Improvement of the Zdanovskii−Stokes−Robinson Model for Mixtures Containing Solutes of Different Charge Types

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The Zdanovskii−Stokes−Robinson (ZSR) relationship [Stokes and Robinson (*J. Phys. Chem.* **1966**, *70*, 2126−2130)] enables the solvent content of a liquid mixture to be estimated, for a specified solvent activity, from data for pure solutions of each of the individual solutes. There is an analogous relationship for the activity coefficients of the solutes. The method has been shown to be exact, in the limit of extreme dilution, only for mixtures containing either all uncharged (neutral) solutes or electrolytes all of the same charge type, and in practice it is found to be most accurate for such mixtures. Here we derive an addition to the ZSR equations which removes this limitation by incorporating simple Debye−Hückel terms into the equations for solvent mass and solute activity coefficients. This addition, in its simplest form, does not involve any new fitted parameters or require any further thermodynamic information. The relationship is general, and not limited to particular Debye−Hückel expressions. Application of the revised model to activity and osmotic coefficient data for the system NaCl−Na_2SO_4−H_2O at 298.15 K shows that errors are reduced, compared to predictions of the standard model, by up to a factor of 2. Solubilities of NaCl(cr), $Na_2SO_4\cdot10H_2O$(cr), and Na_2SO_4(cr) in that system are similarly better predicted. Activity coefficients of uncharged solutes in salt solutions calculated using the revised model are now largely consistent with the empirically observed Setchenow relationship.

1. Introduction

The Zdanovskii−Stokes−Robinson (ZSR) relationship, or linear isopiestic relation, enables the solvent content of a liquid mixture to be estimated, for a specified solvent activity, from data for pure solutions of the individual solutes. This approximate relationship was first discovered empirically by Zdanovskii[1] and later derived independently by Stokes and Robinson.[2] Some of the underlying theory has been reviewed by Frolov,[3] and other recent studies include a number of practical applications.[4−7] The ZSR relationship has also been applied to the estimation of volumetric and thermal properties of mixtures,[8,9] the speed of sound,[10] and freezing point depression.[11] In addition to the expression for solvent content, corresponding ZSR equations exist for solute activity coefficients,[2] and the method has been extended to include ternary (two solute, single solvent) mixture parameters whose values are determined from experimental data.[12−14] Clegg et al.[14] have demonstrated the application of the extended model to reciprocal salt and other systems, and have also derived expressions for cases in which a subset of solutes within a mixture have their osmotic and activity coefficients described by some other model within the overall ZSR expression.

Solution water content (hence osmotic coefficient) and solute activity coefficients predicted by the ZSR relationship are least accurate for aqueous mixtures containing electrolytes of different charge types and for mixtures containing both electrolytes and nonelectrolytes. In the latter case, for example, predicted activity coefficients of the nonelectrolyte in salt solutions are not consistent with the Setchenow relationship.[14,15] This represents a significant limitation in the practical application of the model. These observations are consistent with the analysis of Mikhailov[16] who showed that, for extremely dilute solutions, the ZSR relationship is exact only for mixtures of electrolytes of the same charge type, or for mixtures of nonelectrolytes.

In this work we derive simple correction terms, not involving any new parameters, for ZSR expressions for both solvent content and solute activity coefficients in indefinitely complex mixtures. Expressions for the terms corresponding to the different model cases treated by Clegg et al.[14] are given. The effects of the new terms are explored in a number of examples, including osmotic coefficients and salt solubilities in NaCl−Na_2SO_4−H_2O at 298.15 K and activity coefficients of uncharged solutes in aqueous salt solutions.

2. Theory

2.1. Solvent Properties. The water activity (a_w) and osmotic coefficient (ϕ) of an aqueous solution are related by the standard equation[17]

$$\ln(a_w) = -M_w\phi\sum_i m_i \qquad (1)$$

where M_w (0.0180152 kg) is the molar mass of water, and m_i is the molality of each individual solute species (ion or uncharged molecule) in the mixture. The ZSR relationship is expressed in terms of the properties of solutions of individual salts, or uncharged molecules. For a mixture containing just two solutes, 1 and 2, we have

$$1/m = x_1/m_1^\circ + x_2/m_2^\circ \qquad (2)$$

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where m is the total molality of the solutes in the mixture, and m_1° and m_2° are the molalities of pure solutions of solutes 1 and 2, respectively, at the solvent activity of the mixture. Quantity x_1 is the mole fraction $n_1/(n_1 + n_2)$, and similarly for x_2, where n_1 and n_2 are the numbers of moles of each species present. For this system of two solutes, eq 1 can be written as

$$\ln(a_\mathrm{w}) = -M_\mathrm{w}(m_1\nu_1 + m_2\nu_2)\phi \tag{3a}$$

or

$$\ln(a_\mathrm{w}) = -M_\mathrm{w}m(x_1\nu_1 + x_2\nu_2)\phi \tag{3b}$$

where ν_i is the number of moles of particles produced by the dissociation in water of solute i. For example, ν_i would be 2 for the salt NaCl, 3 for Na_2SO_4, and unity for a nondissociating molecule. Rearranging eq 3b, we obtain

$$1/m = -(M_\mathrm{w}/\ln(a_\mathrm{w}))(x_1\nu_1 + x_2\nu_2)\phi \tag{4}$$

and for pure aqueous solutions of each solute i:

$$1/m_i^\circ = -(M_\mathrm{w}/\ln(a_\mathrm{w}))\nu_i\phi_i^\circ \tag{5}$$

where superscript ° indicates that the quantity is for a pure aqueous solution of i at the same water activity as the mixture. Finally, multiplying eq 5 for each solute by x_i and substituting into eq 4 yield

$$1/m = x_1/m_1^\circ + x_2/m_2^\circ - (M_\mathrm{w}/\ln(a_\mathrm{w}))[(x_1\nu_1 + x_2\nu_2)\phi - x_1\nu_1\phi_1^\circ - x_2\nu_2\phi_2^\circ] \tag{6}$$

The ZSR relationship, eq 2, is obtained from eq 6 by assuming that the final term in $1/\ln(a_\mathrm{w})$ is negligible—hence $(x_1\nu_1 + x_2\nu_2)\phi \approx (x_1\nu_1\phi_1^\circ + x_2\nu_2\phi_2^\circ)$. Mikhailov[16] has shown that this is indeed true for very dilute solutions containing solutes of the same charge type, for which $\phi \approx \phi_1^\circ \approx \phi_2^\circ$ at constant water activity. This can be understood intuitively, as for salts in such solutions the osmotic coefficients will all have values close to the Debye−Hückel limiting slope (which is a function of ionic strength only), or in the case of a mixture of uncharged solutes the osmotic coefficients will all be very close to unity. However, this is not true for mixtures containing solutes of different charge types (i.e., 1:1, 2:1, and 2:2 electrolytes, etc.), and this can have a significant effect on solute activity coefficients estimated using ZSR.

We have found that a worthwhile improvement in the ZSR relationship can be obtained by approximating ϕ, ϕ_1°, and ϕ_2° in eq 6 by molality-based expressions for the Debye−Hückel limiting law. The desirable features of such expressions are, first, that they reproduce satisfactorily the osmotic coefficients of both pure electrolyte solutions and mixtures at high dilutions, including the correct limiting law behavior as m tends to zero. Second, at moderate to high concentrations the calculated osmotic coefficient should tend to some small, approximately constant, value that is greater than zero. This is so that the principal influence of the term is restricted to very high water activities. Third, there should be a corresponding analytical expression for the Debye−Hückel contribution to the activity coefficient of each solute. The Pitzer activity coefficient model[18] contains a suitable expression:

$$\phi = 1 - (2/\sum_i m_i)A^\phi I^{3/2}/(1 + b\sqrt{I}) \tag{7}$$

where the summation is as in eq 1, A^ϕ is the molal Debye−Hückel coefficient (0.3915 at 298.15 K),[19] b is a constant that usually takes the value 1.2, and I is the molal ionic strength of the mixture. This is given by $I = 0.5\sum_i m_i z_i^2$, where z_i is the charge on ion i. The value of an osmotic coefficient calculated from eq 7 is the same for all solutions containing only electrolyte(s) of the same charge type at the same water activity, and is unity for all solutions containing only uncharged solute(s). For these two cases the terms in square brackets in eq 6 cancel, and the ZSR relationship reverts to its normal form. Notice that eq 7 does not contain any solute-specific parameters, so that this extension to the ZSR expression does not require any additional thermodynamic information. However, other choices are possible. For example, eq 7 can be extended with an additional term $+\ \beta_{ca}^{(1)}\exp(-\alpha I^{1/2})$, where α is a constant (a value of 2.0 is often used) and $\beta_{ca}^{(1)}$ is a temperature-dependent parameter specific to each electrolyte ca.[18] The effect of this term is confined to dilute solutions. An alternative, and probably more flexible, equation can be obtained by replacing the single value of b in eq 7 by an individual constant b_ca for each electrolyte. The development of this equation is described in the Appendix.

