Effect of Revisions of Debye–Hückel Limiting Law Coefficients on the Thermodynamic Parameters for Strong-Electrolyte Solutions

Donald G. Archer

Electrolyte Data Center, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

In order to treat properly the thermodynamics of mixed aqueous electrolytes, parameters obtained from the binary systems must have all been calculated with the same Debye–Hückel limiting law slope. Improvements in experiment and correlation of experimental dielectric constant and *PVT* measurements cause subsequent changes in calculated values of Debye–Hückel limiting law slopes. A method is described for the adjustment of ion-interaction parameters, resulting from differences in the Debye–Hückel limiting law coefficients. This method, for many equations, obviates the need for refitting the entire data base with the new Debye–Hückel coefficients. Illustration of the method is provided for the conversion of ion-interaction parameters obtained with an earlier dielectric constant equation to values obtained with a recently formulated dielectric constant equation.

Introduction

At high dilution, the concentration dependence of thermodynamic properties of aqueous electrolyte solutions approaches values that, in principle, can be calculated from the Debye–Hückel limiting law. Thus, the Debye–Hückel limiting behavior is usually included in empirical or semiempirical equations used to represent the experimentally determined concentration dependence of thermodynamic properties of aqueous electrolyte solutions. However, Debye–Hückel limiting law coefficients also require both experimentally determined values and representations of experimentally determined values for their calculation. These experimental values include fundamental constants (k, N, e, etc.) and the density and dielectric constant of the solvent. The fundamental constants are now well enough known so that the small revisions that occur from time to time do not make significant changes in the Debye–Hückel coefficients. On the other hand, the dielectric constant and density of water, as well as their derivatives with respect to temperature and pressure, are not as well-known. Therefore, as improvements are made in experimental results for the properties of water and their representations, experimentally significant changes of the Debye–Hückel limiting law values are simultaneously made.

In the past, equations that represented experimental determinations of dielectric constant for a region of temperature from the 0.1-MPa freezing temperature of water to temperatures in excess of the critical temperature were generally not of sufficient accuracy to give the most accurate values of Debye–Hückel limiting law coefficients in the temperature regimes where the most accurate experimental results existed. Equations that spanned smaller regions of temperature gave more accurate values of Debye–Hückel limiting law slopes in those regions but were not applicable over the entire range of temperature that is now experimentally accessible to enthalpy of dilution, heat capacity, and density measurements. This obviously produced a quandary for those attempting to represent these measurements. A recent representation of the dielectric constant of water has ameliorated this difficulty (*1*).

Revisions of Debye–Hückel limiting law coefficients would not seem to be of importance if one's attention is constrained to only individual binary electrolyte + water systems and if no attempt to transport the individual binary system results to any other system or theory is to be made. In other words, the equations fitted to the original experimental results give adequate representations of the results, regardless of small differences in the Debye–Hückel coefficients. However, it is often necessary to include the virial coefficients, or ion-interaction parameters, obtained from the representations for the binary electrolyte + water systems in calculations for mixed aqueous electrolyte solutions. This results in the obvious question: If different values for the properties of water were used in the different representations of the binary systems, then how does one use the so-obtained parameters in the calculations for the mixture?

The task of refitting to the experimental results for the aqueous electrolytes in order to obtain the revised empirical parameters, as well as thermodynamic consistency, is a task both tremendous and horrific. The present work will show that, for many cases, an alternative method makes refitting the experimental results unnecessary. What is actually desired is a method to obtain the revised coefficients without refitting to all of the experimental results. Such a method is described and demonstrated here.

The present method is applicable for most equations that are linear in their parameters as well as for some equations that are not. It is not meant for chemical-equilibrium model representations of experimental results for very dilute solutions. For the present demonstration, Pitzer's (*2*) ion-interaction equation is used. This choice was made because of widespread use of this equation, as well as the development of a large data base of ion-interaction coefficients based on this equation. The demonstration explores the differences caused in these ion-interaction parameters resulting from a change of Debye–Hückel coefficients, for example, the difference of those calculated from the dielectric constant equation of Bradley and Pitzer (*3*) and the equation of state of Haar et al. (*4*) from those calculated from a more recent dielectric constant equation (*1*) and the equation of state for water (*5*). The difference of the Debye–Hückel limiting law coefficient for the osmotic coefficient calculated from these two sets of equations is shown in Figure 1.

