

Real Ionic Solutions in the Mean Spherical Approximation. 2. Pure Strong Electrolytes up to Very High Concentrations, and Mixtures, in the Primitive Model

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Activity and osmotic coefficients for aqueous solutions of pure nonassociating salts and their mixtures are described in the framework of the primitive model of ionic solutions in which the solvent is a dielectric continuum, using the mean spherical approximation (MSA). Expressions for these quantities are given which verify the Gibbs–Duhem relation, in the Lewis–Randall (experimental) molality scale. The model involves concentration-dependent ion size and effective permittivity. In contrast to other previous descriptions, variation of these parameters can be interpreted in terms of ionic hydration effects. The model has been applied to fit data for aqueous solutions of pure alkali halides up to very high concentrations (19 mol kg⁻¹ for LiCl, 20 mol kg⁻¹ for LiBr, ...), acids such as HCl (to 16 mol kg⁻¹), LiNO₃, two alkali perchlorates, and uranyl perchlorate, and two-salt mixtures without a common cation. A property of the model is used to predict the behavior of two-salt mixtures with a common cation from the results for pure salt solutions. Generalization of the model to an arbitrary number of salts is tested in the case of three-salt mixtures. Generally, the calculations have been carried out up to the highest concentration for which data are available, at 25 °C. In all cases, the results agree with the experimental measurements to within the experimental error.

Introduction

The present paper is the continuation of previous work¹ (hereafter cited as P1), in which the mean spherical approximation (MSA) was used for the description of thermodynamic excess functions of pure ionic solutions.

It seems that, besides the Pitzer method,² the MSA represents a promising alternative method, which has been receiving constant interest in the past 20 years.^{3–14} The classic primitive MSA has been used with fixed ionic diameters^{3,6,8,9} or with the cation's diameter that varied linearly with concentration.⁴ In another work¹² osmotic coefficients were fitted to very high concentrations, such as 20 mol kg⁻¹ for LiBr, with the use of a cation's diameter that was expressed as a polynomial of the second degree for the concentration. Recently, a modification of the original MSA consisted of using the experimental solution permittivity rather than the pure solvent permittivity together with an adjustable average diameter.¹³

In P1, we used a varying cation's diameter and solvent permittivity. Both are ways of including hydration effects, which are not taken into account at the first level of the primitive model. We did not use experimental solution permittivity values because this quantity constitutes information on electronic interactions at large ionic separations. It may be expected not to be the relevant quantity at high concentration for the calculation of the energy of the system. Moreover, experimental permittivities are known to contain not only equilibrium contributions but also dynamical ones, with many uncertainties in estimating the latter, even at low concentrations.^{15–17}

It must be emphasized that, in P1, the dependence of the parameters on concentration was explicitly taken into account in the expression of the activity and osmotic coefficients. This led to additional terms, which have a significant contribution at moderate and high concentration (typically above 1 mol kg⁻¹). The method was applied to the description of mean activity coefficients in pure alkali halide solutions, below 6 mol kg⁻¹.

In P1, the classic conversion of the activity coefficients from the molarity to the molality scale was performed in the Lewis–Randall (LR) system (eq 16 below). However, it must be stressed that no similar conversion formula exists for the osmotic coefficient in the LR system. Thus, it was not possible to get expressions that verified the Gibbs–Duhem relation in the LR (experimental) system. These difficulties have been overcome with the use of a MacMillan–Mayer-to-LR conversion. The basic ingredients of this conversion have been given some time ago,¹⁸ and recently, an approximate simple conversion procedure has been tested.¹⁹ The interesting properties of the conversion are that (i) both activity and osmotic coefficients can be obtained at the LR level (molality scale) from expressions obtained in P1 at the MacMillan–Mayer (MM) level (molarity scale) and (ii) the converted activity and osmotic coefficients still verify the Gibbs–Duhem relation.

It must be underlined that this conversion should be performed in any study using the primitive MSA because, in this framework, the thermodynamic excess functions are calculated at the MM level.²⁰ The MM framework is characterized by two features: the solvent is regarded as a continuum that manifests itself through its permittivity, and the thermodynamic properties are calculated at constant solvent chemical potential. Although the effect of the conversion is negligible at relatively low concentrations, it becomes significant as concentration is increased, typically above 1–2 mol/kg.¹⁹

In this paper, a consistent description of activity and osmotic coefficients is presented. The expressions for these thermodynamic quantities, derived in P1 at the MM level are combined with a MM-to-LR conversion for comparison with experimental data. The treatment is applied to fit data for aqueous pure strong electrolytes and two-salt mixtures without a common cation. A property of the model is used to predict the behavior of two-salt mixtures with a common cation from the results for pure salt solutions. Generalization of the model to an arbitrary number of salts is tested in the case of three-salt mixtures.

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Theory

The basic assumptions of the model are as follows. The ions, to which some solvent molecules are possibly bound, are modeled as hard spheres that interact through Coulomb forces in a continuum of relative permittivity ϵ . The sizes of the ions and the permittivity are allowed to vary with concentration.

Most of the theoretical relations used in this paper have been derived in P1. However, we first recall some of them that can be rewritten in a more convenient form. Besides, we give the activity coefficient of a salt in a mixture. The expressions are given in SI units.

