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Activity Coefficient Derivatives of Ternary Systems Based on Scatchard's Neutral Electrolyte Description

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Abstract

Activity coefficient derivatives with respect to molality are presented for the Scatchard Neutral Electrolyte description of a ternary common-ion electrolyte system. These quantities are needed for the calculation of "diffusion Onsager coefficients" and in turn for tests of the Onsager Reciprocal Relations in diffusion. The usually-omitted b_{23} term is included. The direct SNE binary approximations and a further approximation are discussed. Binary evaluation strategies other than constant ionic strength are considered.

Keywords Ternary system · Scatchard Neutral Electrolyte description · Activity coefficient derivatives · Binary approximations · Binary evaluation strategies

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1. Introduction

There are many ways to represent the osmotic and activity coefficients of single and mixed electrolyte systems. Pitzer's equations and their extensions [1] are currently the most popular representations. For mixed electrolyte systems, other representations include the Scatchard Neutral Electrolyte [2-7], Scatchard Ion Component [8,9], Reilly-Wood et al. [10,11,7], and Friedman [7,12].

The goodness of fit to experimental data for ϕ and $\ln\gamma_i$ is especially important because the thermodynamic applications to transport processes require the activity coefficient *derivatives*. However, taking derivatives magnifies the errors. Pitzer's equations and their extensions do provide quite adequate values of ϕ and $\ln\gamma_i$ for most practical applications. However, the fits to binary data often show considerable cycling of residuals, especially at higher concentrations [13-15]. In this circumstance, the use of representations that have more adjustable constants can yield better derivatives for both binary and ternary systems.

Our particular concern is thermodynamic analysis of ternary diffusion systems, in particular the testing of the Onsager Reciprocal Relations (ORR). These require the Onsager diffusion coefficients in either the volume-fixed reference frame $(L_{ij})_V$ [16] or the solvent-fixed frame $(L_{ij})_0$ [17-19]. These in turn require either the four experimental volume-fixed $(D_{ij})_V$ or the four solvent-fixed diffusion coefficients $(D_{ij})_0$, which can be calculated from the $(D_{ij})_V$ [18,19]. The Onsager coefficients also require the derivatives of the chemical potentials μ_{ij} with respect to the concentration C_i in mol dm^{-3}, where

$$\mu_{ij} = \frac{\partial \mu_i}{\partial C_j} \tag{1}$$

These μ_{ij} are obtained from the derivatives of the activity coefficients $\partial \ln \gamma_i / \partial m_j$ multiplied by the concentration derivative $\partial m_j / \partial C_j$, which can be calculated from densities or partial molar volumes $\overline{V}_i$ [16]. Here γ_i is the mean molal activity coefficient and m_i is the molality of solute i in mol·(kg H_2O)$^{-1}$.

Further determination of the ternary *ionic* Onsager coefficients l_{ij} requires the transference numbers t_i and the equivalent conductance Λ [20-22]. These ionic coefficients are useful in estimating the vector transport properties of multicomponent systems [21,23-25], although experimental values of the transference numbers are rarely available.

Ternary diffusion systems composed of electrolytes must have a common ion. In contrast, a solution of two non-common ion electrolytes is a 4-component system for diffusion, unlike ternary equilibrium systems [16,26].

In the case of a ternary common-ion system, the Scatchard Neutral Electrolyte (SNE) description is simpler than the various ion-component descriptions Scatchard, Reilly et al., Friedman, and Pitzer. We have found that it usually fits ternary osmotic coefficient data better than Pitzer's equations over large molality ranges [14,28], given sufficient adjustable parameters in the mixing terms. There is also the advantage that the binary approximation part of the osmotic coefficient and the activity coefficients can be based on fits to other binary equations, including Pitzer's, rather than elaborate functional form of Scatchard's original formulation.

The SNE mixing terms are related to the excess Gibbs energy of mixing ΔG^{ex} and can be related to Friedman's work on pair, triplet, quadruplet, etc. interactions [7,29]. In either case, ϕ and $\ln\gamma$ are derivatives of ΔG^{ex}, and their derivatives in turn are our interest.

