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Quaternary diffusion coefficients for the sucrose–NaCl–KCl–water system at 25 °C[☆]

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ABSTRACT

Transport properties of saccharide–salt aqueous mixtures are important for basic research and applications in the biochemical and biotechnological fields. We have experimentally determined the nine multi-component diffusion coefficients for the sucrose (0.25 M) + NaCl (0.50 M) + KCl (0.50 M) + H₂O quaternary system at 25 °C. Our results are compared with those previously obtained for all the corresponding ternary systems and binary systems. A simple excluded-volume model can be used to successfully predict the effect of sucrose on salt cross-term diffusion coefficients for ternary and quaternary systems. We have found that the ternary cross-term diffusion coefficients can be used to make reasonable estimates of the corresponding quaternary coefficients. These estimates can replace the corresponding experimental data when they cannot be measured with satisfactory precision.

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1. Introduction

Carbohydrates are essential components of biological systems. They are not only the main energy source for living organisms but they are essential moieties of biological macromolecules, such as glycoproteins and glycolipids. Furthermore, they also act as osmolytes and help organisms survive extreme osmotic stress [1].

In the pharmaceutical and biotechnological industries, saccharides such as sucrose are important components of formulations because they can be used as cryoprotectant against the destabilization and degradation of enzymes and drugs during lyophilization procedures [2].

It has been shown that salts can be used to modulate the cryoprotectant action of saccharides on biological macromolecules. This has been attributed to thermodynamic effects such as changes in saccharide hydration and changes in viscosity, diffusion and crystallization kinetics [3]. Thus, experimental characterization of thermodynamic and transport properties of saccharide–salt aqueous mixtures is important not only for basic research, but also for applications in the biochemical and biotechnological fields. In this paper, we characterize the diffusion properties of the sucrose + NaCl + KCl + water quaternary system.

Understanding diffusion processes often makes use of Fick's first law for isothermal diffusion in a single phase with $N + 1$ components.

Fick's first law relating solute fluxes J_i to solute concentration gradients ∇C_j may be written [4]:

$$-J_i = \sum_{j=1}^N D_{ij} \nabla C_j \quad i = 1 \dots N. \quad (1)$$

(We denote the solvent components with subscripts $i, j = 0$.) The diffusion coefficients of Eq. (1) depend on a reference frame. Typically the D_{ij} are measured on the volume-fixed reference frame defined by the equation:

$$\sum_{i=0}^N J_i \bar{V}_i = 0 \quad (2)$$

where \bar{V}_i is the partial molar volume of component i . We write the volume-fixed diffusion coefficients as: $(D_{ij})_V$ [5].

It is common practice to describe solute diffusion transport in terms of only N solute pseudo-binary diffusion coefficients and their respective concentration gradients [6]. This simplification may be practical, but is sufficient for only the case of weakly interacting non-electrolytes at relatively low concentrations. Nevertheless, N^2 diffusion coefficients are required for a full description of transport in N solute systems and may be needed for an acceptable estimation of transport properties. Of these N^2 coefficients, we identify N 'main-term' diffusion coefficients $(D_{ii})_V$ that relate flux of a solute due to its own concentration gradient, and $N(N - 1)$ 'cross-term' diffusion coefficients, $(D_{ij})_V$ (with $i \neq j$), that relate the flow of solute i to the gradient of solute j .

In systems with multiple salt components, cross-term diffusion coefficients for the salt–salt component interactions become significant at all concentrations and generally cannot be ignored. For

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example, in the ternary system NaCl + MgCl₂ + H₂O at 25 °C measured values of the four $(D_{ij})_V$ indicate that at higher NaCl concentrations, a cross-term $(D_{ij})_V$ can be larger than both main-term $(D_{ii})_V$. Furthermore, at higher NaCl concentrations, a gradient of MgCl₂ may cause NaCl with an equal gradient in the opposite direction to diffuse from lower concentration to higher concentration [7].

At relatively low total salt concentrations, the infinitesimal-concentration Nernst–Hartley (NH) equations [8], can give useful estimations of all main-term and cross-term diffusion coefficients calculated from limiting ionic mobilities. At high salt concentrations, however, the NH equations may be very incorrect and misleading. The NH equations do not predict the NaCl + MgCl₂ + H₂O results noted above, and are seriously incorrect in this case [7].

