075	0.146	43,200
	15B	1.387	16.380	4.92	7.107	25.195	1.21	18.070	3.933	0.020	0.146	43,200

TABLE 23

LOW SOLIDS DATA FOR 1-HEXANOL

Temp. (° C)	Sample Number	P (atm)	$A_D \times 10^{-6}$ (vapor)	$\sigma / \bar{x}$ (%)	$C_V \times 10^{6}$ (g/ml)	$A_D \times 10^{-5}$ (liquid)	$\sigma / \bar{x}$ (%)	$C_L \times 10^{3}$ (g/ml)	$k \times 10^{3}$	$\sigma \times 10^{3}$	S	Time (sec)
60°	WA	1.086	4.145	0.55	7.45	26.770	0.21	1.496	4.983	0.03	0	320,400
	WB	1.082	4.105	2.83	7.36	26.935	0.45	4.887	4.887	0.14	0	320,400
	WC	1.103	6,486	0.48	11.88	4.449	8.17	47.650	47.650	3.90	0	2,792
	WD	0.961	5.733	0.46	9.13	6.553	0.84	24.930	24.930	0.24	0	5,560
	15A	1.082	3.330	0.83	5.97	17.643	3.25	5.088	5.088	0.17	0.143	320,400
	15B	1.075	3.896	3.74	6.94	17.495	0.61	5.966	5.966	0.27	0.141	320,400
75°	WA	1.114	9.457	0.37	16.69	30.390	14.71	7.514	7.514	1.11	0	165,600
	WB	1.116	9.535	0.82	16.84	30.275	11.84	7.613	7.613	0.90	0	165,600
	WC	1.184	10.505	0.61	19.69	6.821	2.26	39.500	39.500	0.92	0	3,740
	WD	1.182	11.535	0.43	21.57	10.460	3.11	28.220	28.220	0.89	0	7,007
	15A	1.117	9.294	0.43	16.44	27.175	3.25	6.958	6.958	0.32	0.140	165,600
	15B	1.113	9.176	0.55	16.17	29.970	0.00	6.207	6.207	0.03	0.140	165,600
90°	WA	1.289	17.595	0.20	40.79	52.290	0.46	14.900	14.900	0.07	0	57,600
	WB	1.299	15.260	3.06	35.63	55.390	0.08	12.290	12.290	0.38	0	57,600
	WC	1.257	18.860	1.35	42.61	25.530	0.42	31.880	31.880	0.45	0	3,763
	WD	1.288	22.210	0.76	51.43	21.110	0.40	46.540	46.540	0.44	0	7,463
	15A	1.272	18.530	1.14	42.39	48.625	5.92	14.000	14.000	0.84	0.146	57,600
	15B	1.157	17.140	5.53	35.65	50.155	2.50	11.420	11.420	0.69	0.146	57,600

TABLE 24

DIFFUSION DATA FOR 2-BUTANONE

Sample Number	60° C			75° C			90° C		
	M_t/M_∞	l (cm)	D (cm^2/sec)	M_t/M_∞	l (cm)	D (cm^2/sec)	M_t/M_∞	l (cm)	D (cm^2/sec)
WC	0.185	1.80	1.07×10^{-5}	0.194	1.80	3.49×10^{-5}	0.191	1.80	8.76×10^{-5}
WD	0.248	1.80	1.28×10^{-5}	0.273	1.80	4.49×10^{-5}	0.269	1.80	1.48×10^{-5}
30C	0.856	0.45	1.97×10^{-5}	0.143	0.45	2.38×10^{-5}	0.992	0.45	9.16×10^{-5}
30D	0.950	0.45	1.33×10^{-5}	0.466	0.45	1.09×10^{-5}	0.865	0.45	3.30×10^{-5}
50C	0.500	0.45	4.73×10^{-6}	0.272	0.45	5.20×10^{-6}	0.977	0.45	3.57×10^{-5}
50D	0.892	0.45	9.84×10^{-6}	0.341	0.45	4.46×10^{-6}	0.706	0.45	1.65×10^{-5}
70C	0.856	0.15	1.70×10^{-6}	0.500	0.15	1.69×10^{-6}	0.484	0.15	1.76×10^{-6}
70D	0.950	0.15	1.31×10^{-6}	0.632	0.15	1.35×10^{-6}	0.950	0.15	3.37×10^{-6}
80C	0.234	0.15	1.06×10^{-6}	0.198	0.15	1.44×10^{-7}	0.198	0.15	2.40×10^{-7}
80D	0.480	0.15	3.18×10^{-7}	0.356	0.15	2.66×10^{-7}	0.296	0.15	3.00×10^{-7}