Figure 1 shows osmotic coefficients (ϕ°) for aqueous solutions of eight 1:1 electrolytes, together with values calculated using eq 7 for a range of parameter b. If only a single value is to be adopted then $b = 1.2$ is satisfactory. However, the plots also suggest that some optimization, i.e., individual values of b_ca, may be worthwhile to improve agreement between observed ϕ° and eq 7 at very low molality.

A similar comparison for some 1:2 and 2:1 electrolytes is shown in Figure 2. Here, calculated osmotic coefficients for b equal to 1.2 fall below the true ϕ° of most of the salts, and values of 2.0 to 3.0 would yield better agreement. We also note that for higher charge types such as 2:2 electrolytes it is essential to adopt a value of b in eq 7 greater than 1.2, to avoid negative osmotic coefficients being predicted at high molalities.

Denoting osmotic coefficients calculated using eq 7 with a prime, we generalize the modified ZSR relationship by writing eq 6 for an indefinite number of solutes s:

$$1/m = \sum_s x_s/m_s^\circ - (M_\mathrm{w}/\ln(a_\mathrm{w}))\sum_s x_s\nu_s(\phi' - \phi_s^{\circ\prime}) \tag{8}$$

Multiplying through by the total moles of solutes ($\sum_s n_s$) in the mixture, eq 8 can be rewritten for the total mass of water (W_total, in kg):

$$W_\mathrm{total} = \sum_s w_s^\circ + (W'_\mathrm{total} - \sum_s w_s^{\circ\prime}) \tag{9}$$

where w_s° is the mass of water associated with n_s moles of solute s in a pure solution of s at the water activity of the mixture, and $w_s^{\circ\prime}$ is the same quantity but calculated using eq 7 to obtain the Debye−Hückel approximation to the osmotic coefficient $\phi_s^{\circ\prime}$. Similarly W'_total is the approximation to the total mass of water in the mixture calculated using eq 7 to obtain ϕ'.

Equation 9 can be compared to eq 7 of Clegg et al.[14] which, in addition to the first term in eq 9, contains a summation involving solute−solute mixture parameters. That reference should be consulted for details.

2.2. Solute Activity Coefficients. Values of the molal activity coefficient, or mean activity coefficient in the case of electrolytes, that are thermodynamically consistent with eq 9 are obtained by applying the McKay−Perring equation.[20] For a

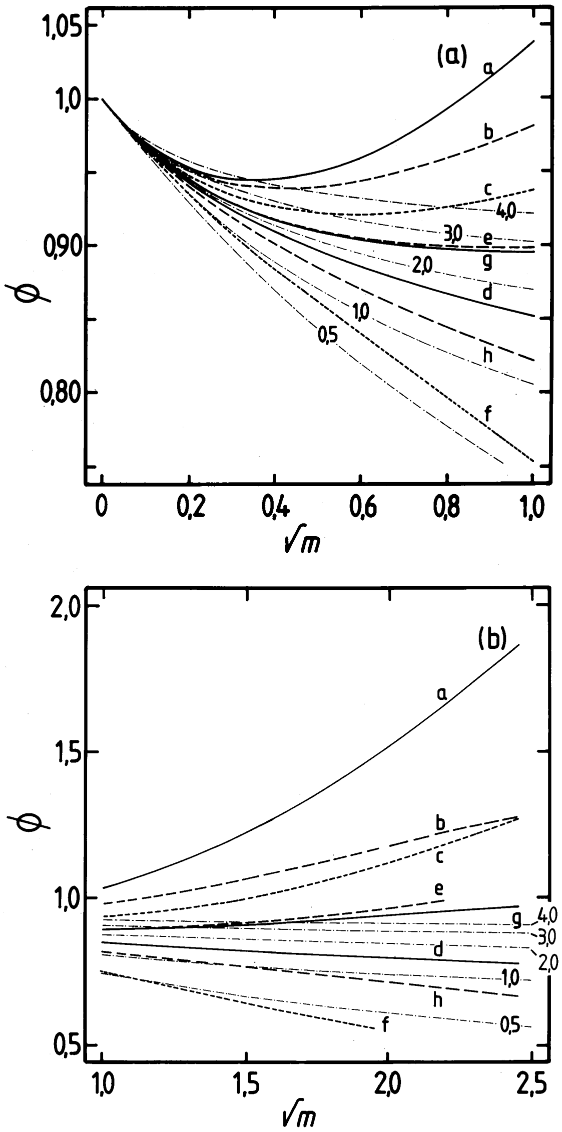

Figure 1. Molal osmotic coefficients (ϕ) of aqueous solutions of eight 1:1 electrolytes at 298.15 K, compared with values calculated using the Debye−Hückel expression (eq 7) for different values of the parameter *b*. (a) For $\sqrt{m} \leq 1.0$ mol$^{1/2}$ kg$^{-1/2}$, where *m* is the molality of the electrolyte. (b) For higher $\sqrt{m}$. Solid, dashed, and dotted lines: a, HCl(aq); b, HNO$_3$(aq); c, NaCl(aq); d, NaNO$_3$(aq); e, KCl(aq); f, KNO$_3$(aq); g, NH$_4$Cl(aq); h, NH$_4$NO$_3$(aq). Fine dash−dot lines: calculated using eq 7 with values of *b* from 0.5 to 4.0 as shown on the plot.

solution containing two solutes this is

$$\ln(\gamma_1) = \ln(\gamma_1^\circ) + \ln(k_1 m_1^\circ/m^*) + \left(\frac{1}{M_w}\right)\left(\frac{k_1}{\nu_1}\right) \times \int_0^{\ln a_w} \left\{ -\left(\frac{1}{m^{*2}}\right)\left(\frac{\partial m^*}{\partial \ln \mathbf{r}_2}\right)_{a_w} - \frac{1}{m^*} + \frac{1}{k_1 m_1^\circ} \right\} \mathrm{d}\ln(a_w) \quad (10)$$

where γ_1 is the activity coefficient of solute 1 in the mixture, γ_1° is its activity coefficient in a pure aqueous solution of 1 at the water activity of the mixture, k_1 is an arbitrary proportionality constant for solute 1 (here set the same as ν_1), and m^* is equal to ($k_1m_1 + k_2m_2$) or ($\nu_1m_1 + \nu_2m_2$). The ratio $\mathbf{r}_2$ is equal to ν_2m_2/m^*, or $1 - \mathbf{r}_1$ where $\mathbf{r}_1 = \nu_1m_1/m^*$. Note that these ratios can be expressed in terms of the moles of each solute in the mixture, and so do not vary with water activity. Equation 10 can now be rewritten in the form that is used here:

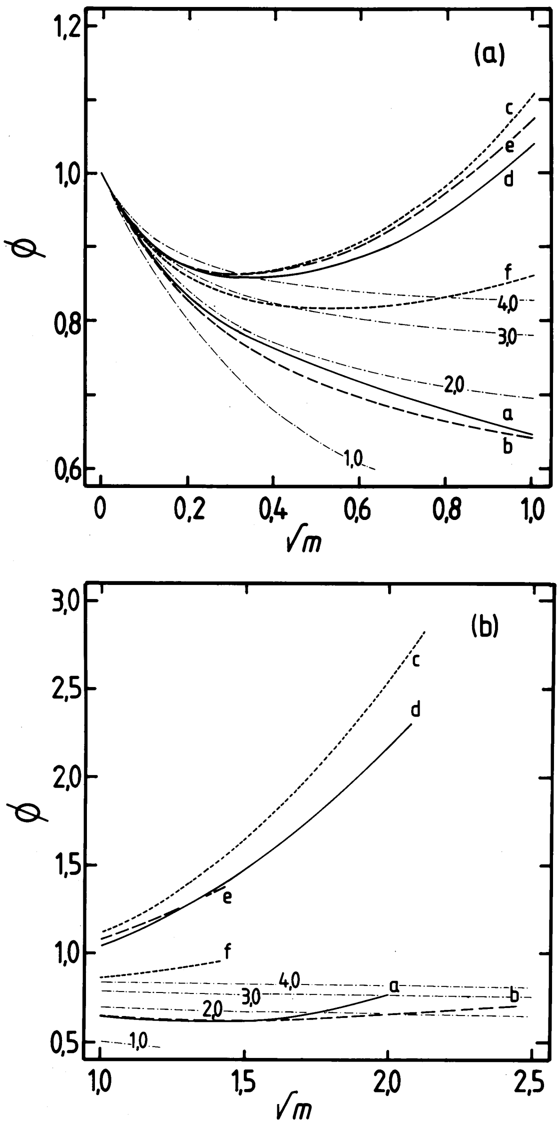

Figure 2. Molal osmotic coefficients (ϕ) of aqueous solutions of six 2:1 and 1:2 electrolytes at 298.15 K, compared with values calculated using the Debye−Hückel expression (eq 7) for different values of the parameter *b*. (a) For $\sqrt{m} \leq 1.0$ mol$^{1/2}$ kg$^{-1/2}$, where *m* is the molality of the electrolyte. (b) For higher $\sqrt{m}$. Solid, dashed, and dotted lines: a, Na$_2$SO$_4$(aq); b, (NH$_4$)$_2$SO$_4$(aq); c, MgCl$_2$(aq); d, CaCl$_2$(aq); e, Mg(NO$_3$)$_2$(aq); f, Ca(NO$_3$)$_2$(aq). Fine dash−dot lines: calculated using eq 7 with values of *b* from 1.0 to 4.0 as shown on the plot.

$$\ln(\gamma_1) = \ln(\gamma_1^\circ) + \ln(k_1 m_1^\circ/m^*) + \left(\frac{1}{M_w}\right)\left(\frac{k_1}{\nu_1}\right) \times \int_0^{\ln a_w} \left\{ \mathbf{r}_2 \left(\frac{\partial 1/m^*}{\partial \mathbf{r}_2}\right)_{a_w} - \frac{1}{m^*} + \frac{1}{k_1 m_1^\circ} \right\} \mathrm{d}\ln(a_w) \quad (11)$$

For the standard ZSR expression for the relationship between solution water content and solvent activity (eq 2) the integral above is zero, and the activity coefficient of solute 1 equal to the first two terms in eq 11.[2,14]

Next, we obtain expressions for the terms in the McKay−Perring integral corresponding to the extended ZSR relationship. Equation 6 is first rewritten in terms of osmotic coefficients:

$$1/m = -(M_w/\ln(a_w))[x_1\nu_1\phi_1^\circ + x_2\nu_2\phi_2^\circ + (x_1\nu_1 + x_2\nu_2)\phi' - x_1\nu_1\phi_1^{\circ\prime} - x_2\nu_2\phi_2^{\circ\prime}] \quad (12)$$

Multiplying through by m/m^* and recognizing that $\mathbf{r}_i = \nu_i m_i/(\nu_1 m_1 + \nu_2 m_2) = \nu_i m_i/m^*$, and $\mathbf{r}_1 = 1 - \mathbf{r}_2$, eq 12 becomes

$$l/m^* = -(M_\mathrm{w}/\ln(a_\mathrm{w}))[(1 - \mathbf{r}_2)\phi_1^\circ + \mathbf{r}_2\phi_2^\circ + \phi' - (1 - \mathbf{r}_2)\phi_1^{\circ\prime} - \mathbf{r}_2\phi_2^{\circ\prime}] \quad (13)$$

Differentiating eq 13 with respect to $\mathbf{r}_2$ at constant water activity yields

$$\left(\frac{\partial 1/m^*}{\partial \mathbf{r}_2}\right)_{a_\mathrm{w}} = -\left(\frac{M_\mathrm{w}}{\ln(a_\mathrm{w})}\right)\left[-\phi_1^\circ + \phi_2^\circ + \left(\frac{\partial \phi'}{\partial \mathbf{r}_2}\right)_{a_\mathrm{w}} + \phi_1^{\circ\prime} - \phi_2^{\circ\prime}\right] \quad (14)$$

Finally, inserting eq 13 and eq 14 into the McKay−Perring equation, and substituting $-(M_\mathrm{w}/\ln(a_\mathrm{w}))\phi_1^\circ$ for $1/k_1 m_1^\circ$, yields

$$\ln(\gamma_1) = \ln(\gamma_1^\circ) + \ln(k_1 m_1^\circ/m^*) + \frac{k_1}{\nu_1}\int_\mathrm{o}^{\ln(a_\mathrm{w})} \left\{\mathbf{r}_2\left(\frac{\partial \phi'}{\partial \mathbf{r}_2}\right)_{a_\mathrm{w}} + \phi' - \phi_1^{\circ\prime}\right\} \frac{\mathrm{d}\ln(a_\mathrm{w})}{\ln(a_\mathrm{w})} \quad (15)$$

As expected, the only terms remaining within the integral in eq 15 involve the extension to the ZSR expression. The value of the integral can be obtained by considering a solution containing the same two solutes, whose osmotic coefficient (ϕ') is given by eq 7. For this solution the McKay−Perring equation yields

$$\ln(\gamma_1') = \ln(\gamma_1^{\circ\prime}) + \ln(k_1 m_1^{\circ\prime}/m^{*\prime}) + (1/M_\mathrm{w})\frac{k_1}{\nu_1}\int_\mathrm{o}^{\ln(a_\mathrm{w})} \left\{\mathbf{r}_2\left(\frac{\partial 1/m^{*\prime}}{\partial \mathbf{r}_2}\right)_{a_\mathrm{w}} - \frac{1}{m^{*\prime}} + \frac{1}{k_1 m_1^{\circ\prime}}\right\} \mathrm{d}\ln(a_\mathrm{w}) \quad (16)$$

where the prime indicates properties calculated using the simplified Debye−Hückel expression. In this case $l/m^{*\prime}$ is equal to $-(M_\mathrm{w}/\ln(a_\mathrm{w}))\phi'$ and $1/k_1 m_1^{\circ\prime}$ is equal to $-(M_\mathrm{w}/\ln(a_\mathrm{w}))\phi_1^{\circ\prime}$, so that

$$\ln(\gamma_1^\circ) = \ln(\gamma_1^{\circ\prime}) + \ln(k_1 m_1^{\circ\prime}/m^{*\prime}) + \frac{k_1}{\nu_1}\int_\mathrm{o}^{\ln(a_\mathrm{w})} \left\{\mathbf{r}_2\left(\frac{\partial \phi'}{\partial \mathbf{r}_2}\right)_{a_\mathrm{w}} + \phi' - \phi_1^{\circ\prime}\right\} \frac{\mathrm{d}\ln(a_\mathrm{w})}{\ln(a_\mathrm{w})} \quad (17)$$

Clearly the integral in eq 17 is identical to that in eq 15. The values of both $\ln(\gamma_1^\circ)$ and $\ln(\gamma_1^{\circ\prime})$ can be calculated directly from the expression for solute activity coefficients that corresponds to eq 7. Where solute 1 is an electrolyte $\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}$ then we have[18]

$$\ln(\gamma_1') = -|z_\mathrm{M} z_\mathrm{X}|\mathrm{A}^\phi[\sqrt{I}/(1 + b\sqrt{I}) + (2/b)\ln(1 + b\sqrt{I})] \quad (18)$$

where I is the ionic strength of the solution mixture at the specified water activity, calculated using eq 7 (for ϕ') and eq 1. The value of $\ln(\gamma_1^{\circ\prime})$ is also calculated using eq 18, except that in this case the ionic strength is that of a pure aqueous solution of $\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}$ at the water activity of the mixture. For solutions containing only neutral (uncharged) solutes ϕ' is equal to unity and both $\ln(\gamma_1')$ and $\ln(\gamma_1^{\circ\prime})$ are equal to zero under all conditions.