Basic Relations. For the electrostatic contribution to the individual ionic activity coefficient we have

$$\Delta \ln y_i^{\text{MSA}} = L_i + \sum_j \rho_j q_j \frac{\partial \sigma_j}{\partial \rho_i} + \beta \Delta E^{\text{MSA}} \epsilon \frac{\partial \epsilon^{-1}}{\partial \rho_i} \quad (1)$$

with

$$L_i = -\lambda \left[\frac{\Gamma z_i^2}{1 + \Gamma \sigma_i} + \eta \sigma_i \left(\frac{2z_i - \eta \sigma_i^2}{1 + \Gamma \sigma_i} + \frac{\eta \sigma_i^2}{3} \right) \right]$$

$$\lambda = \beta e^2 / (4\pi \epsilon_0 \epsilon)$$

$$q_j = \lambda \left[\frac{\Gamma^2 z_j^2}{(1 + \Gamma \sigma_j)^2} + \eta \frac{\sigma_j^2 (2 - \Gamma^2 \sigma_j^2) - 2z_j}{(1 + \Gamma \sigma_j)^2} \right]$$

ϵ_0 the permittivity of a vacuum, ϵ the relative permittivity of the solution, z_i the charge number of species i , ρ_i its number density and other quantities as defined in P1.

The parameter λ is a characteristic length whose value for pure water at 25 °C is $\lambda_W \approx 7.1$ Å. It is also twice the Bjerrum critical distance for ion-pair formation.²¹

The mean activity coefficients read

$$\Delta \ln y_{\pm}^{\text{MSA}} = \frac{\beta \Delta E^{\text{MSA}}}{\rho_t} - \lambda \frac{2}{\pi} \frac{\eta^2}{\rho_t} + \frac{1}{\rho_t} \sum_j \rho_j q_j D(\sigma_j) + \frac{\beta \Delta E^{\text{MSA}}}{\rho_t} \epsilon D(\epsilon^{-1}) \quad (2)$$

with the notation

$$D = \sum_k \rho_k \frac{\partial}{\partial \rho_k} \quad (3)$$

and²²

$$\Delta \ln y_{\pm}^{\text{HS}} = \left(\frac{X_2^3}{X_0 X_3^2} - 1 \right) \ln x + \frac{X_3}{x} + \frac{3X_1 X_2 (2 - X_3)}{X_0 x^2} + \frac{X_2^3 (1 + 2X_3 - X_3^2)}{X_0 X_3^3} + \frac{1}{\rho_t} \sum_j \rho_j Q_j D(\sigma_j) \quad (4)$$

with

$$\rho_t \equiv \sum_j \rho_j$$

Further, consider a binary salt S, one mole of which releases ν_+ moles of cations and ν_- moles of anions. Then the mean

contributions to the activity coefficient for this salt in a mixture are

$$\Delta \ln y_S^{\text{MSA}} = L_S + \frac{1}{\nu} \sum_j q_j C_j \frac{\partial \sigma_j}{\partial C_S} + \frac{1}{\nu} (\beta \Delta E^{\text{MSA}} 10^{-3}/N) \epsilon \frac{\partial \epsilon^{-1}}{\partial C_S} \quad (5)$$

$$\Delta \ln y_S^{\text{HS}} = M_S + \frac{1}{\nu} \sum_j Q_j C_j \frac{\partial \sigma_j}{\partial C_S} \quad (6)$$

with C_i and C_S the molar concentrations (in mol/L) of species i and salt S, respectively, for which

$$\rho = 10^3 NC$$

in mol m⁻³, with N the Avogadro's number. Moreover, $\nu \equiv \nu_+ + \nu_-$, and L_S and M_S are the mean of L_i and M_i (the analogue of L_i in the hard sphere part), respectively, for the two ions of the salt S

$$X_S \equiv (\nu_+ X_+ + \nu_- X_-) / \nu$$

with $X = L$ or M .

The electrostatic contribution to the osmotic coefficient can be written as

$$\Delta \phi^{\text{MSA}} = -\frac{\Gamma^3}{3\pi \rho_t} - \lambda \frac{2}{\pi} \frac{\eta^2}{\rho_t} + \frac{1}{\rho_t} \sum_j \rho_j q_j D(\sigma_j) + \frac{\beta \Delta E^{\text{MSA}}}{\rho_t} \epsilon D(\epsilon^{-1}) \quad (7)$$

In P1, interesting results were obtained for solutions of pure salts when the anion size was kept constant (equal to its crystallographic value) and the diameter of the cation and ϵ^{-1} were chosen as linear functions of the concentration,

$$\sigma = \sigma^{(0)} + \sigma^{(1)} C_S \quad (8)$$

$$\epsilon^{-1} = \epsilon_W^{-1} (1 + \alpha C_S) \quad (9)$$

where C_S is the molar concentration of the salt and ϵ_W is the relative permittivity of pure water. From these relations we get

$$D(\sigma) = \sigma - \sigma^{(0)} \quad (10)$$

$$\epsilon D(\epsilon^{-1}) = 1 - \epsilon / \epsilon_W \quad (11)$$

where D is defined by eq 3. It can be shown that these last two relations will remain valid hereafter for salt mixtures.

Any individual or mean activity coefficients at the MM level reads

$$\ln y^{(\text{MM})} = \Delta \ln y^{\text{MSA}} + \Delta \ln y^{\text{HS}} \quad (12)$$

The osmotic coefficient in the same reference system is

$$\phi^{(\text{MM})} = 1 + \Delta \phi^{\text{MSA}} + \Delta \phi^{\text{HS}} \quad (13)$$

MM-to-LR Conversion. These quantities need to be converted to the LR (experimental) reference system for comparison with experimental data. Approximate relations¹⁹

may be used for this purpose. For the conversion of the osmotic coefficient we get

$$\phi^{(\text{LR})} = \phi^{(\text{MM})} (1 - CV_{\pm}) \quad (14)$$

where $\phi^{(\text{LR})}$ and $\phi^{(\text{MM})}$ are the osmotic coefficients at the LR and MM level, respectively. In eq 14, $\phi^{(\text{MM})}$ is the osmotic coefficient calculated from eq 13. Besides, C is the total solute concentration

$$C = m/V$$

with m the total solute molality

$$m \equiv \sum_i m_i$$

and V is the volume of solution per mass of solvent in the LR system, and V_{\pm} is the mean solute partial molal volume.

