Correlating Diffusion Coefficients in Concentrated Carbohydrate Solutions

The diffusivities and the vapor-liquid equilibrium coefficients of two organic components, 1-hexanol and 2-butanone, were measured in concentrated malto-dextrin solutions using newly developed techniques. Accurate determination of these quantities required complete material balances of the two phases and control of the water concentration in the experimental cell. The diffusion coefficients of these solutes correlated with solution viscosity to the ½ power over a range of temperatures and concentrations. Other literature data for diffusion coefficients in concentrated malto-dextrin and sugar solutions are shown to correlate with viscosity.

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SCOPE

The retention of flavors and other volatiles during the drying of liquid foods is an important problem in the food industry. The ability to predict accurately volatile diffusivities over ranges of temperature and water contents is critical to good process design. Examples of such cases include the spray drying of liquid foods when diffusion in the liquid droplet phase is rate-limiting (*Kieckbusch* and King, 1980) and flavor loss during the drying of cereals.

For the spray-drying case, mass transfer depends on the diffusivity of the flavor components as functions of temperature and water content, as well as their equilibrium solubilities. In addition, the possibility of surface cracks and rupture of internal bubbles can complicate modeling attempts. Several methods for correlating the diffusion coefficients of volatile components in foods or model food systems have been proposed. Concentrated sugar and malto-dextrin solutions are often used as model food systems since they have high viscosities at spray-drying conditions, are good film formers, and tend to retain some volatiles.

Rulkens and Thijssen (1972) have proposed that volatile retention is enhanced when a film of high solids concentration impermeable to flavors is formed on the drying droplet. The film acts as a barrier to larger flavor molecules through selective diffusion, allowing smaller water molecules to diffuse while retaining the flavors. Menting et al. (1970) proposed that the log of the acetone diffusivity in malto-dextrin solutions varied with the negative inverse of the square root of the water concentration. Chandrasekaran and King (1972) have shown that the log of the reduced diffusivity of a flavor (ratio of the diffusivity in the model food system to the diffusivity in pure water) is proportional to the log of the water content for sucrose solutions.

The above studies do not provide a consistent basis by which to correlate diffusion coefficients with solution properties and temperature. In addition, the previous studies included data taken at less than 45°C, much less than the temperatures expected in drying operations. The objective of this study was to take diffusivity and solubility data of a sparingly soluble solute, 1-hexanol, and a partially soluble solute, 2-butanone, in malto-dextrin solutions over wide ranges in temperature and water content of the solution phase. These data were analyzed to determine scaling relations that would permit rapid estimation of mass transfer properties in the liquid phase.

CONCLUSIONS AND SIGNIFICANCE

Correlations of volatile compound diffusivity with solution viscosity accurately represent data for solute diffusion in concentrated sugar and malto-dextrin solutions. This type of correlation permits extrapolation over a range of temperatures and solids concentrations. A comparison of literature data suggests that the viscosity exponent may change for one solute in different carbohydrate solutions or for different solutes in the same carbohydrate solution.

INTRODUCTION

Spray drying is an energy-efficient method for dehydrating foods, but it has high flavor losses compared to freeze drying. Carbohydrate solutions have been used as surrogates for food liquids to study the flavor loss mechanisms during spray drying. The rate of flavor loss from a spray-dried droplet may depend on either the rate of mass transfer through the droplet or the rate of mass transfer from the gas film surrounding the droplet. Our purpose for studying flavor diffusion through carbohydrate solutions is to provide a basis for modeling the flavor loss through the liquid phase of drying food.

Volatile loss in the liquid phase rate-limiting region of spray

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drying or in cereal drying will depend on the diffusivity of the flavor through and its equilibrium solubility in the food. Measurement techniques and correlating criteria for both quantities will be needed for process design. This paper considers the problem of correlating volatile flavor diffusion coefficients in model food systems (concentrated sugar and malto-dextrin solutions).

Data were taken on the diffusivity of two flavor components, 1-hexanol and 2-butanone, in concentrated malto-dextrin solutions over the temperature range 60 to 90°C and over the concentration range 0 to 80 wt. % malto-dextrin. While the temperature range was lower than that often experienced in spray drying water-based foods, it was higher than that used in previous studies. The upper limit of the wt. % solids was less than that obtained in commercial systems but was at the upper limit at which properties could be accurately determined.

The two flavor analogs have low molecular weights, but 1-hexanol is only sparingly soluble in water solutions. 2-Butanone has a much higher solubility in water than 1-hexanol (22 vs. 0.5 wt. % at 30°C). Data on the diffusivity of flavor components in concentrated sugar and malto-dextrin solutions were also taken from the literature.

Diffusivity Correlations

The diffusion coeffients of solutes in dilute solution can usually be related to temperature using an Arrhenius expression:

$$D = D_o \exp(-E_d/RT) \qquad (1)$$

The activation energy for diffusion, E_d, may be considered to be a function of solution composition. The Stokes-Einstein group, $D\mu/T$, has been used to scale diffusion coefficients. For large spherical particles in solution, the Stokes-Einstein group is inversely proportional to the particle radius (Bird et al., 1960). The radius of the particle can be related to the molar volume of the solute. Several theories and correlations (Reid and Sherwood, 1966) suggest that diffusivity is inversely proportional to viscosity at constant temperature:

$$D\mu^{\epsilon} = \text{constant} \qquad (2)$$

where ϵ is equal to 1.0 for the diffusion of large solute molecules in dilute solution with a solvent of small molecules.