This work was originally done in 1974 (without the b_{23} term, see below) in anticipation of testing the ORR for various ternary diffusion systems. The results have been applied to the calculation of the $(L_{ij})_0$ and testing of the ORR from the systematic sets of diffusion results for the NaCl-MgCl$_2$-H$_2$O system [30-34]. These tests are now being prepared for publication. Our 1974 results are contained in John Mitchell's thesis [35]. The results below have been extended to include the b_{23} term.

2 The Scatchard Neutral Electrolyte Equations

Although we are primarily interested in values of the $\left(\partial \ln \gamma_i / \partial m_j \right)$, we include the general expressions for $\ln\gamma_i$ and ϕ as well.

It can be shown [28,36] from the elaborate original Scatchard forms [2] that the binary approximation for ϕ can be re-written as

$$\phi = h_1 \, \phi_1^0 + h_2 \, \phi_2^0 \tag{2}$$

where h_i is the osmolality fraction of solute i, and ϕ_i^0 is the osmotic coefficient of solute i in its binary solution typically evaluated at the ionic strength I of the ternary mixture. The osmolality O is $(r_1 m_1 + r_2 m_2)$, $h_i = r_i m_i / O$ and r_i and m_i are defined below.

Then the SNE expression for ϕ and $\ln \gamma_i$ can be written in terms of the binary approximation above (Eq. 2) and the mixing terms [14,28] as follows.

$$\phi = h_1 \phi_1^0 + h_2 \phi_2^0 +$$
$$\frac{z_1 z_2 y_1 y_2}{2(z_2 y_1 + z_1 y_2)} \left[\left(b_{01} I + b_{02} I^2 + b_{03} I^3 \right) + \left(y_1 - y_2 \right) \left(b_{12} I^2 + b_{13} I^3 \right) + \left(y_1 - y_2 \right)^2 b_{23} I^3 \right] \tag{3}$$

$$\ln \gamma_1 = \ln \gamma_1^0 + z_1 \left\{ y_2 \, \Phi + \frac{y_2}{2}[\;]_{11} - \frac{y_2^2}{2}[\;]_{12} + \frac{y_2^3}{2}[\;]_{13} \right\} \tag{4}$$

$$\ln \gamma_2 = \ln \gamma_2^0 + z_2 \left\{ -y_1 \, \Phi + \frac{y_1}{2}[\;]_{21} - \frac{y_1^2}{2}[\;]_{22} - \frac{y_1^3}{2}[\;]_{23} \right\} \tag{5}$$

where ϕ is the osmotic coefficient of the ternary, ϕ_i^0 and γ_i^0 are the respective osmotic coefficient and activity coefficient of the binary system with solute i at the ionic strength I of the ternary, z_i is $-z_{ic} z_{ia} = |z_{ic} z_{ia}|$, z_{ic} is the charge on the cation of solute i, z_{ia} is the charge of the anion of solute i, $r_i = r_{ic} + r_{ia}$ is the total number of ions of solute i, r_{ic} and r_{ia} are the number of cations and anions respectively from the ionization of solute i, y_i is the ionic strength fraction of solute i in the ternary, b_{ij} are the mixing parameters and are not functions of I, ϕ is the osmotic coefficient of the ternary, and Φ is the function

$$\Phi = \left[\frac{\left(\phi_2^0 - 1 \right)}{z_2} - \frac{\left(\phi_1^0 - 1 \right)}{z_1} \right] \tag{6}$$

The $[\;]_{ij}$ are as follows:

$$[\;]_{11} = \left[b_{01} I + \left(b_{02} + b_{12} \right) I^2 + \left(b_{03} + b_{13} + b_{23} \right) I^3 \right] \tag{7}$$

$$[\;]_{12} = \left[\left(\frac{b_{02}}{2} + \frac{3 b_{12}}{2} \right) I^2 + \left(\frac{2 b_{03}}{3} + 2 b_{13} + \frac{10 b_{23}}{3} \right) I^3 \right] \tag{8}$$

$$[\;]_{13} = \left[\left(\frac{2 b_{13}}{3} + \frac{8 b_{23}}{3} \right) I^3 \right] \tag{9}$$

$$[\;]_{21} = \left[b_{01} I + \left(b_{02} - b_{12} \right) I^2 + \left(b_{03} - b_{13} + b_{23} \right) I^3 \right] \tag{10}$$

$$[\;]_{22} = \left[\left(\frac{b_{02}}{2} - \frac{3 b_{12}}{2} \right) I^2 + \left(\frac{2 b_{03}}{3} - 2 b_{13} + \frac{10 b_{23}}{3} \right) I^3 \right] \tag{11}$$

$$[]_{23} = \left[\left(\frac{2b_{13}}{3} - \frac{8b_{23}}{3} \right) I^3 \right] \tag{12}$$

