Multicomponent Diffusion and Vapor-Liquid Equilibria of Dilute Organic Components in Aqueous Sugar Solutions

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A technique for direct measurement of the differential diffusion coefficients in a ternary system of water, sugar, and a dilute organic species is described. The individual sugars were d-fructose, d-glucose, and sucrose; and ethyl alcohol, ethyl acetate, *n*-butyl acetate, and *n*-hexanal individually constituted the dilute organic species. The four ternary diffusivities were obtained over a range of sugar concentrations by the use of horizontal diaphragm cells, a differential interferometer, a flame-ionization gas-liquid chromatograph and postulation of the validity of the Onsager reciprocal relations. The equilibrium partial pressures of the dilute organic species over these solutions have also been measured, using a vapor head space chromatographic technique.

Two main approaches have been utilized for the determination of multicomponent liquid diffusivities. Pseudo steady state diffusion through a porous diaphragm has been one method (*1* to *4*), while unsteady state diffusion from an initially sharp boundary is the second (*5* to *9*).

In this study, the existing binary diffusion data for aqueous sugar solutions are used as a partial basis for a diaphragm cell study of diffusion in a ternary mixture of water, sugar, and a dilute organic species. The ternary diffusion data were required for the analysis of the mechanism of volatiles loss during the drying of food liquids; that analysis is reported in the following paper. For the analysis one of the cross-diffusion terms is highly significant; hence it was necessary that cross-diffusion coefficients as well as straight diffusion coefficients be determined for these systems. The individual sugars were two monosaccharides, d-fructose and d-glucose, and one disaccharide, sucrose. Ethyl alcohol, ethyl acetate, *n*-butyl acetate, and *n*-hexanal individually constituted the dilute organic species. From a single experiment with a diaphragm cell and two independent experimental measurements, together with known binary diffusion data for aqueous sugar solutions, the three independent ternary diffusion coefficients are determined. The fourth diffusion coefficient is then obtained from these three ternary diffusivities by the use of the Onsager reciprocal relationship. The variation of these diffusion coefficients with sugar concentration is experimentally obtained. The extent of nonideality of the systems is evaluated by measuring the activity coefficients of the dilute organic components as a function of sugar concentration. These data are required for using the Onsager reciprocal relation.

THEORY

The description of the diffusion flux in a binary system of species A and B requires that the diffusion coefficient D_{AB} be related to the flux J_A in a fixed volume frame of reference by Equation (1):

$$J_A = -D_{AB} \nabla C_A \qquad (1)$$

where C_A is the molar concentration of component A. The mutual diffusion coefficients D_{AB} and D_{BA} are equal, but they are concentration dependent. Equation (1) is equivalent to other definitions of the Chapman-Cowling diffusion coefficient if it is assumed that there is no volume change upon mixing and that the system is isothermal and isobaric, or having zero coefficient of expansion.

The transport process in a ternary system of species 1, 2, and 3 can be described by means of the general equations for the fluxes of the two solutes 1 and 2 in a fixed volume frame of reference (*6, 7, 10*):

$$J_1 = -D_{11} \nabla C_1 - D_{12} \nabla C_2 \qquad (2)$$

$$J_2 = -D_{21} \nabla C_1 - D_{22} \nabla C_2 \qquad (3)$$

Equations (2) and (3) are a generalization of Fick's equation for two independent diffusional flows. The flows are related to the gradients of concentration of two solutes by four diffusion coefficients—two straight coefficients D_{11} and D_{22} and two cross coefficients D_{12} and D_{21}. Because of the volume-fixed frame of reference, J_3 is determined once J_1 and J_2 are known, and the flux equation for J_3 is not independent.

Equations (2) and (3) can now be compared to the Onsager reciprocal equations based on independent chemical potential gradients (*10, 11*). The dependence of chemical potential on position is caused by the local changes of the solute concentration C_1 and C_2. For a volume-fixed frame of reference, Miller (*10*) has shown that the diffusion coefficients of Equations (2) and (3) can be related to the Onsager coefficients by the following equations:

$$D_{11} = L_{11} A_{11} + L_{12} A_{21} \qquad (4a)$$

$$D_{12} = L_{11} A_{12} + L_{12} A_{22} \qquad (4b)$$

$$D_{21} = L_{21} A_{11} + L_{22} A_{21} \qquad (4c)$$

$$D_{22} = L_{21} A_{12} + L_{22} A_{22} \qquad (4d)$$

where A_{ij} is a function of the chemical potential gradients, concentrations, and the partial molar volumes.

The thermodynamic requirement $L_{12} = L_{21}$ does not lend to the equality of the coefficients D_{12} and D_{21}. Equation (4) can be rearranged to give the following relationship among diffusion coefficients:

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$$D_{11}A_{12} - D_{12}A_{11} = D_{22}A_{21} - D_{21}A_{22} \quad (5)$$

If we reduce the parameters A_{ij} given by Miller (*10*) in his Equation (79) (his *a*, *b*, *c* and *d*) for the case of component 1 being present at high dilution, Equation (5) becomes (*12*)

$$\frac{D_{12}}{C_1} = \left[\frac{1}{C_2}\frac{\partial \ln \gamma_1}{\partial \ln C_2} + \frac{V_1}{1 - C_2\bar{V}_2}\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln C_2}\right)\right] (D_{11} - D_{22}) + \frac{1}{C_2(1 - C_2\bar{V}_2)}\left(1 + \frac{\partial \ln \gamma_2}{\partial \ln C_2}\right) D_{21} \quad (6)$$

where γ is the activity coefficient in solution, C the molar concentration, and $\bar{V}$ is the partial molar volume. It should be noted that this equation involves a knowledge of the solution non-idealities, that the quantity on the right-hand side is a unique function of C_2 and not the gradient of C_1 or C_2, and that when component 1 is highly dilute D_{12} is directly proportional to C_1.