Method

In the process of fitting an equation that incudes a Debye–Hückel limiting law term to experimental results, it is often (and usually implicitly) assumed that an adequate representation of the experimental results does not reuire that the Debye–Hückel coefficient be absolutely accurate. In other words, the assumption exists that the same set of experimental results can be fitted equally well, and within its uncertainty, with a small range of values of the Debye–Hückel parameter. This assumption recognizes that small errors in the Debye–Hückel coefficient are compensated by the values of the adjustable parameters. Two least-squares-fitted ion-interaction equations for the electrolyte (MX) + water system, each of which contains

Table I. Values of $\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$ and δC^ϕ_{MX} for Different Types of Electrolytes[a]

type	α_1/ (kg mol^{-1})$^{1/2}$	$\delta\beta^0_{MX}$/ (kg mol^{-1})	$\delta\beta^1_{MX}$/ (kg mol^{-1})	$\delta\beta^2_{MX}$/ (kg mol^{-1})	δC^ϕ_{MX}/ (kg mol^{-1})	I/ (mol kg^{-1})
1–1	2.0	0.1167	2.729		-5.611×10^{-3}	10.2
1–2, 2–1	2.0	0.3363	14.99		-1.741×10^{-2}	30.2
1–2, 2–1[b]	1.4	0.2451	7.486		-1.028×10^{-2}	30.2
3–1, 1–3	2.0	0.8988	39.98		-7.583×10^{-3}	30.2
4–1, 1–4	2.0	1.868	83.30		−0.2280	30.2
5–1, 1–5	2.0	3.363	149.9		−0.5507	30.2
6–1, 1–6	2.0	5.493	244.9		−1.149	30.2
2–2[c]	1.4	0.8801	26.23	606.3	-7.025×10^{-3}	30.2

[a] I is the maximum molality of the fitted range of molality. [b] Holmes and Mesmer (*6*) found a better fit to aqueous alkali-metal sulfate results, using $\alpha_1 = 1.4$ (kg mol^{-1})$^{1/2}$. [c] Representation of the aqueous 2–2 metal sulfate data requires the inclusion of $\delta\beta^{2,i}_{MX}\exp(-\alpha_2 I^{1/2})$ in eqs 1 and 2 [$\alpha_2 = 12$ (kg mol^{-1})$^{1/2}$ for 298.15 K; for these cases $\alpha_1 = 1.4$ (kg mol^{-1})$^{1/2}$] (*7*). The addition of consequential terms to eqs 3–7 is straightforward.

a different Debye–Hückel coefficient, may be written. For each experimental osmotic coefficient these two equations are:

$$\phi - 1 = -|z_X z_M| A^B_\phi I^{1/2}/(1 + bI^{1/2}) + 2m\nu_M\nu_X[\beta^{0,B}_{MX} + \beta^{1,B}_{MX}\exp(-\alpha_1 I^{1/2})]/\nu + 2m^2(\nu_M\nu_X)^{3/2}C^{\phi,B}_{MX}/\nu + \epsilon^B \quad (1)$$

and

$$\phi - 1 = -|z_X z_M| A^A_\phi I^{1/2}/(1 + bI^{1/2}) + 2m\nu_M\nu_X[\beta^{0,A}_{MX} + \beta^{1,A}_{MX}\exp(-\alpha_1 I^{1/2})]/\nu + 2m^2(\nu_M\nu_X)^{3/2}C^{\phi,A}_{MX}/\nu + \epsilon^A \quad (2)$$

where ϕ is the experimentally determined osmotic coefficient and A^B_ϕ, A^A_ϕ refer to the two different Debye–Hückel limiting law slopes for osmotic coefficient. The least-squares determined estimates of the parameters of eqs 1 and 2 are $\beta^{0,B}_{MX}$, $\beta^{1,B}_{MX}$, $C^{\phi,B}_{MX}$ and $\beta^{0,A}_{MX}$, $\beta^{1,A}_{MX}$, $C^{\phi,A}_{MX}$, respectively. The difference between the fitted equation and each experimental value is denoted either ϵ^B or ϵ^A. In general, if the difference in A_ϕ is not too large, both equations can be fitted to the experimental results within their experimental uncertainty. For each experimental observation, eq 2 can be subtracted from eq 1 and the difference rearranged, yielding

$$|z_M z_X| I^{1/2}/(1 + bI^{1/2}) = 2m\nu_M\nu_X[\delta\beta^0_{MX} + \delta\beta^1_{MX}\exp(-\alpha_1 I^{1/2})]/\nu + 2m^2(\nu_M\nu_X)^{3/2}\delta C^\phi_{MX}/\nu + \delta\epsilon \quad (3)$$

where

$$\delta\beta^0_{MX} = (\beta^{0,B}_{MX} - \beta^{0,A}_{MX})/\delta A_\phi \quad (4)$$

$$\delta\beta^1_{MX} = (\beta^{1,B}_{MX} - \beta^{1,A}_{MX})/\delta A_\phi \quad (5)$$

$$\delta C^\phi_{MX} = (C^{\phi,B}_{MX} - C^{\phi,A}_{MX})\delta A_\phi \quad (6)$$

$$\delta\epsilon = (\epsilon^B - \epsilon^A)/\delta A_\phi \quad (7)$$

$$\delta A_\phi = A^B_\phi - A^A_\phi \quad (8)$$

The quantity $\delta\epsilon$ is related to the difference between the residuals from the least-squares fitted eqs 1 and 2 for each data point. The coefficients $\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$, and δC^ϕ_{MX} are independent of temperature and pressure. They are dependent on the electrolyte's charge type but not its identity.