Note that we have included the usually-missing b_{23} term that completes the quadruplet interactions as described by Leifert and Wigent [29], and whose contributions to ϕ and $\ln\gamma_i$ had been previously presented by Rush [6]. Rard and Miller [28] used this term for trial fits to ϕ data for the system $NaCl\text{-}MgCl_2\text{-}H_2O$.

The Friedman g_i are related to the b_{ij} as follows [29]:

$$g_0 = b_{01} + \frac{b_{02}\,I}{2} + \frac{b_{03}\,I^2}{3} + ... \tag{13}$$

$$g_1 = \frac{b_{12}\,I}{2} + \frac{b_{13}\,I^2}{3} + ... \tag{14}$$

$$g_2 = \frac{b_{23}\,I^2}{3} + ... \tag{15}$$

The expressions for the excess part of ϕ and the excess Gibbs energy as polynomials of $y_1 y_2$ and $(y_1 - y_2)^n$ are also related to the empirical suggestions of Redlich and Kister [37] for non-electrolytes.

3. Activity coefficient derivatives

We proceed to differentiate eq 4 and 5, making use of a number of auxiliary equations and definitions. These are listed below in the Appendix. After some algebra, we find that

$$\left(\frac{\partial \ln \gamma_1}{\partial m_1} \right)_{m_2} = \frac{r_1 z_1^2}{2} \left\{ \begin{array}{l} \left[\displaystyle\sum_{i=1}^{2} \frac{y_i}{z_i} \frac{d \ln \gamma_i^0}{dI} - \frac{2y_2}{I} \Phi \right] \\[2ex] + \dfrac{y_2}{2} \left[(b_{02} + b_{12}) I + 2 (b_{03} + b_{13} + b_{23}) I^2 \right] \\[2ex] - \dfrac{y_2^2}{2} \left[\left(\dfrac{2b_{03}}{3} + 2b_{13} + \dfrac{10b_{23}}{3} \right) I^2 \right] \end{array} \right\} \tag{16}$$

$$\left(\frac{\partial \ln \gamma_1}{\partial m_2} \right)_{m_1} = \frac{r_2 z_1 z_2}{2} \left\{ \begin{array}{l} \left[\displaystyle\sum_{i=1}^{2} \frac{y_i}{z_i} \frac{d \ln \gamma_i^0}{dI} + \frac{(y_1 - y_2)}{I} \Phi \right] \\[2ex] + \dfrac{1}{2} \left[(b_{01} + (b_{02} + b_{12}) I + (b_{03} + b_{13} + b_{23}) I^2) \right] \\[2ex] + \dfrac{y_2}{2} \left[-2b_{12} I + \left(\dfrac{2b_{03}}{3} - 2b_{13} - \dfrac{14b_{23}}{3} \right) I^2 \right] \\[2ex] - \dfrac{y_2^2}{2} \left[\left(\dfrac{2b_{03}}{3} - \dfrac{14b_{23}}{3} \right) I^2 \right] \end{array} \right\} \tag{17}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} = \frac{r_1 z_1 z_2}{2} \left\{ \begin{array}{l} \left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln\gamma_i^0}{dI} + \frac{(y_1-y_2)}{I}\Phi\right] \\[2mm] + \frac{1}{2}\left[\left(b_{01} + (b_{02}-b_{12})I + (b_{03}-b_{13}+b_{23})I^2\right)\right] \\[2mm] + \frac{y_1}{2}\left[2b_{12}I + \left(\frac{2b_{03}}{3}+2b_{13}-\frac{14b_{23}}{3}\right)I^2\right] \\[2mm] - \frac{y_1^2}{2}\left[\left(\frac{2b_{03}}{3}-\frac{14b_{23}}{3}\right)I^2\right] \end{array} \right\} \tag{18}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial m_2}\right)_{m_1} = \frac{r_2 z_2^2}{2} \left\{ \begin{array}{l} \left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln\gamma_i^0}{dI} + \frac{2y_1}{I}\Phi\right] \\[2mm] + \frac{y_1}{2}\left[(b_{02}-b_{12})I + 2(b_{03}-b_{13}+b_{23})I^2\right] \\[2mm] - \frac{y_1^2}{2}\left[\left(\frac{2b_{03}}{3}-2b_{13}+\frac{10b_{23}}{3}\right)I^2\right] \end{array} \right\} \tag{19}$$

