

Figure 3. $Y_1 - X_1$ vs. X_1 diagram for the *p*-xylene-tetrachloroethane system.

parison of the two correlations.

Thermodynamic Consistency

The thermodynamic consistency of T - X - Y data has to be tested by using the rigorous Gibbs-Duhem equation

$$I_1 + I_2 + I_3 = 0 \quad (8)$$

where

$$I_1 = \int_0^1 \log(\gamma_1/\gamma_2) dX_1 \quad (9)$$

$$I_2 = - \int_0^1 (H^E / (2.303RT^2)) (dT/dX_1) dX_1 \quad (10)$$

$$I_3 = \int_0^1 (V^E / RT) (dP/dX_1) dX_1 \quad (11)$$

The volume change on mixing for the *p*-xylene-1,1,2,2-tetrachloroethane is negligible. However, the enthalpy of mixing at 308.15 K ranges from -300 J mol^{-1} at $X_1 = 0.03$ to -600 J mol^{-1} at $X_1 = 0.9$ with a minimum of -3400 J mol^{-1} at $X_1 = 0.36$. Similar but slightly higher negative values are obtained at 298.15 K. Therefore, it is essential to consider I_1 and I_2 in testing the thermodynamic consistency of the data. The integral I_1 was evaluated graphically. To evaluate I_2 , we fitted the bubble temperature-composition data to the relation

$$T = \sum_{i=1}^4 B_i X_i^{-1} \quad (12)$$

Equation 12 fitted the T - X data with an average absolute deviation of 0.006% and a maximum deviation of 0.01% with $B_1 = 415.589$, $B_2 = -9.109$, $B_3 = 8.334$, and $B_4 = -7.553$, the constants being evaluated by using the least-squares technique. Using eq 12 to get the necessary derivative, we evaluated I_2 numerically with Simpson's rule. The excess enthalpies of mixing measured at 308.15 K (4) were used in evaluating I_2 . The values of I_1 and I_2 were 0.00508 and -0.00465 , respectively, giving a value of 0.00043 for $I_1 + I_2$ and indicating the consistency of the data. The data were also checked for consistency by using Herington criteria (11). It was found that the data are internally consistent with $D = 10.63$ and $J = 2.88$, thus giving a value of $D - J < 10$. An error analysis performed on experimental values revealed the maximum errors in γ_1 and γ_2 to be 0.57% and 0.69%, respectively. The errors in pressure, composition, and temperature measurements were $\pm 0.1 \text{ mm Hg}$, ± 0.0001 , and $\pm 0.05 \text{ K}$, respectively. Figure 3 reveals that there were no random errors. Taking all these into consideration together with the purity of the chemicals, the accuracy of measurements, and the agreement of the vapor pressure data with the literature values, the data presented in this paper should be reliable and accurate.

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Diffusion Coefficients of Acetates in Aqueous Sucrose Solutions

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Diffusivities of ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl acetates in 0-55% w/w solutions of sucrose in water were measured at 25 and 45 °C and high dilution of the acetates by using glass diaphragm cells. The results agree well with previous data, where comparisons can be made. The data are also rationalized in terms of absolute rate theory and the functionality between solute diffusivity and solution viscosity.

Introduction

Relatively few experimental data are available for diffusion coefficients of homologous series of solutes in a given solvent system, or for diffusion coefficients of solutes in aqueous carbohydrate solutions covering a wide range of composition and viscosity. Among other applications, such data are valuable for interpretation of measurements of retention of volatile flavor and aroma components during concentration and drying processes for liquid foods.

Several methods have been employed to measure diffusivities in such systems. Chandrasekaran and King (1) used stirred diaphragm cells to measure the diffusivities of trace amounts of organic components in aqueous sucrose solutions. Menting et al. (2) obtained diffusion coefficients for similar systems by measuring the rate of absorption of organic components into a gelled slab. The observed large decrease in diffusivity of organic solutes at high concentrations of dissolved solids in such systems is a widely accepted explanation of the relatively high retentions of the volatile components during drying (3, 4).

The purpose of the present study was to extend the existing data on diffusion of homologous series of organic solutes in aqueous sucrose solutions. Ethyl, *n*-propyl, *n*-butyl, and *n*-pentyl acetates were used as solutes at several sucrose concentration levels and temperatures. Because of the large range of viscosity encountered in these experiments, these data are also useful for evaluating correlations for diffusion coefficients of trace components in ternary mixtures.