For the conversion of activity coefficients we may use the following relationship

$$\ln y_i^{(\text{LR})} = \ln y_i^{(\text{MM})} - C V_i \phi^{(\text{MM})} \quad (15)$$

in which $y_i^{(\text{MM})}$ is given by eq 12, V_i is the partial molal volume of species i , and $y_i^{(\text{LR})}$ is the LR activity coefficients in the molarity scale, *i.e.*,²¹

$$y_i^{(\text{LR})} = \gamma_i^{(\text{LR})} V d_w \quad (16)$$

with $\gamma_i^{(\text{LR})}$ the experimental activity coefficient in the molality scale and d_w the density of pure solvent.

For a salt S in a mixture, the conversion gives

$$\ln y_S^{(\text{LR})} = \ln y_S^{(\text{MM})} - C V_S \phi^{(\text{MM})}/\nu \quad (17)$$

with V_S the mean partial molal volume of salt S in the mixture and ν having the same meaning as in eqs 5 and 6.

Equation 16 is valid also for the mean salt activity coefficients.

Calculation of Mean Partial Molal Volumes. The quantity V_{\pm} , the mean solute partial molal volume, can be computed from density data as follows.

It can be defined¹⁸ as the mean of the individual partial molal volumes

$$V_{\pm} = \sum_i x_i V_i \quad (18)$$

where x_i designates the mole fraction of species i ,

$$x_i \equiv m_i/m \quad (19)$$

and

$$V_i \equiv \frac{\partial V}{\partial m_i} \quad (20)$$

Besides, it stems from eq 20 that

$$dV = \sum_i V_i dm_i \quad (21)$$

from which we get, by virtue of eqs 18 and 19,

$$V_{\pm} = \left[\frac{\partial V}{\partial m} \right]_{x_i} \quad (22)$$

where the derivative is performed with all x_i 's constant.

Now we have

$$V = (1 + \sum_i m_i M_i)/d \quad (23)$$

with M_i the molar mass of species i and d the density of the solution. Thus, by using eqs 22 and 23, we arrive at

$$V_{\pm} = \frac{M - d'}{d - C d'} \quad (24)$$

where

$$M = \frac{1}{m} \sum_i m_i M_i$$

or

$$M = \frac{1}{m} \sum_S m_S M_S$$

in which the subscript S indicates a salt, m_S its molality, M_S its molar mass, and

$$d' \equiv \left[\frac{\partial d}{\partial C} \right]_{x_i}$$

In the same way, it can be shown that V_S , the mean partial molal volume of a salt S in a mixture, can be calculated from the following expression

$$V_S = \frac{M_S - d'_S}{d - C_S d'_S} \quad (25)$$

where M_S is the molar mass of S, C_S its molar concentration, and $d'_S = \partial d / \partial C_S$.

Application to Solutions of Pure Salts

In the present treatment, it has been assumed that the solution is made up of strong electrolytes. So in the following, real aqueous solutions, for which there is no clear evidence of ionic association²³ or which are commonly regarded so, have been considered. Moreover, data for these solutions have been taken at 25 °C only.

Solutions of the following salts have been treated. As 1-1 salts, they are the following: alkali halides MX, in which M and X stand for Li, Na, K, Rb, or Cs, and Cl, Br, or I, respectively; HCl, HBr, and HI; LiNO₃; LiClO₄ and NaClO₄; some symmetrical tetraalkylammonium halides. As 2-1 salts, they are the following: alkaline earth metal halides M'X₂; perchlorates M'(ClO₄)₂, with M' = Mg, Ca, Sr, or Ba; uranyl perchlorate.

Equations 13 and 14 have been used together with eqs 8 and 9 for a least-square adjustment of osmotic coefficients.

Values for osmotic data have been taken from compilation articles for uni-univalent electrolytes²⁴ (except for tetraalkylammonium salts²⁵) and for alkaline earth metal halides^{26a} and perchlorates.^{2,26b}

Calculations have been performed from 0.1 mol/kg to saturation or to the highest molality for which experimental data are available. For some of these salts, this molality can be very high: 16 mol/kg for HCl, 19 mol/kg for LiCl, 20 mol/kg for LiBr and LiNO₃, 12 mol/kg for NaI, and 11 mol/kg for CsCl.

In the MM-to-LR conversion, V_{\pm} has been calculated by using density data and eq 24. The density of a solution was calculated by using a parametrization

$$d = d_w + d_1 C_S - d_2 C_S^{3/2} \quad (26)$$

where values for d_1 and d_2 are tabulated²⁷ and C_S is the molar concentration of the salt. In the case of the tetraalkylammonium salts, density data have been found in various sources of the literature and fitted to eq 26. Table 1 gives values of the parameters for these salts. In the absence of data for uranyl perchlorate, parameters were empirically estimated from data concerning uranyl chloride.²⁷ This led to $d_1 \approx 0.408$ kg/mol and $d_2 \approx 7 \times 10^{-3}$ kg L^{1/2} mol^{-3/2}.