For an isothermal, isobaric set of experimental results, the right-hand side of eq 3 can be viewed simply as a truncated series representation of the set of $|z_M z_X| I^{1/2}/(1 + bI^{1/2})$, which correspond to the experimental concentrations. If the series coefficients for the right-hand side of eq 3 are available, then a simple recipe for the desired correction of the ion-interaction parameters is at hand.

In order to obtain these coefficients, it was assumed that a linear least-squares procedure could be used to approximate the values of $\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$, and δC^ϕ_{MX}. Values of $\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$, and δC^ϕ_{MX} were determined for several different valence-type electrolytes in the following manner. For each type of electrolyte, a column of evenly spaced $I^{1/2}$ values (increment = 0.05 mol$^{1/2}$ kg$^{-1/2}$) was generated. The values of $\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$, and δC^ϕ_{MX} were then obtained from a linear least-squares fit to this column of values. The least-squares-estimated values of $\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$, and δC^ϕ_{MX} and the range of ionic strength that was used in the least-squares process are given in Table I. Adjustment of the ion-interaction parameters, for a change in the Debye–Hückel coefficient, δA_ϕ, is accomplished by applying eqs 4–6 and the values in Table I.

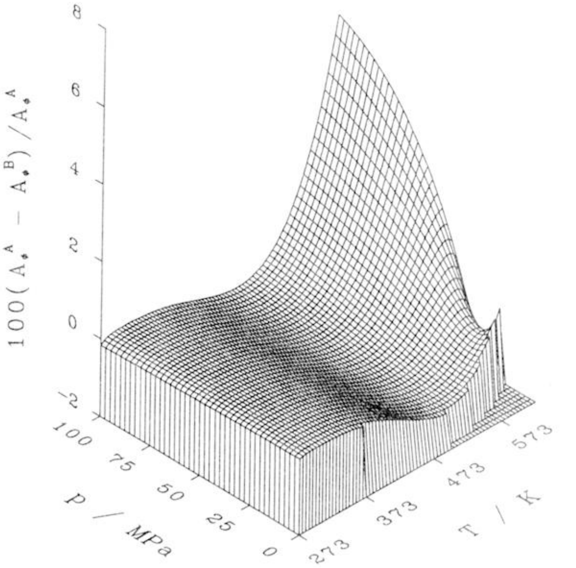

Figure 1. Percentage difference in Debye–Hückel limiting law coefficient for osmotic coefficient calculated from the equations of Bradley and Pitzer (*3*) and Haar et al. (*4*), A^B_ϕ, and that calculated from the equations of Archer and Wang (*1*) and Hill (*5*), A^A_ϕ, against temperature and pressure and for the liquid phase.

An example of the results of such a conversion is as follows. For NaCl(aq) for 573.15 K and 100 MPa, Pitzer et al. (*8*) calculated a value of A_ϕ of 0.7256 kg$^{1/2}$ mol$^{-1/2}$ from the equations of Bradley and Pitzer (*3*) and Haar et al. (*4*). For this temperature and pressure, they list values of β^0_{MX}, β^1_{MX}, and C^ϕ_{MX} as 0.0542 kg mol^{-1}, 0.5192 kg mol^{-1}, and -1.00×10^{-3} kg^2 mol^{-2}. The value of A_ϕ calculated from the more recent dielectric constant equation (*1*) and equation of state for water (*5*) is 0.7366. Applying eqs 4–6 and the parameters of Table I gives revised values of β^0_{MX}, β^1_{MX}, and C^ϕ_{MX} of 0.0556 kg mol^{-1}, 0.5487 kg mol^{-1}, and -1.06×10^{-3} kg^2 mol^{-2}. The difference in osmotic coefficient calculated with the two sets of parameters is less than ±0.0003 for molalities from 0.25 to 10.0 mol kg^{-1}; for molalities from 0.01 to 0.1 mol kg^{-1}, the difference in ϕ is slightly smaller than ±0.001. These differences are within the uncertainty of the calculated osmotic coefficient (*8*).