Experimental Section

Apparatus. The measurement of diffusion coefficients was carried out in stirred horizontal glass diaphragm cells identical with those described by Holmes et al. (5). The cells incorporated type E fritted disks (Ace Glass Co.). The temperature bath and other auxiliary equipment are also described by Holmes et al. (5) but were modified to provide for more reliable operation. The bath temperature was controlled to within $\pm 0.1^\circ\text{C}$ with a proportional temperature controller. The cell constants (β) were obtained by calibration with 0.1 N HCl diffusing across a small concentration difference. The method described by Stokes (6) was used to account for the concentration dependence of the diffusivity of HCl in water. Values for the cell constants did not change noticeably during the experiments and were generally reproducible to within $\pm 3\%$.

Chemicals. Reagent-grade sucrose, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, and *n*-pentyl acetate were used without additional purification. The distilled water used to make sucrose solutions was passed through a Milli-Q filter apparatus (Millipore Corp.) and was degassed before use. It was found necessary to add 50 ppm of merthiolate (thimersal; sodium ethylmercurithiosalicylate) to the sucrose solutions to inhibit the growth of microorganisms during the experiments.

Procedure. One cell compartment was filled with sucrose solution and held above the empty side of the cell. A vacuum was then applied to the empty side of the cell to force solution downward through the diaphragm. The empty side of the cell was rinsed and then filled with a sucrose solution of the same concentration but containing a small amount (100–500 ppm w/w) of each of the four acetates. A typical run lasted from 6 to 35 days, depending upon the sucrose concentration. The stirring speed was held at 350 rpm in all of the experiments. Correlations developed by Holmes et al. (5), as well as experimental data for these cells from Chandrasekaran (7), show that, at these stirring rates, the resistance to mass transfer lies entirely within the diaphragm. At the end of an experimental run, the cell contents were analyzed by the gas-chromatographic headspace analysis described by Kieckbusch and King (8). The reproducibility of this analysis was generally within $\pm 1\%$.

Analysis of Data. The four diffusion coefficients which describe a ternary system are defined by the equations

$$J_1 = -D_{11}\nabla C_1 - D_{12}\nabla C_2 \quad (1)$$

$$J_2 = -D_{21}\nabla C_1 - D_{22}\nabla C_2 \quad (2)$$

Several authors (1, 9, 10) have presented methods for determining these diffusivities from experimental data derived from diaphragm-cell experiments. Cullinan and Toor (11) have

Table I. Diffusivities of Acetates at 25 °C

| acetate | wt % sucrose | $10^5 D_{11}$, cm ² /s | | |
|------------------|--------------|------------------------------------|------|------|
| | | 0 | 15 | 30 |
| ethyl | | 1.18 | 0.90 | 0.47 |
| <i>n</i> -propyl | | 1.12 | 0.81 | 0.41 |
| <i>n</i> -butyl | | 1.04 | 0.75 | 0.38 |
| <i>n</i> -pentyl | | 0.98 | 0.71 | 0.35 |

Table II. Diffusivities of Acetates at 45 °C

| acetate | wt % sucrose | $10^5 D_{11}$, cm ² /s | | | | |
|------------------|--------------|------------------------------------|------|------|------|------|
| | | 0 | 15 | 30 | 45 | 55 |
| ethyl | | 1.83 | 1.34 | 0.84 | 0.46 | 0.25 |
| <i>n</i> -propyl | | 1.69 | 1.24 | 0.75 | 0.41 | 0.21 |
| <i>n</i> -butyl | | 1.59 | 1.16 | 0.70 | 0.38 | 0.19 |
| <i>n</i> -pentyl | | 1.52 | 1.12 | 0.67 | 0.37 | 0.18 |

Table III. Diffusivity of Ethyl Acetate at High Dilution in Water

| ref | binary diffusivity $\times 10^5$, cm ² /s | | | | |
|-----------|---|-------|-------|-------|-------|
| | 20 °C | 25 °C | 30 °C | 35 °C | 45 °C |
| 13 | 1.00 | | 1.75 | | |
| 1 | | 1.32 | | 1.66 | |
| this work | | 1.18 | | | 1.83 |

shown that, as C_1 approaches zero, the diaphragm-cell equation for component 1 in a ternary mixture reduces to

$$\frac{1}{\beta t} \ln \frac{\Delta C_1^0}{\Delta C_1^F} = D_{11} \quad (3)$$

where β is a constant determined experimentally for each cell. A comparison of the magnitudes of the terms in the diaphragm-cell equation, as given by Chandrasekaran and King (1), shows that, for the values of C_1 used in this study ($C_1 < 10^{-2}$ mol/L), eq 3 yields values of D_{11} which differ from those obtained from the exact solution by substantially less than the experimental error. For this reason, eq 3 was judged to be adequate for obtaining values of D_{11} . Values for the cross diffusion coefficients were not obtained. The correction for the finite holdup in the diaphragm (12) was found to be of negligible importance.