In the case of the alkali halides the fits of the parameters appearing in eqs 8 and 9 have been conducted according to the following guide lines. (1) Equations 8 and 9 have been plugged into the expression for the total osmotic coefficient (eqs 13 and 14). (2) Crystallographic diameters have been adopted for the diameters of the halides in order to reduce the number of adjustable parameters and because the hydration number of halide ions is believed to be low.^{35,36} (3) For a given cation M, the data concerning the salts MCl, MBr, and MI have been fitted at the same time with a common value for the parameter $\sigma^{(0)}$. In this procedure, three parameters need therefore be adjusted, with the constraint on $\sigma^{(0)}$ as expressed by condition 3.

In the case of LiNO₃ solutions, the diameter of Li⁺ at infinite dilution, $\sigma^{(0)}$, has been taken consistently from the fit of the lithium halides and the diameter of nitrate has been determined so as to yield an optimum adjustment of the data for LiNO₃. When the data were fitted to the maximum concentration of 20 mol/kg, the adjustment was not as good as for the halides (average absolute relative deviation (AARD) = 1.3% at best). This result is likely to be due to a possible association in very concentrated solutions and/or to the fact that nitrate is a complex ion with a planar geometry. Consequently, the molality range has been reduced to 10 mol/kg. In this range the AARD is 0.4% with the diameter of nitrate equal to 3.40 Å.

The perchlorates were treated as follows. The salts LiClO₄ and the four alkaline earth perchlorates were fitted at the same time²¹ using, for the cations, the $\sigma^{(0)}$ values determined previously. It resulted that the optimum perchlorate diameter was 4.53 Å. Then the data for sodium and uranyl perchlorates were adjusted with this size for the perchlorate ion.

The results have been collected in Table 2. This table gives the maximum concentration, the values of the fitted parameters, and the AARD for each salt.

Plots of the calculated and experimental osmotic coefficients for LiCl, LiBr, and LiNO₃ are shown in Figure 1.

It is satisfying to notice that excellent fits have been obtained not only to 6 mol/kg but to very high concentrations. As quoted above, the calculations involve only three parameters for these adjustments. A similar finding has been obtained previously by other workers,¹² also within the MSA but with a different method. In contrast, fitting thermodynamic data to such concentrations with Pitzer's equations has been shown³⁷ recently to require five adjustable parameters.

Besides, one can notice that the present method yields a more homogeneous set of values for the parameters as compared to those obtained in P1. Unlike what was done in P1, a common value for $\sigma^{(0)}$ for the three halides of a given cation is preferable for approaching the case of salt mixtures, and this procedure yields values for the parameters that show some satisfying and interesting features described below.

(1) As mentioned previously in P1, the cation's diameter at infinite dilution, $\sigma^{(0)}$ falls below the Pauling diameter for Rb⁺, and this anomaly is still more pronounced for Cs⁺. It may be explained³⁸ by the effect of short-range forces between ions. It is worth noting that these forces may be caused not only by

TABLE 1: Fit of Density Data for Tetraalkylammonium Halide Solutions

salt	ref	max m (mol kg ⁻¹)	$10^3 d_1$ (kg mol ⁻¹)	$10^3 d_2$ (kg L ^{1/2} mol ^{-3/2})	10^4SD^a
Me ₄ NCl	28	22	-0.3522	-2.299	4
Me ₄ NBr	29	5.5	38.17	-0.8496	2
Me ₄ NI	30, 31	0.25	73.94	-1.682	0.1
Et ₄ NCl	28	9.9	-3.001	-5.940	5
Et ₄ NBr	29	10	32.69	-6.169	2
Et ₄ NI	32	0.1	103.1	101.6	16
Pr ₄ NCl	33	1.7	-12.23	-9.907	2
Pr ₄ NBr	29	10	34.39	-0.7192	2
Pr ₄ NI	34	0.25	63.13	-5.812	3

^a SD: standard deviation of fit.

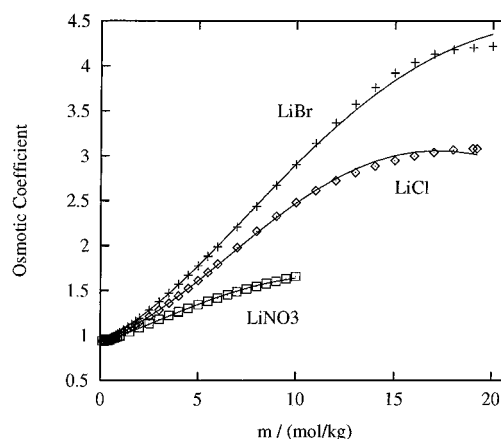


Figure 1. LR experimental and calculated osmotic coefficients for LiCl (◇), LiBr (+), and LiNO₃ (□) as a function of the salt molality.

effects involving the solvent, such as the overlap of hydration spheres (Gurney forces), but also by an additional short-range Coulomb attraction due to the high polarizability of the rubidium, cesium, and halide ions.^{39,40} Besides, as concerns the alkali halides, the results for $\sigma^{(0)}$ agree with the current notions about ionic hydration. Moreover, the divalent cations (alkaline earth and uranyl cations) are found to be significantly bigger than the alkali ions.

(2) The parameters $\sigma^{(1)}$ and α for lithium nitrate and perchlorate form a consistent set with those for the lithium halides.