Several investigators (*6, 8, 10, 13*) have tested the validity of the Onsager reciprocal relations in various systems, including systems of sugars and water, and have found that the difference between L_{12} and L_{21} is no more than a few percent. On this basis, the validity of the reciprocal equation was assumed in the analysis of ternary diffusion.

EXPERIMENT

Diffusion

Apparatus. The stirred diaphragm cell technique was used for the determination of the diffusion coefficients. The cells were of the horizontal type described by Holmes et al. (*14, 15*), and a number of the cells were the same as used by Holmes et al. (*14, 15*) and by Byers and King (*16*). The two solution compartments are horizontally opposed across a vertical fritted glass diaphragm with a nominal pore diameter of 3 to 8 μm. Each compartment was approximately 125 cu.cm. in volume and was stirred by a 1-in. teflon-covered magnetic stirrer bar. The temperature bath and other auxiliary equipment are also described by Holmes et al. (*14, 15*). Temperatures in the surrounding bath were controlled to $\pm$ 0.05 K in all cases.

The classical diaphragm cell equation with no net volume flux across the diaphragm (*17*) was used with the reported diffusion data for the binary system of water and sucrose (*18*) to calibrate the cells:

$$\ln\left[\frac{\Delta C^0}{\Delta C}(1 - \lambda/6)\right] = \beta\, Dt(1 - \lambda/6) \quad (7)$$

where ΔC^0 and ΔC are the concentration differences across the diaphragm at time equal to zero and t respectively, and β is the cell constant. The term $(1 - \lambda/6)$ is a correction for finite hold up in the fritted diaphragm which was first proposed by Gordon (*17*).

Only differential measurements were made, and the initial molar concentration difference was always below 2.2×10^{-2} kg. sucrose/m^3. Thus the density difference between the two cell compartments was very small and mass transfer from free convection through the diaphragm was absent (*16*). The effect of liquid viscosity over the range of 10 to 400 N-s/m^2 on β, as determined by calibration with the known binary sucrose-water data, was found to be less than 5% with no confirmable trend, at stirring speeds of 5.8 rev./s and greater. The correction for solute hold up in the diaphragm $\lambda/6$ was less than 0.01 for these particular cells. Furthermore, mass balance calculations confirmed that the total amount of sugar distributed between the cell compartments did not change with time. Most of the calibrations were performed at 298 $\pm$ .05 K, with some at a higher temperature of 308 $\pm$ .05 K. The effect of temperature over this range on β was less than 5%, with no confirmed trend.

Interpretation of Data

Analysis of the ternary diffusion data is more complicated. Assuming no net volume flux and a negligible correction term λ, the solution of Equation (2) for the conditions of the diaphragm cell leads to (*1, 7, 12*)

$$\left(\frac{\Delta C_1}{\Delta C_1^0}\right) = -\frac{(B + \beta D_{11})}{(A - B)}e^{At} + \frac{(A + \beta D_{11})}{(A - B)}e^{Bt} + \frac{\Delta C_2^0 \beta D_{12}}{\Delta C_1^0 (A - B)}(e^{Bt} - e^{At}) \quad (8a)$$

$$\left(\frac{\Delta C_2}{\Delta C_1^0}\right) = \frac{(A + \beta D_{11})(B + \beta D_{11})}{\beta D_{12}(A - B)}(e^{At} - e^{Bt}) + \frac{\Delta C_2^0}{\Delta C_1^0 (A - B)}[(A + \beta D_{11})e^{At} - (B + \beta D_{11})e^{Bt}] \quad (8b)$$

where ΔC^0 and ΔC are the concentration differences across the diaphragm frit at times zero and t respectively, β is the cell constant, and A and B are quantities which arise as the roots of an auxiliary equation.

$$A, B = \frac{\beta}{2}\left[-(D_{11} + D_{22}) \pm \sqrt{(D_{11} - D_{22})^2 + 4D_{12}D_{21}}\right] \quad (9)$$

Direct solutions of Equations (8) would be very tedious, but an algebraic transformation leads to Equations (10).

$$\frac{\Delta C_1}{\Delta C_1^0} = 1 - \left(D_{11} + \frac{\Delta C_2^0}{\Delta C_1^0}D_{12}\right)\beta t + \left[(D_{11}^2 + D_{12}D_{21}) + D_{12}(D_{11} + D_{22})\frac{\Delta C_2^0}{\Delta C_1^0}\right]\frac{\beta^2 t^2}{2} + \cdots \quad (10a)$$

$$\frac{\Delta C_2^0 - \Delta C_2}{\Delta C_1^0} = \left(D_{21} + D_{22}\frac{\Delta C_2^0}{\Delta C_1^0}\right)\beta t - \left[D_{21}(D_{11} + D_{22}) + \frac{\Delta C_2^0}{\Delta C_1^0}(D_{22}^2 + D_{12}D_{21})\right]\frac{\beta^2 t^2}{2} + \cdots \quad (10b)$$

For the run times used in this study, terms in Equations (10) beyond the first bracket on the right are only 2 or 3% of the leading terms.

Chemicals

Analytical reagent grade d-fructose, d-glucose, and sucrose crystals were used. Solutions of these individual sugars with distilled water were prepared with concentrations of the sugars ranging from 15 to 65% by weight. Some solutions were also prepared containing a mixture of these three sugars. Reagent grade ethyl alcohol, ethyl acetate, *n*-hexanal, and *n*-butyl acetate were used as the dilute organic species. The maximum concentration of these organic compounds was approximately 6.0×10^{-2} kg.-moles/m^3.