It is clear that the $\delta\epsilon$ of eq 3 do not form a normal distribution; i.e. the $\delta\epsilon$ are not a random error. Two consequences of this fact are (1) confidence intervals and probability tests for the parameters of Table I are not valid and (2) either ϵ^A or ϵ^B, or both, possess a component that is not normally distributed. This non normally distributed component of ϵ^i arises from the small error in Debye–Hückel coefficient and is often much smaller than the other sources of imprecision and inaccuracy of the experiment and/or the model bias in the fitted function (other than the Debye–Hückel portion). Also, it is observed that as δA_ϕ approaches zero, so must both $\epsilon^B - \epsilon^A$ and $\delta\epsilon$.

The adjusted parameters will not be identical with those calculated from repeating the least-squares fitting to the complete data base with the new A_ϕ value. However, the difference will be reasonably small compared to the change in the value. The small difference occurs because the distribution of experimental results, as a function of ionic strength, is not the same as that used in the generation of Table I.

The method described above can also be applied to equations that were fitted to apparent molar properties, e.g. $C_{p,\phi}$, V_ϕ, and H_ϕ. As an example, the analogue of eq 3 is constructed for the V_ϕ equation given by Rogers and Pitzer (*9*). Their equation for the apparent molar volume of solution, V_ϕ, was

$$V_\phi = V_\phi{}^\circ + \nu|z_M z_X|A_v h(I) + 2\nu_M\nu_X RT(mB^V_{MX} + \nu_M z_M m^2 C^V_{MX}) \quad (9)$$

where

$$h(I) = \ln(1 + bI^{1/2})/2b \quad (10)$$

$$B^V_{MX} = (\partial\beta^0_{MX}/\partial p)_T + 2(\partial\beta^1_{MX}/\partial p)_T[1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})]/(\alpha_1{}^2 I) \quad (11)$$

$$C^V_{MX} = (\partial C^\phi_{MX}/\partial p)_T/(2|z_M z_X|^{1/2}) \quad (12)$$

Proceeding as for eq 3, eqs 13–19 are obtained.

$$-\nu|z_M z_X|h(I) = \delta V_\phi{}^\circ + 2\nu_M\nu_X mRT[\delta(\partial\beta^0_{MX}/\partial p)_T + 2\delta(\partial\beta^1_{MX}/\partial \mathrm{p})[1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})]/(\alpha_1{}^2 I)] + m^2\nu_M{}^{3/2}\nu_X{}^{3/2}RT\delta(\partial C^\phi_{MX}/\partial p)_T + \delta\epsilon \quad (13)$$

where

$$\delta V_\phi{}^\circ = (V_\phi{}^{\circ,B} - V_\phi{}^{\circ,A})/\delta A_v \quad (14)$$

$$\delta(\partial\beta^0_{MX}/\partial p)_T = RT[(\partial\beta^{0,B}_{MX}/\partial p)_T - (\partial\beta^{0,A}_{MX}/\partial p)_T]/\delta A_v \quad (15)$$

$$\delta(\partial\beta^1_{MX}/\partial p)_T = RT[(\partial\beta^{1,B}_{MX}/\partial p)_T - (\partial\beta^{1,A}_{MX}/\partial p)_T]/\delta A_v \quad (16)$$

$$\delta(\partial C^\phi_{MX}/\partial p)_T = RT[(\partial C^{\phi,B}_{MX}/\partial p)_T - (\partial C^{\phi,A}_{MX}/\partial p)_T]/\delta A_v \quad (17)$$

$$\delta\epsilon = (\epsilon^B - \epsilon^A)/\delta A_v \quad (18)$$

$$\delta A_v = A^B_v - A^A_v \quad (19)$$

V_ϕ is related to the difference in density between solution, ρ, and solvent, ρ_w. This relation is such that the error in V_ϕ is as follows: (1) A molality-independent error in density behaves as $1/m$. Additionally, there is an error in determination of the molality or concentration of a solution. This error in molality determination can be a larger relative error than the error in density determination, for large concentrations, and thus cannot be neglected. Both of these errors require appropriate weighting in the conversion procedure. (2) A small percentage error in the value for the density of solvent creates an approximately corresponding percentage error in V_ϕ. This percentage error in V_ϕ will almost always be smaller than the other sources of error in V_ϕ, and its representation. Thus, this small percentage error, which arises due to the use of different equations of state, is neglected in the procedure for V_ϕ. The values of $\delta V_\phi{}^\circ$, $\delta(\partial\beta^0_{MX}/\partial p)_T$, $\delta(\partial\beta^1_{MX}/\partial p)_T$, and $\delta(\partial C^\phi_{MX}/\partial p)_T$