(3) $\sigma^{(1)}$ is negative for most of the salts, and it increases in absolute value with the size of the halide. Somewhat amazingly, this result agrees with the simple picture in which the effective cation size conveys the degree of hydration of the ion: the bigger the anion the more rapidly the size of a given cation decreases with concentration. In contrast, $\sigma^{(1)}$ is positive for the halides of Rb and Cs, and the tetraalkylammonium salts.

(4) As expected, α is positive (with two exceptions), thus entailing a decrease in the permittivity with salt concentration. Moreover, as observed in experimental measurements,⁴¹ the decrease rate of the permittivity is greatest for lithium salts in the series of alkali halides and for alkaline earth halides. However, our equilibrium permittivity decreases more slowly than the experimental "static" permittivity. So by fitting permittivity data to high concentrations⁴¹ with the use of eq 9, "experimental" values for α for some alkali halides were in the range 0.2–0.3, and for LiNO₃ and CaCl₂ they were close to 0.26 and 0.47, respectively. Lastly, we notice that α decreases with the size of the anion for the more hydrated, order-producing³⁸ cations Li⁺, Na⁺, and all the alkaline earth metals, while it is nearly constant for K⁺ and varies in reverse order for the less hydrated, order-destroying cations Rb⁺ and Cs⁺. However, there does not seem to be any clear reason at hand to interpret these results.

TABLE 2: Values of Parameters from Fit of Osmotic Coefficients for Pure Salts

salt	max m^a	$\sigma^{(0)b}$	$10^2 \sigma^{(1)c}$	$10^2 \alpha^d$	AARD ^e
HCl	16	5.040	-8.216	6.266	0.2
HBr	11	5.040	-8.132	2.921	0.9
HI	0	5.040	-9.502	3.216	0.9
LiCl	19.2	5.430	-9.147	15.45	0.5
LiBr	20	5.430	-9.676	14.56	0.8
LiI	3	5.430	-13.01	12.71	0.7
LiNO ₃	10	5.430	-9.563	14.39	0.4
LiClO ₄	4.5	5.430	-13.32	16.55	0.07
NaCl	6.1	3.870	-2.164	6.930	0.1
NaBr	9	3.870	-4.208	4.819	0.5
NaI	12	3.870	-4.710	4.196	0.5
NaClO ₄	6	3.870	-5.639	16.06	0.5
KCl	5	3.450	-0.5272	6.964	0.04
KBr	5.5	3.450	-1.860	7.272	0.1
KI	4.5	3.450	-5.820	6.921	0.06
RbCl	7.8	2.700	0.2984	2.458	0.2
RbBr	5	2.700	0.09538	4.262	0.02
RbI	5	2.700	1.966	7.277	0.3
CsCl	11	1.870	3.890	0.1151	0.4
CsBr	5	1.870	6.432	2.327	0.1
CsI	3	1.870	0.2686	4.296	0.1
Me ₄ NCl	6	1.000	51.62	-6.867	0.6
Me ₄ NBr	5.5	1.000	43.27	2.134	0.6
Me ₄ NI	0.25	1.000	449.4	62.90	0.2
Et ₄ NCl	6	0.3170	143.5	-15.19	0.7
Et ₄ NBr	6	0.3170	110.3	6.892	0.2
Et ₄ NI	1.2	0.3170	213.6	50.32	1
(Pr ₄ NCl)	1.6	3.721	125.2	1.087	(0.5)
(Pr ₄ NBr)	2	0.1090	221.1	13.23	(0.3)
(Pr ₄ NI)	0.25	0	1113	170.9	(0.5)
MgCl ₂	5.9	6.710	-21.17	9.043	0.3
MgBr ₂	5.6	6.710	-23.15	4.372	0.3
MgI ₂	5	6.710	-26.45	2.719	0.2
Mg(ClO ₄) ₂	2	6.710	-26.49	3.530	0.6
CaCl ₂	7.5	7.030	-24.14	18.11	0.5
CaBr ₂	7.7	7.030	-24.58	16.86	0.7
CaI ₂	1.9	7.030	-32.00	13.63	0.1
Ca(ClO ₄) ₂	2	7.030	-36.14	15.34	0.3
SrCl ₂	3.5	6.690	-20.38	16.19	0.7
SrBr ₂	2.1	6.690	-20.59	14.58	0.07
SrI ₂	2	6.690	-26.46	11.41	0.2
Sr(ClO ₄) ₂	2.5	6.690	-35.29	12.89	0.6
BaCl ₂	1.8	6.010	-18.82	11.51	0.4
BaBr ₂	2.3	6.010	-22.00	8.107	0.1
BaI ₂	2	6.010	-26.00	0.8903	0.6
Ba(ClO ₄) ₂	2	6.010	-32.38	11.76	0.2
UO ₂ (ClO ₄) ₂	5.5	7.916	-43.62	10.42	0.3

^a Given in mol kg⁻¹. ^b In Å. ^c In Å mol⁻¹ L. ^d In mol⁻¹ L. ^e AARD is the average relative deviation for the calculated osmotic coefficients: AARD(%) = (100/ N) $\sum_{k=1}^N |\phi_{\text{cal}}(k) - \phi_{\text{exp}}(k)| / \phi_{\text{exp}}(k)$, with N the number of data points.

It is worth mentioning that the tetraalkylammonium halides could not be treated as easily and satisfactorily as the other halides studied. Osmotic data at very high concentrations could not be fitted accurately, and the maximum concentration of fit had to be lowered accordingly. Moreover, the tetrapropylammonium halides could not be treated consistently as regards the parameter $\sigma^{(0)}$, and for Pr₄NI no value at all could be determined as a best value in the adjustment. For information, the results from fitting individually these salts are also given in Table 2 in parentheses; it is seen that the value of $\sigma^{(0)}$ for Pr₄NCl is much greater than that for Pr₄NBr, which made a consistent fit impossible. Besides, for the methyl and ethylammonium salts, the values of $\sigma^{(0)}$ are surprisingly low, and $\sigma^{(1)}$ is positive and sometimes quite large. Lastly, Me₄NCl and Et₄NCl are the only halides for which α is negative.