TABLE 25

DIFFUSION DATA FOR 1-HEXANOL

Sample Number	60° C			75° C			90° C		
	M_t/M_∞	l (cm)	D (cm^2/sec)	M_t/M_∞	l (cm)	D (cm^2/sec)	M_t/M_∞	l (cm)	D (cm^2/sec)
WC	0.104	1.80	1.42×10^{-6}	0.192	1.80	6.36×10^{-6}	0.426	1.80	6.07×10^{-5}
WD	0.198	1.80	2.89×10^{-6}	0.268	1.80	7.16×10^{-6}	0.292	1.80	1.30×10^{-5}
30C	0.735	0.45	1.53×10^{-5}	0.304	0.45	4.09×10^{-6}	0.251	0.45	5.72×10^{-6}
30D	0.348	0.45	1.07×10^{-6}	0.560	0.45	6.02×10^{-6}	0.738	0.45	1.65×10^{-5}
50C	0.234	0.45	5.36×10^{-7}	0.388	0.45	4.05×10^{-6}	0.218	0.45	1.99×10^{-6}
50D	0.254	0.45	3.64×10^{-7}	0.454	0.45	2.55×10^{-6}	0.472	0.45	3.98×10^{-6}
70C	0.547	0.15	7.66×10^{-7}	0.399	0.15	5.99×10^{-7}	0.370	0.45	6.89×10^{-7}
70D	0.593	0.15	3.16×10^{-7}	0.537	0.15	5.43×10^{-7}	0.443	0.45	4.31×10^{-7}
80C	0.187	0.15	4.74×10^{-8}	0.328	0.15	2.21×10^{-7}	0.173	0.45	9.19×10^{-8}
80D	0.210	0.15	3.09×10^{-8}	0.400	0.15	1.85×10^{-7}	0.200	0.45	8.01×10^{-8}

TABLE 26

THE STOKES-EINSTEIN GROUP DATA, LOG $(D\mu/T)$

Sample Number	2-Butanone			1-Hexanol		
	60° C	75° C	90° C	60° C	75° C	90° C
WC	-7.863	-7.451	-7.148	-8.740	-8.191	-7.307
WD	-7.782	-7.342	-6.918	-8.431	-8.139	-7.975
30C	-6.360	-6.140	-5.881	-6.379	-7.057	-7.247
30D	-6.515	-6.667	-6.407	-7.467	-6.898	-6.775
50C	-6.179	-6.171	-5.579	-7.002	-6.572	-6.764
50D	-5.945	-6.256	-5.903	-7.183	-6.431	-6.581
70C	-5.125	-5.160	-5.054	-5.739	-6.115	-5.925
70D	-5.178	-5.267	-4.789	-6.177	-6.191	-6.175
80C	-3.654	-4.591	-4.095	-6.015	-5.471	-5.546
80D	-4.337	-4.462	-4.256	-5.903	-5.598	-5.605

TABLE 27

ACTIVITY COEFFICIENT DATA FOR 2-BUTANONE AND 1-HEXANOL

Sample Number	2-Butanone			1-Hexanol		
	60° C	75° C	90° C	60° C	75° C	90° C
WA	59.6	72.6	61.3	492	335	319
WB	69.2	67.6	-	483	339	263
15A	95.3	92.0	40.8	467	288	278
15B	95.2	95.5	40.8	548	257	229
30A	85.3	43.7	41.2	243	157	161
30B	91.2	41.4	46.2	239	139	176
50A	78.3	30.7	33.9	191	98	88
50B	84.9	40.2	34.5	164	119	95
70A	83.2	33.3	25.1	126	74	60
70B	73.5	30.3	25.7	114	73	68
80A	140.0	32.9	43.0	98	66	145
80B	79.8	32.1	42.7	98	67	87

TABLE 28

pH DATA FOR HEXANOL AT 90° C

Sample Number	P (atm)	$\Lambda_D \times 10^{-7}$	$\sigma/\bar{x}$ (%)	$C_V \times 10^6$ (g/ml)	Λ_D/Λ_{IS}	$\sigma/\bar{x}$ (%)	W_S (g)	W_{IS} (g)	$C_L \times 10^6$ (g/ml)	$k \times 10^3$	$\sigma \times 10^3$	S	t (sec)
6A	1.311	2.425	2.16	5.526	0.0712	1.73	0.0992	0.01115	58.73	9.409	0.260	0.537	62,000
6B	1.317	2.438	0.67	5.585	0.0645	1.31	0.1120	0.01380	57.98	9.633	0.140	0.521	62,000
6C	1.329	2.455	3.05	5.673	0.0269	6.72	0.2858	0.01510	10.30	55.070	4.000	0.510	1,374
6D	1.320	2.473	3.37	5.675	0.0664	0.15	0.3365	0.01175	16.54	34.320	1.200	0.474	2,881
8A	1.332	2.531	0.89	5.860	0.0852	0.95	0.1595	0.01310	52.72	11.120	0.145	0.477	62,000
8B	1.330	2.553	0.78	5.905	0.0770	1.73	0.1281	0.01268	58.14	10.160	0.193	0.502	62,000
8C	1.343	1.929	1.06	4.507	0.0302	8.02	0.4426	0.01317	6.78	66.490	5.380	0.479	860
8D	1.336	2.521	0.53	5.856	0.0582	1.88	0.4166	0.01413	14.94	39.20	0.766	0.485	2,536

TABLE 29

DIFFUSION DATA FOR pH SAMPLES

Sample Number	M_t/M_∞	l (cm)	D (cm^2/sec)
6C	0.173	0.45	2.03×10^{-6}
6D	0.277	0.45	2.61×10^{-6}
8C	0.160	0.45	2.90×10^{-6}
8D	0.271	0.45	2.96×10^{-6}