Procedure

One compartment of the cell was completely filled with a pure sugar solution. The cell was now held vertically with the liquid side up, and this pure sugar solution was forced through the diaphragm by applying a vacuum to the other empty compartment to purge all the air from the pores. In other words, the pores of the diaphragm were completely filled with the pure sugar solution containing none of the trace organic component. The other compartment was washed and filled to the same vertical level with a sugar solution of very nearly the same molar water concentration as the lean side, but contain-

ing a trace amount of an organic species. A run normally lasted 5 to 10 days, after which time the cell contents were sampled and analyzed. This time duration was necessary particularly when high concentration sugar solutions were employed.

Since the initial molar concentration difference of the trace organic species never exceeded 6.0×10^{-2} kg.-moles/m^3, the diffusion coefficients are differential in nature.

The diffusion coefficients in the ternary systems, trace organic species (1) : water (2) : sugar (3), were calculated using Equations (10a) and (10b). It was postulated that the straight Onsager coefficient L_{22} of water is the same as the Onsager coefficient of water in the binary water : sugar system under similar concentration conditions. This conclusion follows from the fact that Component 1 is so dilute that there is virtually no influence of 1 on 2-3 interactions. Hence gradients in chemical potential of Component 2 are unaffected by the prevailing level or gradient of Component 1. Thus L_{22} should reflect only 2-3 interactions and should be the same as in a binary solution of the same sugar/water ratio. This statement implies that D_{22} differs by no more than 1 or 2% from the binary D for the 2-3 system.

The coefficients D_{11}, D_{12}, and D_{21} were calculated from Equations (6), (10a), and (10b) by an iterative procedure. In these diffusion experiments, the initial concentration difference ΔC_2^0 of water is less than 10% of the initial concentration difference ΔC_1^0 of the dilute organic species. As an initial approximation, terms other than the first D_{11} term on the right-hand side of Equation (10a) are neglected, and the straight diffusion coefficient D_{11} of the trace organic species is computed. The cross diffusion coefficient D_{21} of water is then computed from Equation (10b) after neglecting terms beyond the first main term on the right-hand side. In a few of the runs, the D_{22} contribution in the first main term is as much as 15 to 20% of the leading D_{21} term. Now from knowledge of D_{21} and the nonideality of the system, the cross diffusion coefficient D_{12} of the trace organic species is computed using Equation (6). The value of the diffusion coefficient D_{11} is now further refined by substituting for the other terms in Equation (10a). Similarly the value of the coefficient D_{21} is refined by reusing Equation (10b) with the new value of D_{11}, and the value of D_{12} is refined through Equation (6). Convergence was generally achieved within 1 to 2 iterations.

Analysis. For each run it was necessary to analyze the difference in concentrations of both the dilute organic species and the sugar species between the two sides of the cell. A Varian Aerograph No. 1740 gas chromatograph equipped with a flame ionization detector was used to analyze the dilute organic species. A 150 cm Porapak-Q column was used. The column temperature was varied from 393 to 473 K depending upon the particular compound being analyzed. The carrier gas was pure helium, and purified hydrogen and breathing quality compressed air were used for the detector flame. The dilute organic species content was obtained by directly injecting 2.5 mm^3 of liquid sample. In order to prevent contamination of the instrument by sugar, a 90 mm $\times$ 6 mm pyrex capillary tube was inserted in the injection port of the chromatograph. This insert was periodically changed as the sugar charred along the inside of the tube. The products of pyrolysis of the sugar did not interfere with the determination of the dilute organic species, although some drift of the baseline of the recorder was observed at high sensitivities. The peak areas for the dilute organic species were compared with previously determined calibration curves. At these low concentration levels, the peak areas were found experimentally to be linear with concentration.

A Carl Zeiss differential interferometer model no. G-1, sensitive to 10^{-7} refractive index difference, was used to analyze the difference in sugar concentration between the solutions on either side of the diaphragm cells. The calibration curve of interferometer reading difference in molar concentration depends upon the sugar concentration level and is linear over the small concentration differences encountered here. It should be noted that the difference in refractive index between the two solutions results in part from the difference in dilute organic species content as well as from the sugar concentration difference. The dilute organic species contribution is accounted for from the chromatograph measurements to determine the actual difference in sugar concentration between the two sides of the diaphragm cell. The correction to the interferometer reading for the dilute organic species is under 10%, assuming that the effects of the different solutes upon refractive index are additive.

Activity Coefficients

Procedure. The effect of sugar concentrations on the activity coefficients or the relative volatilities of the dilute organic components with respect to water was also studied. 50 cm^3 of sugar solutions of various concentrations ranging from 0 to 70% by weight were placed in 250 cm^3. Erlenmeyer flasks sealed at the top with aluminium foil. 2.5 mm^3 of each of the following organic components—ethyl alcohol, ethyl acetate, *n*-hexanal, *n*-butyl acetate, ethyl-2-methyl butyrate, and *n*-hexyl acetate—were injected into each flask through the aluminium foil. The flasks were placed in a thermostatted bath maintained at 298 $\pm$ .05 K. After the solutions had been allowed to equilibrate, 5 cm^3 of the vapor space was removed through the foil with a gas-tight syringe and injected as a vapor sample into the chromatograph. The amount of the particular dilute organic component present in the vapor space is a measure of the activity coefficient or relative volatility of that component in the given sugar solution.

Analysis. For vapor and liquid phases in equilibrium in two different sugar solutions, 1 and 2, we have (19):

$$\frac{v_{S1}}{v_{S2}} = \frac{K_{S1}}{K_{S2}} \left[\frac{L_2 + K_{S2}V}{L_1 + K_{S1}V} \right] \tag{11}$$

where v_S is the number of moles of component S in the vapor phase, and L and V are the total number of moles in the liquid and vapor phases, respectively. K_S is the equilibrium ratio of component S and can be expressed as

$$K_S = \frac{\gamma_S P_S^0}{P}$$

where γ_S is the activity coefficient of component S, and P_S^0 and P are the vapor pressure of S and the total pressure, respectively.