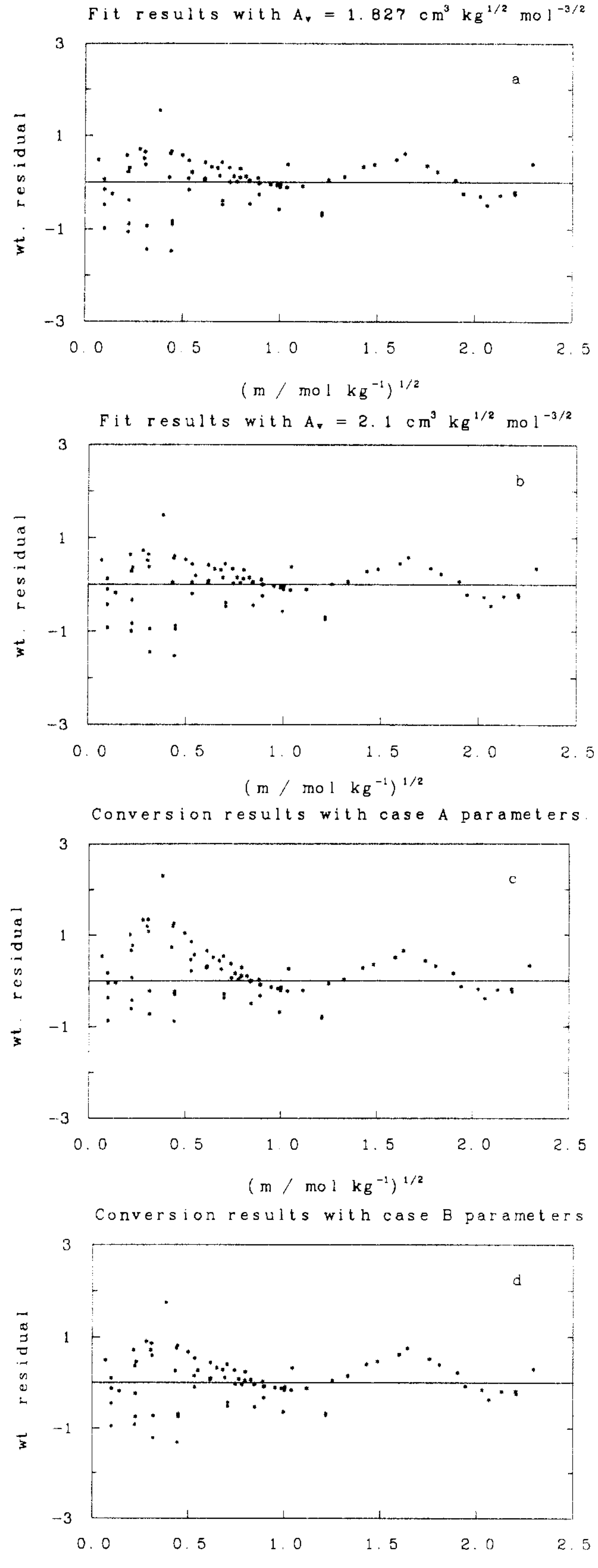

Figure 2. Weighted residual, $[V_\phi(\mathrm{obsd}) - V_\phi(\mathrm{calcd})]/\epsilon V_\phi$, against the square root of molality: (a) calculated from a fit to the experimental results using A_v = 1.827 cm³ kg$^{1/2}$ mol$^{-3/2}$; (b) calculated from a fit to the experimental results using A_v = 2.1 cm³ kg$^{1/2}$ mol$^{-3/2}$; (c) calculated by adjusting the ion-interaction parameters from the fit for b, by means of the case A parameters of Table II, and combining these ion-interaction parameters with the Debye–Hückel contribution with A_v = 1.827 cm³ kg$^{1/2}$ mol$^{-3/2}$; (d) calculated as that as in c with the exception that the case B parameters of Table II were used rather than the case A parameters.

Table II. Values of $\delta V_\phi°$, $\delta(\partial\beta^0_{MX}/\partial p)_T$, $\delta(\partial\beta^1_{MX}/\partial p)_T$, and $\delta(\partial C^\phi_{MX}/\partial p)_T$ for a 2-1, 1-2 Electrolyte, Obtained with Different Values of c' and MW

case[a]	$\delta V_\phi°$/ (cm^3 mol^{-1})	$\delta(\partial\beta^0_{MX}/\partial p)_T$/ (kg mol^{-1} bar^{-1})	$\delta(\partial\beta^1_{MX}/\partial p)_T$/ (kg mol^{-1} bar^{-1})	$\delta(\partial C^\phi_{MX}/\partial p)_T$/ (kg^2 mol^{-2} bar^{-1})	I/ (mol kg^{-1})
A	−0.153	−0.094	−4.06	5.67×10^{-3}	30.2
B	−0.447	−0.101	−3.48	6.35×10^{-3}	30.2

[a] Case A corresponds to values of c' and MW equal to 60 g^2 cm^{-3} mol^{-1} and 95 g mol^{-1}, respectively. Case B corresponds to values of c' and MW equal to 250 g^2 cm^{-3} mol^{-1} and 391.1 g mol^{-1}, respectively.