Notice the two cross derivatives look different but are similar in form. However, they can be shown to satisfy the cross differentiation relation

$$r_1\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = r_2\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} \tag{20}$$

It turns out that we can get a common and simpler looking result by adding the appropriate terms and dividing by 2; namely,

$$r_1\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = r_2\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} = \frac{r_1 r_2 z_1 z_2}{2} \left\{ \begin{array}{l} \left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln\gamma_i^0}{dI} + \frac{(y_1-y_2)}{I}\Phi\right] \\[2mm] + \frac{1}{2}\left[b_{01} + b_{02}I + (b_{03}+b_{23})I^2\right] \\[2mm] + \frac{(y_1-y_2)}{2}\left[b_{12}I + b_{13}I^2\right] \\[2mm] + \frac{y_1 y_2}{2}\left[\left(\frac{2b_{03}}{3}-\frac{14b_{23}}{3}\right)I^2\right] \end{array} \right\} \tag{21}$$

In Eq. 16–20, the derivatives $d\ln\gamma_i^0/dI$ of the binary system are functions only of I, and are evaluated at the ionic strength I of the ternary.

4. Comments on binary approximations

In the absence of mixing data, it is often necessary to approximate the ternary osmotic coefficients, activity coefficients, and the activity coefficient derivatives from their binary expressions. The Scatchard Neutral Electrolyte equations for ternary common ion systems are useful here. We note that the Pitzer equations can also be used for binary approximations, but as mentioned earlier, the results can be limited by the quality of the binary fits.

Extracting the binary terms from the above equations yields the approximations:

$$\phi = h_1\,\phi_1^0 + h_2\,\phi_2^0 \tag{2}$$

$$\frac{\ln \gamma_1}{z_1} = \frac{\ln \gamma_1^0}{z_1} + y_2\,\Phi \tag{22}$$

$$\frac{\ln \gamma_2}{z_2} = \frac{\ln \gamma_2^0}{z_2} - y_1\,\Phi \tag{23}$$

$$\left(\frac{\partial \ln \gamma_1}{\partial m_1}\right)_{m_2} = \frac{r_1 z_1^2}{2}\left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln \gamma_i^0}{dI} - \frac{2y_2}{I}\Phi\right] \tag{24}$$

$$r_1\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = r_2\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} = \frac{r_1 r_2 z_1 z_2}{2}\left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln \gamma_i^0}{dI} + \frac{(y_1-y_2)}{I}\Phi\right] \tag{25}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial m_2}\right)_{m_1} = \frac{r_2 z_2^2}{2}\left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln \gamma_i^0}{dI} + \frac{2y_1}{I}\Phi\right] \tag{26}$$

where again, Φ, a function of the binary osmotic coefficients, is given by Eq. 2.

Equations 22 and 23, *i.e.*, where all the b_{ij} are 0, correspond to the conditions on the Harned's Rule coefficients that $\alpha_{12}/z_1 = -\alpha_{21}/z_2$, $\beta_{12}/z_1 = -\beta_{21}/z_2$, *etc.*, as can be obtained by writing Eq. 22 and 23 in Harned Rule form. These conditions have often been found to be valid or nearly valid [38,39].

A still further approximation allows us to get the ternary $\ln \gamma_i$ in terms of only the $\ln \gamma_i^0$, without needing the binary osmotic coefficients ϕ_i^0 in Φ. This approximation, also based on Harned Rule studies, is that

$$\frac{\ln \gamma_1^{tr}}{z_1} = \frac{\ln \gamma_2^{tr}}{z_2} \tag{27}$$

where γ_i^{tr} is the activity coefficient of a trace amount of solute i in a in finite concentration of solute j. This further approximation has also been found to be valid for some systems [38,39].