Results

Each diffusion coefficient was measured 3 times in three different cells. The results of the experiments are shown in Tables I and II. The mean deviation from the reported average tends to increase with sucrose concentration and molecular weight of the acetate and varies from 3% to 10% at 25 °C and from 1% to 6% at 45 °C.

Discussion

The measured diffusion coefficients of ethyl acetate at high dilution in water are compared to those from other sources in Table III. An extrapolation of the diffusivities of ethyl acetate obtained in the present study to 20 °C yields a value of 1.05×10^{-5} cm²/s, which is in reasonable agreement with the diffusivity reported by Lewis (13). The diffusivity reported by Chandrasekaran and King at 25 °C is 10% larger than the value obtained in this study. It should be noted that the Lewis data exhibit a temperature dependence which is over twice as large as that observed either in this study or by Chandrasekaran and King. The diffusivities of ethyl acetate in aqueous sucrose solutions obtained in this study show considerably less scatter than those obtained by Chandrasekaran and King. This seems to be primarily due to improvements in the analytical technique.

The diffusivities of the four acetates at various sucrose concentrations at 45 °C are plotted logarithmically against the solution viscosity in Figure 1. Since the experimental points

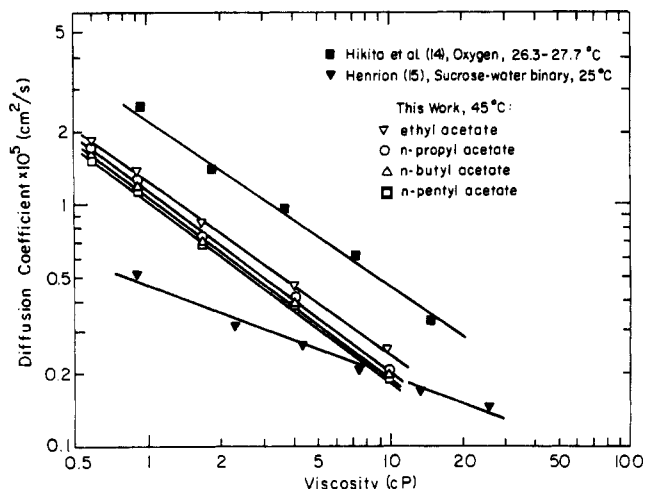


Figure 1. Diffusivities of acetates, oxygen, and water in sucrose solutions, as functions of viscosity.

Table IV. Effect of Sucrose Concentration on the Ratio $D_{11}(\text{ethyl acetate})/D_{11}(\text{n-butyl acetate})$ at 25 and 45 °C

| | $D_{11}(\text{ethyl acetate})/D_{11}(\text{n-butyl acetate})$ | | | | | |
|-------|---|------|------|------|------|------|
| | wt % sucrose | 0 | 15 | 30 | 45 | 55 |
| 25 °C | | 1.14 | 1.20 | 1.25 | | |
| 45 °C | | 1.15 | 1.16 | 1.20 | 1.21 | 1.26 |

lie on reasonably straight lines, the diffusivity can be seen to be approximately proportional to an inverse power of solution viscosity. Previous studies (16, 17) have indicated that, in viscous solutions where the molecular size of the solute is much smaller than the size of the solvent, the diffusivity is approximately proportional to the $-2/3$ power of the solution viscosity. Alternately, the Stokes-Einstein relationship (18), which applies when the solute is significantly larger than the solvent, predicts that the diffusivity should be proportional to the -1 power of solution viscosity.

The diffusivities in this study are inversely proportional to a power of viscosity whose value increases slightly with increasing molecular weight of the acetate, decreases slightly with increasing temperature, and varies from 0.72 for ethyl acetate at 45 °C to 0.90 for *n*-pentyl acetate at 25 °C. By comparison, diffusivities of oxygen in aqueous sucrose solutions, as measured by Hikita et al. (14), are proportional to the $-2/3$ power of viscosity. Figure 1 also indicates that the diffusivities of the acetates decrease more rapidly than the diffusivity of water as the sucrose concentration increases. This observation is in agreement with the selective-diffusion concept for the transport of organic solutes through carbohydrate solutions as put forward by Thijssen and co-workers (3, 4).