Table III. Values of $\delta V_\phi°$, $\delta(\partial\beta^0_{MX}/\partial p)_T$, $\delta(\partial\beta^1_{MX}/\partial p)_T$, and $\delta(\partial C^\phi_{MX}/\partial p)_T$ for Different Types of Electrolytes

type	$\delta V_\phi°$/ (cm^3 mol^{-1})	$\delta(\partial\beta^0_{MX}/\partial p)_T$/ (kg mol^{-1} bar^{-1})	$\delta(\partial\beta^1_{MX}/\partial p)_T$/ (kg mol^{-1} bar^{-1})	$\delta(\partial C^\phi_{MX}/\partial p)_T$/ (kg^2 mol^{-2} bar^{-1})	I/ (mol kg^{-1})
1-1[a]	−0.2150	−0.031 23	−0.6393	1.6433×10^{-3}	10.2
1-2, 2-1[b]	−0.3398	−0.099 12	−3.6900	6.2154×10^{-3}	30.2
1-2, 2-1[c]	−0.9157	−0.068 26	−1.7219	3.2886×10^{-2}	30.2

[a] c' = 100 g^2 cm^{-3} mol^{-1}, MW = 165.4 g mol^{-1}, α_1 = 2.0 (kg mol^{-1})$^{1/2}$. [b] c' = 130 g^2 cm^{-3} mol^{-1}, MW = 200 g mol^{-1}, α_1 = 2.0 (kg mol^{-1})$^{1/2}$. [c] c' = 130 g^2 cm^{-3} mol^{-1}, MW = 200 g mol^{-1}, α_1 = 1.4 (kg mol^{-1})$^{1/2}$.

Table IV. Effect of Adjustment Procedure on $C°_{p,\phi}$[a]

T/K	$(\delta A_c/R)$/ (kg/mol)$^{-1/2}$	$\Delta C°_{p,\phi}/R$	$\delta A_c\delta C°_{p,\phi}/R$	$\lvert\Delta C°_{p,\phi} - \delta A_c\delta C°_{p,\phi}\rvert/R$	$\epsilon C_{p,\phi}(0.2\ m)/R$
298.15	−0.408	0.070	0.088	0.018	0.18
340.0	0.046	−0.005	−0.010	0.005	0.72
450.0	1.050	−0.148	−0.226	0.078	0.96
550.0	0.265	−0.041	−0.057	0.016	1.80
575.0	4.490	−0.687	−0.966	0.279	2.28
600.0	24.906	−3.816	−5.355	1.539	3.85

[a] Results for 17.9 MPa (*13*).

were obtained by using the same procedure as described for eqs 3–8, with the exception that a nonunity weighting factor was assigned to each calculated value of $-\nu|z_M z_X|h(I)$.

The error in V_ϕ, ϵV_ϕ, resulting from an absolute error in density determination and a relative error in molality determination can be expressed as

$$(\epsilon V_\phi)^2 = (\epsilon m)^2\{1000c'[(\rho°\rho_s m)^{-1} - (\rho_s{}^2 m)^{-1}] - \mathrm{MW}c'/\rho_s{}^2\}^2 + (\epsilon\rho)^2[-1000/(m\rho_s{}^2) - \mathrm{MW}/\rho_s{}^2]^2 \quad (20)$$

where

$$\rho_s = \rho° + c'm \quad (21)$$

and where $\rho°$ is the density of the solvent, m is the stoichiometric molality, MW is the solute molecular weight, ϵm is the error in molality determination, $\epsilon\rho$ is the error in density determination, c' is a constant that approximates the slope of the empirical density-molality relationship, and ρ_s is an approximation of the solution density. Equations 20 and 21 are not exact, but they do give a reasonable approximation of the uncertainty in V_ϕ due to measurement errors. The appearance of c' in eq 20 and 21 implies the possibility that a conversion process based on equations of the form of eqs 13–19 might not be sufficiently general as to be useful.