When pseudo-binary diffusion coefficients alone are insufficient for a useful description of ternary systems, it is possible, given suitable apparatus and sufficient experience, to measure all four diffusion coefficients at an acceptable accuracy. ('Acceptable accuracy' is influenced by the relative sizes of the eigenvalues of the diffusion coefficient matrix and the relative values of the refractive index increments defined below.) Moreover, experimental and theoretical investigations on ternary systems play a chief role in the comprehension of multicomponent diffusion because cross-term diffusion coefficients describe the net interaction between two different solutes. In systems with four components or more, cross-term diffusion coefficients should be closely related to those obtained in the corresponding ternary systems. This facilitates the characterization of these higher-order multicomponent systems because, for these cases, direct measurements of the diffusion coefficients become much more difficult and the accuracy of measurement becomes a serious issue. Thus, it is of interest to examine whether sets of four D_{ij} values from corresponding ternary systems could help develop useful estimates of the D_{ij} required for the full description of the quaternary system.

Recent studies have reported all 9 diffusion coefficients for the quaternary system Lysozyme + Tetra(ethyleneglycol) + NaCl + H₂O [9] and the system Lysozyme + PEG2000 + NaCl + H₂O [10]. There were useful correlations between the ternary and quaternary diffusion coefficients for these systems. However, because of the relatively larger differences of the sizes the solutes in the quaternary Lysozyme systems, the cross-term diffusion coefficients for these systems are more precise than those sucrose-and-salt systems reported here.

In this paper we report the measured 9 quaternary diffusion coefficients of the aqueous system: sucrose (0.25 M) + NaCl (0.5 M) + KCl (0.5 M) + H₂O at 25.0 °C. This is a system for which reliable sets of diffusion coefficients exist for each of the corresponding binary and ternary subsystems [11–14]. We denote the components sucrose, NaCl, and KCl, by 1, 2, and 3, respectively, in equations below.

We examine the use of ternary $(D_{ij})_V$ to estimate the quaternary $(D_{ij})_V$ for this case. Our measured cross-term quaternary D_{ij} are generally less accurate than the corresponding ternary cross-term diffusion coefficients. This introduces the possibility that for some diffusion coefficients the estimates may be as accurate and more precise than the measured quaternary values.

2. Materials and methods

Reagent-grade NaCl and KCl were purchased from Mallinckrodt, dried at 450 °C for 7 h, and used without further purification. The purity of these salts was listed as 99.9% by the supplier. Ultrapure Bioreagent sucrose was purchased from J. T. Baker and used as received without drying or other purification. Distilled water was run through a sequence of four Millipore filters and used to prepare all solutions. All solutions were prepared gravimetrically. The formula

weights were: H₂O 18.015 g mol⁻¹; sucrose 342.299 g mol⁻¹; NaCl 58.443 g mol⁻¹; KCl 74.551 g mol⁻¹.

Densities of all solutions were measured with a Mettler–Parr DMA/40 vibrating densitometer that had been interfaced to a computer for time averaging. The temperature was controlled with water from a large water bath at 25.00 °C whose accuracy is ±0.01 °C and maintained at constant temperature ±0.001 °C. The vibrating densitometer was calibrated using water (0.997045 g cm⁻³) and air as standards. An accurate value of density air was calculated using a state equation that shows explicit dependence on pressure, temperature (25.00 °C), and humidity. The measured density values are reported in Table 1. These data were fit with the following equation by the method of least squares to obtain the least-squares parameters \bar{d} and H_i [15]:

$$d = \bar{d} + H_1(C_1 - \bar{C}_1) + H_2(C_2 - \bar{C}_2) + H_3(C_3 - \bar{C}_3) \quad (3)$$

where d and \bar{d} are the densities and mean density respectively, C_i and \bar{C}_i molar solute concentrations and mean molar solute concentrations (0.25 M, 0.5 M, and 0.5 M) respectively. The calculated values of the least-squares parameters are: $\bar{d} = (1.072185 \pm 0.000002) \text{ g/cm}^3$, $H_1 = (0.12866 \pm 0.00006) \text{ kg/mol}$, $H_2 = (0.03845 \pm 0.00002) \text{ kg/mol}$, $H_3 = (0.04421 \pm 0.00002) \text{ kg/mol}$.

