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

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coupled diffusion

A B S T R A C T
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 \( \nabla C_j \) may be written [4]:

\[
-J_i = \sum_{j=1}^{N} D_{ij} \nabla C_j \quad i = 1...N.
\]  

(1)

(We denote the solvent components with subscripts \( ij = 0 \).) 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:

\[
\sum_{i=0}^{N} J_i \tilde{V}_i = 0
\]  

(2)

where \( \tilde{V}_i \) 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 \( (D_{ij})_V \) 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...
example, in the ternary system NaCl+MgCl2+H2O at 25 °C measured values of the four (Dij)V indicate that at higher NaCl concentrations, a cross-term (DiJ)V can be larger than both main-term (Di) 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 Dij values from corresponding ternary systems could help develop useful estimates of the DiJ 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, of the relatively larger differences of the sizes the solutes in the quaternary systems were useful correlations between the ternary and quaternary 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 (DiJ)V to estimate the quaternary (DiJ)V for this case. Our measured cross-terntary DiJ 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 ±0.01 °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 d and H1 [15]:

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

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

<table>
<thead>
<tr>
<th>C1(M)</th>
<th>C2(M)</th>
<th>C3(M)</th>
<th>d (g/cm³)</th>
<th>C1(M)</th>
<th>C2(M)</th>
<th>C3(M)</th>
<th>d (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1500</td>
<td>0.4000</td>
<td>0.0600</td>
<td>1.059893</td>
<td>0.2500</td>
<td>0.5000</td>
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<td>0.5000</td>
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<td>0.49997</td>
<td>1.076699</td>
</tr>
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<td>1.069008</td>
<td>0.2500</td>
<td>0.38237</td>
<td>0.50003</td>
<td>1.067277</td>
</tr>
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<td>0.49996</td>
<td>1.076696</td>
<td>0.2499</td>
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</tr>
<tr>
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<td>1.077075</td>
</tr>
<tr>
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<td>0.05354</td>
<td>1.077068</td>
<td>0.23886</td>
<td>0.44188</td>
<td>0.44148</td>
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<td>1.068115</td>
<td>0.27265</td>
<td>0.50002</td>
<td>0.50002</td>
<td>1.075114</td>
</tr>
</tbody>
</table>
We also calculate the solvent \( V_0 = (18.039 \pm 0.0007) \text{ cm}^3 \text{ mol}^{-1} \) and \( C_0 = 51.075 \text{ M} \) using the equations:

\[
\sum_{i=0}^{3} C_i M_i = \hat{d}
\]

(5)

and

\[
\sum_{i=0}^{3} C_i V_i = 1.
\]

(6)

All diffusion coefficient measurements were made with the Gosting Diffusimeter operating in the Rayleigh interferometric mode [16–18]. The light source of the diffusimeter 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 m \times 10 \mu m) pixel linear array, which was stepped horizontally through the pattern in 10 \mu m 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 \( C_1 \) but a different set of ratios of the three \( \Delta C_i \). However, to improve precision, 18 experiments were performed. The \( \Delta C_i \) are the differences between the top and bottom solution concentrations.

3. Results

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

The number of fringes \( J \) and the three corresponding \( \Delta C_i \) 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:

\[
J = R_1 \Delta C_1 + R_2 \Delta C_2 + R_3 \Delta C_3.
\]

(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.

<table>
<thead>
<tr>
<th>Exp</th>
<th>( \Delta C_1 ) (M)</th>
<th>( \Delta C_2 ) (M)</th>
<th>( \Delta C_3 ) (M)</th>
<th>( J ) (1–7)</th>
<th>( J ) (8–14)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.2382</td>
<td>100.55</td>
<td>100.41</td>
</tr>
<tr>
<td>2.9</td>
<td>0.0000</td>
<td>0.2352</td>
<td>0.0000</td>
<td>100.45</td>
<td>100.36</td>
</tr>
<tr>
<td>3.10</td>
<td>0.0453</td>
<td>0.0000</td>
<td>0.0000</td>
<td>100.39</td>
<td>100.47</td>
</tr>
<tr>
<td>4.11</td>
<td>0.0000</td>
<td>0.1176</td>
<td>0.1191</td>
<td>100.39</td>
<td>100.47</td>
</tr>
<tr>
<td>5.12</td>
<td>0.0226</td>
<td>0.0000</td>
<td>0.1191</td>
<td>100.49</td>
<td>100.42</td>
</tr>
<tr>
<td>6.13</td>
<td>0.0226</td>
<td>0.1176</td>
<td>0.0000</td>
<td>100.37</td>
<td>100.28</td>
</tr>
<tr>
<td>7.14</td>
<td>0.0151</td>
<td>0.0784</td>
<td>0.0794</td>
<td>100.61</td>
<td>100.43</td>
</tr>
</tbody>
</table>

\[a\] 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.

\[d\] \( \Delta C = -0.0006 \text{ M} \) for exp (9).