It is demonstrated here that the choice of c', within reasonable values, does not greatly affect the choice of conversion parameters. Table II gives values of $\delta V_\phi°$, $\delta(\partial\beta^0_{MX}/\partial p)_T$, $\delta(\partial\beta^1_{MX}/\partial p)_T$, and $\delta(\partial C^\phi_{MX}/\partial p)_T$ calculated for a 2-1 or 1-2 electrolyte with the values c' and MW of 60 g^2 cm^{-3} mol^{-1} and 95.0 g mol^{-1} and of 250 g^2 cm^{-3} mol^{-1} and 391.1 g mol^{-1}. These values approximately correspond to $MgCl_2$ and BaI_2 for 298.15 K and 0.1 MPa and thus represent a partial range of the possible values for 2-1 electrolytes. The values of $\epsilon\rho$ and ϵm assumed for eqs 20 and 21 were 10×10^{-6} g cm^{-3} and $1 \times 10^{-3}m$, respectively. Figure 2 shows the weighted residuals, $[V_\phi(\mathrm{obsd}) - V_\phi(\mathrm{calcd})]/\epsilon V_\phi$, calculated from fitting eqs 9–12 to the 298.15 K experimental results for $MgCl_2$ of Lo Surdo et al. (*10*) and Chen et al. (*11*) by using a value of A_v = 1.827 cm^3 kg$^{1/2}$ mol$^{-3/2}$ and a value of A_v = 2.1 cm^3 kg$^{1/2}$ mol$^{-3/2}$. Also shown in Figure 2 are values of the weighted residuals calculated from a conversion of the ion-interaction parameters, which had been obtained with A_v = 2.1 cm^3 kg$^{1/2}$ mol$^{-3/2}$, using both sets of conversion parameters given in Table II. (The value of A_v = 2.1 cm^3 kg$^{1/2}$ mol$^{-3/2}$ is approximately the value recommended by Beyers and Staples (*12*). This value is not very accurate. It was chosen for this example because it provides one of the largest δA_v, for 298.15 K, producible with values found in the current literature.) The high degree of accuracy and precision of the experimental $\rho - \rho_w$, combined with this large difference in A_v, makes this example a fairly strenuous test of both the effect of weighting factors and the conversion process.

It can be seen from Figure 2 that either set of parameters can adjust the virial coefficients, for this fairly large difference in A_v, such that both adjusted ion-interaction equations can reproduce the results within experimental error. Thus, the adjustment parameters are not greatly dependent on the exact value of c' and MW in eqs 20 and 21. Table III gives values appropriate for conversion of V_ϕ results for 1-1, 2-1, and 1-2 electrolytes.

An example of a conversion is as follows. Rogers and Pitzer gave a value of A^B_v, for 573.15 K and 8.6 MPa, of 98.73 cm^3 kg$^{1/2}$ mol$^{-3/2}$. The value of A^A_v calculated from the more recent equations (*1*, *5*) is 107.08 cm^3 kg$^{1/2}$ mol$^{-3/2}$. For 573.15 K and 8.6 MPa, Rogers and Pitzer gave the values −95.68 cm^3 mol^{-1}, -5.167×10^{-5} kg mol^{-1} bar^{-1}, 0.0 kg mol^{-1} bar^{-1}, and 3.17×10^{-6} kg^2 mol^{-2} bar^{-1} for $V_\phi°$, $(\partial\beta^0_{MX}/\partial p)_T$, $(\partial\beta^1_{MX}/\partial p)_T$, and $(\partial C^\phi_{MX}/\partial p)_T$, respectively. Applying the correction procedure gives the values −97.47 cm^3 mol^{-1}, -5.714×10^{-5} kg mol^{-1} bar^{-1}, -1.120×10^{-4} kg mol^{-1} bar^{-1}, and 3.46×10^{-6} kg^2 mol^{-2} bar^{-1} for $V_\phi°$, $(\partial\beta^0_{MX}/\partial p)_T$, $(\partial\beta^1_{MX}/\partial p)_T$, and $(\partial C^\phi_{MX}/\partial p)_T$, respectively. For molalities from 0.25 to 10 mol kg^{-1}, the maximum difference for $\rho - \rho_w$ calculated from the two sets of parameters was approximately 0.04% (this difference occurs for molalities of about 0.5 mol kg^{-1}). This small difference is well within the estimated uncertainty of the equation (*9*).