TABLE 30

GAS CHROMATOGRAPH STANDARDS FOR HIGH SOLIDS SAMPLES

Standard	Temp. (° C)	Samples	Vapor Standard		Liquid Standard	
			V_{STD}/A_{STD} (ml)	C_{STD} (g/ml)	W_D/W_{IS}	A_{IS}/A_D
2-Butanone	60°	A, B	7.71×10^{-10}	0.0160	0.0492	23.4
	60°	C, D	1.99×10^{-10}	0.0160	0.0492	23.4
	75°	A, B, C, D	1.78×10^{-10}	0.0160	0.0492	23.1
	90°	A, B, C, D	1.41×10^{-10}	0.0160	0.0492	22.2
1-Hexanol	60°	A, B, C, D	5.21×10^{-11}	0.0315	0.1102	6.35
	75°	A, B, C, D	5.00×10^{-11}	0.0315	0.1102	6.71
	90°	A, B, C, D	5.68×10^{-11}	0.0315	0.1102	6.12
	90°	pH6	5.50×10^{-11}	0.0315	0.1102	5.46
	90°	pH8	5.50×10^{-11}	0.0315	0.1102	5.76

TABLE 31

GAS CHROMATOGRAPH STANDARDS FOR LOW SOLIDS SAMPLES

Standard	Temp. (° C)	Sample	Vapor Standard $\frac{V_{STD}}{A_{STD}} \times 10^{11}$ (ml)	Liquid Standard $A_{STD} \times 10^{-7}$	Vapor And Liquid Standard C_{STD} (g/ml)
2-Butanone	60°	W, 15	5.44	8.74	0.0680
	75°	W, 15	6.43	7.62	0.0680
	90°	W, 15	4.59	9.48	0.0680
1-HEXANOL	60°	W	5.24	5.64	0.0315
	60°	15	5.24	6.79	0.0315
	75°	W	5.00	4.31	0.0315
	75°	15	5.00	5.13	0.0315
	90°	W	5.68	6.02	0.0315
	90°	15	5.68	7.17	0.0315

APPENDIX II

SAMPLE CALCULATIONS

Vapor Concentration, C_V

The concentration of the diffusant in the vapor phase was determined using an external standard technique. In early runs, a series of injections of standard produced a standard curve of peak area versus volume of injection for each run. These standard curves were linear. So, in subsequent runs, 5 μl injections were used to calibrate the response.

The external standard technique is outlined by Gudzinowicz (1967). The equation used to calculate the vapor phase concentration was

$$C_V = P \frac{A_D}{V_S} \left(\frac{C_{STD} V_{STD}}{A_{STD}} \right) \quad . \tag{65}$$

The following is an example for 1-hexanol, 60° C, sample 30 A.

$P = 1.078$ atm

$A_D = 4.42 \times 10^6$

$V_S = 1.0$ ml

$C_{STD} = 0.3153$ g/ml

$V_{STD}/A_{STD} = 5.207 \times 10^{-11}$ ml

$$C_V = (1.078)\ \left(\frac{4.43 \times 10^6}{1.0\ \text{ml}}\right)\ (0.03153\ \text{g/ml})$$

$$\times\ (5.207 \times 10^{-11}\ \text{ml})$$

$$C_V = 7.866 \times 10^{-6}\ \text{g/ml}$$

Liquid Concentrations, C_L

The concentration of diffusant in the liquid phase was measured in one of two ways. For low percent solids samples (less than 30 wt % solids), an external standard technique similar to the vapor phase analysis was used. An internal standard technique was used for the rest of the samples (Gudzinowicz, 1967).

Low solids samples were injected directly onto the gas chromatograph (G. C.) column. The G. C. response was calibrated using 3 µl injections of an aqueous standard solution. The liquid phase concentration was

$$C_L = \frac{A_D}{V_S}\,\frac{C_{STD}V_{STD}}{A_{STD}} \quad . \tag{66}$$

In this case, $V_S = V_{STD} = 3$ µl or

$$C_L = \frac{A_D}{A_{STD}}\,C_{STD} \quad . \tag{67}$$

The following is an example for 1-hexanol, 60° C, sample W A.

$A_D = 2.677 \times 10^6$

$C_{STD} = 0.03153$ g/ml

$A_{STD} = 5.643 \times 10^7$

$$C_L = \left(\frac{2.677 \times 10^6}{5.643 \times 10^6}\right)\ (0.03513\ \text{g/ml})$$

$C_L = 1.496 \times 10^{-3}$ g/ml

Samples containing greater than 30 wt % solids were analyzed by the internal standard technique outlined by Gudzinowicz (1967). A standard solution containing a known weight ratio of diffusant and internal standard was injected. The weight ratio of diffusant weight to sample weight was

$$\frac{W_D}{W_S} = \frac{A_D}{A_{IS}} \frac{W_{IS}}{W_S} \left(\frac{A_{IS}}{A_D} \right)_{STD} \left(\frac{W_D}{W_{IS}} \right)_{STD} . \tag{68}$$

The concentration in the liquid phase was

$$C_L = \rho \frac{W_D}{W_S} . \tag{69}$$

The density was shown to be a linear function of weight percent solids.

$$\rho = A + BS . \tag{70}$$

The constants A and B were obtained by a least-squares fit of the density data for 30, 50, 70 and 80 wt % solids solutions.

