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THE THERMODYNAMICS OF UNSYMMETRICAL ELECTROLYTE
MIXTURES: ENTHALPY AND HEAT CAPACITY

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The Thermodynamics of Unsymmetrical Electrolyte Mixtures:

Enthalpy and Heat Capacity

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(Abstract)

There is a purely electrostatic contribution
to the thermodynamic properties of electrolytes
for the mixing of ions of different charge but
the same sign. The previous treatment, which was
limited to activity or osmotic coefficients, is
extended to enthalpies and heat capacities and
applied to the measurements of Cassel and Wood
on the heat of mixing in the systems $NaCl-BaCl_2$
and $NaCl-Na_2SO_4$.

Introduction

For electrolytes involving unsymmetrical mixing of ions of different charges of the same sign there is a higher-order limiting law. Friedman[1] derived this law by the cluster integral method which was developed for electrolytes by Mayer.[2] A method of practical application to unsymmetrical mixtures of realistic concentration was developed by the writer.[3] While the limiting law alone is inadequate, it was shown that one could define a new function, valid at finite molalities. With this function an anomaly in the thermodynamics of $HCl-AlCl_3$ was removed. This new function has the same character as the limiting law; it depends only on the charges on the ions, and solvent properties, i.e., dielectric constant and density, as well as the temperature. The Debye-Hückel limiting law has these characteristics. The new function becomes zero for mixing ions of the same charge.

Cassel and Wood[4] measured heats of mixing of NaCl with $BaCl_2$ and of NaCl with Na_2SO_4 in dilute aqueous solution with the intent of testing the corresponding limiting law for heat of unsymmetrical mixing. While they found a significant effect of the right sign as the ionic strength approached zero, they were unable to verify the law quantitatively. Even between ionic strengths of 0.02 and 0.05 mol kg^{-1} their slope was less than half the theoretical limiting value. In this paper we extend to enthalpies the derivation of the unsymmetrical mixing function derived earlier[3] for free energy, and obtain good agreement with Cassel and Wood's measurements.

Friedman and Krishnan[5] have made calculations in the HNC approximation with parameters specifically chosen for the $NaCl-BaCl_2$ system and at the molalities of measurement. They obtained reasonable agreement. However, their calculations are much more complex and less general than the method presented here.

The heat of mixing is, of course, related to the temperature dependence of activity and osmotic coefficients for mixed electrolytes, and in a companion paper Roy, et al.,[6] present new and precise measurements of the activity coefficient of HCl in HCl-LaCl$_3$ mixtures at several temperatures.

The appropriate equations for the heat capacity of unsymmetrical mixtures are derived, although these do not appear to be any experimental data at present for which this effect would be significant. The molecular-level implications are also discussed.

Equations for Unsymmetrical Mixed Electrolytes

It was shown[3] that this limiting law for unsymmetrical mixing could easily be incorporated in the general equations for mixed electrolytes of Pitzer and Kim;[7] these equations comprise a Debye-Hückel term together with virial coefficients for short range interparticle forces. In most cases it is sufficient to include only second and third virial coefficients for binary and ternary interactions, and one deletes the third virial coefficient if all three ions are of the same sign. The higher-order mixing function appears as a term in the second virial coefficient for unlike ions of the same sign.

The terms in the equations arising from short-range forces are evaluated empirically. The more important terms, which are for ions of opposite sign, are evaluated from data on solutions of a single solute. Very small terms for the difference in short range forces between pairs of unlike ions of the same sign as compared to the averages for pairs of like ions must be evaluated from the data for mixtures. Since ions of the same sign are seldom close enough to one another for short-range forces to arise, these terms are expected to be small and are often negligible. For for ions of different charge of the same sign, there is this small but significant effect of the long-range electrical forces.

A most impressive application of the equations for mixed electrolytes is found in the work of Harvie and Weare[8] on the mineral solubilities related to the many components of seawater. They found that these higher-order electrostatic terms were essential in the interpretation of the solubility of $CaSO_4$ in NaCl or in seawater.

Practically all of the applications to date of these higher-order electrostatic terms have been to activity or osmotic data at 25°C. In the present paper we extend the derivations to the enthalpy and the heat capacity.