Knowing both $\ln(\gamma_1')$ and $\ln(\gamma_1^{\circ\prime})$ from eq 18 and also the terms in solute amounts and molalities in eq 17, the value of the integral in eq 15 and eq 17 is obtained just by subtracting the first two terms on the right-hand side of eq 17 from $\ln(\gamma_1')$ on the left. Incorporating the result into eq 15, and rewriting in terms of water amounts, gives the complete expression for $\ln(\gamma_1)$ in a two-solute system for the extended model:

$$\ln(\gamma_1) = \ln(\gamma_1^\circ) + \ln(\gamma_1'/\gamma_1^{\circ\prime}) + \ln\left(\frac{W_\mathrm{total}}{W'_\mathrm{total}}\frac{w_1^{\circ\prime}}{w_1^\circ}\right) \quad (19)$$

Note that the final term in eq 19 can also be written in terms of molalities; hence, w_1° and $w_1^{\circ\prime}$ in this equation are calculated for an arbitrary (though the same) amount of solute 1, rather than the amount actually present in the mixture. The distinction is important where eq 19 is being used to calculate the activity coefficient of a solute at trace (i.e., zero) molality in a mixture, for which $w_1^{\circ\prime}/w_1^\circ$ (equivalent to $m_1^\circ/m_1^{\circ\prime}$) has a finite value. This consideration also applies to other activity coefficient equations derived below.

In mixture of solutes that are all of the same charge type the second term in eq 19 is equal to zero ($\gamma_1' = \gamma_1^{\circ\prime}$) since in such a solution the activity coefficients given by the Debye−Hückel expression in eq 18 depend on the ionic strength only. This would not be the case, though, if different values b_ca were being used.

The McKay−Perring equation for the activity coefficient of solute 1 in a two solute mixture can be applied straightforwardly to a multicomponent mixture by treating the other $n - 1$ solutes ($n = 2, 3, ...$) as a single combined "solute" in which all they are present in fixed ratios to one another. Repeating the above derivation on this basis leaves eq 19 unchanged, thus it can be applied to *all* solution mixtures.

2.3. Combining Models within ZSR. In many practical applications osmotic and activity coefficients of one or more subgroups of solutes may be either known directly or calculated by some other method than ZSR. For example, the properties of the electrolyte components of a mixture might be estimated with an ion interaction model such as that of Pitzer,[18] while the properties of the uncharged solutes are either determined using another model such as UNIFAC[21] (which is then incorporated into the ZSR scheme) or are treated individually. It is desirable to incorporate these submodels into the overall ZSR approach in order to retain as much accuracy as possible in the prediction of osmotic and activity coefficients in the mixture. In the derivation below we follow Clegg et al.[14] in a similar analysis of the use of solute−solute mixture parameters within ZSR.

First consider a solution containing a number of solutes s, subdivided into two groups r and q. The properties of mixtures containing only solutes r can be calculated directly by some arbitrary model, whose predictions we wish to incorporate into the ZSR framework, while each solute q is treated as an individual component. The expression for the total mass of water in the system is

$$W_\mathrm{total} = w^{\circ,r} + \sum_q w_q^\circ + (W'_\mathrm{total} - w^{\circ,r\prime} - \sum_q w_q^{\circ\prime}) \quad (20)$$

where $w^{\circ,r}$ is the mass of water associated with the group of solutes r in the mixture, and calculated using the arbitrary model referred to above, and w_q° is the mass of water associated with each individual solute q at the water activity of the mixture. The meaning of W'_total is as given earlier, $w^{\circ,r\prime}$ is also calculated using eq 7 for the osmotic coefficient, but only for the group of solutes r, and each $w_q^{\circ\prime}$ is calculated using eq 7 for pure aqueous solutions of each individual solute q.

The expression for the activity coefficient of solute Q, a member of group q, is obtained as follows. Assuming, for simplicity, that solute group q has two solutes q_1 and q_2, the extended ZSR expression for the water content of the solution is

$$1/m = x_r/m_r^\circ + x_{q_1}/m_{q_1}^\circ + x_{q_2}/m_{q_2}^\circ - (M_\mathrm{w}/\ln(a_\mathrm{w}))[(x_r\nu_r + x_{q_1}\nu_{q_1} + x_{q_2}\nu_{q_2})\phi' - x_r\nu_r\phi_r^{\circ\prime} - x_{q_1}\nu_{q_1}\phi_{q_1}^{\circ\prime} - x_{q_2}\nu_{q_2}\phi_{q_2}^{\circ\prime}] \quad (21)$$

where m_r° is the total molality of all solutes r, in a solution containing only these solutes, at the water activity of the mixture. Osmotic coefficient $\phi_r^{\circ\prime}$ is calculated using eq 7, also for a solution containing solutes r only. Note that the use of subscript r on its own refers to the whole group of solutes r together. Quantities x_r and m_r are defined below:

$$x_r = (\sum_r n_r)/\sum_s n_s \quad (22)$$

$$\nu_r = (\sum_r n_r\nu_r)/\sum_r n_r \quad (23)$$

The expression for $\ln(\gamma_\mathrm{Q})$ is obtained first by converting the three initial terms in eq 21 to osmotic coefficients, and multiplying through by m/m^* to get the expression for $1/m^*$:

$$1/m^* = -(M_\mathrm{w}/\ln(a_\mathrm{w}))[\mathbf{r}_r\phi_r^\circ + \mathbf{r}_{q_1}\phi_{q_1}^\circ + \mathbf{r}_{q_2}\phi_{q_2}^\circ + \phi' - \mathbf{r}_r\phi_r^{\circ\prime} - \mathbf{r}_{q_1}\phi_{q_1}^{\circ\prime} - \mathbf{r}_{q_2}\phi_{q_2}^{\circ\prime}] \quad (24)$$

where

$$\mathbf{r}_r = (\sum_r n_r\nu_r)/\sum_s n_s\nu_s \quad (25)$$

$$\mathbf{r}_{q_i} = (n_{q_i}\nu_{q_i})/\sum_s n_s\nu_s \quad (26)$$

Assuming that solute Q is q_1, then the differential of $1/m^*$ in the McKay−Perring equation is with respect to the ratio $\mathbf{r}$ for the combined solutes r and q_2 (i.e., all solutes except the selected q_1). Defining $\mathbf{r}_\mathrm{c} = \mathbf{r}_r + \mathbf{r}_{q_2}$ for these combined solutes, eq 24 can be written as

$$1/m^* = -(M_\mathrm{w}/\ln(a_\mathrm{w}))[\mathbf{r}_r\phi_r^\circ + (1 - \mathbf{r}_\mathrm{c})\phi_{q_1}^\circ + \mathbf{r}_{q_2}\phi_{q_2}^\circ + \phi' - \mathbf{r}_r\phi_r^{\circ\prime} - (1 - \mathbf{r}_\mathrm{c})\phi_{q_1}^{\circ\prime} - \mathbf{r}_{q_2}\phi_{q_2}^{\circ\prime}] \quad (27)$$

The expression for $\mathbf{r}_\mathrm{c}[(\partial\, 1/m^*)/\partial\mathbf{r}_\mathrm{c}]_{a_\mathrm{w}}$ can be obtained straightforwardly from eq 27, recognizing that $\mathrm{d}\mathbf{r}_r/\mathrm{d}\mathbf{r}_\mathrm{c} = \mathbf{r}_r/\mathbf{r}_\mathrm{c}$, and $\mathrm{d}\mathbf{r}_{q_2}/\mathrm{d}\mathbf{r}_\mathrm{c} = \mathbf{r}_{q_2}/\mathbf{r}_\mathrm{c}$:

$$\mathbf{r}_\mathrm{c}\left(\frac{\partial 1/m^*}{\partial\mathbf{r}_\mathrm{c}}\right)_{a_\mathrm{w}} = -\left(\frac{M_\mathrm{w}}{\ln(a_\mathrm{w})}\right)\left[\mathbf{r}_r\phi_r^\circ - \mathbf{r}_\mathrm{c}\phi_{q_1}^\circ + \mathbf{r}_{q_2}\phi_{q_2}^\circ + \mathbf{r}_\mathrm{c}\left(\frac{\partial\phi'}{\partial\mathbf{r}_\mathrm{c}}\right)_{a_\mathrm{w}} - \mathbf{r}_r\phi_r^{\circ\prime} + \mathbf{r}_\mathrm{c}\phi_{q_1}^{\circ\prime} - \mathbf{r}_{q_2}\phi_{q_2}^{\circ\prime}\right] \quad (28)$$

Substituting eq 27 and eq 28 into the McKay−Perring expression in the same way as for the two-solute case described earlier yields essentially the result in eq 16, but with solute Q replacing solute 1 and $\mathbf{r}_\mathrm{c}$ replacing $\mathbf{r}_2$. The value of the integral is obtained in the same way as before, yielding the following final result:

$$\ln(\gamma_\mathrm{Q}) = \ln(\gamma_\mathrm{Q}^\circ) + \ln(\gamma_\mathrm{Q}'/\gamma_\mathrm{Q}^{\circ\prime}) + \ln\left(\frac{W_\mathrm{total}}{W_\mathrm{total}'}\frac{w_\mathrm{Q}^{\circ\prime}}{w_\mathrm{Q}^\circ}\right) \quad (29)$$

This expression is similar to eq 19. The only difference is that the total water content of the system (W_total) is calculated using eq 20 rather than eq 9.