The partial molar volumes of the solute components were calculated by using the equations [15]:

$$\bar{V}_i = \frac{M_i - 1000H_i}{\bar{d} - \sum_{j=1}^3 H_j C_j} \quad (i = 1, 2, 3) \quad (4)$$

Here the M_i are the formula weights of solute i . The partial molar volumes are: \bar{V}_1 (sucrose) = $(213.92 \pm 0.06) \text{ cm}^3 \text{ mol}^{-1}$, \bar{V}_2 (NaCl) = $(20.02 \pm 0.02) \text{ cm}^3 \text{ mol}^{-1}$ and \bar{V}_3 (KCl) = $(30.39 \pm 0.03) \text{ cm}^3 \text{ mol}^{-1}$.

Table 1
Sucrose(1) + NaCl(2) + KCl(3) + H₂O measured densities.

C ₁ (M)	C ₂ (M)	C ₃ (M)	d (g/cm ³)	C ₁ (M)	C ₂ (M)	C ₃ (M)	d (g/cm ³)
0.15001	0.40003	0.60004	1.059893	0.25000	0.50000	0.61911	1.077446
0.35004	0.60009	0.40007	1.084486	0.25000	0.50000	0.38087	1.066908
0.24999	0.50000	0.61910	1.077438	0.24999	0.61762	0.49997	1.076699
0.25000	0.49998	0.38088	1.066908	0.25001	0.38237	0.50003	1.067661
0.24998	0.61761	0.49996	1.076696	0.24999	0.61762	0.49997	1.076698
0.27265	0.50002	0.50000	1.075123	0.25001	0.38237	0.50002	1.067659
0.22735	0.50000	0.50000	1.069277	0.24999	0.61760	0.49997	1.076700
0.27265	0.50002	0.50000	1.075114	0.25001	0.38239	0.50003	1.067661
0.22735	0.49999	0.49999	1.069275	0.27265	0.50002	0.50002	1.075111
0.27265	0.50001	0.50001	1.075106	0.22735	0.49999	0.50000	1.069277
0.22735	0.49998	0.50000	1.069273	0.24999	0.55880	0.55955	1.077075
0.24998	0.61762	0.49997	1.076696	0.25000	0.44118	0.44045	1.067283
0.25001	0.38238	0.50001	1.067642	0.26132	0.50001	0.55957	1.076273
0.24999	0.55879	0.55954	1.077068	0.23868	0.49999	0.44044	1.068094
0.25000	0.44118	0.44044	1.067275	0.26131	0.55881	0.49998	1.075895
0.26133	0.50002	0.55957	1.076292	0.23868	0.44117	0.50001	1.068468
0.23868	0.50001	0.44045	1.068115	0.25754	0.53920	0.53969	1.076412
0.26132	0.55879	0.49998	1.075891	0.24245	0.46079	0.46030	1.067949
0.23868	0.44119	0.50000	1.068468	0.25754	0.53920	0.53970	1.076405
0.26132	0.55882	0.49999	1.075903	0.24245	0.46078	0.46030	1.067950
0.23868	0.44120	0.50001	1.068484	0.26510	0.46078	0.57942	1.076136
0.23122	0.55671	0.49813	1.071890	0.23490	0.53919	0.42057	1.068241
0.26132	0.55882	0.49999	1.075917	0.26511	0.46081	0.57944	1.076141
0.23869	0.44119	0.50001	1.068488	0.23490	0.53920	0.42057	1.068235
0.25755	0.53921	0.53971	1.076416	0.24621	0.59801	0.49998	1.075465
0.24245	0.46079	0.46030	1.067953	0.25378	0.40198	0.50002	1.068901
0.25755	0.53922	0.53971	1.076423	0.26699	0.44119	0.58937	1.076059
0.24246	0.46080	0.46029	1.067950	0.23301	0.55882	0.41065	1.068324