The general form of a virial equation for the excess Gibbs energy of electrolytes is[9]

$$\frac{G^{ex}}{n_w RT} = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) + \sum_i \sum_j \sum_k m_i m_j m_k \; \mu_{ijk} \cdots \tag{1}$$

where n_w is the number of kg of solvent and $f(I)$ is a general function of the ionic strength I related to the electrical forces and containing the Debye-Hückel limiting law. The expression selected[9] for $f(I)$ is an extended form

$$f(I) = -A_\phi (4I/b) \ln(1 + bI^{1/2}) \tag{2}$$

$$A_\phi = \frac{1}{3} (2\pi N_o d_w/1000)^{1/2} \ell^{3/2} \tag{3}$$

$$\ell = e^2/DkT \tag{4}$$

where A_ϕ is the Debye-Hückel parameter and b is a parameter given the value 1.2 $kg^{1/2}$ $mol^{-1/2}$ for all solutions. Expansion of the logarithm in (2) gives the limiting law as the leading term. In equation (4) e is the charge on the electron, D the dielectric constant of the solvent while k and T have the usual meanings. In SI units $4\pi\epsilon_o$ must be inserted

in the denominator of equation (4) with ϵ_o the vacuum permitivity.

The quantities $\lambda_{ij}(I)$ are the second virial coefficients for pairwise interaction between ions (or other solute particles) i and j and are functions of I. The ionic strength dependence may be neglected for the third virial coefficients μ_{ijk}. Higher order coefficients can be added but are not ordinarily needed.

The virial coefficients depend on the short-range forces, effective in the solvent, between solute particles. For ions the individual coefficients cannot be measured; hence one defines the measurable coefficients which are for electrically neutral combinations. We repeat here only the expressions for the second virial coefficients since the higher order electrical terms are at that level.

$$B_{MX} = \lambda_{MX} + |z_X/2z_M|\lambda_{MM} + |z_M/2z_X|\lambda_{XX} \tag{5}$$

$$\theta_{MN} = \lambda_{MN} - (z_N/2z_M)\lambda_{MM} - (z_M/2z_N)\lambda_{NN} \tag{6}$$

Here M, N are ions of one sign and X is an ion of the opposite sign. The B terms appear for pure electrolytes, hence they can be evaluated empirically from pure-electrolyte data. The θ terms arise for mixtures and can be evaluated from simple, common-ion mixtures such as HCl-NaCl or NaCl-Na_2SO_4. Since the λ's depend on the ionic strength, so, in principle, do the B's and θ's. The empirical expressions chosen for this ionic strength dependence of the B's are given elsewhere.[7-10] For the θ's it is found that the ionic strength dependence is negligible except for the special electrostatic effects to be discussed below.

Before proceeding further it is convenient to rewrite equation (1) in terms of the measurable coefficients B and θ and the corresponding third virial coefficients C and ψ which are given in various papers[7-10]

$$\frac{G^{ex}}{n_w RT} = f(I) + 2 \sum_c \sum_a m_c m_a [B_{ca} + (\Sigma mz)C_{ca}]$$

$$+ \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'} + \sum_a m_a \psi_{cc'a}/2]$$

$$+ \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'} + \sum_c m_c \psi_{caa'}/2] \tag{7}$$

Here the sums are over the various cations c, c' and the various anions a,a' while the quantity (Σmz) is just the total electrical positive (or negative) charge molality, i.e., $\Sigma m_c z_c$.

The theoretical basis for this formulation is found in the cluster-integral method introduced for electrolytes by Mayer[2] and applied with generality by Friedman.[1] Since the theoretical infrastructure is extensive, it will not be repeated here. Including only interactions between pairs of solute ions, Friedman obtains the following equation for the excess Helmholtz energy.

$$\frac{A^{ex}}{VkT} = -\frac{\kappa^3}{12\pi} + \sum_i \sum_j c_i c_j [\frac{2\pi z_i z_j \ell}{\kappa^2} J_{ij}(\kappa, z_i, z_j, \ldots)] \tag{8}$$