The ratio of D_{11} for *n*-ethyl acetate to D_{11} for *n*-butyl acetate at various sucrose concentrations and temperatures is shown in Table IV. This ratio increases somewhat with increasing sucrose concentration. Similar trends can be observed for the other acetates. For comparison, Ratcliff and Lusi (19) measured the diffusivities of ethyl acetate and *n*-butyl acetate in chloroform and found the ratio of diffusivities to be 1.18. The Wilke-Chang correlation (20) predicts that this ratio should be 1.24 in all solvent systems.

The absolute rate theory of Eyring applied to multicomponent solutions yields the following equation (21):

$$\frac{D_{11\mu}}{T} = \frac{k}{\xi} \left(\frac{N}{V_s} \right)^{1/3} \exp \left(\frac{E_\mu - E_D}{RT} \right) \quad (4)$$

where the geometrical factor ξ equals 6 for most small organic molecules (22). Experimental values of $D_{11\mu}/T$ for ethyl acetate are plotted against mole fraction of sucrose in Figure 2.

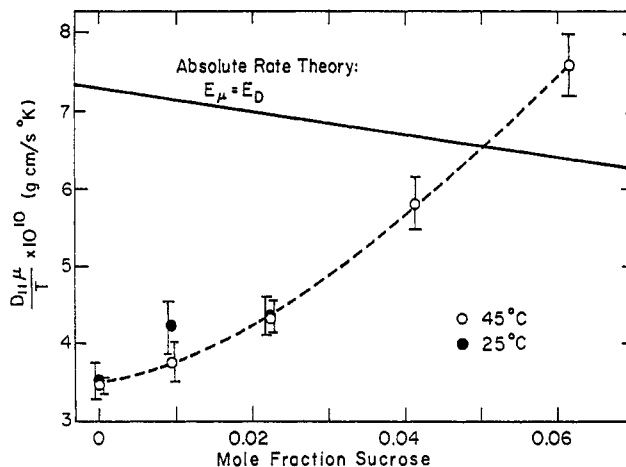


Figure 2. $D_{11\mu}/T$ for ethyl acetate at 25 and 45 °C. (Error bars denote the range of values obtained in three separate experiments.)

Values of $D_{11\mu}/T$ calculated from eq 4 with $E_\mu = E_D$ are also shown in the figure.

The lack of any appreciable temperature dependence in $D_{11\mu}/T$ in solutions of low to moderate sucrose concentrations indicates that in this range, $E_\mu = E_D$ with a possible error of approximately 1 kcal/g-mol. Since the discrepancy between the experimental values of $D_{11\mu}/T$ and the values calculated from absolute rate theory can be accounted for by a value for $E_\mu - E_D$ of -400 cal/g-mol, it seems apparent that the data in this study do not contradict eq 4 in any obvious way. Activation energies at higher sucrose concentrations were not measured since the time required for an experimental run at high sucrose concentrations and low temperatures was prohibitively long. However, the rapid increase in $D_{11\mu}/T$ at 45 °C with increasing sucrose concentration suggests that, at higher sucrose concentrations, $E_\mu - E_D$ becomes appreciably larger. This type of behavior is observed in the sucrose-water binary system where, at 64% sucrose, E_μ has a value of 10.5 kcal/g-mol and E_D has a value of 7.3 kcal/g-mol (23).

Glossary

| | |
|---------|--|
| C | concentration, g-mol/cm ³ |
| D | diffusion coefficient, cm ² /s |
| E_D | activation energy for diffusion, cal/g-mol |
| E_μ | activation energy for viscosity, cal/g-mol |
| J | flux in a fixed-volume frame of reference, g-mol/(cm ² s) |
| k | Boltzmann constant, erg/K |
| N | Avogadro's number |
| R | gas constant, cal/(g-mol K) |
| T | temperature, K |
| t | time, s |
| V_s | molar volume, cm ³ /g-mol |

Greek Letters

| | |
|----------|---------------------------------|
| β | cell constant, cm ⁻² |
| ∇ | gradient operator |
| Δ | difference operator |
| ξ | geometrical factor |
| μ | viscosity, cP |

Superscripts

| | |
|---|---------------|
| 0 | initial value |
| F | final value |

Subscripts

| | |
|------|--------------------|
| 1, 2 | components 1 and 2 |
|------|--------------------|

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Osmotic and Activity Coefficients of Some Amino Acids and Their Hydrochloride Salts at 298.15 K

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Osmotic and activity coefficient data are reported for lysine (Lys), arginine (Arg), lysine hydrochloride (Lys-HCl), arginine hydrochloride (Arg-HCl), and histidine hydrochloride (His-HCl). The order of the coefficients for the hydrochlorides is lysine > histidine > arginine. A comparison of the coefficients of lysine and ϵ -aminocaproic acid furnishes additional evidence that the lysine zwitterion is formed with the ϵ -amino group.