For the case of a small solute molecule diffusing in a viscous solvent of larger molecules. Eyring's rate theory suggests that the diffusion coefficient is proportional to the solvent's viscosity to the $-2/3$ power (Hiss and Cussler, 1973); that is

$$D\mu^{2/3} = \text{constant} \qquad (3)$$

Eyring's rate theory can also predict an exponent of 1.0 for viscosity for Eq. 2.

Many empirical correlations have been proposed for predicting the diffusivity in binary solutions. The Wilke-Chang correlation (1955) predicts that the diffusivity varies with the molecular weight of the solvent to the $1/2$ power and the molar volume of the solute to the -0.6 power. Othmer and Thaker (1953) developed a similar correlation that relates the diffusivity to the solute molar volume and solution viscosity. The viscosity exponent is 1.1.

Few correlations are available for the variation of diffusivities in ternary or more complicated systems. Perkins and Geankoplis (1969) scaled ternary diffusion coefficients with viscosity to the 0.8 power. Kett and Anderson (1969a,b) have used hydrodynamic theory to scale ternary diffusion coefficients with viscosity to the 1.0 power.

EXPERIMENT

Measuring diffusion coefficients in malto-dextrin solutions at temperatures and wt. % solids near those experienced in spray drying is not straightforward. The solutions change from viscous liquids to pourable semisolids as the water contents or temperatures are reduced. Previous data (Menting et al., 1970) covered either a range of temperatures at one malto-dextrin concentration or a range of malto-dextrin concentrations at one temperature. Measuring diffusivities over ranges of both temperature and solid concentrations was thought to be important to improve the accuracy of correlations. At high concentrations, the solutions are opaque, precluding the use of an interferometer. They are also too viscous to study in a diaphragm cell, since they cannot be effectively stirred near the diaphragm surface.

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.

An experiment was designed to allow flavor components to diffuse from the vapor phase of a closed gas space into a known solution volume with a limited diffusion path length. Since malto-dextrin solutions tend to lose water at experimental conditions, the water concentration is the vapor space had to be controlled so that the wt. % solids in the solution remained constant over the run time of the experiment. The vapor volume was large compared to the solution volume so that the solute concentration in the vapor phase would change only a small amount during the experiments.

Table 1 lists the chemicals used in this study and their sources. Table 2 lists the properties of the malto-dextrin sample, which had an average degree of polymerization of 10.

The diffusion cell used in this study is shown in Figure 1. Malto-dextrin solutions were placed in the diffusion tray, either by pipet or by spatula. The diffusion trays were rectangular blocks of Teflon with a racetrack oval machined in the upper surface. The depression was either 0.45 or 0.15 mm in height. The diffusion rate of the solutes into the Teflon was orders of magnitudes lower than the diffusion rate into the solution. The malto-dextrin solution could be made level with the upper surface of the block so that the sample thickness was known.

Lead shot was used to weight the serum vials so that they would be completely immersed in a water bath. The valve on the vial could be opened so that the vapor space could be sampled using a gas-tight syringe. The valve could seal against pressures up to 1.5 atm.

All experiments of this study were done with dilute solute concentrations in the vapor phase. Water or solute condensation inside the vial during a run usually ruined the material balances by causing unusually high solute concentrations in the sample or changing the sample's water content. Solution samples were equilibrated with the vapor phase at the experimental temperature before the solute was introduced into the vial. Small amounts of water were added to the vapor phase to limit the evaporation of water from the sample. Samples were conditioned for at least 24 h before solute was added.

Diffusant was injected as a liquid to start the diffusion experiment, taking care not to drop any directly on the solid sample. The total amount of diffusant added varied with temperature and did not exceed 20 μl for 1-hexanol and 200 μl for 2-butanol.

Solute diffusivities were determined at 60, 75, and 90°C for four different wt. % malto-dextrin solutions (30, 50, 70, and 80 wt. %). Solute was injected in the sample vials after they had equilibrated to experimental conditions. At specific times, samples were analyzed to determine the concentration of solute in the vapor phase, the concentration of solute in the solution, and the water content of the solution.

In order to compute the diffusivity of the solute, the equilibrium solubility in malto-dextrin solutions had to be known for the conditions of each unsteady state experiment. Solutions were allowed to equilibrate with diffusant for 1 to 4 days, depending on the temperature and wt% solids.

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
wt. per ft^3	30 lb
Carbohydrate composition	(Approx. D.B.)
Monosaccharides	1%
Disacchardies	4%
Trisaccharides	5%
Tetrasaccharides and Higher	90%

SI Conversion: kg = lb × 0.454; m^3 = ft^3 × 0.0283

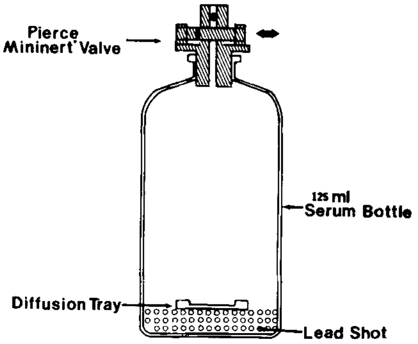

Figure 1. Cross-sectional view of diffusion equipment.

Then the vapor and solution phases were analyzed for solute, and the wt. % solids of the solution was determined. The malto-dextrin solutions were too viscous for other equilibria measurement techniques to be used (Kieckbusch and King, 1980). A Hewlett-Packard 5840 A gas chromatograph with a flame ionization detector was used to analyze both vapor and liquid samples.