Here V is the volume, κ is the usual Debye-Hückel parameter, c_i is the concentration and z_i the number of charges (sign included) on the ith ion. The function J depends on the interionic potential and κ. If the potential is

$$v_{ij} = u_{ij} + z_i z_j \ell/r \tag{9}$$

where the short-range potential u_{ij} is a function of interionic distance r, then J is

$$J_{ij} = - \frac{\kappa^2}{z_i z_j 1} \int_0^\infty [\exp(q_{ij} - u_{ij}/kT) - 1 - q_{ij} - \frac{1}{2} q_{ij}^2] r^2 \, dr \qquad (10)$$

with

$$q_{ij} = -(z_i z_j \ell/r) e^{-\kappa r} \qquad (11)$$

The analogy between the terms on the right in equations (1) and (8) is apparent. Note, of course, that (8) contains no third virial or higher terms. Since the virial terms in (1) are to be determined empirically, they can absorb the small differences between concentrations and molalities, between the Helmholtz and Gibbs energies, etc. The first term in (8) is the Debye-Hückel limiting law and it is contained exactly in $f(I)$ in (1). One could limit $f(I)$ to that expression, but it proved more effective to use the extended form of equation (2). The additional terms in the expansion of the logarithm in (2) can be expressed as second virial terms with I dependence; hence there is no difference in principle arising from the difference in the initial terms of (1) and (8).

The integral in equation (10) for the theoretical second virial coefficients cannot be evaluated, in general, without explicit knowledge of the short-range interionic potential u_{ij}. Since that is not available these terms are ordinarily evaluated empirically. But for the particular case of ions of the same sign, an approximation yields useful results.

Ions of the same sign repel one another strongly enough that they seldom approach one another closely; hence the short-range potential should have little or no effect. This can be seen mathematically in

eq (10). If q_{ij} is large and negative for the range of r for which u_{ij} differs from zero, then the value of $\exp(q_{ij})$ is extremely small through-out this range. Thus, provided u_{ij} is positive (or if negative, is small), the effect of u_{ij} will be negligible.

In view of this situation, we can evaluate the effect of electro-static forces on the difference terms θ_{MN} without making any detailed assumption about short-range forces. Let us write

$$\theta_{MN} = {}^{S}\theta_{MN} + {}^{E}\theta_{MN} \tag{12}$$

where the first term on the right arises from the combined effects of short-range forces acting directly or through the solvent, of the use of molalities instead of concentration, and of the difference in the Debye-Hückel term in eq. (8) from that in (1). The second term ${}^{E}\theta_{MN}$ will be calculated from the corresponding terms of the cluster-integral theory with the omission of short-range forces. From the definition of θ_{MN}, we have

$$^{E}\theta_{MN} = {}^{E}\lambda_{MN} - (z_{N}/2z_{M})^{E}\lambda_{MM} - (z_{M}/2z_{N})^{E}\lambda_{NN} \tag{13}$$

$$^{E}\lambda_{ij} = (z_{i}z_{j}/4I)J_{ij} \qquad \text{with} \qquad u_{ij} = 0 \tag{14}$$

$$J_{ij} = \frac{\kappa^{2}}{z_{i}z_{j}\ell} \int_{0}^{\infty} (1 + q_{ij} + \frac{1}{2}q_{ij}^{2} - e^{q_{ij}})r^{2}\,dr \tag{15}$$

With the substititions

$$y = \kappa r \tag{16}$$

$$x = z_{i}z_{j}\ell\kappa \tag{17}$$

$$q = -(x/y)e^{-y} \tag{18}$$

$$J(x) = x^{-1} \int_0^\infty (1 + q + \frac{1}{2} q^2 - e^q) y^2 \, dy \tag{19}$$

In our working units

$$x_{ij} = 6 z_i z_j A_\phi I^{1/2} \tag{20}$$

where for ions of the same sign x_{ij} is always positive. Also

$${}^E\theta_{MN} = (z_M z_N / 4I) [J(x_{MN}) - \frac{1}{2} J(x_{MM}) - \frac{1}{2} J(x_{NN})] \tag{21}$$