We also calculate the solvent $\bar{V}_0 = (18.039 \pm 0.0007) \text{ cm}^3 \text{ mol}^{-1}$ and $C_0 = 51.075 \text{ M}$ using the equations:

$$\sum_{i=0}^3 C_i M_i = \bar{d} \quad (5)$$

and

$$\sum_{i=0}^3 C_i \bar{V}_i = 1. \quad (6)$$

All diffusion coefficient measurements were made with the Gosting Diffusometer operating in the Rayleigh interferometric mode [16–18]. The light source of the diffusometer was a 543.5 nm HeNe laser. The diffusion cell channel was 10 cm in vertical length, 2.5 cm in horizontal depth, and 3 mm in width. Initially the higher-density bottom solution filled the entire diffusion channel, and preliminary baseline scans were performed to correct for optical imperfections. Then a needle was inserted into the channel down to the 5 cm level at the center of the channel. A sharp boundary was formed by drawing bottom and top solutions from the reservoirs up through the needle with a peristaltic pump. The pump was run at a slow rate to allow the boundary sharpening process to clear residual bottom solution from the upper channel walls. The needle was then removed, and the channels sealed at the top and bottom of the cell to start the experiment. The Rayleigh patterns were scanned with a 6 cm long 6000 (10 $\mu\text{m} \times 10 \mu\text{m}$) pixel linear array, which was stepped horizontally through the pattern in 10 μm steps. A total of 50 scans at even time intervals were made during the course of each experiment. The initial scan was performed after sufficient time had elapsed for initial boundary imperfections and optical aberrations to become insignificant [19]. The final scan was performed before significant concentration changes could occur at the top and bottom of the diffusion channel. Scanning and data gathering processes were under computer control.

Separation of Creeth Pairs [19] were used to analyze the fringe patterns. The equations used for analysis of the quaternary Rayleigh patterns were those given by Miller [20]. In principle, at least three diffusion experiments must be performed, each with the same \bar{C}_i but a different set of ratios of the three ΔC_i . However, to improve precision, 18 experiments were performed. The ΔC_i are the differences between the top and bottom solution concentrations.

3. Results

We performed 18 diffusion experiments. The ΔC_i values for all 18 experiments are listed in Table 2. Experiments 1–7 and 8–14 represent two nearly identical sets of experiments. Comparison of diffusion coefficients calculated using set 1–7 and 8–14 provide an indicator of experimental error. In all cases, except experiment 17, the ΔC_i were chosen to give a total of 100 Rayleigh fringes (J in Table 2). For experiments 7 and 14 the ΔC_i of each component contributed 33.33 fringes. When there was only one zero ΔC_i , the other two nonzero ΔC_i contributed 50 fringes each.

The number of fringes J and the three corresponding ΔC_i for each set of experiments (1–7 and 8–14) were used to obtain the R_i coefficients by applying the method of least squares to the equation:

$$J = R_1 \Delta C_1 + R_2 \Delta C_2 + R_3 \Delta C_3. \quad (7)$$

For set 1–7: $R_1 = 2216.5 \pm 1.6 \text{ M}^{-1}$, $R_2 = 427.2 \pm 0.3 \text{ M}^{-1}$, and $R_3 = 422.1 \pm 0.3 \text{ M}^{-1}$. For set 8–14: $R_1 = 2215.8 \pm 1.7 \text{ M}^{-1}$, $R_2 = 427.6 \pm 0.3 \text{ M}^{-1}$, and $R_3 = 421.5 \pm 0.3 \text{ M}^{-1}$. For set 1–18: $R_1 = 2217.0 \pm 1.0 \text{ M}^{-1}$, $R_2 = 427.2 \pm 0.18 \text{ M}^{-1}$, and $R_3 = 422.0 \pm 0.2 \text{ M}^{-1}$.

Table 2
Sucrose(1, 0.25 M) + NaCl(2, 0.50 M) + KCl(3, 0.50 M) + H₂O concentration differences across the initial boundaries for both sets of experiments.