An external standard technique (Gudzinowicz, 1967) was used to determine the concentration in the vapor phase. The pressure in the vapor space of the vial was measured by a U-tube manometer. The column packing was 5% SP 2100 and the precision of the technique was ±2%.

Low concentration malto-dextrin solutions (30 wt. %) could be injected directly into the GC for analysis. Higher solids samples were analyzed using an internal standard technique (Gudzinowicz, 1967) on a 5% Carbowax 20 M column. This technique requires the solution density at experimental conditions in order to compute the liquid phase concentration. Malto-dextrin solution densities were linear with solids concentration at constant temperature. The malto-dextrin concentrations were determined by sampling the liquid phase, measuring an initial weight, and drying the sample to constant weight.

The equilibrium experiment data were used to calculate the dilute solution activity coefficient:

$$\Upsilon_i = \frac{P\, y_i}{P_{sat}\, x_i} \tag{4}$$

Equation 4 defines the activity coefficient for conditions at which the vapor phase is an ideal gas, i.e., when the pressure is 1 atm or less. The activity coefficients varied with solids concentration and temperature. Curves were drawn through the data so that activity coefficients could be interpolated for specific diffusion experiments. The activity coefficient was used to calculate the equilibrium solubility of the diffusant in the sample for that run (M_∞). The malto-dextrin was assumed to have a degree of polymerization of 10 for the calculations of the activity coefficients.

The diffusion coefficients were analyzed by modeling the experiment as diffusion from a gas phase of limited volume into a stagnant solution phase. The solutions were sufficiently viscous to prevent convective mixing. Since the gas phase diffusivities were at least 4 orders of magnitude greater than those of the liquid phase, the gas phase was considered well mixed compared to the liquid phase. Since the diffusant concentration was dilute, it was assumed that only the diffusant concentration was changing in the vapor space; no net flux of water occurred from the solution to the gas. We also assumed that there was no volume change of the solution and that the diffusion coefficient was independent of diffusant concentration in this dilute region. The diffusion coefficients were obtained by solving Eq. 5 for the specified boundary and initial conditions (Crank, 1975). That is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{5}$$

with initial conditions that the solute concentration is zero in the slab at the start of the experiment.

$$C = 0, \quad 0 < x < \ell, \quad t = 0$$

where ℓ is the slab thickness, C is the solute concentration, t is time, and D is the diffusion coefficient. The boundary conditions are

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = 0, \quad t > 0 \tag{6a}$$

at the bottom of the tray and

$$\frac{KV_v}{A}\frac{\partial C}{\partial t} = -D\frac{\partial C}{\partial x}; \quad x = \ell, \quad t > 0 \tag{6b}$$

where V_v is the vapor volume, K is the vapor-liquid equilibrium coefficient (defined as the inverse of the partition coefficient given by Crank, 1975), and A is the slab surface area. The small time asymptotic solution to the equation is

$$\frac{M_t}{M_\infty} = (1+\alpha)\left[1 - \exp\left(\frac{B}{\alpha^2}\right)\operatorname{erfc}\left(\frac{B}{\alpha^2}\right)^{1/2}\right] \tag{7a}$$

where

$$\alpha = K\, Vv/V_L \tag{7b}$$

and

$$B = Dt/\ell^2 \tag{7c}$$

The partition and activity coefficients for the solute were determined by performing equilibrium experiments. D was calculated in an iterative procedure using the above equation. Mass fluxes and concentrations were used to describe the system since the malto-dextrin was not monodisperse. Since the diffusants were dilute, it is assumed that they did not change any associations between water and malto-dextrin and that these components could be treated as a single solvent. It was further assumed that diffusivity of a solute was independent of its concentration in the malto-dextrin solution.

The run times for the unsteady state diffusion experiments were targeted so that the solution solute concentration would reach about 20% of its equilibrium solubility. This gave reasonable experimental times and accurate concentration measurements.

Solution Property Measurements

Solution viscosities were measured using Ostwald-Fenske and Ferranti Couette viscometers with glycerin as a calibration standard. With these viscometers, only solutions of less than 65 wt. % malto-dextrin could be analyzed. Solutions of higher malto-dextrin concentrations tended to lose water and form films, making rheological measurements difficult. A Weissenberg rheogoniometer was tried for measuring viscosity of more concentrated solutions, but the material dried in the gap before accurate measurements could be made. The correlation used to estimate the viscosity of these solutions is described in the next section.

RESULTS

Viscosity Correlations

Malto-dextrin solution viscosity could be measured only for solutions of less than 65 wt. % malto-dextrin. Correlations were made for these data so that solution viscosity could be estimated for all diffusion coefficient data. The simplest correlation form that gave good agreement was

$$\log \mu = E + F \log W \tag{8}$$

Temperature dependence was added to the above equation by letting the constants E and F be inversely proportional to temperature. The resulting equation was

$$\log \mu = E1 + F1 \log W + \frac{(E2 + F2 \log W)}{T} \tag{9}$$

where $E1$, $F1$, $E2$, and $F2$ are constants.

This form correctly accounted for the effects of temperature, and the correlation coefficient was greater than 0.99. Equations 8 and 9 will also correlate viscosity and wt% data for sugar solutions, although they both tend to underestimate the solution viscosity at very high sugar concentrations. Extrapolation is probably valid only over limited ranges. There was no evidence of non-Newtonian behavior during the measurement of viscosity for the malto-dextrin solutions.

Viscosity estimates were needed to analyze literature data taken for diffusion in sugar solutions at 25°C. Viscosity data for glucose and sucrose solutions (Powell, 1914; Circular C 440, 1942) were fit with Eq. 9 so that test solution viscosities could be calculated. The viscosity data for glucose were assumed applicable to fructose solutions since both sugars are monosaccharides. Concentrated sugar solutions are Newtonian.