If the activity coefficients at infinite dilution are known for various trace organic species in sugar-free solution, the respective activity coefficients in concentrated sugar solutions can be determined from measured values of v_S using Equation (11). Limiting activity coefficients in sugar-free solution were obtained from a variety of sources, including reported solubility

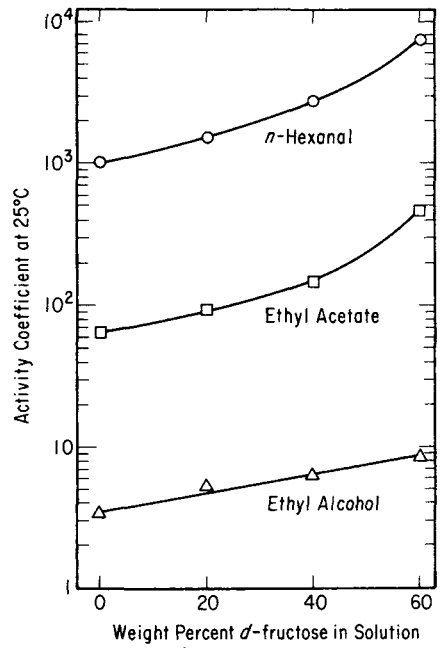

Fig. 1. Variation of activity coefficients of trace organic species for d-fructose solutions.

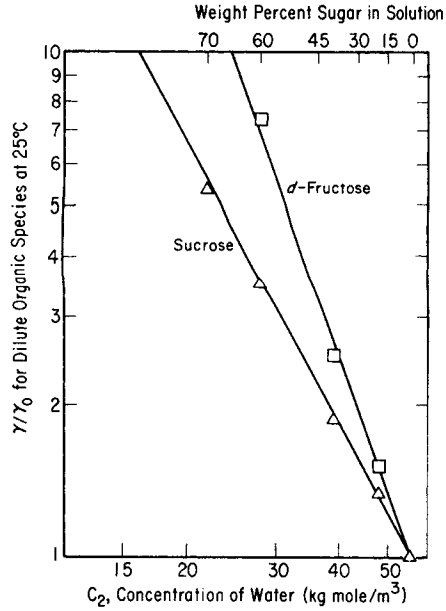

Fig. 2. Variation of (γ/γ^0) for various organic species with respect to sugar-water composition.

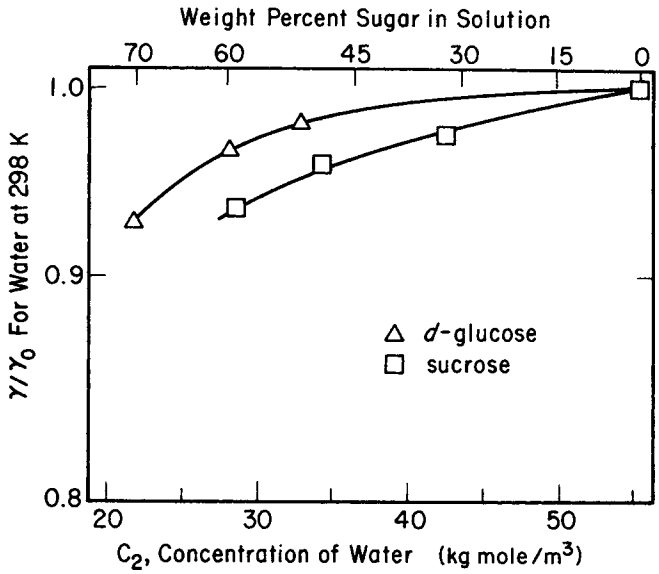

Fig. 3. Variation of (γ/γ^0) for water with respect to sugar-water composition, after Timmermans (22).

measurements (20) and correlations of Pierotti et al. (21). The activity coefficients in sugar solutions were calculated relative to these limiting activity coefficients in sugar-free solution. These limiting activity coefficients agreed within 10% with independent calculations of the activity coefficient from measurements at high dilution made in the present work (12).

RESULTS

Activity Coefficients

The variations of the activity coefficients of three of the trace organic species in d-fructose solutions are shown in Figure 1. The measured activity coefficients for all six trace components in sucrose solutions have been presented elsewhere (19). It is apparent that the experimentally determined activity coefficients of the selected trace organic components increase with increasing sugar concentration. Furthermore, this increase is larger in d-fructose solutions as compared to the equilibrium behavior in sucrose solutions. Glasstone and Pound (20) have determined activity coefficients for ethyl acetate in solutions of d-glucose, d-fructose, and sucrose through solubility measurements. The agreement between their values for the latter two solutions, and the activity coefficients obtained in this study is good; the difference being less than 3% at high sugar concentrations for both d-fructose and sucrose solutions. Glasstone and Pound (20) also found that the activity coefficient of ethyl acetate in d-glucose solutions is greater than in d-fructose solutions, and that the absolute difference becomes larger with increasing sugar concentration.

It is possible to correlate these activity coefficients in sugar solutions with respect to those in sugar-free water solution. The ratio of the activity coefficient at a particular sugar-water composition γ to the activity coefficient in pure water γ^0 versus sugar-water composition expressed as molar water concentration C_2 is presented in Figure 2. Each point in Figure 2 represents the average for all the different trace organic solutes. The deviation of γ/γ^0 for the various trace organic components from the average at a particular sugar-water composition was generally less than 5%. The advantage of correlating the data in this manner is that the equations representing the straight lines in Figure 2 can be used readily in obtaining solutions to Equations (5) and (6).