With Eq. 27 given in terms of Eq. 22 (with $y_2=1$) and eq 23 (with $y_1=1$),

$$\left[\frac{\ln \gamma_1^{tr}}{z_1} = \frac{\ln \gamma_1^0}{z_1} + \Phi\right] = \left[\frac{\ln \gamma_2^0}{z_2} - \Phi = \frac{\ln \gamma_2^{tr}}{z_2}\right] \qquad (28)$$

Solving Eq. 28 for Φ and eliminating the result from Eqs. 22 and 23 gives expressions for $\ln \gamma_i$ in terms of $\ln \gamma_1^0$ and $\ln \gamma_2^0$. A little manipulation gives the final result for a ternary common ion mixture:

$$\frac{\ln \gamma_i}{z_i} = \frac{1}{2} \frac{\ln \gamma_i^0}{z_i} + \frac{1}{2}\left[y_1 \frac{\ln \gamma_1^0}{z_1} + y_2 \frac{\ln \gamma_2^0}{z_2}\right] \qquad (29)$$

This result was obtained for 1-1 ternary common-ion mixtures by the author in ref. [16] using a similar argument. Lietzke and Stoughton [40] subsequently presented an equation for higher valence mixtures that is exactly equivalent to Eq. 29 for ternary common-ion mixtures.

The activity coefficient derivatives based on Eq. 29 are also independent of the osmotic coefficients:

$$\left(\frac{\partial \ln \gamma_1}{\partial m_1}\right)_{m_2} = \frac{r_1 z_1^2}{2}\left[\frac{\ln \gamma_1^0}{2 z_1 I} + \sum_{i=1}^{2} \frac{y_i}{2 z_i}\left(\frac{d \ln \gamma_i^0}{dI} - \frac{\ln \gamma_i^0}{I}\right)\right] \qquad (30)$$

$$r_1\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = r_2\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} =$$
$$\frac{r_1 r_2 z_1 z_2}{2}\left[\frac{1}{2}\left(\frac{\ln \gamma_1^0}{2 z_1 I} + \frac{\ln \gamma_2^0}{2 z_2 I}\right) + \sum_{i=1}^{2} \frac{y_i}{2 z_i}\left(\frac{d \ln \gamma_i^0}{dI} - \frac{\ln \gamma_i^0}{I}\right)\right] \qquad (31)$$

$$\left(\frac{\partial \ln \gamma_2}{\partial m_2}\right)_{m_1} = \frac{r_2 z_2^2}{2}\left[\frac{\ln \gamma_2^0}{2 z_2 I} + \sum_{i=1}^{2} \frac{y_i}{2 z_i}\left(\frac{d \ln \gamma_i^0}{dI} - \frac{\ln \gamma_i^0}{I}\right)\right] \qquad (32)$$

5. Comments on binary evaluation strategies and mixing term functions

There are other *binary evaluation strategies* (BES) for the binary part of these expressions besides constant ionic strength. Examples are evaluation at constant equivalents E, constant molality m, or constant osmolality O. These arise from the arbitrary choice of "ideal mixing" of the binaries [7,41]. All require the use of osmolality fractions for ϕ_i^0, which are a consequence of the definition of excess Gibbs energy. However, other concentration measures and other fractions could be used in the mixing term.

The issue of binary evaluation strategies has been discussed in detail for volumes [42] and conductances [43], and applied earlier to volumes [44] and heats of mixing [45]. It is expected that at low concentrations ($I<0.1$ mol·kg^{-1}), evaluation at constant I will be better. However, at higher concentrations, it has frequently been found that evaluation at constant E yields a better binary

approximation (smaller mixing term) than constant *I* for volumes **[42,44]**, heats **[45,46]**, and osmotic coefficients.

Although the use of equivalents is de-emphasized in elementary chemistry courses, they have an important role in electrolyte theory and practice. For example, Pitzer's equations have terms in *E* and E_i, as do the Reilly and Wood mixing equations. Also the general expression for chemical potential derivatives of common-ion mixtures contains *E* in one term **[16]**. Furthermore, Reilly and Wood point out that in Young's rule mixings, each ion sees the same number of other ions in constant *E* mixings **[45,46]**, so that the oppositely-charged pairwise interactions nearly cancel.