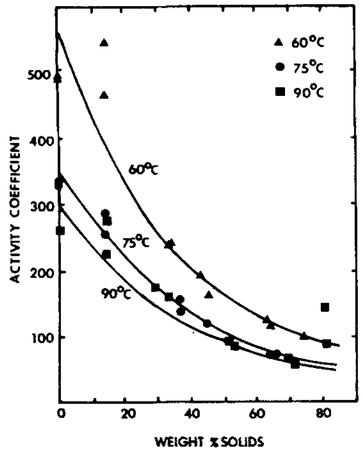

Figure 2. Activity coefficient vs. weight percent solids for 1-hexanol in malto-dextrin solutions.

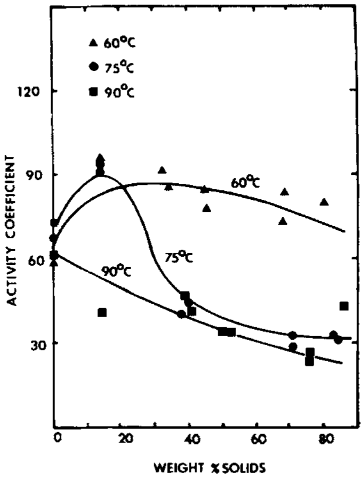

Figure 3. Activity coefficient vs. weight percent solids for 2-butanone in malto-dextrin solutions.

Activity Coefficients

Dilute solution activity coefficients were calculated from data on the diffusant concentrations in the liquid and solid phases. Figures 2 and 3 show the activity coefficients as functions of the wt. % solids. The activity coefficients for water solutions are comparable to those calculated by the Analytic Solution of Groups (Wilson and Deal, 1962; Palmer, 1975).

For 1-hexanol, solubility increases as temperature or solid fraction increases. For 2-butanone, there is an apparent maximum in the soublity in malto-dextrin solutions at 60 and 75°C. Solubility data for 2-butanone in water (Stephan, 1963) show a maximum solubility at 90°C, consistent with the data at 0 wt. % solids in Figure 3.

These data indicate that the 1-hexanol strongly interacts with the malto-dextrin, possibly through hydrogen bonding. 2-Butanone may also interact at higher temperatures, but the relative change in the activity coefficient is much less than that for 1-hexanol.

Diffusion Coefficients

Table 3 lists the diffusion coefficients of 1-hexanol and 2-butanone in concentrated malto-dextrin solutions. Data for diffusivities in pure water solution were not as accurate by our method as desired due to the possibility of convective mixing in solutions with low viscosities. When large differences existed between replicate runs in pure water, the diffusivity of the solute as computed by the Othmer-Thakar correlation (1963) was substituted for the experimental values. It was difficult to determine the precision of the malto-dextrin experiments since many of the replicate experiments had slightly different wt% solids. No experiments were considered valid if the material balance on the diffusant was in error by greater tha 20% or if condensation occurred in the sample vial. The material balances were reasonable considering the experimental difficulties of working with sparingly soluble solutes. Sample shrinkage, in which the sample would pull away from the edges of the Teflon tray and increase the surface area for diffusion, was also a possible source of error. Water injection was used to prevent this problem.

In general, the diffusivity of both the sparingly soluble solute, 1-hexanol, and the partially soluble solute, 2-butanone, increased with temperature and decreased with increasing solids in the solutions. Similar phenomena have been reported by Menting et al. (1970) for the diffusion of acetone and other organic solutes through malto-dextrin solutions at 21°C.

The diffusion data for both solutes were correlated with solution

TABLE 3. DIFFUSION COEFFICIENTS FOR 1-HEXANOL AND 2-BUTANONE IN MALTO-DEXTRIN SOLUTIONS

60°C		75°C		90°C	
W	D, m^2/s	W	D, m^2/s	W	D, m^2/s
		1-Hexanol			
1.00	1.53×10^{-9}[a]	1.00	1.97×10^{-9}[a]	1.00	2.62×10^{-9}[a]
0.661	1.53×10^{-10}	0.641	4.09×10^{-10}	1.00	6.07×10^{-9}
0.647	1.07×10^{-10}	0.643	6.02×10^{-10}	0.678	5.72×10^{-10}
0.510	5.36×10^{-11}	0.544	4.05×10^{-10}	0.675	1.65×10^{-10}
0.512	3.64×10^{-11}	0.485	2.55×10^{-10}	0.484	1.99×10^{-10}
0.361	7.66×10^{-11}	0.353	5.99×10^{-11}	0.505	3.98×10^{-10}
0.367	3.16×10^{-11}	0.357	5.43×10^{-11}	0.304	6.89×10^{-11}
0.270	4.74×10^{-12}	0.250	1.85×10^{-11}	0.309	4.31×10^{-11}
0.246	3.09×10^{-12}	0.246	2.21×10^{-11}	0.194	9.19×10^{-12}
				0.194	8.08×10^{-12}
		2-Butanone			
1.00	1.98×10^{-9}[a]	1.00	3.40×10^{-9}	1.00	8.76×10^{-9}
0.680	1.97×10^{-9}	1.00	4.49×10^{-9}	1.00	3.40×10^{-9}
0.677	1.33×10^{-9}	0.609	2.38×10^{-9}	0.640	9.16×10^{-9}
0.530	4.73×10^{-10}	0.649	1.09×10^{-9}	0.659	3.30×10^{-9}
0.544	9.84×10^{-10}	0.483	5.20×10^{-10}	0.496	3.57×10^{-9}
0.332	1.70×10^{-10}	0.496	4.46×10^{-10}	0.494	1.65×10^{-9}
0.326	1.31×10^{-10}	0.298	1.69×10^{-10}	0.258	1.76×10^{-10}
0.207	3.18×10^{-11}	0.299	1.35×10^{-10}	0.259	3.37×10^{-10}
0.197	1.06×10^{-10}	0.180	2.66×10^{-11}	0.147	3.00×10^{-11}
		0.172	1.44×10^{-11}	0.134	2.40×10^{-11}

W = water weight fraction; D = diffusivity.