The liquid concentration was

$$C_L = (A + BS) \left(\frac{A_D}{A_{IS}} \right) \left(\frac{W_{IS}}{W_S} \right) \left(\frac{A_{IS}}{A_D} \right)_{STD} \left(\frac{W_D}{W_{IS}} \right)_{STD} . \tag{71}$$

The following is an example for 1-hexanol, 60° C, sample 30 A.

A = 0.9503 g/ml

B = 0.5414 g/ml

S = 0.343

$$\frac{A_D}{A_{IS}} = 0.03881$$

$$W_{IS} = 0.01352 \text{ g}$$

$$W_S = 0.16540 \text{ g}$$

$$\left(\frac{A_{IS}}{A_D}\right)_{STD} = 6.353$$

$$\left(\frac{W_D}{W_{IS}}\right)_{STD} = 0.1102$$

$$C_L = [0.9503 \text{ g/ml} + (0.5414 \text{ g/ml})(0.343)](0.03881) \times \left(\frac{0.01352 \text{ g}}{0.16540 \text{ g}}\right)(6.353)(0.1102)$$

$$C_L = 2.523 \times 10^{-3} \text{ g/ml}$$

Vapor-Liquid Equilibrium Coefficient, K

In this work, the vapor-liquid equilibrium coefficient, K, was defined as the ratio of vapor and liquid concentrations at equilibrium or

$$K = \lim_{t\to\infty} \frac{C_V}{C_L} \tag{72}$$

or, simply,

$$K = \frac{C_V}{C_L} \tag{73}$$

where equilibrium between the bulk vapor and liquid phases is assumed.

The following is an example for 1-hexanol, 60° C, sample 30 A.

$$C_V = 7.866 \times 10^{-6} \text{ g/ml}$$

$C_L = 2.523 \times 10^{-3}$ g/ml

$K = \dfrac{7.866 \times 10^{-6} \text{ g/ml}}{2.523 \times 10^{-3} \text{ g/ml}}$

$K = 3.118 \times 10^{-3}$

Vapor-Liquid Equilibrium Coefficient Standard Deviation, σ_K

The relative standard deviation of a calculated value (eg. K) is the square root of the sum of the squares of the relative standard deviations of each measured value (Skoog and West, 1976). That is, the relative standard deviations for the partition coefficient was

$$\frac{\sigma_K}{K} = \sqrt{\left(\frac{\sigma_{CV}}{C_V}\right)^2 + \left(\frac{\sigma_{CL}}{C_L}\right)^2} \quad (74)$$

or

$$\sigma_K = K\sqrt{\left(\frac{\sigma_{CV}}{C_V}\right)^2 + \left(\frac{\sigma_{CL}}{C_L}\right)^2} \quad (75)$$

The following is an example for 1-hexanol, 60° C, sample 30 A.

$\dfrac{\sigma_{CV}}{C_V} = 0.0132$

$\dfrac{\sigma_{CV}}{C_L} = 0.0029$

$\sigma_K = 3.118 \times 10^{-3} \sqrt{(0.0132)^2 + (0.0029)^2}$

$\sigma_K = 0.042 \times 10^{-3}$

Diffusivity, D

The solution to the unsteady state diffusion equation is given by Crank (1975) as

$$\frac{M_t}{M_\infty} = (1 + \alpha)\left[1 - \exp\left(\frac{T}{\alpha^2}\right) \text{erfc}\left(\frac{T}{\alpha^2}\right)^{1/2}\right] . \tag{76}$$

M_t / M_∞ is the ratio of the bulk concentration of diffusant in the liquid phase at time t to the bulk concentration at steady state. This ratio may be represented as

$$\frac{M_t}{M_\infty} = \frac{k_{eq}}{k_t} . \tag{77}$$

Where k_{eq} and k_t are not equilibrium constants, but are convenient ratios of concentrations for calculation purposes. They are defined as

$$k_{eq} = \frac{C_V}{C_L} \tag{78}$$

at large values of t, and as

$$k_t = \frac{C_V}{C_L} \tag{79}$$

at small values of t. In this work

$$k_{eq} = K \tag{80}$$

since equilibrium is reached at large values of t. The ratio of the mass of diffusant in the vapor phase to the mass of diffusant in the liquid phase at steady state was α, or

$$\alpha = \frac{M_V}{M_L} = \frac{C_V V_V}{C_L V_L} \tag{81}$$

or

$$\alpha = K \frac{V_V}{V_L} \quad . \tag{82}$$

Table 32 gives values of V_V/V_L for the samples. Dimensionless lime, T, is defined as

$$T = \frac{Dt}{l^2} \quad . \tag{83}$$

To obtain a diffusivity from the data, M_t/M_∞ and α were first obtained. M_t/M_∞ was calculated from the steady state and unsteady state concentration ratios and k_{eq} was taken as the k_{eq} that has a weight percent solids value closest to the weight percent solids of the short time sample being calculated.