In this context, we examined in 1986 three large ϕ data sets at 298.15 K for NaCl-MgCl$_2$-H$_2$O **[28]**; NaCl-SrCl$_2$-H$_2$O **[27]**; and for NaCl-Na$_2$SO$_4$-H$_2$O from R. F. Platford that was not published until recently **[47]**, plus a smaller number of points from **[4,48]** taken from ref. **[6]**. We found but did not report that the mixing term

$$\phi - h_1 \phi_1^0 + h_2 \phi_2^0 \tag{33}$$

was smallest overall when ϕ_i^0 is evaluated at constant *E* for NaCl-MgCl$_2$-H$_2$O and NaCl-Na$_2$SO$_4$-H$_2$O, but smallest at constant *I* for NaCl-SrCl$_2$-H$_2$O. The overall standard deviations are in **Table 1**. Still earlier, based on data in Rush's compilation **[6]**, we found in 1974 that the mixing term was smaller for constant *I* at three compositions of NaCl-LaCl$_3$-H$_2$O, whereas for two compositions of NaCl-CaCl$_2$-H$_2$O and one of NaCl-BaCl$_2$-H$_2$O the mixing terms were smaller for constant E.

As noted earlier, it is not necessary to use Scatchard's choice of equations to fit the binaries. The choice of concentration function to represent the binary ϕ_i^0 and $\ln \gamma_i^0$ can be the choice that gives the best fit to each binary system data with the minimum of parameters and minimum cycling of residuals. This means, for example, that Pitzer's equations may be appropriate for both binaries **[49]**, or Pitzer's equations for one binary and a polynomial in $I^{1/2}$ for the other. We note that the derivative of the binary Pitzer equation for a 2-2 salt is given in Miller et al. **[50]** Appendix I, and can be specialized for other than 2-2 and 3-3 valence types simply by setting $\beta^{(2)}$ equal to zero.

In general, the binary evaluation strategy that gives the smallest overall deviations from the ternary data is important because the mixing terms will be fewer in number and will provide a better fit. Consequently, the derivatives will also have smaller errors, and the $(L_{ij})_0$ obtained both from them and the diffusion coefficients will be more reliable.

However, at high concentrations, a poorer binary approximation may actually be better, with the mixing coefficients compensating for the larger deviations. This situation arises when the concentration type in the BES exceeds the solubility of the least soluble or the lowest valence-type electrolyte. For given molalities of the electrolytes, the total osmolality *O* or ionic strength *I* are larger than the total equivalent concentration *E*, which in turn is larger than the total molality *m*. Consequently, the values of *O*, *I*, *E*, or *m* for a binary corresponding to that of the mixture may exceed the solubility of the binary. Therefore the equations describing the binary ϕ_i^0 and $\ln \gamma_i^0$ will be extrapolated beyond their region of validity.

For example, consider a solution of that is 0.5 mol·kg^{-1} in NaCl and 2.5 mol·kg^{-1} in MgCl$_2$. The total molality *m* equals 3.0 mol·kg^{-1}, the equivalent concentration *E*=5.5, *I*=8, and *O*=8.5. The molality m_1 of the 1-1 binary NaCl corresponding to the total value of *m*, *E*, *I* or *O* is just the total value of *m*, *E*, *I*

or O, respectively. Therefore, the last two are considerably beyond the solubility of NaCl, which is 6.16 mol·kg^{-1}. For the 2-1 MgCl$_2$, the corresponding m_2 of the binary are 3.0, 2.75, 2.667, and 2.833, respectively, and all are within the solubility of MgCl$_2$ (5.81 mol·kg^{-1}). Consequently, using constant E or m for the BES avoids the extrapolation of the binary equations for ϕ_1^0 and $\ln \gamma_1^0$ of NaCl. Then the mixture quantities must make up for the possible poorer binary approximation.