For enthalpies we need the temperature derivative of θ and therefore of J while for heat capacities we need the second derivative. Thus we shall consider the evaluation of J, J', and J'' where

$$J' = \partial J / \partial x \tag{22a}$$

$$J'' = \partial^2 J / \partial x^2. \tag{22b}$$

For J the integrals of the second and third terms in the parentheses in eq (19) are straightforward with the results

$$J = \frac{1}{4} x - 1 + J_2 \tag{23}$$

$$J' = \frac{1}{4} - (J_2 / x) + J_3 \tag{24}$$

$$J'' = \frac{J_2}{x^2} - \frac{2 J_3}{x} - J_4 \tag{25}$$

$$J_2 = x^{-1} \int_0^\infty (1 - e^q) y^2 \, dy \tag{26}$$

$$J_3 = x^{-1} \int_0^\infty \exp(q - y) y \, dy \tag{27}$$

$$J_4 = x^{-1} \int_0^\infty \exp(q - 2y) \, dy \tag{28}$$

There are no simple integrals for J_2, J_3, and J_4 but they are readily evaluated numerically with modern computers. The resulting functions J, J', J" are shown in figure 1 . The accompanying paper includes further comments on the evaluation of these functions.

The equations for the excess enthalpy $L = H^{ex}$ and heat capacity $J = C_p^{ex}$ follow directly from differentiation of eq (7).

$$\frac{L}{n_w RT^2} = \frac{A_H I}{RT^2 b} \ln(1 + bI^{1/2}) - 2 \sum_c \sum_a m_c m_a [B_{ca}^L + (\Sigma mz)C_{ca}^L]$$

$$- \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'}^L + \sum_a m_a \psi_{cc'a}^L /2]$$

$$- \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'}^L + \sum_c m_c \psi_{caa'}/2] \tag{29}$$

$$\frac{J}{n_w RT^2} = \frac{A_J I}{RTb} \ln(1 + bI^{1/2}) - 2 \sum_c \sum_a m_c m_a [B_{ca}^J + (\Sigma mz)C_{ca}^J]$$

$$- \sum_c \sum_{c'} m_c m_{c'} [\theta_{cc'}^J + \sum_a m_a \psi_{cc'a}^J /2]$$

$$- \sum_a \sum_{a'} m_a m_{a'} [\theta_{aa'}^J + \sum_c m_c \psi_{cca'}^J /2] \tag{30}$$

where

$$B^L = \partial B/\partial T, \quad B^J = \partial^2 B/\partial T^2 + (2/T)\partial B/\partial T \tag{31}$$

$$C^L = \partial C/\partial T, \quad C^J = \partial^2 C/\partial T^2 + (2/T)\partial C/\partial T \tag{32}$$

$$\theta^L = \partial \theta/\partial T, \quad \theta^J = \partial^2 \theta/\partial T^2 + (2/T)\partial \theta/\partial T \tag{33}$$

$$\psi^L = \partial \psi/\partial T, \quad \psi^J = \partial^2 \psi/\partial T^2 + (2/T)\partial \psi/\partial T \tag{34}$$

Do not confuse J, the excess heat capacity, with J(x) the function of

eq (10) etc. The second virial coefficients B, B^L, and B^J all have the ionic strength dependence given by

$$B_{ca} = \beta_{ca}^{(0)} + (2\beta_{ca}^{(1)}/\alpha^2 I)[1-(1+\alpha I^{\frac{1}{2}})\exp(-\alpha I^{\frac{1}{2}})]$$

where α is a general parameter equal to 2.0 $kg^{\frac{1}{2}}$ $mol^{-\frac{1}{2}}$ while $\beta_{ca}^{(0)}$ and $\beta_{ca}^{(1)}$ are parameters specific to the electrolyte c,a.