It is highly likely that the difficulties met with these salts have the same origin as the many peculiarities that have long been recognized.^{29,30,42}

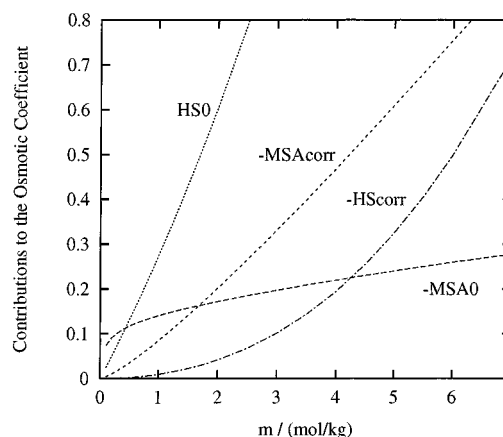


Figure 2. Contributions to the osmotic coefficient (at the MM level): “HSO” is for $\Delta\phi_0^{\text{HS}}$, and “-HScorr, -MSA0, -MSAcorr” are for the opposites of $\Delta\phi_{\text{corr}}^{\text{HS}}$, $\Delta\phi_0^{\text{MSA}}$, and $\Delta\phi_{\text{corr}}^{\text{MSA}}$, respectively.

Lastly, it is interesting to examine the various contributions to the calculated osmotic coefficient and estimate the influence of the corrective terms that arise from the variation of σ and ϵ with concentration. It is easily seen that the electrostatic and hard-sphere contributions can be written as

$$\Delta\phi^{\text{MSA}} = \Delta\phi_0^{\text{MSA}} + \Delta\phi_{\text{corr}}^{\text{MSA}} \quad (27)$$

and

$$\Delta\phi^{\text{HS}} = \Delta\phi_0^{\text{HS}} + \Delta\phi_{\text{corr}}^{\text{HS}} \quad (28)$$

in which the subscript “corr” indicates corrective terms comprising $D(\sigma_i)$ and $D(\epsilon)$ arising from the effect of the concentration dependence of the sizes and permittivity.

In Figure 2 these four contributions (at the MM level) are plotted as a function of the molality of LiCl. For clarity, the curves are plotted up to 7 mol/kg. For this salt, both corrections are negative. At low density (below 0.4 mol/kg), the electrostatic contribution dominates and causes the osmotic coefficient to decrease. Above, the hard-sphere contribution has a greater and greater effect, eventually producing a rise in the osmotic coefficient. Above 1.8 mol/kg the MSA corrective term becomes the dominant electrostatic contribution and increases much more rapidly than $\Delta\phi_0^{\text{MSA}}$. Above typically 10 mol/kg (not shown), hard-sphere effects govern the increase in the osmotic coefficient. At 19 mol/kg we get $\Delta\phi_0^{\text{MSA}} \approx 0.45$, $\Delta\phi_{\text{corr}}^{\text{MSA}} \approx -2.7$, $\Delta\phi_0^{\text{HS}} \approx 13.6$, and $\Delta\phi_{\text{corr}}^{\text{HS}} \approx -7.2$.

Application to Mixtures of Two Salts

The case of two-salt mixtures can now be examined. From the study of solutions of pure salts we have to distinguish between mixtures with a common cation and other types of mixtures. Moreover, we notice that two types of experiments have been reported in the literature. On the one hand, isopiestic vapor pressure measurements have provided osmotic data for most of the salt mixtures. On the other hand, electromotive force measurements have been used for the estimation of activity coefficients of acids such as HCl or HBr. In this section, we first consider the case of mixtures with a common cation that have been studied only by the isopiestic method.

Predictions for Mixtures with a Common Cation. In this case one may try the following scheme for a mixture of two salts A and B. Once the data for pure solutions of A and B have been fitted, one may generalize eqs 8 and 9 by writing

$$\sigma = \sigma^{(0)} + \sigma_A^{(1)} C_A + \sigma_B^{(1)} C_B \quad (29)$$

and

$$\epsilon^{-1} = \epsilon_w^{-1} (1 + \alpha_A C_A + \alpha_B C_B) \quad (30)$$

where $\sigma^{(0)}$ is the common cation's diameter at infinite dilution for the salts A and B, and the other parameters are for the pure salts A and B whose concentration in the solution are C_A and C_B . Hence, in this particular case there is no new parameter to introduce, and osmotic coefficients can be predicted from the study of the pure solutions.

Among the two-salt mixtures that can be prepared with the salts considered in the previous section, osmotic data have been reported for three of them in the literature: NaCl + NaBr, KCl + KBr, and LiCl + LiNO₃ systems. The results given in the previous section have been used to compute the osmotic coefficients for these mixtures. The calculations have been performed to the highest molality for which experimental data are available.

Densities have been estimated by using a relationship²⁷ for mixtures similar to eq 26, namely,

$$d = d_w + \sum_S d_{1,S} C_S - (\sum_S d_{2,S}^{2/3} C_S)^{3/2}$$

where summations are made on all the salts present in the mixture, and $d_{1,S}$ and $d_{2,S}$ are the parameters for the pure salt S .