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

<table>
<thead>
<tr>
<th>( D_{ij} ) and eigenvalues, ( \lambda_i ) calculated from experiment set 1–7</th>
<th>( D_{ij} ) and eigenvalues, ( \lambda_i ) calculated from experiment set 8–14</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{11} ) = 0.443 ± 0.003</td>
<td>( D_{11} ) = 0.442 ± 0.002</td>
</tr>
<tr>
<td>( D_{12} ) = 0.04 ± 0.08</td>
<td>( D_{12} ) = 0.049 ± 0.012</td>
</tr>
<tr>
<td>( D_{13} ) = 0.25 ± 0.06</td>
<td>( D_{13} ) = 0.165 ± 0.012</td>
</tr>
<tr>
<td>( \lambda_1 ) = 0.438 ± 0.013</td>
<td>( \lambda_1 ) = 0.165 ± 0.012</td>
</tr>
<tr>
<td>( \lambda_2 ) = 1.651 ± 0.017</td>
<td>( \lambda_2 ) = 1.533 ± 0.011</td>
</tr>
<tr>
<td>( \lambda_3 ) = 1.533 ± 0.007</td>
<td>( \lambda_3 ) = 1.533 ± 0.007</td>
</tr>
</tbody>
</table>

\[a\] 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 \(\text{NaCl (0.5 M)} + \text{KCl (0.5 M)} + \text{H}_2\text{O}\) are 0.842 and 0.846 respectively. This fractional decrease represents the effect of adding the disaccharide to the ternary \(\text{NaCl} + \text{KCl} + \text{H}_2\text{O}\) system. These fractional shifts are the same well within experimental error. This shift is also found for the \((D_{22})_{V}\) 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, 0.5M KCl 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]:

\[
D = D^0(1 - 1.5\phi)
\]

where \(D\) is the mutual diffusion coefficient of small particles in the presence of large particles with volume fraction \(\phi\), 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 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 \quad \text{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 + \(\text{NaCl} + \text{H}_2\text{O}\) and sucrose + \(\text{KCl} + \text{H}_2\text{O}\). 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 \((D_{23})_{V}\) 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 \(\text{NaCl(2)}\) and \(\text{KCl(3)}\) 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: \(-J_C = (D_{21})_V (\partial C_2/\partial x_C)_V\) 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 \(J^*_C\) 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: \(-J_C = (D_{21})_V (\partial C_2/\partial x_C)_V\), where \(C_2 = C_2(1 - C_1/V_1)\) and \(J^*_C = J_C(1 - C_1/V_1)\). Since \((\partial C_2/\partial x_C)\) can be written as \(\partial (C_1/V_1)\), we can relate \((D_{21})_V\) to \((D_{21})_V\) using the equation [23]:

\[
(D_{21})_V = C_2 \frac{V_1}{1 - C_1} (D_{22})_V.
\]

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 \(V_1\). These calculated values of \(V_1\) for the SN 0.5, SN 1.0, SK 0.5, and SK 1.0 systems are respectively: 220, 212, 217, and 188 cm³ mol⁻¹ with an average of 209 cm³ mol⁻¹. This average is not too different than the 213–214 cm³ mol⁻¹ that were obtained from density measurements.
for these systems and 214 cm$^3$ mol$^{-1}$ from density measurements of the quaternary system. The agreement between experimental ternary results and Eq. (9) indicates that $V_1$ 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 $C_i^* = C_i/(1 - C_i V_1)$ with $i = 2, 3$. The equation $J_i = (D_{ij})_V (\partial C_i / \partial x)_{C_j C_i}$ relates the flux of component $i$ due to a gradient of component 1, at constant $C_2$ and $C_3$. The interstitial flux $J_i^* = J_i/(1 - C_i V_1)$ of the two salts will be given by:

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

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

$$(D_{11})_V = \frac{V_1}{1 - C_1 V_1} \left[ C_i (D_{1i})_V + C_j (D_{ij})_V \right] \quad (i,j = 2, 3 \text{ and } i \neq j). \quad (11)$$

Using Eq. (11), we estimate $(D_{21})_V \approx 0.13 \times 10^{-5}$ cm$^2$ s$^{-1}$ by using the experimental values of $(D_{22})_V$ and $(D_{23})_V$ and $(D_{31})_V \approx 0.18 \times 10^{-5}$ cm$^2$ s$^{-1}$ by using the values of $(D_{33})_V$ and $(D_{31})_V$ 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) + H$_2$O 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. Moreover, 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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References