Exp ^a	ΔC_1 (M) ^b	ΔC_2 (M)	ΔC_3 (M)	J (1–7) ^c	J (8–14)
1,8	0.0000	0.0000	0.2382	100.55	100.41
2,9	0.0000	0.2352	0.0000 ^d	100.45	100.36
3,10	0.0453	0.0000	0.0000	100.39	100.47
4,11	0.0000	0.1176	0.1191	100.39	100.47
5,12	0.0226	0.0000	0.1191	100.49	100.42
6,13	0.0226	0.1176	0.0000	100.37	100.28
7,14	0.0151	0.0784	0.0794	100.61	100.43
<i>Experiments 15–18 for set 1–18</i>					
15	0.0302	−0.0784	0.1588	100.53	
16	0.0302	−0.0784	0.1588	100.53	
17	−0.0075	0.1960	0.0000	66.92	
18	0.0340	−0.1175	0.1787	100.61	

^a An additional two figures, not shown, were carried in all calculations to avoid round-off errors.

^b Concentrations are expressed in moles per liter.

^c Number of fringes in the Rayleigh pattern.

^d $\Delta C_3 = -0.0006 \text{ M}$ for exp (9).

Reported in Table 3 are the $(D_{ij})_V$ for isothermal diffusion at 25 °C in the quaternary system. Examination of the propagation-of-error values for the main-term diffusion coefficients $(D_{ii})_V$ indicate an error of roughly 1% of their value. Comparison of results from sets 1–7 and 8–14 indicate that these main-term diffusion coefficients $(D_{ii})_V$ are within the propagation-of-error values. The cross-term diffusion coefficients $(D_{12})_V$ and $(D_{13})_V$ for the fluxes of the sucrose due to gradients of NaCl(2) and KCl(3) respectively are less than 5% of $(D_{11})_V$. The comparison of results from the two sets of experiments shows close agreement. The cross-term coefficients $(D_{21})_V$ and $(D_{31})_V$ for the flux of NaCl(2) and KCl(3) due to a gradient of sucrose have very large propagation-of-error values and large differences between the two sets of experiments. This is a consequence of the two salts having diffusion coefficients whose values that are not too different, particularly compared to the differences between sucrose(1) and the salts(2,3). The cross-term coefficients $(D_{23})_V$ and $(D_{32})_V$ have error values that are in the general range as those for the main-terms $(D_{22})_V$ and $(D_{33})_V$. These relate flux of one salt to the gradient of the other salt when the gradient of the sucrose(1) is zero. For $(D_{32})_V$ the values from the 1–7 and 7–14 sets of experiments are within 10% each other. Note that the value of $(D_{32})_V$ is comparable to its error. This is expected since the value of $(D_{23})_V$ is expected to be one order of magnitude smaller than that of $(D_{32})_V$ from calculations based on NH equations.

Table 3
Sucrose(1, 0.25 M) + NaCl(2, 0.50 M) + KCl(3, 0.50 M) + H₂O Measured diffusion coefficients.

$(D_{ij})_V^a$ and eigenvalues, λ_i , calculated from experiment set 1–7		
$(D_{11})_V = 0.443 \pm 0.003$	$(D_{12})_V = 0.019 \pm 0.008$	$(D_{13})_V = 0.014 \pm 0.010$
$(D_{21})_V = 0.04 \pm 0.08$	$(D_{22})_V = 1.167 \pm 0.019$	$(D_{23})_V = 0.008 \pm 0.018$
$(D_{31})_V = 0.25 \pm 0.06$	$(D_{32})_V = 0.136 \pm 0.016$	$(D_{33})_V = 1.532 \pm 0.012$
$\lambda_1 = 0.438 \pm 0.013$	$\lambda_2 = 1.165 \pm 0.019$	$\lambda_3 = 1.539 \pm 0.011$
<i> </i>		
$(D_{ij})_V$ and eigenvalues, λ_i , calculated from experiment set 8–14		
$(D_{11})_V = 0.442 \pm 0.002$	$(D_{12})_V = 0.019 \pm 0.005$	$(D_{13})_V = 0.014 \pm 0.006$
$(D_{21})_V = 0.16 \pm 0.05$	$(D_{22})_V = 1.155 \pm 0.012$	$(D_{23})_V = 0.006 \pm 0.012$
$(D_{31})_V = 0.14 \pm 0.04$	$(D_{32})_V = 0.150 \pm 0.010$	$(D_{33})_V = 1.533 \pm 0.008$
$\lambda_1 = 0.437 \pm 0.001$	$\lambda_2 = 1.156 \pm 0.011$	$\lambda_3 = 1.538 \pm 0.007$
<i> </i>		
$(D_{ij})_V$ and eigenvalues, λ_i , calculated from experiment set 1–18		
$(D_{11})_V = 0.442 \pm 0.003$	$(D_{12})_V = 0.019 \pm 0.008$	$(D_{13})_V = 0.014 \pm 0.011$
$(D_{21})_V = 0.10 \pm 0.07$	$(D_{22})_V = 1.170 \pm 0.013$	$(D_{23})_V = 0.009 \pm 0.019$
$(D_{31})_V = 0.20 \pm 0.06$	$(D_{32})_V = 0.133 \pm 0.016$	$(D_{33})_V = 1.531 \pm 0.024$
$\lambda_1 = 0.437 \pm 0.001$	$\lambda_2 = 1.169 \pm 0.098$	$\lambda_3 = 1.537 \pm 0.012$