The results of comparison with experimental results have been collected in Table 3. They are very good, particularly in the case of the last system for which the maximum ionic strength is quite high. This is an encouraging result for the treatment of mixtures, which may lend support to the present scheme. A plot of the experimental and calculated osmotic coefficients is shown in Figure 3 for the mixture LiCl + LiNO₃. The results are given for three values of the fraction of LiNO₃. Agreement is good up to the maximum total molality of 10 mol/kg, and it is surprisingly best at the highest concentrations.

Mixtures without a Common Cation. For the case of mixtures of two salts A and B without a common cation, we have to account for the variation of a cation's diameter arising from the influence of the other salt. Obviously, the preceding results suggest the following expressions for the diameter of the cations

$$\sigma_A = \sigma_A^{(0)} + \sigma_A^{(1)} C_A + \sigma_{B \rightarrow A}^{(1)} C_B \quad (31)$$

(with a similar relationship for σ_B) and to keep eq 30. In these relations, σ_A stands for the diameter of the cation of salt A, and $\sigma_A^{(0)}$ and $\sigma_A^{(1)}$ are determined by fitting the data for the pure salts A and B. The parameter $\sigma_{B \rightarrow A}^{(1)}$ represents the effect of salt B on the cation size of salt A. So we have now two cross terms to be adjusted: $\sigma_{B \rightarrow A}^{(1)}$ and $\sigma_{A \rightarrow B}^{(1)}$.

When isopiestic ratios were given in the references, the experimental osmotic coefficients of the mixed electrolytes have been deduced by interpolating the osmotic coefficients of the reference salts. Interpolation has been carried out by using fitting expressions given in the papers^{24,26} quoted above.

The results for mixtures that were studied with the isopiestic method have been collected in Table 4. The table gives the values for the cross terms $\sigma_{A \rightarrow B}^{(1)}$ and $\sigma_{B \rightarrow A}^{(1)}$, and the AARD of fit. For comparison, the average relative deviation AARD₀ for the case where the cross terms $\sigma_{B \rightarrow A}^{(1)}$ and $\sigma_{A \rightarrow B}^{(1)}$ are set to zero in eq 31 is also given. For many systems it is noticed that agreement is poor in the latter case, especially at high concentration.

TABLE 3: Results for Two-Salt Mixtures with Common Cation

system A + B	ref	max I^a	AARD ^b (%)
NaCl + NaBr	43	4.3	0.5
KCl + KBr	43	4.3	0.09
LiCl + LiNO ₃	44	10	0.7

^a I is the ionic strength: $I = 1/2 \sum Z_i^2 m_i$ expressed in mol/kg.

^b Defined in Table 2.

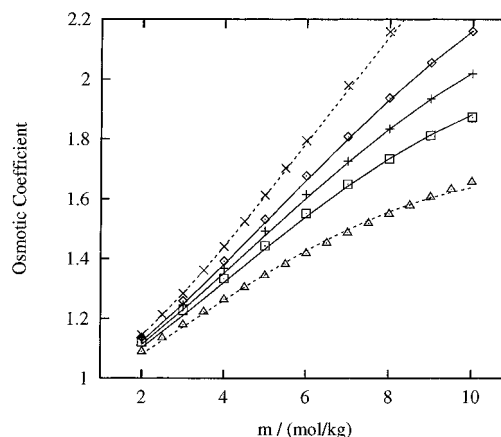


Figure 3. LR experimental and calculated osmotic coefficients for the mixture LiCl + LiNO₃ for three values of x , the fraction of LiNO₃, as a function of the total molality: $x = 0.3066$ (\diamond), $x = 0.4662$ ($+$), and $x = 0.6414$ (\square). Lines are the calculated curves. The results for the pure salts LiCl and LiNO₃ are recalled: $x = 0$ (\times) and $x = 1$ (\triangle).

TABLE 4: Results for Two-Salt Mixtures without Common Cation (Osmotic Data)

system A + B	ref	max I^a	$10^2 \sigma_{B \rightarrow A}^{(1)b}$	$10^2 \sigma_{A \rightarrow B}^{(1)b}$	AARD ^c	AARD ₀ ^d
LiCl + NaCl	45	6	-8.248	1.806	0.5	4.4
LiCl + KCl	44	5	-9.919	1.492	0.4	7
LiCl + CsCl	46	6	3.219	-16.56	0.3	3.4
NaCl + KCl	47	4	18.33	-28.59	0.04	2.2
NaCl + CsCl	48	6	15.14	-26.91	0.2	0.7
KCl + CsCl	46	5	1.110	5.043	0.1	1.1
NaCl + KBr	43	4.5	11.78	-18.96	0.1	1.3
KCl + NaBr	43	4.3	23.25	-37.65	0.06	4.4
NaBr + KBr	43	4.3	38.91	-67.15	0.3	2.4
NaCl + MgCl ₂	49	5.9	-1.759	-9.326	0.1	2.8
NaCl + CaCl ₂	50	8	0.9981	-12.47	0.2	7.3
KCl + CaCl ₂	51	6.3	41.77	-36.90	0.3	6
LiCl + BaCl ₂	52	4.3	-25.83	9.232	0.3	1.5
NaCl + BaCl ₂	53	4.8	8.002	-16.14	0.1	1.9
KCl + BaCl ₂	53	4.5	59.76	-53.45	0.2	3.6
CsCl + BaCl ₂	52	4	-97.19	8.537	0.6	1.8
MgCl ₂ + CaCl ₂	54	12	-21.33	-23.82	0.4	46
LiClO ₄ + NaClO ₄	55	5.8	-13.07	-3.052	0.4	7

^a I is the ionic strength: $I = 1/2 \sum Z_i^2 m_i$ in mol/kg. ^b In Å mol⁻¹ L.