The following is an example for 1-hexanol, 60° C, sample 30 C.

$$k_t = 8.723 \times 10^{-3}$$

$$k_{eq} = 3.118 \times 10^{-3}$$

$$\frac{M_t}{M_\infty} = \frac{3.118 \times 10^{-3}}{8.723 \times 10^{-3}}$$

$$\frac{M_t}{M_\infty} = 0.7347$$

The value of α was calculated using equation 82.

The following is an example for 1-hexanol, 60° C, sample 30 C.

$$K = 3.118 \times 10^{-3}$$

$$\frac{V_V}{V_L} = 889.0$$

TABLE 32

VOLUME RATIO AND DIFFUSION PATH LENGTH FOR THE DIFFUSION SAMPLES

Sample	V_V/V_L	l (cm)
W	114.3	1.8
30, 50	296.3	0.45
70, 80	889.0	0.15

$\alpha = (3.118 \times 10^{-3})\ (889.0)$

$\alpha = 0.9240$

The unsteady state diffusion equation (equation 76) was solved by trial and error for T.

The following is an example for 1-hexanol, 60° C, sample 30 C.

$\frac{M_t}{M_\infty} = 0.7347$

$\alpha = 0.9240$

$$0.7347 = (1 + 0.9240) \left\{ 1 - \exp\left[\frac{T}{(0.9240)^2} \right] \times \operatorname{erfc}\left[\frac{T}{(0.9240)^2} \right]^{1/2} \right\}$$

$$0.7347 = 1.9240 \left[1 - \exp\left(\frac{T}{0.8538} \right) \operatorname{erfc}\left(\frac{T^{1/2}}{0.9240} \right) \right]$$

Trial and error gives T = 0.2095.

Given a dimensionless value of time, T, the diffusivity was obtained by rearranging equation 83.

$$D = \frac{Tl^2}{t} \tag{84}$$

The following is an example for 1-hexanol, 60° C, sample 30 C.

$T = 0.2095$

$l = 0.45$ cm

$t = 2779$ sec

$D = \frac{(0.2095)\ (0.45\ \text{cm})^2}{2779\ \text{sec}}$

$D = 1.526 \times 10^{-5}\ \text{cm}^2/\text{sec}$

Activity Coefficient, γ

The activity coefficient, γ, was calculated from the vapor-liquid equilibrium data, K. The molar vapor-liquid equilibrium coefficient was defined as

$$\tilde{K} = \frac{y}{x} = \frac{\gamma P^{sat}}{P} \quad . \tag{85}$$

The vapor phase mole fraction was

$$y = \frac{n_{DV}}{n_{TV}} \tag{86}$$

where n_{DV} and n_{TV} were the diffusant and total vapor molar concentrations, respectively. The diffusant molar concentration was

$$n_{DV} = \frac{C_V}{M_D} \tag{87}$$

where C_V was the vapor phase mass concentration of diffusant and M_D was the diffusant molecular weight. Assuming an ideal gas for the vapor phase, n_{TV} became

$$n_{TV} = \frac{P}{RT} \tag{88}$$

where P was the total pressure, R was the ideal gas constant and T was absolute temperature. The vapor mole fraction became

$$y = \frac{C_V RT}{PM_D} \quad . \tag{89}$$

The liquid mole fraction was

$$x = \frac{n_{DL}}{n_{TL}} \tag{90}$$

where n_{DL} and n_{TL} were the diffusant and total liquid molar concentration, respectively. The diffusant liquid molar concentration was

$$n_{DL} = \frac{C_L}{M_D} \quad . \tag{91}$$

The total liquid molar concentration was

$$n_{TL} = n_{DL} + n_{WL} + n_{SL} \tag{92}$$

where n_{WL} and n_{SL} were the water and solids (malto-dextrin) liquid molar concentration, respectively. The diffusant concentration was assumed to be negligible. The water and solids concentration became

$$n_{WL} = \frac{W\rho}{M_W} \tag{93}$$

and

$$n_{SL} = \frac{S\rho}{M_S} \tag{94}$$

where ρ was the solution density, S and W were the solids and water weight fraction, and M_W and M_S were the water and solids molecular weight. The water and solids weight fractions were related by

$$W = 1 - S. \tag{95}$$

The density was correlated by

$$\rho = A + BS \ . \tag{96}$$

So, the liquid mole fraction became

$$x = \frac{C_L}{M_D \ (A + BS) \ \left(\frac{1 - S}{M_W} + \frac{S}{M_S} \right)} \quad . \tag{97}$$

The activity coefficient was calculated by

$$\gamma = \frac{P^{sat}}{P} \frac{y}{x} \tag{98}$$

or

$$\gamma = \frac{KRT\ (A + BS)}{P^{sat}} \quad \frac{1 - S}{M_W} \frac{S}{M_S} \quad . \tag{99}$$

The following is an example for 1-hexanol, 60° C, sample 30 A.