Second, we determine the equation for the activity coefficient of a solute R from group r. The total amount of water associated with the mixture is given by eq 20, and $1/m^*$ by eq 24. Assuming, for simplicity, that group r contains two solutes r_1 and r_2, and that the selected solute R is r_1, then we can define $\mathbf{r}_\mathrm{c} = \mathbf{r}_{r_2} + \mathbf{r}_{q_1} + \mathbf{r}_{q_2}$. The osmotic coefficients ϕ', ϕ_r°, and $\phi_r^{\circ\prime}$ in eq 24 all have nonzero differentials with respect to $\mathbf{r}_\mathrm{c}$, leading to a relatively lengthy expression for $(\partial 1/m^*)/\partial\mathbf{r}_\mathrm{c}$ and more complex integral. The complete derivation of the equation for $\ln(\gamma_\mathrm{R})$ from eq 20, eq 24, and the McKay−Perring equation is given in the Supporting Information to this paper. Below we give only the final result:

$$\ln(\gamma_\mathrm{R}) = \ln(\gamma_\mathrm{R}^{\circ,r}) + \ln(\gamma_\mathrm{R}'/\gamma_\mathrm{R}^{\circ,r\prime}) + \ln\left(\frac{W_\mathrm{total}}{W_\mathrm{total}'}\frac{w^{\circ,r\prime}}{w^{\circ,r}}\right) \quad (30)$$

This expression differs from that for $\ln(\gamma_\mathrm{Q})$ in that the water amounts w° in the final term are those associated with the entire group of solutes r rather than just the solute of interest. Also, the activity coefficient $\gamma_\mathrm{R}^{\circ,r}$ is the value (calculated by the arbitrary model that is being included in the ZSR scheme), for a solution containing only solutes r. The activity coefficient $\gamma_\mathrm{R}^{\circ,r\prime}$ is determined using eq 18, also for a solution containing only solutes r.

2.4. ZSR Model with Mixture Parameters. Clegg et al.[14] have recently derived expressions for additional terms to the ZSR equations for mixture water content and solute activity coefficients that take into account interactions between pairs of solutes. The expressions are based upon earlier work by Chen et al.[13] and in particular by Kirgintsev and Lukyanov,[12] and they include parameters whose values are obtained from experimental data that yield solute or solvent activities. The effect of using these additional terms is to increase the accuracy of model predictions in complex mixtures.

The equations derived by Clegg et al.[14] correspond to the different cases treated above, but do not of course include the extension that we have derived here. The results of both papers are straightforwardly combined by adding the mixture expressions of Clegg et al.[14] to the equations in sections 2.1−2.3 above. Thus:

$$W_\mathrm{total} = w^{\circ,r} + \sum_q w_q^\circ + (W_\mathrm{total}' - w^{\circ,r\prime} - \sum_q w_q^{\circ\prime}) + (\sum_s n_s)\sum_{s<s'}\sum x_s x_{s'}(A_{s,s'}^0 + A_{s,s'}^1 y_{s,s'} + B_{s,s'}a_\mathrm{w}) \quad (31)$$

where $A_{s,s'}^0$, $A_{s,s'}^1$ and $B_{s,s'}$ are the interaction parameters for pairs of solutes s and s', and $y_{s,s'}$ is equal to $n_{s'}/(n_s + n_{s'})$. In a mixture of a number of solutes s, all of which are treated as individual components within ZSR, the activity coefficient of a solute S is given by

$$\ln(\gamma_\mathrm{S}) = \ln(\gamma_\mathrm{S}^\circ) + \ln(\gamma_\mathrm{S}'/\gamma_\mathrm{S}^{\circ\prime}) + \ln[(W_\mathrm{total}/W_\mathrm{total}')(w_\mathrm{S}^{\circ\prime}/w_\mathrm{S}^\circ)] - (1/(M_\mathrm{w}\nu_\mathrm{S}))(1 - x_\mathrm{S})^2[(\mathbf{A}_\mathrm{S} - \mathbf{A}_\mathrm{S}')\ln(a_\mathrm{w}) - (\mathbf{B}_\mathrm{S} - \mathbf{B}_\mathrm{S}')(1 - a_\mathrm{w})] \quad (32)$$

Finally, for the cases where the solution is treated as a containing a group of solutes r, and a number of individual solutes q

$$\ln(\gamma_\mathrm{Q}) = \ln(\gamma_\mathrm{Q}^\circ) + \ln(\gamma_\mathrm{Q}'/\gamma_\mathrm{Q}^{\circ\prime}) + \ln[(W_\mathrm{total}/W_\mathrm{total}')(w_\mathrm{Q}^{\circ\prime}/w_\mathrm{Q}^\circ)] - (1/(M_w\nu_\mathrm{Q}))(1 - x_\mathrm{Q})^2[(\mathbf{A}_\mathrm{Q} - \mathbf{A}_\mathrm{Q}')\ln(a_w) - (\mathbf{B}_\mathrm{Q} - \mathbf{B}_\mathrm{Q}')(1 - a_\mathrm{w})] \quad (33)$$

$$\ln(\gamma_\mathrm{R}) = \ln(\gamma_\mathrm{R}^{\circ,r}) + \ln(\gamma_\mathrm{R}'/\gamma_\mathrm{R}^{\circ,r\prime}) + \ln[(W_\mathrm{total}/W_\mathrm{total}') \times (w^{\mathrm{o},r\prime}/w^{\mathrm{o},r})] - (1/(M_\mathrm{w}\nu_\mathrm{R}))(1 - x_\mathrm{R})^2[(\mathbf{A}_\mathrm{R} - \mathbf{A}_\mathrm{R}')\ln(a_\mathrm{w}) - (\mathbf{B}_\mathrm{R} - \mathbf{B}_\mathrm{R}')(1 - a_\mathrm{w})] \quad (34)$$

The mixture functions **A**, **A′**, **B**, and **B′** in eqs 32−34 incorporate the parameters $A^0_{s,s'}$, $A^1_{s,s'}$, and $B_{s,s'}$. The definitions of these functions are given in section 2.2 of Clegg et al.[14] and are not repeated here.

2.5. Solute Amounts in Multicomponent Electrolyte Solutions. The only further requirement for carrying out calculations for solutions containing multiple ions is a method of assigning the mixture composition in terms of electrolytes rather than ions as components, as required by the ZSR method. A mixing rule should be adopted as this cannot be done uniquely for mixtures containing >2 ions of each charge type. Some of the possible approaches are discussed by Zhong and Friedman.[22] Clegg et al.[14] and Clegg and Simonson[23] have shown that the mixing rule of Reilly and Wood[24] gives satisfactory results. The amounts of each electrolyte are determined from the numbers of equivalents of each cation and anion present ($n_c z_c$, $n_a|z_a|$). The equation for the amount of electrolyte $M_{\nu_+}X_{\nu_-}$ (n_{MX}) present in an arbitrarily complex mixture is[14]

$$n_{MX} = 2n_M n_X(z_M|z_X|/(\nu_{M(X)}\nu_{X(M)}))^{1/2}/(\sum_c n_c z_c + \sum_a n_a|z_a|) \qquad (35)$$

where $\nu_{M(X)}$ is the number of ions of cation M in one molecule of electrolyte $M_{\nu_+}X_{\nu_-}$ (and similarly for $\nu_{X(M)}$ and anion X). The summations are over all cations *c* and anions *a*.

The amount of each solute *s* present in a solution mixture is therefore as follows: for an uncharged (nondissociating) species, such as an organic molecule, n_s is simply the number of moles of that molecule that are present in the mixture; where solute *s* is an electrolyte then the amount present is calculated using eq 35.