Activity coefficients for water may be determined from reported vapor-liquid equilibrium data for sugar-water solutions (22). The ratio of the activity coefficient of water at a particular sugar-water composition to the activity co-

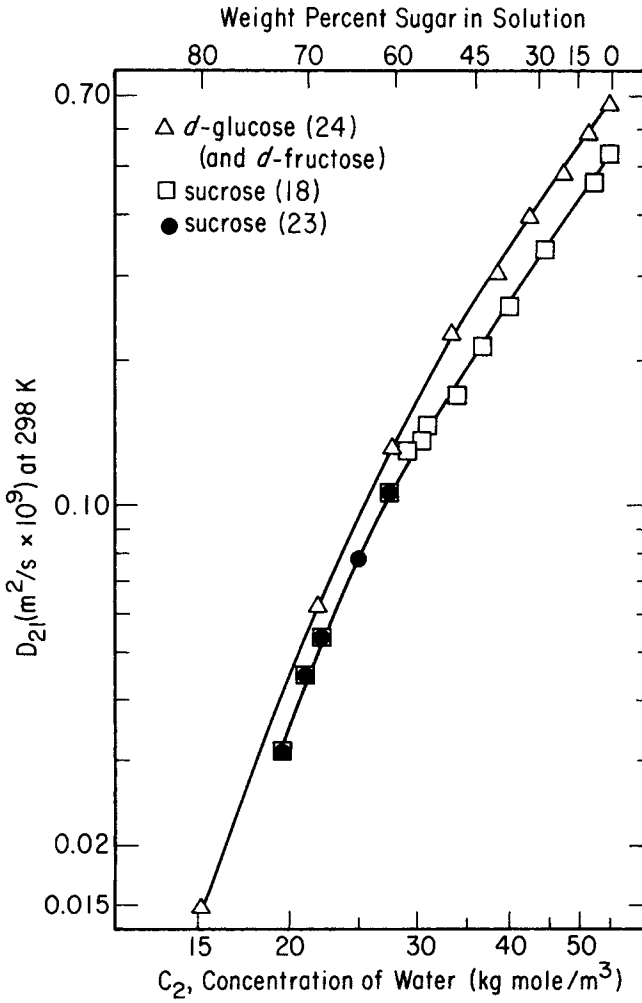

Fig. 4. Variation of water diffusion coefficients in sugar solution.

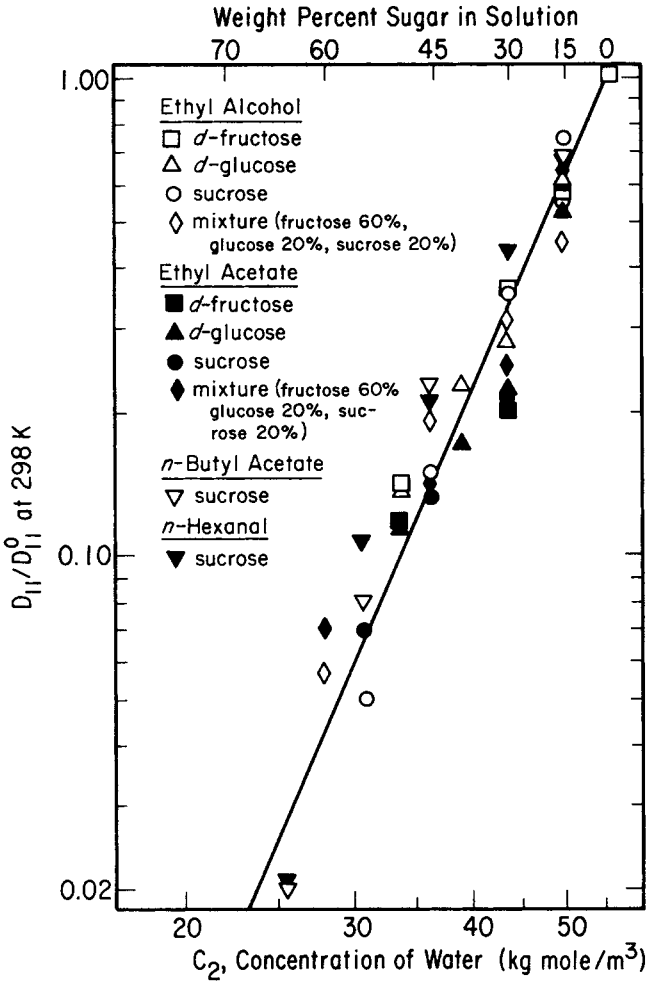

Fig. 5. Variation of (D_{11}/D_{11}^0) with water concentration at 298°K.

efficient of pure water is presented in Figure 3 as a function of the sugar-water composition. It can be seen that γ/γ^0 for water decreases with increasing sugar content, unlike the behavior of the dilute organic species.

Diffusion

The variation of reported diffusion coefficients for water in the binary water : sugar system as a function of sugar-water composition is shown in Figure 4 (*18, 23, 24*). It is interesting to notice that the reported data at high sugar concentrations extend into the supersaturated region of these solutions. Data reported for the water-d-fructose system are limited, but the diffusion behavior appears to be similar to the water-d-glucose system (*12*).

The ratio of the measured diffusion coefficient D_{11} at a particular sugar concentration to the measured diffusion coefficient D_{11}^0 in pure water for the various trace organic species at 298 K is presented in Figure 5 as a function of the sugar-water composition. There is some scatter of the experimental data, but the variation of (D_{11}/D_{11}^0) can be fitted to a reasonable approximation by a logarithmic straight line relation. This functionality seems to be the same for all three sugars and their mixtures. Sugar mixtures of d-fructose, d-glucose, and sucrose in a weight ratio of 6:2:2 respectively are actually more than a ternary diffusion situation, but they were considered as a pseudoternary by taking all the sugars as a single component. The values of the experimentally determined diffusion coefficients D_{11}^0 for the trace organic species in sugar-free water solutions are presented in Table 1. A comparison is made between measured values and previous reported experimental diffusivities for these organic compounds at high dilution in water. Figure 5 and Table 1 together may be used to obtain specific measured experimental diffusivities D_{11} for different trace organic compounds.