$K = 3.118 \times 10^{-3}$

$R = 62{,}400 \ \frac{\text{cm}^3 \text{ Torr}}{\text{g mole } ^\circ\text{K}}$

$T = 333.2\ ^\circ\text{K}$

$A = 0.9503\ \text{g/cm}^3$

$B = 0.5388\ \text{g/cm}^3$

$S = 0.343$

$P^{sat} = 11.10\ \text{Torr}$

$M_W = 18.01\ \text{g/g mole}$

$M_S = 1641.2\ \text{g/g mole}$

$$\gamma = \frac{(3.118 \times 10^{-3}) \left(62{,}400 \ \frac{\text{cm}^3 \text{ Torr}}{\text{g mole } ^\circ\text{K}}\right) \ (333.2\ ^\circ\text{K})}{11.10\ \text{Torr}}$$

$$\times \left[0.9503\ \text{g/cm}^3 + 0.5388\ \text{g/cm}^3\ (0.343)\right]$$

$$\times \left(\frac{1 - 0.343}{18.01\ \text{g/g mole}}\right) \left(\frac{0.343}{1641.2\ \text{g/g mole}}\right)$$

$\gamma = 243$

APPENDIX III

VISCOSITY CORRELATION ATTEMPTS

An extention of the Einstein equation was used to fit the data (Willey and Macosko, 1978)

$$\mu_R = \frac{\mu}{\mu_W} = 1 + 2.5\ \phi + K\ \phi^2 \qquad (100)$$

where ϕ is the volume fraction. An ideal mixing rule was assumed for water and malto-dextrin,

$$\phi = \frac{V_S}{V_S + V_W} \qquad (101)$$

where

$$V_S = \frac{S}{\rho_S} \qquad (102)$$

and

$$V_W = \frac{W}{\rho_W} \qquad (103)$$

or

$$\phi = \frac{1}{1 + \frac{W}{S}\,\frac{\rho_S}{\rho_W}} \qquad (104)$$

where S is the solids weight fraction, W is the water weight fraction, ρ_S and ρ_W are the density of pure malto-dextrin and water, respectively. K in equation 100 was a strong function of the percent solids. Table 33

TABLE 33

EINSTEIN CONSTANT K FOR EQUATION 100

Wt % Solids	Temperature (°C)		
	60°	75°	90°
31.1	153	180	220
47.2	370	498	661
63.2	2202	3348	5724

gives calculated values for K. This correlation does not work because it is meant for use with suspension of spheres. The malto-dextrin studied here has, on average, a chain length of 10 dextrose molecules. In solution, the malto-dextrin molecules should not be spheres. There should be a much greater dependency of the viscosity on the mean molar volume of the solution, since the malto-dextrin chains should extend when a shearing force is exerted on them.

Numerous empirical correlations were tried. One of which was the Martin equation (Bird, et al., 1960),

$$\mu - \mu_S = \mu_S \, [\mu] \, C \exp\left(K'' \, [\mu] \, C\right) \tag{105}$$

where μ_S is the solvent viscosity, C is concentration in g/ml, K" is an adjustable parameter and $[\mu]$ is given by

$$[\mu] = \lim_{C \to 0} \frac{\mu - \mu_S}{\mu_S} \quad . \tag{106}$$

This equation correlated very well. Table 34 and the correlation coefficient, r, gives $[\mu]$, K" for the temperatures at which the viscosity was measured. This correlation was not used in the calculations because it was fairly complex and the density was not measured over the entire range of percent solids of interest.

Menting, et al. (1970a), have shown that the diffusivity of acetone correlates well with exp $(BC_W^{-1/2})$. That is,

$$\log D = A + BC_W^{-1/2} \tag{107}$$

Since the diffusivity and viscosity might have a similar

TABLE 34

CONSTANTS FOR EQUATION 105

Temp. (°C)	[μ]	K"	r
60°	1.51	2.48	0.994
75°	1.67	2.07	0.996
90°	1.76	1.83	0.994

mechanism, the form of a correlation for viscosity should follow the same form. That assumption is indeed correct. Log μ correlates well with $C_W^{-1/2}$. Table 35 gives the constants for the viscosity correlation of the form,

$$\log \mu = A_2 + B_2 C_W^{-1/2} . \tag{108}$$

This equation correlates as well as the Martin equation.

Since C is a function of the water fraction, W, a correlation in the form of

$$\log \mu = A_3 + B_3 W^{-1/2} \tag{109}$$

was used. This correlation worked better than the one based on $C_W^{-1/2}$. Table 36 gives the constants A_3 and B_3 and the correlation coefficient.

It was also found that log μ correlates well with $W^{1/2}$ although not as well as with $W^{-1/2}$ or $C_W^{-1/2}$. The correlation becomes

$$\log \mu = A_4 + B_4 W^{1/2} . \tag{110}$$

Table 37 gives the constants A_4 and B_4 and the correlation coefficient.

TABLE 35

CONSTANTS FOR EQUATION 108

Temp. (°C)	A_2	B_2	r
60°	-7.82	7.45	0.994
75°	-7.38	6.89	0.994
90°	-7.06	6.46	0.994

TABLE 36

CONSTANTS FOR EQUATION 109

Temp. (°C)	A_3	B_3	r
60°	-5.20	49.3	0.999
75°	-4.94	45.8	0.999
90°	-4.74	42.9	0.999

TABLE 37

CONSTANTS FOR EQUATION 110

Temp. (°C)	A_4	B_4	r
60°	17.58	1.86	-0.994
75°	16.08	1.73	-0.994
90°	14.83	1.62	-0.994

APPENDIX IV

EARLY EXPERIMENTS

Previous workers had measured D and K by measuring changes in either the vapor or liquid phase concentration. Early experiments in this study were conducted on the same philosophy.