[a] Computed by Othmer-Thakar correlation (1953).

TABLE 4. PARAMETERS FOR THE CORRELATION OF D WITH μ FOR MALTO-DEXTRIN SOLUTIONS

Diffusant	Temp.	Viscosity Exponent	Constant	r^2
1-Hexanol	60°C	0.55	5.9×10^{-9}	0.81
	75°C	0.50	1.4×10^{-8}	0.98
	90°C	0.55	1.9×10^{-8}	0.84
2-Butanone	60°C	0.37	2.3×10^{-8}	0.90
	75°C	0.44	2.9×10^{-8}	0.95
	90°C	0.45	6.7×10^{-8}	0.91

r^2 is the correlation coefficient for the linear least squares fit to the equation $\log D = \epsilon \log \mu + \log C$.

viscosities estimated by the viscosity correlation. Since diffusion data were taken up to 80 wt. % solids but the viscosity could be measured up to 65 wt. % solids, Eq. 9 was extrapolated as the only means for estimating the values. Equation 9 probably underestimated the malto-dextrin viscosities at wt. % solids higher than 65%.

Figures 4 and 5 show the correlation between diffusivity and viscosity for both 1-hexanol and 2-butanone, and Table 4 lists the viscosity coefficients and constants for Eq. 2. Although there is scatter in the data, Eq. 2 does represent the data. As temperature increases, the diffusivities of both solutes increase in the solutions. Data estimated by the Othmer-Thakar correlation for solute diffusivity in pure water are shown as solid points on Figures 4 and 5.

The exponents of viscosity are in the range of ½, which is on the lower end of the range of values reported for the exponent of viscosity for binary diffusion coefficients in other solutions (0.5 to 1.0). The constants for Eq. 2, the diffusivity at a solution viscosity of 1 cp, increase with increasing temperature. If all the isothermal data sets are assumed to scale with viscosity to the ½ power, the activation energy for diffusion (E_d) will be independent of malto-dextrin concentration, or solution viscosity. Based on this assumption, E_d for 2-butanone is 9.1 kcal/mol and E_d for 1-hexanol is 9.4 kcal/mol.

DISCUSSION

Viscosity is not the only choice of variable for correlating diffusion coefficients. The diffusivity, the diffusivity-viscosity product, and the Stokes-Einstein group also correlate with the weight fraction of water of these solutions. In the range of these data, the weight fraction of water also correlates with viscosity. Viscosity is a convenient choice since it has been used to correlate diffusion coefficients in many liquid systems.

The use of Eq. 2 with an appropriate exponent on the viscosity was a reasonable way to correlate the diffusion coefficient data. However, it is not clear what the best choice of the exponent should be. For large solutes diffusing through small solvent molecules, the Stokes-Einstein relation could apply ($\epsilon = 1$). For small solutes diffusing through large solvent molecules, Evring's rate theory could apply ($\epsilon = 2/3$). The malto-dextrin used in this study was a polymer with a degree of polymerization of 10, so the solutes were within the size range of the rest of the solution molecules (water and oligosaccharides). Empirical correlations have viscosity exponents ranging from 0.5 to 1.0 (Wasan et al., 1972). Wasan's data are for the diffusion of oxygen in carboxyl cellulose solutions in which the polymer molecules are very large and the macroscopic viscosity is different from the microscopic viscosity. We have reviewed literature data for diffusion in malto-dextrin and sugar solutions to determine whether Eq. 2 provides a consistent basis for correlating diffusivities with solution properties.

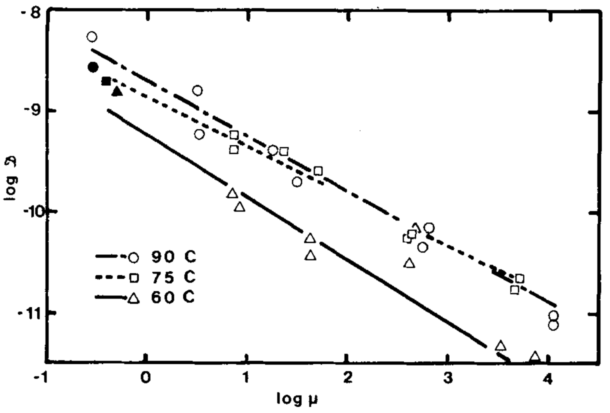

Figure 4. Diffusivity (m²/s) vs. viscosity (cp) for 1-hexanol diffusing in malto-dextrin solutions. Solid points are correlation values (Othmer and Thakar, 1953).