Equations analogous to eq (12) apply to θ^L and θ^J and, with eq (20) and (21), yield

$$^E\theta_{MN}^L = \frac{z_M z_N}{4I}\left[\left(\frac{\partial x_{MN}}{\partial T}\right)J'(x_{MN}) - \frac{1}{2}\left(\frac{\partial x_{MM}}{\partial T}\right)J'(x_{MM})\right.$$

$$\left. - \frac{1}{2}\left(\frac{\partial x_{NN}}{\partial T}\right)J'(x_{NN})\right] \tag{35}$$

$$^E\theta_{MN}^J = \frac{z_M z_N}{4I}\left\{\left(\frac{\partial x_{MN}}{\partial T}\right)^2 J''(x_{MN}) + \left(\frac{\partial^2 x_{MN}}{\partial T^2} + \frac{2}{T}\frac{\partial x_{MN}}{\partial T}\right)J'(x_{MN})\right.$$

$$- \frac{1}{2}\left[\left(\frac{\partial x_{MM}}{\partial T}\right)^2 J''(x_{MM}) + \left(\frac{\partial^2 x_{MM}}{\partial T^2} + \frac{2}{T}\frac{\partial x_{MM}}{\partial T}\right)J'(x_{MM})\right]$$

$$\left. - \frac{1}{2}\left[\left(\frac{\partial x_{NN}}{\partial T}\right)^2 J''(x_{NN}) + \left(\frac{\partial^2 x_{NN}}{\partial T^2} + \frac{2}{T}\frac{\partial x_{NN}}{\partial T}\right)J'(x_{NN})\right]\right\} \tag{36}$$

$$\frac{\partial x_{ij}}{\partial T} = \frac{3z_i z_j A_H}{2RT^2}I^{1/2} \tag{37}$$

$$\frac{\partial^2 x_{ij}}{\partial T^2} + \frac{2}{T}\frac{\partial x_{ij}}{\partial T} = \frac{3z_i z_j A_J}{2RT^2}I^{\frac{1}{2}} \tag{38}$$

where A_H and A_J are the Debye-Hückel parameters for the enthalpy and heat capacity. These quantities are as defined by Bradley and Pitzer[11] who give numerical values for a wide range of T and P; some earlier definitions are larger by the factor 3/2.

Heat of Mixing

We consider, with Cassel and Wood, the case of mixing solutions of a 1-1 salt MX with a 2-1 salt NX_2, each at ionic strength I. Assume a fraction y of the NX_2 solution and (1-y) of MX and a total weight of solvent n_w. Then the ΔH of mixing may be written

$$\frac{\Delta_m H}{n_w RT I^2} = y(1-y)[h_0 + (1-2y)h_1 + ..] \tag{39}$$

and Cassel and Wood[4] report values for h_0 and h_1. After appropriate substitution of the molalities and amounts of solution into eq (29), one obtains

$$h_0 = Q_1 + Q_2 - 2T \, ^E\theta^L_{MN}/3 \tag{40}$$

$$Q_1 = T(2B^L_{MX}/3 + 11 \, IC^L_{MX}/9 - 2B^L_{NX}/9 - IC^L_{NX}/3) \tag{41}$$

$$Q_2 = -T(2 \, ^S\theta^L_{MN}/3 + 5I \, \psi^L_{MNX}/18) \tag{42}$$

$$h_1 = TI(C^L_{MX}/9 - C^L_{NX}/27 - \psi^L_{MNX}/18). \tag{43}$$

Here Q_1 is the array of "pure electrolyte" terms which are available from heat of dilution measurements. Silvester and Pitzer[12] give these parameters for many electrolytes while Rogers and Pitzer[13] give revised values for Na_2SO_4 and Phutela and Pitzer[14] have recently made revisions for $CaCl_2$. Q_2 is the combination of cation mixing terms arising from short-range forces while the final term in $^E\theta^L_{MX}$ is the electrostatic term for unsymmetrical mixing.

On figures 2 and 3 are plotted for the $NaCl-BaCl_2$ and $NaCl-Na_2SO_4$ mixing systems the values of $Q_2 = (h_0 - Q_1 + 2T \, ^E\theta^L_{MN}/3)$ as circles and the same quantity without the $^E\theta$ term as triangles. One expects a straight line with intercept $-2T \, ^S\theta^L_{MN}/3$ and slope $-5T \, \psi^L_{MNX}/18$. It is apparent that when the $^E\theta$ term is included the results do fall in good straight lines for both systems. The only

somewhat divergent point is that at I = 0.02 for NaCl-BaCl$_2$; the uncertainty

must be quite large for the measurement on this very dilute system. The

resulting parameters for the short-range-force terms are given on first two

lines of Table I for these systems.