^a Units $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

4. Discussion

Listed in Table 4 are the $(D_{ij})_V$ for the quaternary system calculated from the full set 1–18 of experiments plus literature values of the $(D_{ij})_V$ for all the corresponding ternary and binary systems. All values are for measurements 25 °C.

4.1. Main-term $(D_{11})_V, (D_{22})_V, (D_{33})_V$ coefficients

The main-term diffusion coefficients for the flux of a solute component due to its own gradient are included in Table 4. The coefficient $(D_{11})_V$ for the quaternary case is similar to the values for the binary and ternary cases. Any of the corresponding ternary values or even the binary value could be used as a reasonable estimate of the quaternary $(D_{11})_V$. This is consistent with the observed behavior of viscosity. Indeed literature data [21] indicates that viscosities of the aqueous binary salt solutions are not greatly changed by the addition of the salts at the concentrations considered here.

The measured quaternary diffusion coefficients $(D_{22})_V$ and $(D_{33})_V$ divided by the matching values for the ternary system NaCl (0.5 M) + KCl (0.5 M) + H₂O are 0.842 and 0.846 respectively. This fractional decrease represents the effect of adding the disaccharide to the ternary NaCl + KCl + H₂O system. These fractional shifts are the same well within experimental error. This shift is also found for the $(D_{32})_V$ values, but here the error value is too large for this to be meaningful.

When we compare the aqueous binary salt diffusion coefficients to the corresponding aqueous ternary sucrose salt solution main-term diffusion coefficients we find nearly identical comparisons. For 0.5 M NaCl, 1.0 M NaCl, 0.5MKCl and 1.0 M KCl the diffusion coefficient fractions of the before and after sucrose addition are respectively: 0.843, 0.844, 0.844, and 0.844. Thus the ratio of 0.844 may be used in estimating our quaternary data from the corresponding ternary values.

One of the causes of the decrease is the obstruction effect described by [22]:

$$D = D^0(1 - 1.5\phi) \quad (8)$$

where D is the mutual diffusion coefficient of small particles in the presence of large particles with volume fraction ϕ , and D^0 is the corresponding diffusion coefficient at $\phi = 0$. Eq. (8) can be used to estimate the decrease of $(D_{22})_V$ and $(D_{33})_V$ due to the addition of

Table 4

Comparison of the quaternary diffusion coefficients with the ternary and binary diffusion coefficients.

Label	D_{11}^a	D_{12}	D_{13}	D_{21}	D_{22}	D_{23}	D_{31}	D_{32}	D_{33}
D_{ij}^b	0.442	0.019	0.014	0.10	1.170	0.009	0.20	0.133	1.53
D_{ij}^c SN 0.5	0.441	0.019		0.145	1.243				
D_{ij}^d SK 0.5	0.461		0.014				0.179		1.560
D_{ij}^e NK					1.390	0.019		0.157	1.810
D_{ii}^f	0.457				1.474				1.849
D_{ij}^g SN 1.0	0.422	0.019		0.280	1.251				
D_{ij}^h SK 1.0	0.463		0.014				0.315		1.598
D_{ij}^i NK (NH)					1.461	0.014		0.186	1.977
D_{ii}^j (NH)					1.611				1.994

^a Units: $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

^b Calculated from set 1–18 for sucrose (0.25 M) + NaCl (0.50 M) + KCl (0.50 M) + H₂O.