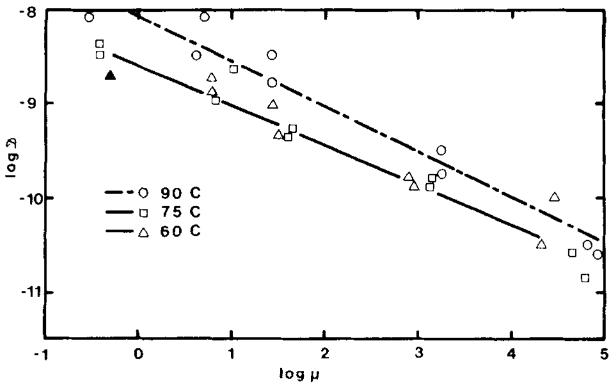

Figure 5. Diffusivity (m²/s) vs. viscosity (cp) for s-butanone diffusing in malto-dextrin solutions. Solid points are correlation values (Othmer and Takar, 1953).

Menting et al. (1970) reported data on the diffusion of water, acetone, and ethyl acetate in malto-dextrin solutions at 21°C. Over the range of moisture contents studied (pure water to 0.10 weight fraction water), the diffusion coefficient of acetone in the solutions was correlated by the equation

$$D_a = G \exp(-H/C_w) \qquad (10)$$

where D_a is the binary diffusion coefficient of acetone in the solution, G and H are constants, and C_w is the water concentration in kg/m³.

Estimating the viscosities for the Menting et al. data meant using Eq. 9 at temperatures below those used to establish the constants. Since the viscosity estimates for malto-dextrin solutions are underestimated at low water contents, none of the Menting et al. data of less than 20 wt. % water was included. It is important to note that the technique used by Menting et al. for controlling the water content of the malto-dextrin solutions could not be replicated in this study. In addition, the diffusants were maintained at saturated vapor pressure in the diffusion chamber, a condition that also led to inaccuracies in this study. If similar effects occurred in the Menting et al. study, this would have the effect of reducing the water content of the solutions from the reported values and increasing the solution viscosities (at high malto-dextrin concentrations) above those calculated by the correlation.

Figure 6 shows the log of the diffusion coefficients plotted versus the log of the malto-dextrin solution viscosity, as estimated by Eq. 9. Over a 5-decade range in the viscosity, Eq. 2 represents the data well. The viscosity exponent for the ethyl acetate was 0.42 and the viscosity exponent for the acetone data was 0.55. Both are within the range of values found for the viscosity exponent for 1-hexanol and 2-butanone in this study. Data for malto-dextrin solutions with lower water contents, 20 to 10 wt. %, fall below the correlation line shown and diverge from it as viscosity increases. Underestimating the viscosity with Eq. 9 could contribute to this divergence.

Taken together, Figures 4, 5, and 6 suggest that the diffusion coefficients of solutes in malto-dextrin solutions can be scaled with solution viscosity. The viscosity exponent for these data ranges from 0.37 to 0.55. All the data can be represented adequately using a viscosity exponent of 0.5.

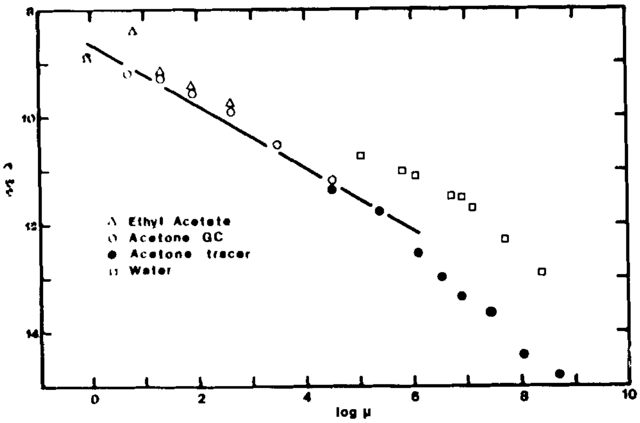

Figure 6. Diffusivity (m^2/s) vs. viscosity (cp) for solutes diffusing in malto-dextrin solutions. Data are from Menting et al. (1970) at 21°C.

The data of Menting et al. have been the basis for the theory that volatiles are retained during spray drying by a film on the droplets permeable to water only. Thijssen and coworkers (Thijssen, 1971; Menting et al., 1970) have interpreted their data as showing that the diffusion coefficients of flavor components, such as acetone, decrease much faster than that of water as the malto-dextrin concentration increases. Above malto-dextrin concentrations of 90 wt. %, they claim that the ratio of the diffusivities of acetone to water is so small that the solution can be considered to be selectively permeable to water only. As shown in Figure 6, the diffusivities of acetone and ethyl acetate may be correlated with solution viscosity despite their differing molar volumes. The diffusivity data at high solids concentrations (Figure 6) suggests that water and acetone show the same power dependence on viscosity even for very concentrated malto-dextrin solutions. The slopes of the two curves are about the same even for viscosities greater than 10^5 cp. If the diffusion coefficients correlate in the same manner with solution viscosity, then the "selectivity" of the solution is about the same over the entire concentration range and might be related to the molar volume. If solute diffusivities are related to molar volume, then flavor components will have much lower diffusivities than water but the diffusivity ratio will be constant and will not necessarily approach zero. We have been unable to establish whether "selectivity" does change at malto-dextrin concentrations greater than 80 wt. % since we could not close material balances at these conditions.

Sugar solutions have also been used as analogs to foods in spray-drying experiments. Data are available for both the diffusion of the water-sugar binary and the diffusion of flavor components. English and Dole (1950) and Gladden and Dole (1953) measured the binary diffusion coefficients of the sugars in sucrose and glucose solutions using interferometry at 25°C. Henrion (1963) measured the binary diffusion coefficients in sucrose solutions using a diaphragm cell. As previously mentioned, viscosity data (Powell, 1914; Circular C 440, 1942) were interpolated to estimate the viscosity of the sugar solutions. For glucose solutions, viscosity data were available from 1.00 to 0.50 water weight fractions. Sucrose viscosity data were available down to 0.20 water weight fraction.