The variation of the cross diffusion coefficient D_{12} with sugar-water composition (expressed as molar water concentration) is shown in Figure 6. The other cross coefficient D_{12} can now be computed using Equation (6). As this computation involves the difference of several terms of comparable magnitudes, the precision of D_{12}/C_1 is approximately $\pm$ 1 $\times$ 10^{-12} m^5/kg.-mole·s (*12*). The resultant values of D_{12}/C_1 over the range of sugar-water compositions are presented in Figure 7 for the case of

Table 1. Diffusion Coefficients of Various Organic Components at High Dilution in Water

Organic species	Temperature, °K.	Diffusion coefficient (m^2/s) $\times$ 10^9 Experimental	Literature (*25*)
Ethyl alcohol	298	1.25	1.24
	308	1.60	—
Ethyl acetate	298	1.30	1.32
	308	1.66	—
n-Butyl acetate	298	0.97	—
n-Hexanal	290	0.93	—

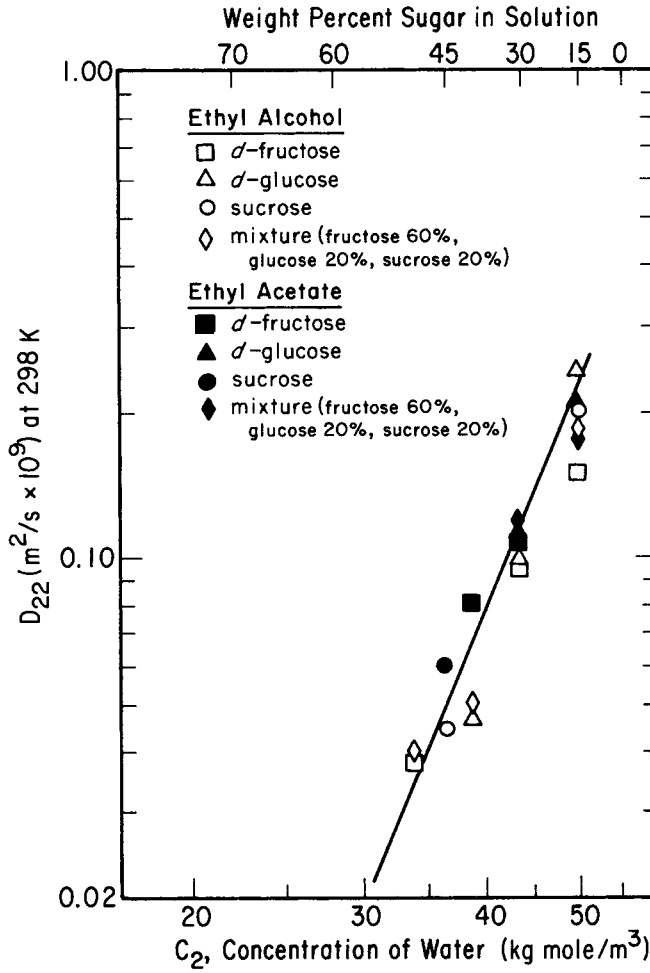

Fig. 6. Variation of D_{21} with water concentration at 298°K.

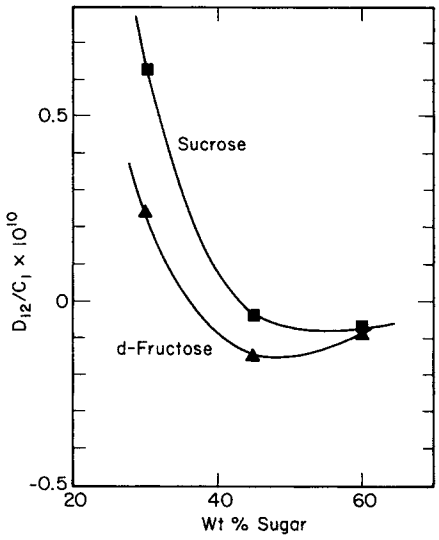

Fig. 7. Variation of D_{12}/C_1 ($m.^3$/kg.-mole) (s) in the system ethyl acetate (1)—water (2)—sugar (3) at 298°K.

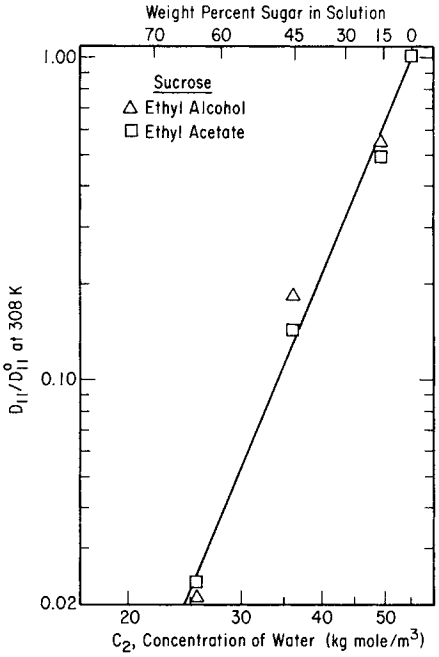

Fig. 8. Variation of D_{11}/D_{11}^0 with water concentration at 308°K.

ethyl acetate as Component 1. The cross diffusion coefficient D_{12} is not presented for d-glucose solutions because of the lack of activity coefficients in concentrated solutions. The change in sign of D_{12} is striking. From Equation (6) we see that the sign change results from two terms: At about 40 wt% sucrose ($D_{11} - D_{22}$) becomes negative. At slightly higher sucrose contents the first main term on the right-hand side of Equation (6) outweighs the second term, and D_{12} becomes negative. ($\partial \ln \gamma_1 / \partial \ln C_2$) is always negative because of the increase of γ_1 with increasing sugar content. At a sucrose content somewhere about 80 wt% that term outweighs the second term in the brackets, making the entire expression in brackets negative and returning D_{12} to a positive sign.