Osmotic and activity coefficients are recorded in the literature for many amino acids. Among the more interesting studies are those involving the effect of increasing the length and complexity of the aliphatic carbon chain (1, 2) and the effect of increasing the dipolar distance between the functional groups (3). The osmotic coefficients of the amino-*n*-butyric acids are in the order $\alpha > \beta > \gamma$ for dilute solutions, while the order is exactly reversed for more concentrated solutions. The concentration at which the reversal occurs is about 2.0–2.5 *m*. Data are also reported for ϵ -aminocaproic acid (3). Lysine has a similar structure except that there is an additional amino group in the α position. It was felt that a comparison of the coefficients of these two amino acids might yield further evidence as to which amino group participates in the formation of the zwitterion. Data are also reported for arginine which has still more amino groups in the δ and more distant positions. Other similar amino acids histidine and norleucine were too insoluble for isopiestic studies. Data for the hydrochloride salts of lysine, arginine, and histidine are reported. These salts are similar to the monosodium and potassium salts of glutamic acid which have been previously reported (4) in that the complex ions all contain three ionic groups but a net charge of unity.

Method

The amino acids and hydrochloride salts were either Fisher reagent or Fisher certified grade from Fisher Scientific Co. except that the lysine was Baker grade from J. T. Baker Co. The 1,3-dimethylurea was Fisher reagent grade. All chemicals were dried in a vacuum dessicator over P_2O_5 , and their purity was checked by titration. The pH of a 0.1 *m* solution of lysine

Table I. Experimental Results for Molalities of Isopiestic Solutions at $T = 298.15$ K

| NaCl | DMU ^a | Lys | NaCl | DMU ^a | Arg |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 0.147 ₉ | 0.285 ₁ | 0.300 ₂ | 0.103 ₀ | 0.291 ₆ | 0.299 ₇ |
| 0.250 ₀ | 0.483 ₂ | 0.505 ₆ | 0.201 ₅ | 0.386 ₁ | 0.400 ₇ |
| 0.431 ₂ | | 0.828 ₃ | 0.344 ₄ | 0.676 ₀ | 0.718 ₀ |
| 0.715 ₅ | | 1.290 | 0.421 ₄ | | 0.889 |
| 1.053 | | 1.798 | 0.500 ₅ | | 1.066 |
| 1.517 | | 2.424 | 0.576 ₇ | | 1.237 |
| 1.947 | | 2.970 | 0.705 ₂ | | 1.542 |
| 2.126 | | 3.190 | | | |
| 2.724 | | 3.925 | | | |
| 3.109 | | 4.380 | | | |
| 3.312 | | 4.619 | | | |
| 4.022 | | 5.436 | | | |
| 4.921 | | 6.587 | | | |
| NaCl | Lys-HCl | Arg-HCl | His-HCl | | |
| 0.183 ₁ | 0.193 ₄ | 0.199 ₂ | 0.195 ₅ | | |
| 0.404 ₁ | 0.439 ₂ | 0.470 ₈ | 0.457 ₅ | | |
| 0.628 ₂ | 0.690 ₂ | 0.771 ₄ | 0.735 ₂ | | |
| 0.770 | 0.848 | 0.971 | | | |
| 1.013 | 1.117 | 1.328 | | | |
| 1.301 | 1.429 | 1.763 | | | |
| 1.621 | 1.769 | 2.252 | | | |
| 1.955 | 2.118 | 2.767 | | | |
| 2.278 | 2.458 | 3.272 | | | |
| 2.611 | 2.806 | 3.784 | | | |
| 2.978 | 3.185 | 4.350 | | | |
| 3.508 | 3.743 | 5.177 | | | |
| 3.618 | | 5.333 | | | |
| 3.666 | | 5.404 | | | |

^a 1,3-Dimethylurea.

was 9.72 ($pI = 9.74$) and of arginine was 10.73 ($pI = 10.76$). The isopiestic equilibration of the solutions was carried out in the usual manner with NaCl solutions serving as the reference except that reagent-grade 1,3-dimethylurea solutions were also included in the dilute solution range of the amino acids to facilitate extrapolations of the molality ratios to infinite dilution. Complete experimental details and the method of activity