Figure 7 shows the relations between sugar binary diffusivities and viscosities. Both data sets were well represented by Eq. 2. For sucrose solutions the exponent on viscosity is 0.37, and for glucose solutions the exponent on viscosity is 0.50. The sucrose solution data were taken by two different techniques so they should be reliable. Since the glucose data were available only over a narrow range of viscosities and none of the investigators performed both diffusion and viscosity experiments, the apparent difference between the slopes of the two curves may not be important. Both slopes are significantly different from the suggested coefficient for small solutes diffusing in large molecules ($\epsilon = 2/3$) and from the suggested coefficient for large solutes diffusing in small molecules ($\epsilon = 1$). They are in the range of the slopes found for Eq. 2 for diffusion in malto-dextrin solutions.

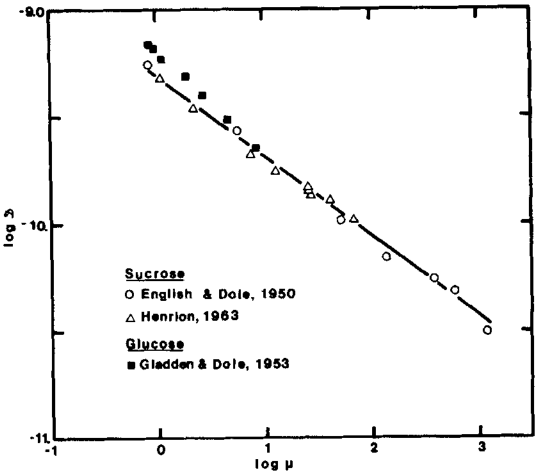

Figure 7. Correlation of binary diffusion coefficients (m^2/s) with viscosity (cp) for sugar solutions. Viscosity data are from Circular C 440 (1942).

Sucrose solutions become saturated at a water weight fraction of 0.321 at 25°C (Circular C 440, 1942), which corresponds to points with viscosities greater than 200 on Figure 7. Binary diffusion coefficients in supersaturated solutions might be affected by clustering (Timkhomiroff, 1965). If clustering occurs, the diffusion coefficients should scale with viscosity to the 1.0 power (Cussler, 1980). The data in Figure 7 seem to follow the correlation line even at high viscosities, so that clustering may not be a problem here. If clustering did occur, it would limit the applicability of Eq. 2 except for those cases in which the viscosity exponent was 1.0.

Chandrasekaran and King (1972) have done an extensive study of the diffusion of various flavor components in sugar solutions at two temperatures, 298 and 308 K, over a range of sugar concentrations. They used a diaphragm cell method to measure ternary diffusion coefficients (the system was organic solute, water and sugar). Fujita and Gosting (1956) have shown that four diffusion coefficients are necessary to describe the mass fluxes of a ternary system. Chandrasekaran and King defined their system by 1 = organic, 2 = water, and 3 = sugar in contrast to the conventional system of naming solutes as components 1 and 2 with 3 denoting the solvent.

The D_{ij} coefficient defines the flux of component i due to the concentration gradient of component j. The D_{22} coefficients were, assumed to be the same as the binary diffusion coefficients for water-sugar systems, but, as will be shown, this assumption may not be valid. The coefficients D_{11}, D_{12}, and D_{21} were calculated from the concentration gradients and the mass flux data. The D_{11} coefficients were presented as a ratio to the diffusion coefficients of the organic solute in pure water. These relative diffusivities were correlated with the viscosities of sugar solutions available in the literature, and the results are shown in Figures 8 and 9. The viscosities of glucose and fructose solutions were assumed to be equivalent. These diffusion coefficients correlate with solution viscosity to the 0.84 and 0.97 power. The cross-diffusion coefficient D_{21} correlates to the 1.1 power, while the D_{11} coefficients at 308 K correlate with the 0.92 power of viscosity. Table 5 summarizes the exponents and constants for these data.

Perkins and Geankoplis (1969) correlated ternary diffusion coefficients with viscosity for a dilute solute in two solvents. All the data correlated with viscosity to the same power, 0.8. Kett and Anderson (1969a,b) applied hydrodynamic theory to ternary diffusion coefficients. In their formulation, all the coefficients, D_{11}, D_{12}, D_{21}, D_{22}, should correlate with viscosity to the 1.0 power. The ternary diffusion coefficients, reported by D_{11} and D_{12} (Chandrasekaran and King), scale with viscosity to the 1.0 power and would appear to be consistent with the above work.

Chandrasekaran and King (1972) assumed that the binary diffusion coefficients for glucose and sucrose solutions would be similar to D_{22} and did not measure this value. Weir and Dole (1958) verified experimentally that a ternary diffusion coefficient was

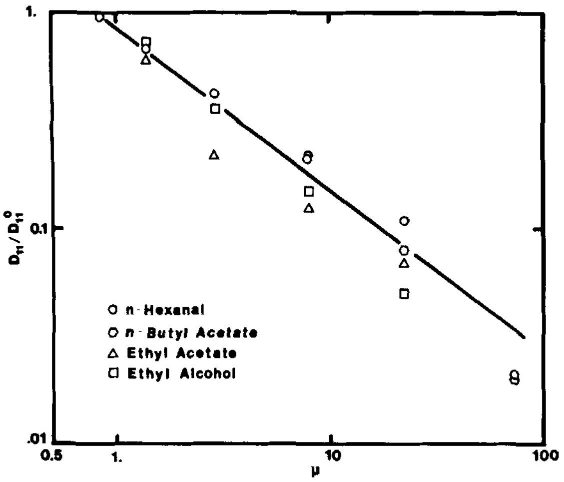

Figure 8. Correlation of a reduced ternary diffusion coefficient with viscosity for flavors in sucrose solutions. Diffusivities are from Chandrasekaran and King (1972) and viscosity data are from Circular C 440 (1942).