A few diffusion experiments were performed at a higher temperature of 308 K. These measurements were less comprehensive because of the difficulty of measuring the water gradients, and were thus designed primarily to yield only the diffusion coefficient D_{11}. The ratio of the diffusion coefficient of ethyl alcohol and ethyl acetate in sucrose solutions to the diffusion coefficients at high dilution in pure water at 308 K are shown in Figure 8 as a function of the sugar-water composition. The functionality is similar to that obtained at the lower temperature of 298 K.

DISCUSSION

By comparing data at temperatures of 298 K and 308 K, activation energies were computed for D_{11} and D_{22}, as well as for viscosity of binary sucrose-water solutions. The results are shown in Figure 9 as a function of composition. The activation energy for D_{11} is approximately equal to that for the viscosity, but is greater than that for D_{22} at high sucrose concentrations. Hence, the viscosity of the solution can be used as a parameter for correlating the main diffusion coefficient D_{11} as a function of temperature by postulating that the group $D_{11}\eta/T$, where η is viscosity, is constant. Similar conclusions were drawn by Henrion (*3*) from measurements of the diffusion of sucrose at infinite dilution in aqueous solutions of d-glucose and d-fructose of varied concentrations.

In solutions of low sucrose content the coefficient D_{11} is larger than D_{22}, but this difference becomes less, and eventually D_{11} becomes smaller than D_{22} as the sugar concentration increases. The variation of the ratio D_{11}/D_{22} is shown in Figure 10 as a function of water concentration. Menting et al. (*26*) measured diffusion coefficients of various dilute organic species in aqueous maltodextrin solutions, and reported effective binary diffusion coefficients, lumping the maltodextrin and water as a single component. The ratio of these effective diffusion coefficients of acetone to the mutual diffusion coefficient in

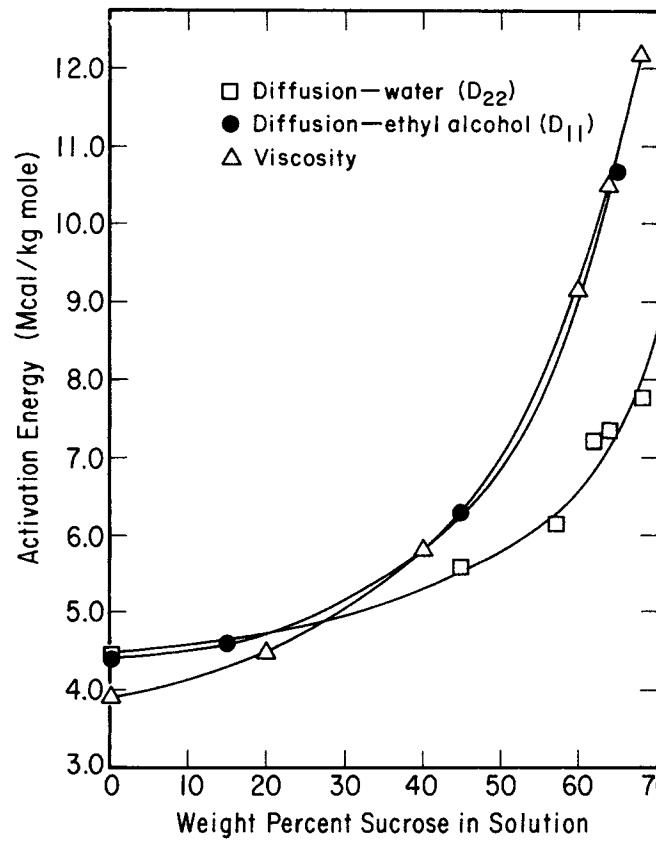

Fig. 9. Activation energies for diffusion and viscous flow in sucrose solutions.

TABLE 2. VARIATION OF THE ONSAGER COEFFICIENTS WITH SUGAR CONCENTRATION AT 298°K.

Weight % sugar	Type of sugar	$L_{22}/C_2 \times 10^6/RT$	$L_{11}\eta/C_1$° $\times 10^6/RT$
15	d-fructose	0.49	1.036
	Sucrose	0.39	1.058
30	d-fructose	0.78	0.960
	Sucrose	0.61	1.096
45	d-fructose	0.81	1.100
	Sucrose	0.65	1.396
60	d-fructose	0.61	1.620
	Sucrose	0.49	2.160

° η is the viscosity of the solution in N.s/m².