3. Applications

3.1. NaCl—Na_2SO_4—H_2O at 298.15 K. The thermodynamic properties of this system, for which extensive data are available, have recently been critically reviewed by Rard et al.[29] Their fitted equations for osmotic and activity coefficients are used here as a reference for comparisons with both standard and extended ZSR models. Figure 3a shows the percentage differences between water masses W_{total} predicted using the standard ZSR relationship (eq 2) and the true values for a range of fixed water activities. Errors are greatest for NaCl fractions of between 0.5 and 0.6, reaching just over −2.5% for $a_w = 0.95$. Figure 3b shows the corresponding results for the extended model (eq 9) in which the value of *b* (used in eq 7 to calculate $\phi^{\circ\prime}$ and hence $w_s^{\circ\prime}$ for both salts) is fixed at 1.2. Here maximum errors only reach about −1.75%, and the magnitudes of the errors for a_w equal to 0.99 and 0.85 are reduced by a factor of 2. While these improvements appear small, they are significant when expressed in terms of osmotic coefficient which can vary steeply with electrolyte concentration particularly for water activities very close to unity (dilute solutions).

Activity coefficients of NaCl, calculated using the standard ZSR model (eq 11, but omitting the integral) and the extended model (eq 19) are compared in Figure 4. The increase in accuracy of the extended model is considerable, with predicted mean activity coefficients of trace NaCl in aqueous Na_2SO_4 being more accurate by over a factor of 2. The result is similar for activity coefficients of Na_2SO_4, and is shown in Figure 5. When calculating the activities of the solutes the mean activity coefficients are squared (NaCl) and cubed (Na_2SO_4). Consequently, the 15% error in the mean activity coefficient of Na_2SO_4 shown in Figure 5a at $x_{NaCl} \approx 1.0$ and $a_w = 0.9$ is equivalent to an error in the calculated Na_2SO_4 activity of almost 40%. It is clear from Figure 5b that this error is essentially removed by the extended model at NaCl mole fractions close to unity, and greatly reduced at lower mole fractions.

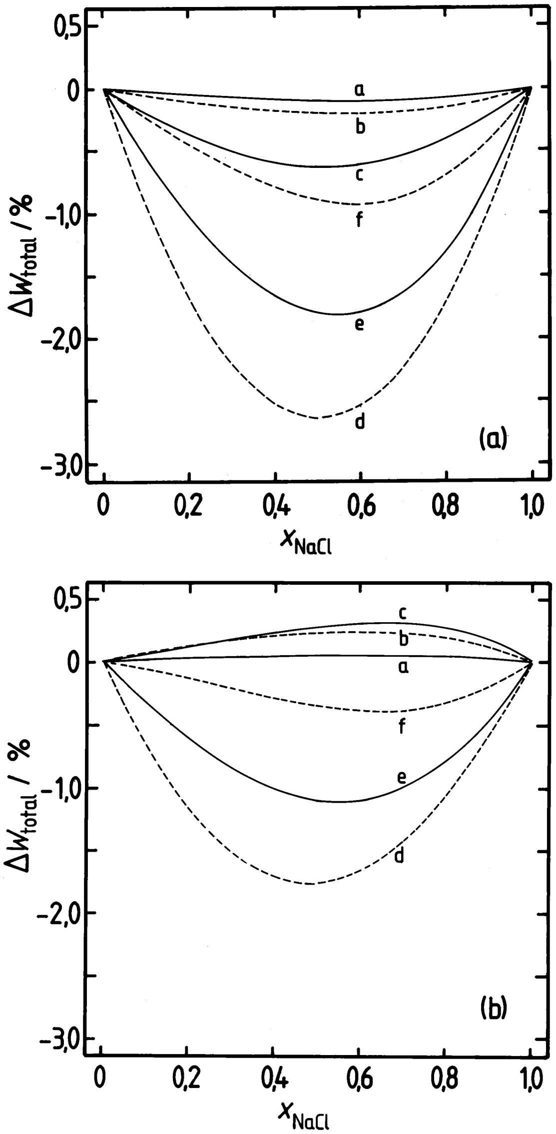

Figure 3. Water content of a mixture containing 1.0 mol of NaCl/Na_2SO_4 calculated using the ZSR model at 298.15 K, shown as the percentage difference (ΔW_{total}) from the true value determined from the model of Rard et al.[29] (a) Standard ZSR model. (b) Extended ZSR model (eq 9). Results are plotted against the dry mole fraction of NaCl in the mixture (x_{NaCl}, equal to $n_{NaCl}/(n_{NaCl} + n_{Na_2SO_4})$) for the following fixed water activities: a, 0.9999; b, 0.999; c, 0.99; d, 0.95; e, 0.90; f, 0.85.

Clegg et al.[14] have modeled the formation of the solids $Na_2SO_4\cdot10H_2O$(cr), Na_2SO_4(cr), and NaCl(cr) in NaCl−Na_2SO_4−H_2O mixtures using the standard ZSR model both with and without fitted mixture parameters A^0 and *B* (see their Figure 1a). Here we repeat the calculation, with the same activity products (K_S) of the solids, but using the extended ZSR model without mixture parameters to determine solute activities. The results are plotted in Figure 6, which shows that the extended model yields a significant improvement in the predicted solubilities, particularly for the two sodium sulfate salts, compared to the standard model without mixture parameters. This is consistent with the water content and activity coefficient comparisons in Figures 4 and 5.

3.2. Activity Coefficients of Uncharged Solutes in Aqueous Salt Solutions. Clegg et al.[14] have shown in their Figure 4 that

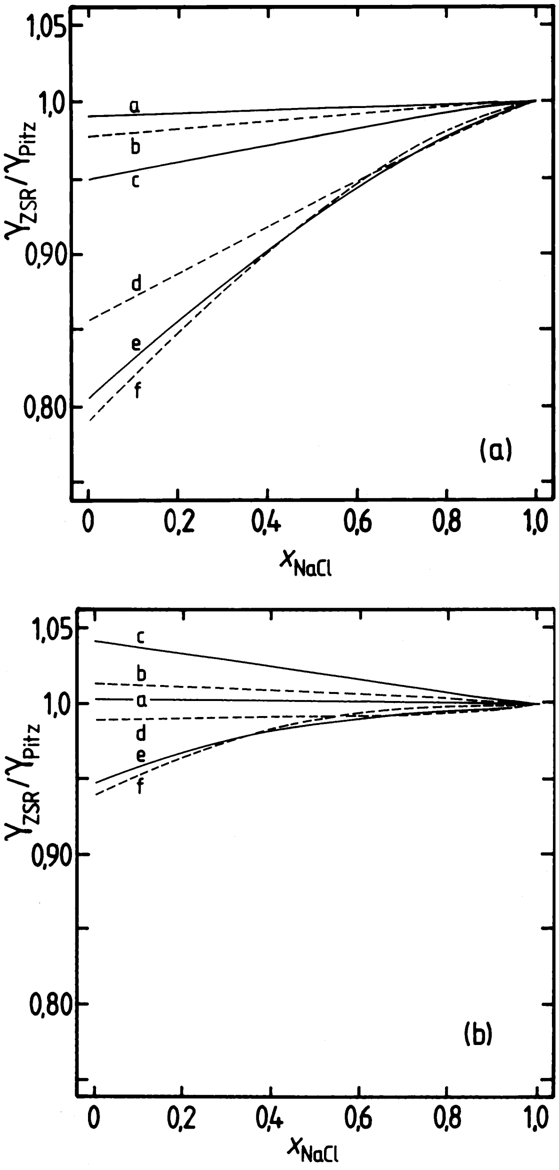

Figure 4. Mean activity coefficients of NaCl in aqueous NaCl/Na_2SO_4 at 298.15 K calculated using the ZSR model (γ_{ZSR}), shown as the ratio to the true value determined from the model of Rard et al.[29] (γ_{Pitz}). (a) Standard ZSR model. (b) Extended ZSR model (eq 19). Results are plotted against the dry mole fraction of NaCl in the mixture (x_{NaCl}, equal to $n_{NaCl}/(n_{NaCl} + n_{Na_2SO_4})$) for the following fixed water activities: a, 0.9999; b, 0.999; c, 0.99; d, 0.95; e, 0.90; f, 0.85.

activity coefficients of uncharged solutes in salt solutions predicted by the standard ZSR model are not consistent with the commonly observed Setchenow relationship.[15] In particular, at very low salt molalities m_S, the values of the activity coefficients are predicted to vary steeply with m_S and only approach unity at extreme dilution—a feature that is not observed in real solutions.