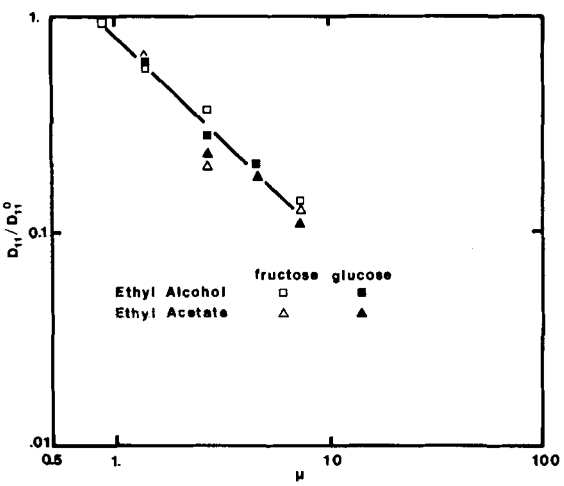

Figure 9. Correlation of a reduced ternary diffusion coefficient with viscosity for flavors in monosaccharide solutions. Diffusivities are from Chandrasekaran and King (1972) and viscosities are from Circular C 440 (1942).

similar to a dilute solution binary diffusion coefficient. Based on the discussion of Kett and Anderson (1969a), the binary diffusion coefficient needed by Chandrasekaran and King would be $D_{23}°$, the coefficient for infinitely dilute water diffusing through sugar. In addition, the binary diffusion coefficients available correlate with viscosity to the ½ power, while Chandrasekaran and King's ternary diffusion coefficients correlate with the 1.0 power. These reasons suggest that the binary diffusion coefficients of Dole and coworkers may not be equivalent to D_{22} as formulated by Chandrasekaran and King.

Frey and King (1982) measured diffusion coefficients of acetates in aqueous sugar solutions at 25 and 45°C. They correlated the D_{11} diffusion coefficients of ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl acetate with solution viscosity. Over a viscosity range of 0.5 to 10 cp, they found that the diffusivities were proportional to the inverse power of solution viscosity. The diffusivity of oxygen in aqueous sucrose solutions has been shown to correlate with the −⅔ power of viscosity (Hikata et al., 1978). As shown in Figure 7, the binary diffusion coefficients of water-sucrose solutions vary with the −½ power of viscosity.

While the diffusivities of solute in sugar solutions correlate well with solution viscosity, different solutes apparently can have different values of the viscosity exponent. The lower value for the viscosity exponent of water-sugar diffusivities in sugar solution is consistent with the selective diffusion concept. However, the diffusion exponents for water and flavor components in malto-dextrin solutions are similar and do not support the selective diffusion concept. The viscosity exponent of ethyl acetate in sugar solutions is different from its value in maltodextrin solutions. These comparisons suggest that studying flavor loss in model food systems should be done with care, since diffusivities may not correlate similarly with solution properties in two different solutions or for two different solutes in the same solution.

NOTATION

A = area of the diffusion sample
B = ratio defined by Eq. 7c
C = solute concentration, g/cm^3
C_w = water concentration, kg/m^3
D = binary diffusion coefficients, m^2/s
D_{ij} = ternary diffusion coefficient, m^2/s
D_o = binary diffusion coefficient, at the reference state
E = constant defined by Eq. 8
E_d = activation energy for diffusion
E_i = constant defined by Eq. 9
F = constant defined by Eq. 8
F_i = constant defined by Eq. 9
K = partition coefficient
ℓ = slab thickness
M_t = wt. of solute in solution at time T
M_∞ = equilibrium wt. of solute in solution
P_{sat} = saturated pressure for solute
P = system pressure
R = ideal gas constant
T = absolute temperature, K
t = time, s
V_v = vapor volume
V_L = liquid volume
W = water weight fraction
y_i = mole fraction of component i in gas phase
x_i = mole fraction of component i in liquid phase

Greek Letters

μ = viscosity, cp
ϵ = power for viscosity
Υ_i = activity coefficient of component i

TABLE 5. CORRELATION OF TERNARY DIFFUSION COEFFICIENTS WITH SOLUTION VISCOSITY FOR FLAVORS DIFFUSING IN SUGAR SOLUTIONS (CHANDRASEKARAN AND KING, 1972)

Diffusion Coefficient	Flavors	Sugar	T,°C	ϵ	Constant	r^2
$D^{11}/D^{11\,o}$	Ethyl acetate Ethyl alcohol	Fructose Glucose	298	0.97	0.81	0.96
	Butyl acetate Ethyl acetate Ethyl alcohol Hexanol	Sucrose	298	0.84	0.89	0.96
D_{21}	Ethyl acetate Ethyl alcohol	Fructose Glucose	298	1.13	3.1×10^{-10}	0.90
$D_{11}D_{11}°$	Ethyl acetate Ethyl alcohol	Sucrose	308	0.92	0.72	0.98

α = defined by Eq. 7c

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