Finally, the use of constant molality or equivalents might be used to obtain the data for one of the binaries in the supersaturated region as follows. Consider a system whose total concentration (E or m) corresponds to a molality in that binary (say binary 1) that exceeds its solubility. Fit the ternary data for example at constant molality using the constant molality binary approximation up to a total molality just below the solubility of binary 1. Then assume the mixing terms can be used at higher total molalities. From the phi data for the ternary and binary, extract what must be the ϕ_1^0 at that total composition. Then use the existing ϕ_1^0 data below the solubility point plus the extracted ϕ_1^0 data above the solubility point to fit a new binary function for the ϕ_1^0 of the whole range. This concept can be tested for systems which have ϕ_i^0 in the supersaturated region.

We now turn to the *mixing term functions*.

The mixing terms must vanish as the total concentration goes to 0, and must also vanish as the composition approaches each binary. This means that if P is a concentration type, and p_i are its fractions, the coefficient of the mixing term must be of the form $p_1 p_2 P$. The rest of the mixing term can be a function of P and $(p_1 - p_2)^n$. Thus in principle, the SNE and Friedman mixing terms, although typically written as polynomials in the concentration factor I, could also be polynomials in $I^{1/2}$ or $\ln(I)$, or still other functions [51-53]. Furthermore, the concentration factor I could also be replaced by E, m, or O. Analogously, the ionic strength fractions y_i could be replaced equivalent fractions x_i, osmolality fractions h_i, or molality fractions. Each of these alternatives gives rise to different constant coefficients analogous to the Scatchard Neutral Electrolyte b_{ij}.

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Table 1. Test of Binary Evaluation Strategies

system	fraction	binary evaluation strategy	concentration range	standard error
NaCl-MgCl$_2$-H$_2$O	osmolality	I	all	0.0187
"	"	E	"	0.0055
"	"	I	I<6.0	0.0144
"	"	E	"	0.0051
NaCl-SrCl$_2$-H$_2$O	osmolality	I		0.0072
"	"	E		0.0120
NaCl-Na$_2$SO$_4$-H$_2$O	osmolality	I	I<10	0.0233
	"	E	"	0.0038

Appendix. Useful Formulas

The coefficient of the mixing term for ϕ in eq 3 (the []) can be written in several ways:

$$\frac{z_1 z_2 y_1 y_2}{2(z_2 y_1 + z_1 y_2)} = \frac{z_1 z_2 h_1 h_2}{2(z_1 h_1 + z_2 h_2)} = \frac{y_1 y_2 I}{(r_1 m_1 + r_2 m_2)} = \frac{y_1 y_2 I}{O} \tag{A1}$$

Other formulas:

$$I = \frac{(r_1 z_1 m_1 + r_2 z_2 m_2)}{2} = I_1 + I_2 \tag{A2}$$

$$m_i = \frac{2 y_i I}{r_i z_i} \tag{A3}$$

$$\left(\frac{\partial I}{\partial m_j}\right)_{m_{k \neq j}} = \frac{r_j z_j}{2} \tag{A4}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial m_j}\right)_{m_{k \neq j}} = \left(\frac{\partial \ln \gamma_i}{\partial I}\right)\left(\frac{\partial I}{\partial m_j}\right)_{m_{k \neq j}} \tag{A5}$$

$$\left(\frac{\partial \ln \gamma_i^0}{\partial m_j}\right)_{m_{k \neq j}} = \left(\frac{\partial \ln \gamma_i^0}{\partial m}\right) \qquad \text{evaluated at } m = \frac{2 I}{r_i z_i} \tag{A6}$$

$$\left(\frac{\partial \phi_i^0}{\partial m_j}\right)_{m_{k \neq j}} = \left(\frac{\partial \phi_i^0}{\partial m}\right) \qquad \text{evaluated at } m = \frac{2 I}{r_i z_i} \tag{A7}$$

$$\left(\frac{\partial y_i}{\partial m_j}\right)_{m_{k}, k \neq j} = \frac{(2 \delta_{ij} - 1) y_1 y_2}{m_j} = \frac{(2 \delta_{ij} - 1) r_j z_j (1 - y_j)}{2 I} \tag{A8}$$

$$\frac{d\phi_i^0}{dm} = \frac{d \ln \gamma_i^0}{dm} - \frac{(\phi_i^0 - 1)}{m} \qquad \text{evaluated at } m = \frac{2 I}{r_i z_i} \tag{A9}$$

$$(y_1 - y_2) = (1 - 2 y_2) = (2 y_1 - 1) \tag{A10}$$