^c Ternary $(D_{ij})_V$ for sucrose (0.25 M) + NaCl (0.5 M) + H₂O [12].

^d Ternary $(D_{ij})_V$ for sucrose (0.25 M) + KCl (0.5 M) + H₂O [12].

^e Ternary $(D_{ij})_V$ for NaCl (0.5 M) + KCl (0.5 M) + H₂O [12].

^f Binary diffusion coefficients [12].

^g Ternary $(D_{ij})_V$ for sucrose (0.25 M) + NaCl (1.0) + H₂O [12].

^h Ternary $(D_{ij})_V$ for sucrose (0.25 M) + KCl (1.0 M) + H₂O [12].

ⁱ Ternary $(D_{ij})_V$ for NaCl (0.5 M) + KCl (0.5 M) + H₂O calculated using Nernst–Hartley (NH) equation [4,8].

^j Binary salt diffusion coefficients calculated using Nernst–Hartley (NH) equation [4,21].

sucrose. If we use $\bar{V}_1 = 214 \text{ cm}^3 \text{ mol}^{-1}$ and $C_1 = 0.25 \text{ M}$, we obtain: $\phi = C_1 \bar{V}_1 = 0.0535$ and the main-term salt diffusion coefficients are predicted to decrease by a factor of 0.92. After applying this correction, the ternary values remain 9% higher than the quaternary values, and the binary values remain also 9% higher than the ternary values. Finally, it is important to remark that a comparison between the quaternary system and the corresponding sucrose–salt ternary systems shows that the effect of sucrose on the ratio between salt main-term diffusion in the presence of the other salt component and salt main-term diffusion in the absence of the other salt component is negligible. This result is consistent with both the obstruction effect and the NH equations.

4.2. Sucrose cross-term $(D_{12})_V$ and $(D_{13})_V$ coefficients

The quaternary values of $(D_{12})_V$ and $(D_{13})_V$ are relatively small, less than 5% of the main-term $(D_{11})_V$ and have error values of similar size. They are virtually the same as the corresponding ternary $(D_{ij})_V$ tabulated for sucrose + NaCl + H₂O and sucrose + KCl + H₂O. Consequently, the ternary values could provide reasonable estimates of the quaternary values.

4.3. Salt cross-term $(D_{23})_V$ and $(D_{32})_V$ coefficients

We noted above that the two main-term salt diffusion coefficients $(D_{22})_V$ and $(D_{33})_V$ were shifted to a lower value by similar fractions by the addition of sucrose to form the quaternary system. It is reasonable to expect the cross-term $(D_{23})_V$ and $(D_{32})_V$ to be similarly shifted. Indeed, both are shifted lower. However, in the case of $(D_{23})_V$, the values of the coefficients are very low, and the shift is nearly within the experimental error. The shift calculated for $(D_{32})_V$ is within experimental error of the shift of $(D_{22})_V$ and $(D_{33})_V$. It would be very reasonable to estimate these cross-term quaternary values from the ternary salt–mixture values by using the percentage shift of the main-term values.

4.4. Salt cross-term $(D_{21})_V$ and $(D_{31})_V$ coefficients

The cross-term diffusion coefficients $(D_{21})_V$ and $(D_{31})_V$ give the fluxes of the salt components NaCl(2) and KCl(3) respectively due to a gradient of the disaccharide(1). These coefficients have very-high relative uncertainty in the quaternary measurements, so the ternary sucrose + salt values may give better estimates.

In this regard, it is of interest to examine these coefficients in terms of expressions for excluded volumes. First we summarize a derivation for a ternary system in which the size of solute ‘1’ is much larger than the size of solute ‘2’. In other words, we treat solute ‘1’ as a second phase. We also assume no association between solutes. The equation: $-J_2 = (D_{21})_V (\partial C_1 / \partial x)_C$ relates the flux of component 2 due to a gradient of component 1, while the stoichiometric concentration C_2 itself is constant. We assume that interstitial flux J_2^* occurs due to an interstitial concentration gradient of component 2 caused by a gradient of component 1 at constant C_2 . We can therefore write: $-J_2^* = (D_{22})_V (\partial C_2^* / \partial x)_C$, where $C_2^* = C_2 / (1 - C_1 \bar{V}_1)$ and $J_2^* = J_2 / (1 - C_1 \bar{V}_1)$. Since $(\partial C_2^* / \partial x)_C$ can be written as $(\partial C_1 / \partial x)_C [C_2 \bar{V}_1 / (1 - C_1 \bar{V}_1)^2]$, we can relate $(D_{21})_V$ to $(D_{22})_V$ using the equation [23]:

$$(D_{21})_V = \frac{C_2 \bar{V}_1}{1 - C_1 \bar{V}_1} (D_{22})_V \quad (9)$$

We have applied Eq. (9) (rearranged) to the sucrose(1) + single salt(2) values $(D_{21})_V$ and $(D_{22})_V$ in Table 4 to calculate \bar{V}_1 . These calculated values of \bar{V}_1 for the SN 0.5, SN 1.0, SK 0.5, and SK 1.0 systems are respectively: 220, 212, 217, and 188 $\text{cm}^3 \text{ mol}^{-1}$ with an average of 209 $\text{cm}^3 \text{ mol}^{-1}$. This average is not too different than the 213–214 $\text{cm}^3 \text{ mol}^{-1}$ that were obtained from density measurements

for these systems and $214 \text{ cm}^3 \text{ mol}^{-1}$ from density measurements of the quaternary system. The agreement between experimental ternary results and Eq. (9) indicates that \bar{V}_1 can be used to estimate sucrose cross-term diffusion coefficients for the ternary and quaternary systems. Hence, the same approach used to obtain Eq. (9) can be extended to the quaternary system. Note that the interstitial flux of each salt will be related to both a main-term and a cross-term diffusion coefficient. We denote the interstitial salt concentrations as $\bar{C}_i^* = C_i/(1 - C_1\bar{V}_1)$ with $i = 2, 3$. The equation $-J_i = (D_{i1})_V (\partial C_i / \partial x)_{C_2, C_3}$ relates the flux of component i due to a gradient of component 1, at constant C_2 and C_3 . The interstitial flux $J_i^* = J_i/(1 - C_1\bar{V}_1)$ of the two salts will be given by:

$$-J_i^* = (D_{ii})_V \left(\frac{\partial C_i^*}{\partial x} \right)_{C_2, C_3} + (D_{ij})_V \left(\frac{\partial C_j^*}{\partial x} \right)_{C_2, C_3} \quad (i, j = 2, 3 \text{ and } i \neq j). \quad (10)$$

Noting that C_2 and C_3 are constant, we can easily obtain the equation:

$$(D_{ii})_V = \frac{\bar{V}_1}{1 - C_1 \bar{V}_1} \left[C_i (D_{ii})_V + C_j (D_{ij})_V \right] \quad (i, j = 2, 3 \text{ and } i \neq j). \quad (11)$$

Using Eq. (11), we estimate $(D_{21})_V \approx 0.13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ by using the experimental values of $(D_{22})_V$ and $(D_{23})_V$, and $(D_{31})_V \approx 0.18 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ by using the values of $(D_{33})_V$ and $(D_{32})_V$ for the quaternary system. These predicted values are consistent with our corresponding experimental values within the experimental error. Given the high uncertainty on the experimental $(D_{21})_V$ and $(D_{31})_V$ values associated with quaternary diffusion measurements and the good agreement between experimental ternary data and Eq. (9), we believe that the values obtained using Eq. (11) can replace the corresponding experimental data when they cannot be measured with satisfactory precision.

5. Summary and conclusions

We have compared our experimental quaternary diffusion coefficients of the system sucrose (0.25 M) + NaCl (0.50 M) + KCl (0.50 M) + H₂O system with the diffusion coefficients of all the corresponding ternary systems and binary systems at 25 °C. We have found that the ternary diffusion coefficients can be used to make reasonable estimates of the quaternary diffusion coefficients. More-

over, we have found that a simple excluded-volume model can be used to successfully predict the effect of sucrose on salt cross-term diffusion coefficients for ternary and quaternary systems. We therefore believe that estimates of $(D_{21})_V$ and $(D_{31})_V$ based on Eq. (11) can replace the corresponding experimental data when they cannot be measured with satisfactory precision.

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