One of the principal reasons for extending the ZSR model was to address this deficiency, although it is emphasized that the model would not be expected to predict quantitatively the effects of different salts without the use of fitted parameters. This is particularly true for solutions in which the uncharged solute is present at very low or trace concentration. We note, though, that thermodynamic properties of some neutral solute/electrolyte mixtures have been modeled satisfactorily using the standard ZSR model over limited ranges of mixture composition.[5]

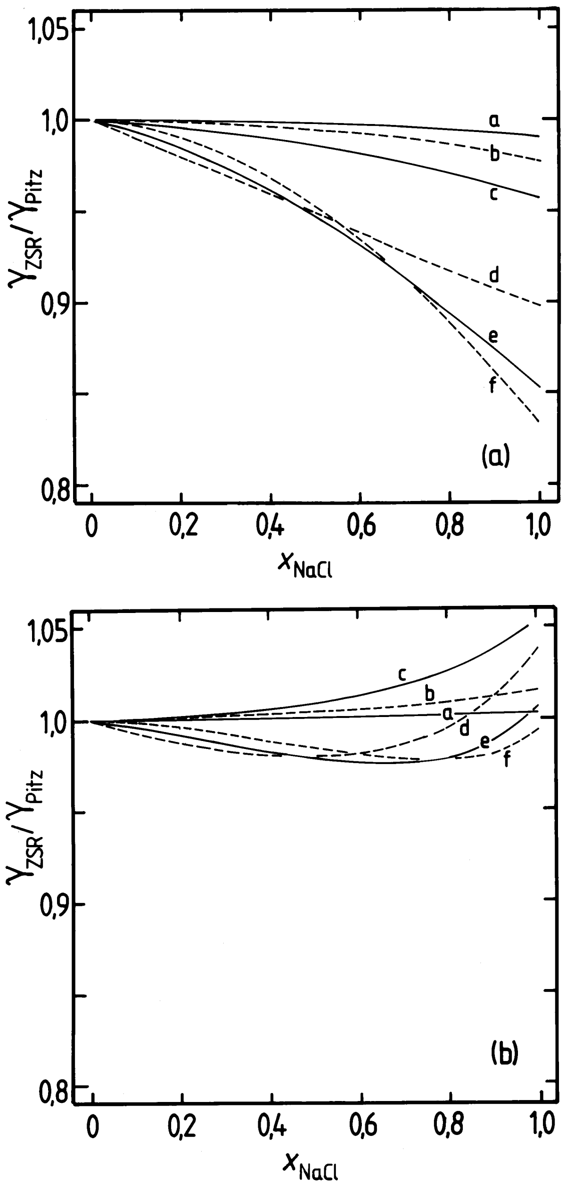

Figure 5. Mean activity coefficients of Na_2SO_4 in aqueous NaCl/Na_2SO_4 at 298.15 K calculated using the ZSR model (γ_{ZSR}), shown as the ratio to the true value determined from the model of Rard et al.[29] (γ_{Pitz}). (a) Standard ZSR model. (b) Extended ZSR model (eq 19). Results are plotted against the dry mole fraction of NaCl in the mixture (x_{NaCl}, equal to $n_{NaCl}/(n_{NaCl} + n_{Na_2SO_4})$) for the following fixed water activities: a, 0.9999; b, 0.999; c, 0.99; d, 0.95; e, 0.90; f, 0.85.

Consider a solution containing an uncharged solute N at trace concentration, and a single salt S. If N behaves ideally in pure aqueous solution ($\gamma_N^\circ = \gamma_N^{\circ\prime} = \gamma_N' = 1.0$) then eq 19 simplifies to

$$\ln(\gamma_N^{\text{trace}}) = \ln(m_N^\circ/(\nu_S m_S)) + \ln(\nu_S m_S'/m_N^{\circ\prime}) \qquad (36)$$

In this example m_N° and $m_N^{\circ\prime}$ are the same at all water activities (since ϕ_N° and $\phi_N^{\circ\prime}$ also equal unity for ideal solutions of N) and

$$\ln(\gamma_N^{\text{trace}}) = \ln(m_S'/m_S) \qquad (37)$$

Values of γ_N^{trace} are plotted in Figure 7 for several salts. For these examples the value of *b* was optimized for each salt by fitting to osmotic coefficients at 298.15 K calculated using the Pitzer model with published parameters,[18] for $\sqrt{m} \leq 0.1$ mol$^{1/2}$

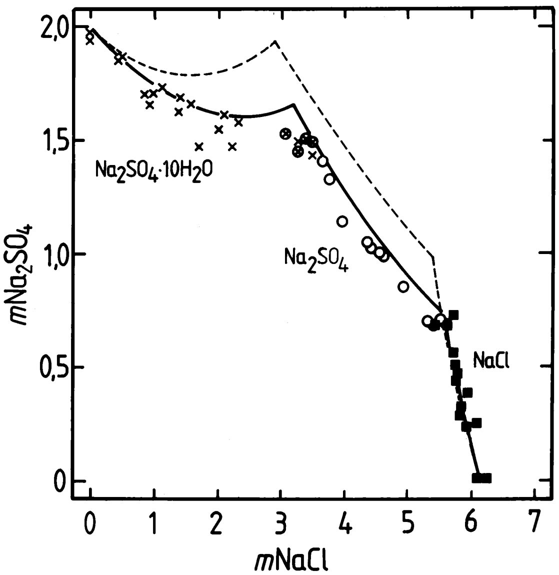

Figure 6. Solid-phase solubilities in aqueous NaCl/Na_2SO_4 mixtures at 298.15 K. Symbols: cross, $Na_2SO_4 \cdot 10H_2O$(cr); open circle, Na_2SO_4(cr); solid square, NaCl(cr). Lines: dashed, standard ZSR model for solution water content and solute activity coefficients; solid, extended ZSR model. Data are from the compilation of Silcock.[32]

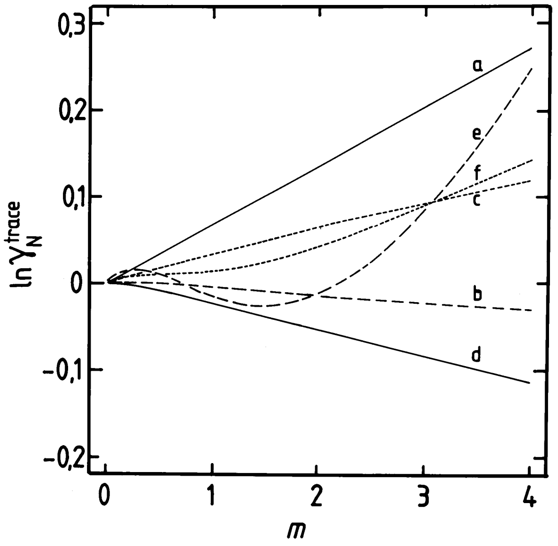

Figure 7. Activity coefficients (γ_N^{trace}) of a nondissociating solute N present at trace concentration in six 1:1 and 2:1 electrolytes at 298.15 K. Solute N is assumed to behave ideally in pure aqueous solution, and γ_N^{trace} is calculated using the extended ZSR model (eq 37), with values of b in eq 7 optimized individually for each electrolyte. Results are plotted against molality m. Lines: a, NaCl(aq); b, $NaNO_3$(aq); c, NH_4Cl(aq); d, NH_4NO_3(aq); e, Na_2SO_4(aq); f, $(NH_4)_2SO_4$(aq).

kg$^{-1/2}$. The values of b are as follows: $b_{NaCl} = 2.21$, $b_{NaNO_3} = 1.71$, $b_{NH_4NO_3} = 1.45$, $b_{NH_4Cl} = 1.097$, $b_{(NH_4)_2SO_4} = 1.56$, $b_{Na_2SO_4} = 1.70$. We note that if $\phi_S^{o\prime}$ were calculated using eq 7 with a fixed value of b, then at a fixed water activity m_S' would be the same for all salts of the same charge type. Hence the activity coefficient γ_N^{trace} would be determined only by $1/m_S$.