^c In %, defined in Table 2. ^d AARD with $\sigma_{B \rightarrow A}^{(1)} = \sigma_{A \rightarrow B}^{(1)} \equiv 0$.

We now turn to the case of solutions involving an acid for which the mean activity coefficient of the acid has been assessed from electromotive force measurements. This quantity can be calculated in the present framework by using eqs 5, 6, 12, 15, and 16.

By virtue of eq 17, the MM-to-LR conversion yields

$$\ln y_{\text{HX}}^{(\text{LR})} = \ln y_{\text{HX}}^{(\text{MM})} - CV_{\text{HX}} \phi^{(\text{MM})}/2 \quad (32)$$

with $X = \text{Cl}$ or Br and in which V_{HX} is the mean partial molal volume of HX in the mixture, which can be evaluated from eq 25. Furthermore, it must be underlined that, in eq 32, the osmotic coefficient $\phi^{(\text{MM})}$ has been calculated consistently from eq 13.

TABLE 5: Results for Two-Salt Mixtures Involving an Acid (Activity Coefficient Data)

system A + B	ref	max I^a	$10^2 \sigma_{B \rightarrow A}^{(1)b}$	$10^2 \sigma_{A \rightarrow B}^{(1)b}$	AARD ^c	AARD ₀ ^d
HCl + LiCl	56	5	-6.640	-8.340	0.5	3.9
HCl + KCl	57	3	-9.123	9.302	0.01	1.4
HCl + CsCl	58	3	39.42	-93.61	0.2	24
HCl + Me ₄ NCl	59	0.1				0.1
HCl + Et ₄ NCl	59	0.1				0.08
HCl + SrCl ₂	60–62	8	-23.50	-2.630	0.8	4.4
HCl + BaCl ₂	63	3	-58.77	29.78	0.5	0.8
HBr + NaBr	64	3	-15.39	14.03	1	1
HBr + KBr	64	3	33.27	-69.17	0.4	1.7

^a I is the ionic strength: $I = \frac{1}{2} \sum Z_i^2 m_i$ in mol/kg.

^b In Å mol⁻¹ L. ^c In %, defined in Table 2. ^d AARD with $\sigma_{B \rightarrow A}^{(1)} = \sigma_{A \rightarrow B}^{(1)} \equiv 0$.

TABLE 6: Results for Three-Salt Mixtures

system	max I^a	AARD ^b (%)
LiCl + NaCl + KCl	3.1	0.7
LiCl + NaCl + CsCl	5.2	0.25
LiCl + NaCl + BaCl ₂	3.3	0.6
NaCl + KCl + BaCl ₂	4.4	0.4
HCl + CsCl + BaCl ₂	2.4	1.7

^a I is the ionic strength: $I = \frac{1}{2} \sum Z_i^2 m_i$ in mol/kg. ^b Defined in Table 2.

The results for the mixtures are summarized in Table 5. Let us mention that no cross term was needed for the mixtures with the two alkylammonium salts because the maximum concentration was low.

Generally, the accuracy of the fits for mixtures is within the experimental uncertainty.

The results given in Tables 4 and 5 deserve one comment. It can be noticed that in most cases the parameters for a given mixture are of opposite sign. Since for all the halides of Li, Na, K, and alkaline earth metals the cation effective size is a decreasing function of concentration, one might have expected a similar behavior in the case of mixtures of these salts. It can be thought that this result is simply caused by the adjustment procedure because for a given mixture one can find generally values for these two parameters that are both negative and lead nearly to the same precision for the fit.

Predictions for Three-Salt Mixtures

As a test, the present model can be used now for the prediction of departures from ideality in three-salt mixtures. The model can be extended to an arbitrary number of salts. The cation's diameter for a salt A and the relative permittivity then read

$$\sigma_A = \sigma_A^{(0)} + \sigma_A^{(1)} C_A + \sum_{S \neq A} \sigma_{S \rightarrow A}^{(1)} C_S \quad (33)$$

$$\epsilon^{-1} = \epsilon_w^{-1} \left(1 + \sum_S \alpha_S C_S \right) \quad (34)$$

where summations are made on the salts S.

With these relations and the results found in the previous sections, we can predict values for osmotic and activity coefficients in salt mixtures. The accuracy of the prediction is exemplified in Table 6. The data have been taken from the same work.⁵³ The first four systems mentioned in the table were studied experimentally with the isopiestic method, while in the last one the activity coefficient of HCl was measured.

Here too, the predictive capability of the present treatment is excellent except for the last system. However, in the latter

case, two points may be in favor of the present result. First, it has been suggested⁵³ that the accuracy of the measurements was likely to be questionable. Second, it has been found that the numerical results from this work agree completely, with a surprising accuracy, with those from two other methods: (i) the Pitzer model² and (ii) the Reilly *et al.* treatment.⁵³

Conclusion

With the present model, the predictions for osmotic and activity coefficients in nonassociating electrolytes agree with the experimental measurements to within the experimental error. In contrast to other previous descriptions, variation with concentration of the parameters introduced in the model can be interpreted in terms of ionic hydration effects.

Moreover, the model can be used up to very high concentrations. In this respect, it should be pointed out that the present treatment has been applied to solutions, such as 20 mol/kg LiBr, that contain nearly as many ions as water molecules.

The purpose of further work will be to account for ionic association effects.

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