The first attempts at measuring the diffusivity and the partition coefficient of 1-hexanol were performed using heavy walled capillary tubes (figure 18). Malto-dextrin solutions were placed inside the capillary tubes with a disposable glass pipette for the low solids solutions. High solids solutions were drawn into the capillary tubes by drawing a vacuum on one end of the capillary tube and placing the other end into a beaker of hot solution. One end of the tube was sealed with several layers of Teflon® tape and a Teflon® cap. The capillary tubes were then placed upright inside the diffusion chamber in a 50 ml beaker. For the equilibrium partition measurements, a thin layer (approximately 0.3 cm thick) of malto-dextrin solution was poured into a 25 ml beaker. This beaker was placed in the diffusion chamber (figure 19) along with the capillary tubes. The diffusion chamber was then placed in the constant temperature water bath and

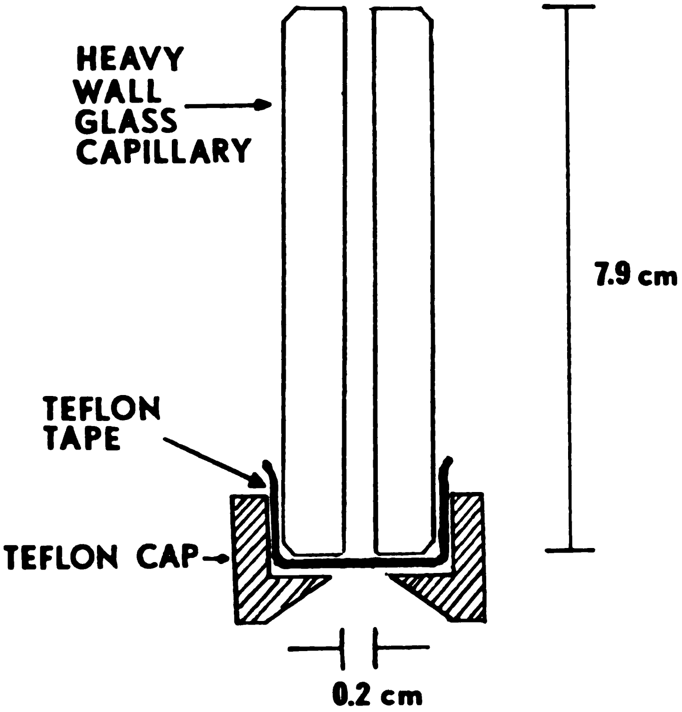

FIGURE 18. GLASS CAPILLARY DIFFUSION TUBE

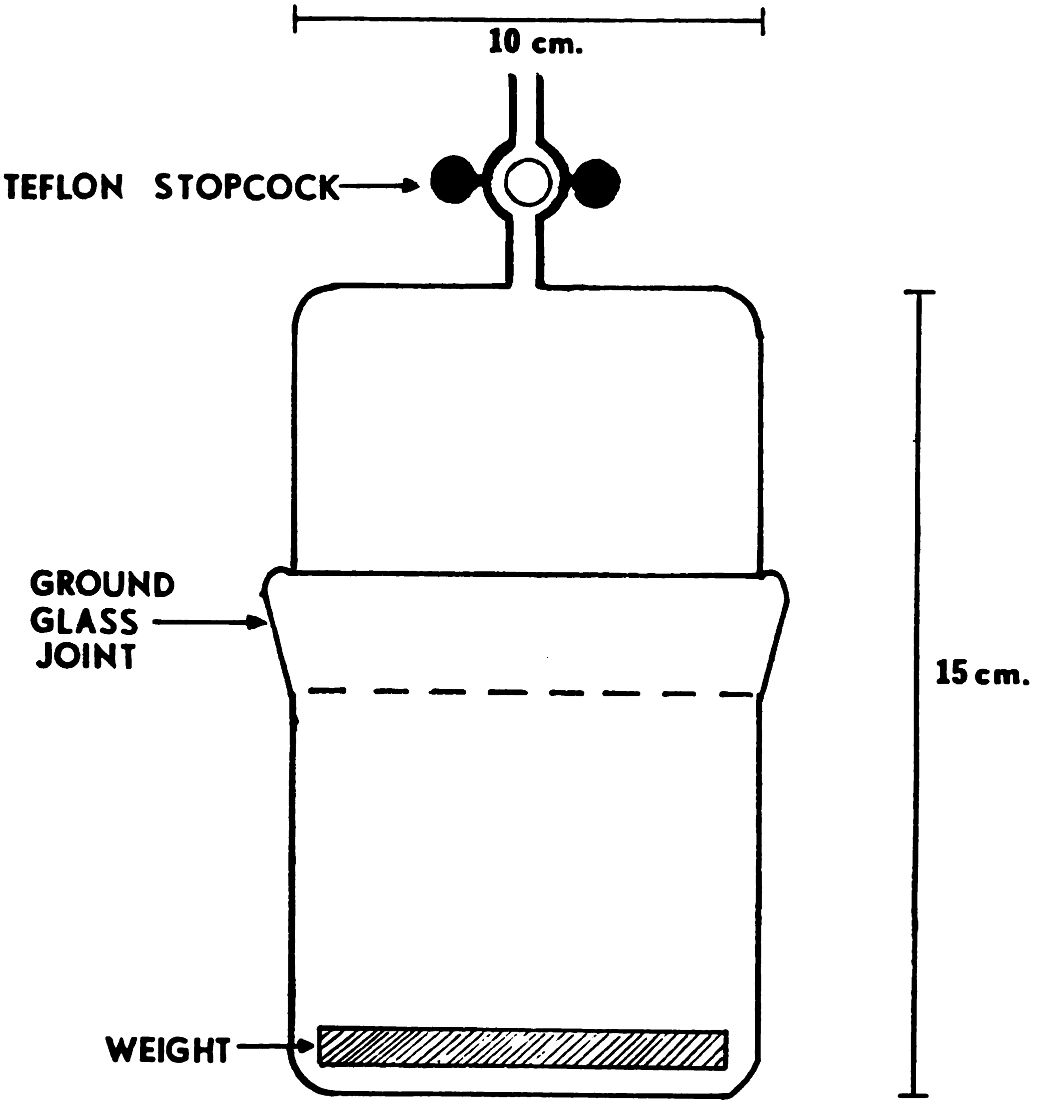

FIGURE 19. GLASS DIFFUSION CELL

the chamber was completely submerged in the water to prevent condensation of water or hexanol on any part of it.

Approximately 4 hours were allowed for the contents of the diffusion chamber to reach the water bath temperature. Then the chamber was removed from the bath and a 25 ml beaker containing about 10 ml of 1-hexanol was placed in the diffusion chamber along with the samples. The chamber was immediately returned to the water bath. The time at which the 1-hexanol was introduced into the diffusion chamber was recorded as the starting time for the run.

The 1-hexanol was allowed to diffuse into the samples for 4 to 48 hours, depending on the percent solids of the sample. Samples of low percent solids solutions were taken by inverting the diffusion tube above a 5 ml serum vial. High percent solids samples were pushed out of the diffusion tube with a metal rod. Samples were taken at different times for each temperature and percent solids. In each run, the very last sample to be taken was the vapor-liquid equilibrium coefficient sample. All samples were analyzed using the internal standard method described in the Experimental Method section. Vapor-liquid equilibrium coefficients were calculated based on the weight percent 1-hexanol in the liquid phase and the saturated vapor pressure of 1-hexanol. It was assumed that the total pressure inside the diffusion chamber was 1 atmosphere since the chamber was opened prior to the introduction of 1-hexanol. The partial pressure of water in the chamber was neglected.