The activity coefficients plotted in Figure 7 in most cases show the expected approximately linear dependence of $\ln(\gamma_N^{trace})$ on m_S in dilute solutions, a large improvement on the standard ZSR model (Figure 4 of Clegg et al.[14]). The results for Na_2SO_4 in Figure 7 differ from the other salts, showing values of γ_N^{trace} either side of unity below about 2 mol kg^{-1} though the variation is not very great. This is related to the difference between $\phi_S^{o\prime}$ obtained from eq 7 and the true value of the osmotic coefficient of aqueous Na_2SO_4 over this molality range. Some optimization is probably possible using, for example, an additional term in $\beta^{(1)}$ in the equations as noted earlier.

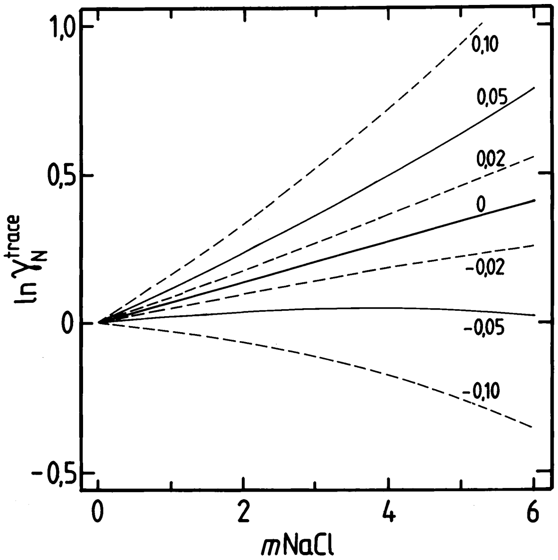

Figure 8. Activity coefficients (γ_N^{trace}) of a nondissociating solute N present at trace concentration in aqueous NaCl 298.15 K. Solute N is assumed to behave ideally in pure aqueous solution, and γ_N^{trace} is calculated using the extended ZSR model (eq 37) for a range of values of the interaction parameter A^0 (indicated on the graph). The line for A^0 equal to zero is the same as the result for NaCl in Figure 7.

Methods of predicting the salt effect on the activity coefficients of uncharged solutes have been reviewed by Millero.[24] These methods can be used to estimate salting coefficients k_S, at least for dilute salt solutions, and the results used to fit the ZSR model parameters A^0 and B for each electrolyte/neutral solute pair of interest. Figure 8 shows calculated values of $\ln(\gamma_N^{trace})$ in aqueous NaCl for a range of values of the mixture parameter A^0. The predicted behavior ranges from a decrease in the activity coefficient (salting in) for $A^0 < -0.05$, to salting out for higher values.

Finally, Clegg et al.[14] have shown that activity coefficients and solid/liquid equilibria in sucrose/NaCl/H_2O solutions can be satisfactorily predicted using the standard ZSR model with mixture parameters. The comparisons shown above suggest that the extended model will yield some improvement but that mixture parameters would still be required.

4. Summary

The Zdanovskii−Stokes−Robinson model is one of the simplest methods of estimating the thermodynamic properties of solution mixtures, based upon the properties of solutions of the individual components. We have derived an extension to the ZSR model which improves its performance for mixtures containing salts of different charge types or salts and uncharged solutes. This can be combined with terms including fitted parameters for the interactions between pairs of solutes, developed previously,[14] to produce a more flexible and accurate model.

The extension to the model involves molality-based Debye−Hückel expressions for osmotic and activity coefficients. In the examples discussed here, the expressions were taken from the Pitzer activity coefficient model,[18] although the method is general and not restricted to a particular equation.

At its simplest, with a fixed value of the parameter b, the extension to ZSR does not require any additional thermodynamic information to the standard model. However, some improvements are possible: optimization of b so that calculated $\phi^{\circ\prime}$, $m^{\circ\prime}$, and $\gamma^{\circ\prime}$ for each electrolyte more closely match its true thermodynamic properties in dilute solution; the inclusion of additional terms including the parameter $\beta^{(1)}$ for the same purpose. We have not explored other possibilities such as the use of unsymmetrical mixing terms (for solutions containing electrolytes of different charge types), also developed by Pitzer.[30]

The extended ZSR model, applied to the system NaCl−Na_2SO_4−H_2O at 298.15 K, yields improved estimates of mixture water content, NaCl and Na_2SO_4 activity coefficients, and solid phase solubilities compared to the standard model. For salt solutions containing trace amounts of nonelectrolytes, the extended model predicts activity coefficients of the nonelectrolytes that are consistent with commonly observed "Setchenow" type behavior, thus addressing a deficiency of the standard model. The use of mixture parameters for the nonelectrolyte/salt interaction allows salting-in or salting-out behavior to be reproduced.

Appendix

Clegg and Pitzer[31] have developed expressions for the Debye−Hückel contributions to solute and solvent activity coefficients, based upon mole fractions rather than molalities, which incorporate the fitted parameter ρ_{ca} (see their eqs 39−45). Analogous equations for the molality scale (with parameter b_{ca}) can be obtained starting from the following expression for the excess Gibbs energy:

$$G^{\mathrm{ex}}/(w_{\mathrm{w}}RT) = -4I(A^{\phi}/b)\ \ln(1 + bI^{1/2}) \qquad \text{(A1)}$$

where w_{w} is the mass of solvent (kg), R (8.3144 J mol^{-1} K^{-1}) is the gas constant, and T (K) is temperature. First we define

$$Y_{ca} = (1/b_{ca})\ \ln(1 + b_{ca}I^{1/2}) \qquad \text{(A2)}$$

where the electrolyte specific parameter b_{ca} will replace b in eq A1. The ionic strength I can be expressed as

$$I = \sum_c\sum_a m_c|z_c|m_a z_a(z_c + z_a)/(\sum_i m_i|z_i|) \qquad \text{(A3)}$$

where z_i is the charge on ion i, and the summations are over all cations c, anions a, and ions i.

Equation A1 can now be rewritten

$$G^{ex}/(w_{\mathrm{w}}RT) = -\,4A^{\phi}\sum_c\sum_a m_c z_c m_a|z_a|(z_c + |z_a|)Y_{ca}/(\sum_i m_i|z_i|) \qquad \text{(A4)}$$

and equations for the osmotic coefficient ϕ and solute activity coefficients γ_i derived using the following relations:

$$\phi - 1 = -\,(\partial(G^{\mathrm{ex}}/RT)/\partial w_{\mathrm{w}})_{n_i}(1/\sum_i m_i) \qquad \text{(A5)}$$

$$1\mathrm{n}(\gamma_i) = (\partial(G^{\mathrm{ex}}/w_{\mathrm{w}}RT)/\partial m_i)_{n_{\mathrm{w}},n_j} \qquad \text{(A6)}$$

yielding

$$\phi - 1 = -(2/\sum_i m_i)A^{\phi}I^{1/2}\sum_c\sum_a m_c z_c m_a|z_a|(z_c + |z_a|)/((1 + b_{ca}I^{1/2})(\sum_i m_i|z_i|)) \qquad \text{(A7)}$$

and for cation M:

$$1\mathrm{n}(\gamma_{\mathrm{M}}) = -\,4z_M(A^{\phi}/\sum_i m_i|z_i|)[\sum_a m_a|z_a|(z_{\mathrm{M}} + |z_a|)Y_{\mathrm{M}a} - \sum_c\sum_a m_c|z_c||m_a||z_a|(z_c + |z_a|)(Y_{ca}/\sum_i m_i|z_i| - z_{\mathrm{M}}/(4(1 + b_{ca}I^{1/2})I^{1/2}))] \qquad \text{(A8)}$$

The equation for anion X is obtained by transposing subscripts X for M, c for a, and a for c:

$$\ln(\gamma_{\mathrm{X}}) = -4|z_{\mathrm{X}}|(A^{\phi}/\sum_i m_i|z_i|)[\sum_c m_c z_c(|z_{\mathrm{X}}| + z_c)Y_{c\mathrm{X}} - \sum_c\sum_a m_c z_c m_a|z_a|(z_c + |z_a|)(Y_{ca}/\sum_i m_i|z_i| - |z_{\mathrm{X}}|/(4(1 + b_{ca}I^{1/2})I^{1/2}))] \qquad \text{(A9)}$$

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Supporting Information Available: Text giving the derivation of eq 30 and the "mixture" contributions to the activity coefficient in eq 32. This material is available free of charge via the Internet at http://pubs.acs.org.

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