It is also noted that eq 9–19, and the parameters of Table III, are sufficiently general for application also to H_ϕ and $C_{p,\phi}$, if the differentiations and temperature factors of eqs 13–19 are taken into account. Gates et al. (*13*) fitted two-cubic spline surfaces to their experimental $C_{p,\phi}$ for aqueous NaCl. The only difference in the two fits was that a different formulation for the dielectric constant of water was used in each. Table IV contains values of the difference in the two sets of Debye–Hückel coefficients, δA_c, and the difference in the value of $C^\circ_{p,\phi}$, $\Delta C^\circ_{p,\phi}$, for 17.9 MPa, from the two fits. The authors' estimate of the experimental accuracy for a determination of $C_{p,\phi}$ for a 0.2 mol kg^{-1} solution, $\epsilon C_{p,\phi}$, is also given in the table. The table gives values of $\delta A_c \delta C^\circ_{p,\phi}$, where $\delta C^\circ_{p,\phi}$ was taken as -0.215 J K^{-1} mol^{-1} (Table III), and the difference between $\Delta C^\circ_{p,\phi}$ and $\delta A_c \delta C^\circ_{p,\phi}$. This difference is seen to be significantly smaller than the uncertainty of the experimental results. This result is interesting for the following reasons: (1) The form of the Debye–Hückel equation used by Gates et al. was different than that used in the generation of the values in Table III. (2) The form of the non-Debye–Hückel, excess property contribution used by Gates et al. was different than that used for Table III. Although the agreement of the differences in Table IV is good, it is recommended that, for equations other than that used in the generation of Tables I and III, the appropriate analogues of the equations presented here be constructed.

These examples demonstrate that the conversion of some equations from a basis on a particular set of Debye–Hückel coefficients to a different set of Debye–Hückel coefficients, without refitting to all of the experimental data, is possible. Because the method is both simple and general, it is not necessary to publish tables of revised parameters for the ion-interaction, or virial coefficient, equations each time that a more accurate dielectric constant representation appears.

Nomenclature

A_ϕ, A_V, A_c, Debye–Hückel limiting law coefficients for osmotic coefficient, apparent molar volume, and apparent molar heat capacity at constant pressure
b, ion size parameter in Pitzer's ion-interaction equation [(b = 1.2 (mol kg^{-1})$^{-1/2}$]
B^V_{MX}, pressure derivative of B_{MX}, a parameter in Pitzer's ion-interaction equation
C^V_{MX}, pressure derivative of C_{MX}, a parameter in Pitzer's ion-interaction equation
C^ϕ_{MX}, parameter in Pitzer's ion-interaction equation
$C_{p,\phi}$, apparent molar heat capacity at constant pressure, J K^{-1} mol^{-1}
$C^\circ_{p,\phi}$, apparent molar heat capacity at constant pressure for infinite dilution, J K^{-1} mol^{-1}
c', slope of the approximate density-molality relationship, g^2 cm^{-3} mol^{-1}
e, charge of the electron, C
$h(I)$, function of ionic strength, defined in eq 10
I, ionic strength (mol kg^{-1} basis)
k, Boltzmann's constant, J K^{-1}
M, Subscript to denote cation
MW, mass of a formula weight of solute, g mol^{-1}
m, molality, mol kg^{-1}
N, Avogadro's constant, mol^{-1}
p, pressure, MPa
R, gas constant, 8.3144 J K^{-1} mol^{-1}
T, thermodynamic temperature, K
V_ϕ, apparent molar volume, cm^3 mol^{-1}
$V_\phi{}^\circ$, apparent molar volume for infinite dilution, cm^3 mol^{-1}
X, subscript to denote anion
z_i, coefficient of the charge of the ion i
α_1, parameter in Pitzer's ion-interaction equation
α_2, parameter in Pitzer's ion-interaction equation for bivalent-metal sulfates
β^0_{MX}, β^1_{MX}, parameters in Pitzer's ion-interaction equation
δA_V, δA_ϕ, δA_c, difference in Debye–Hückel limiting law slope from different sources
$\delta\beta^0_{MX}$, $\delta\beta^1_{MX}$, δC^ϕ_{MX}, Adjustment terms for parameter's in Pitzer's ion-interaction equation, defined in eqs 4–6
$\delta(\partial\beta^0_{MX}/\partial p)_T$, $\delta(\partial\beta^1_{MX}/\partial p)_T$, $\delta(\partial C^\phi_{MX}/\partial p)_T$, adjustment terms for parameter's in Pitzer's ion-interaction equation, defined in eqs 15–17.
$\delta C^\circ_{p,\phi}$, adjustment term for apparent molar heat capacity at constant pressure for infinite dilution, J K^{-1} mol^{-1}
$\delta V_\phi{}^\circ$, adjustment term for apparent molar volume at infinite dilution, cm^3 mol^{-1}
ϵ, difference between a calculated value and an observation
$\epsilon\rho$, ϵm, assumed uncertainties in the experimental determinations of density and molality, respectively, g cm^{-3} and mol kg^{-1}
ρ, density of solution, g cm^{-3}
ρ°, density of solvent, g cm^{-3}
ρ_s, approximate value of the density of a solution, not to be confused with the experimental density of a solution, ρ, g cm^{-3}
ρ_w, density of water, g cm^{-3}
ϕ, osmotic coefficient
ν_i, moles of ion i per mole of electrolyte, assuming complete dissociation
ν, $\nu_M + \nu_X$

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