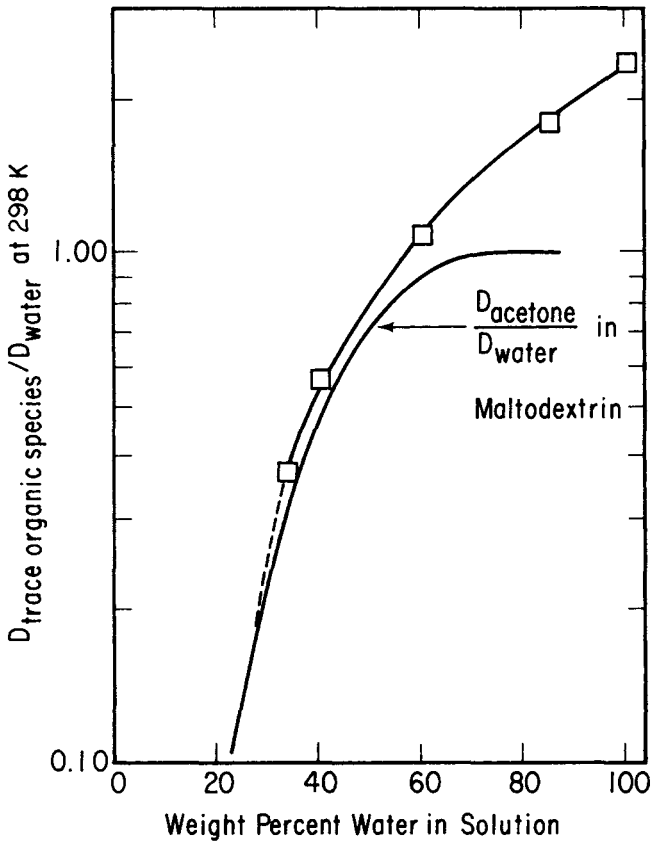

Fig. 10. Effect of sugar concentration on (D_{11}/D_{22}) at 298°K.

water—maltodextrin solutions is also presented in Figure 10 and a similar trend in the data is noticed.

It is apparent that the four diffusion coefficients vary greatly with the sugar concentration of the solution. It was examined whether the Onsager friction coefficients could be more simply correlated. The variation of L_{11} and L_{22} with concentration is shown in Table 2. Under conditions of infinite dilution, L_{11}/C_1 is nearly inversely proportional to the viscosity of the medium. In the case of L_{22} it is found that L_{22}/C_2 is more nearly constant.

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NOTATION

A_{ij} = functionality in Onsager relations
A, B = roots of auxiliary equation
C = concentration
C^0 = initial concentration
D = diffusion coefficient
J = flux
K = equilibrium ratio
L_{ij} = Onsager coefficient
L = total moles in liquid
P = total pressure
P^0 = vapor pressure
t = time elapsed
v = number moles in vapor
V = total moles in vapor
$\overline{V}$ = partial molar volume

Greek Letters

β = diaphragm cell constant
γ = activity coefficient
Δ = difference operator
∇ = gradient operator
λ = correction for hold-up in diaphragm

Subscripts

A, B = Components A and B
i, j = Components i and j
s = Component s
1, 2 = Components 1 and 2

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Volatiles Retention During Drying of Food Liquids

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The retention of trace volatile components in food liquids during low temperature drying processes is analyzed through a ternary diffusion model. Flux equations for both water and trace organic components are solved numerically for typical drying situations. Several effects are found with the ternary analysis which are not evident from a simpler binary model. The sugar-water composition gradient which develops during drying causes an appreciable transport of the trace volatile species. This transport can occur in the same direction as the transport resulting from the concentration gradient of the volatile species, or in the opposite direction, and can result in a local accumulation of the volatile species. Concentration profiles for both water and dilute volatile components were experimentally measured during nearly isothermal drying of gelled slabs of synthetic sugar solutions and natural fruit juice concentrates. The predicted internal maximum in volatiles concentration is borne out by the experiment, and a satisfactory agreement of observed with predicted volatiles retention is found, within the limits of the experiment.

Food liquids are complex aqueous mixtures containing numerous organic compounds. Natural fruit juices, coffee, tea, and other such substances have a high water content, generally between 80 and 98% by weight. From the standpoints of preservation, storage, and transportation it is advantageous to concentrate or totally dehydrate these food liquids. Unfortunately most juices are very sensitive to heat treatment, both because of degradative reactions and because of the volatilization of components essential to the flavor and aroma of the juice. These volatile flavor components are typically trace organic compounds having a high activity coefficient and hence a high volatility over the aqueous solution. These trace species govern the quality and attractiveness of the drink and their retention is of utmost importance. The particular organic compounds constituting the vapor space or aroma above fruit juices and other food liquids are different from substance to substance (*1* to *3*). A mixture of common sugars—two monosacharides, d-fructose and d-glucose, and one disaccharide, sucrose—makes up between 90 and 98 wt.% of the total dissolved solids in fruit juices (*4*, *5*). Thus, to a first approximation, most fruit juices can be treated as aqueous sugar solutions containing trace amounts of volatile organic components.

The retention of volatile flavor compounds during drying at lower temperatures is usually much better than that at higher temperatures. Thijssen and co-workers have analyzed volatiles loss as a selective diffusion process wherein the ratio of the rate coefficient of the transport of the trace organic species to the rate coefficient of transport of water becomes very low as the dissolved solids content increases (*6* to *8*). They show that this picture agrees well with a number of observed characteristics of volatiles loss during air drying of slabs and spray drying.

Freeze-drying gives particularly good volatiles retention. Data for the effects of several process variables upon volatiles retention during freeze-drying have been reported by Sauvageot et al. (*9*) for natural juices and by Flink and Karel (*10*) for synthetic sugar solutions. Flink and Karel (*11*) have demonstrated that rates of volatiles loss, and hence volatiles mobility, depend specifically upon the morphology of molecular aggregation and the degree of crystallinity. Discussions of the qualitative predictions of a diffusion model for the effects of freeze drying on volatiles retention have been presented by King (*12*) and Thijssen and Rulkens (*6*). King (*12* to *14*) has also reviewed the general problem of volatiles retention.

Previous quantitative interpretations of volatiles loss have been made using an effective binary analysis for calculations of diffusion coefficients (*8*, *15*) and for predicting rates of loss during drying. In one case a convective term depending upon the water flux was incorporated (*7*, *16*), but it was a small enough term so that it did not alter the predictions of the binary model greatly.

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