Using the technique just described, it was observed that the diffusion samples lost a considerable amount of water. A drop in the liquid sample capillary of as much as 1 cm was observed for 30 wt % solids samples. A method for controlling the relative humidity above the samples was necessary.

Pre-conditioning similar to that used by Menting, et al. (1970a), was tried. Saturated inorganic salt solutions were placed in the diffusion chambers in 25 ml beakers along with about 10 ml of malto-dextrin solution in a 25 ml beaker. All of the possible combinations of 30, 50, 70, and 80 wt % solids malto-dextrin solutions and saturated solutions of NaBr, KCl, LiCl, $KC_2H_3O_2$ at 60° C were tried. After a conditioning period of 24 hours, all of the solutions had lost most of their water. Some of the solutions had lost so much water that they had to be chipped out of their beakers. Obviously, the vapor pressure of water above the malto-dextrin solutions was considerably greater than that above the saturated salt solutions.

In another attempt, a beaker containing about 100 ml of malto-dextrin solution was placed in the diffusion chamber along with the sample solutions. The 100 ml solution had the same percent solids as the samples. After a conditioning period of 24 hours at 60° C, the solutions showed a water loss similar to that experienced with the saturated salt solutions. The solutions in the diffusion chamber lost a considerable amount of water. This method was rejected for two reasons. First, the solutions lost water during a 24-hour conditioning period. Second, and most important, it was decided that it was important to use a partial pressure of 1-hexanol much lower than the saturated vapor pressure. In order to prevent condensation of 1-hexanol on the solutions during sampling, a partial pressure less than the saturated vapor pressure was needed, but if a low partial pressure was to be used, the vapor phase concentration of 1-hexanol would have to be measured using a gas chromatographic technique. The vapor phase could not be measured from the diffusion chamber due to condensation in stopcock valve. For that reason, a more effective sampling port was needed. The combination of 125 ml serum vials and Pierce Mininert® Valves proved to work satisfactorily.

A large amount of malto-dextrin solution could not be used to control the humidity because there was not enough room in the 125 ml serum bottle for the solutions. The humidity was controlled in the 125 ml serum bottles by injecting a certain amount of distilled water into the bottles before the runs, depending upon the percent solids of the solutions.

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