With the values of ψ_{MNX}^L from Table I one can calculate h_1; the results

are very small values which are not significant in relation to the experi-

mental uncertainty. Cassel and Wood find h_1 to be zero at ionic strength

0.5 mol kg^{-1} and above in agreement with our expectation. For very dilute

solutions, however, Cassel and Wood find substantial values of h_1 which are

apparently larger than the experimental uncertainty.

Friedman and Krishnan[5] made calculations in the HNC approximation with

parameters chosen especially for the NaCl-BaCl$_2$ system and found reasonable

agreement for h_0 but complete disagreement in sign as well as magnitude for

h_1. They note, however, that their HNC results in this case failed to satisfy

certain self-consistency tests and may, therefore, be invalid. Thus we can

only conclude that there is now no theoretical explanation of the h_1 values

of Cassel and Wood for very dilute solutions. If this effect is real, its

explanation must come from triple or higher order electrostatic interactions.

It is difficult to believe that such triple ion interactions can have a

large effect in very dilute solutions; thus we reserve judgment as to the

validity of these large h_1 values for very dilute solutions.

Most measurements of heats of mixing do not extend below an ionic

strength of about 0.5 mol kg^{-1}. Such data cannot give any clear confirmation

of this higher order electrostatic term. It is, nevertheless, desirable to

include the term in reducing the experimental data in order to obtain values

of $^S\theta_{MN}^L$ and ψ_{MNX}^L of maximum accuracy. These parameters can then be used to

predict properties in more dilute solutions.

The experimental heat of mixing data for 6 additional systesms of the

$MX - NX_2$ type yield fully consistent results when treated in this manner. The results and the references for these data are given on the third through the eighth lines of Table I. In the absence of data below 0.5 mol kg^{-1} these $^S\theta$ values are considerably less accurate than the values where the data extend to low concentration. There are also limited measurements for a few other systems which appear to be less consistent and therefore are not included in Table I.

Since the higher order electrostatic term gives a non-linear effect primarily at low molality, one can omit this term for simplified calculations of reasonable accuracy. But the effective θ_{MN}^L should then be taken to be lower than $^S\theta_{MN}^L$ by 3×10^{-4} kg mol^{-1} K^{-1} while at the same time ψ_{MNX}^L should be increased by 1.2×10^{-4} kg^2 mol^{-2} K^{-1}. From the dashed lines on figures 2 and 3 one notes that such effective θ and ψ values can fit quite well above $I = 1$ mol kg^{-1}. Also, for many practical purposes these mixing terms are all unimportant for dilute solutions and in that case the term $^E\theta$ can be neglected as well as the others.

Discussion

The molecular-level explanation of this correcting term for unsymmetrical mixing is quite simple. The radial distribution function implied by the Debye–Hückel limiting law is[19]

$$g_{ij} = 1 + q_{ij} = 1 - (z_i z_j \ell/r) \exp(-\kappa r) \tag{44}$$

This linearized expression can become negative if $q_{ij} < -1$ which is possible, even in water, for multiply charged ions at short but reasonable distances. But a negative distribution function is physically impossible. The correcting term, at the level of binary interactions, is

$$\delta g_{ij} = \exp(q_{ij} - u_{ij}/kT) - 1 - q_{ij} \tag{45}$$

For like-charged ions we can again ignore the short-range potential u_{ij}. Thus the correction consists simply in replacing the linearized expression $1 + q$ by the exponential $\exp(q)$ which cannot become negative.

The "higher order" term just removes the falsely negative portion of the Debye-Hückel distribution. More precisely it replaces the linear approximation by the exponential distribution. In the effect on the total free energy, this is the removal of a falsely negative distribution for a positive energy; hence the absolute effect is a positive contribution. When the difference is taken for mixing, the dominant contribution comes from the pure component with the most highly charged ions. Thus the net effect is a negative contribution to the Gibbs energy of mixing, with $^E\theta$ negative.

For the heat of mixing one has $H = -T^2[\partial(G/T)/\partial T]$ and one finds a positive contribution to ΔH of mixing (but negative $^E\theta^L$). In turn this decreases the remaining enthalpy to be ascribed to the short-range-force contribution as is apparent from figures 2 and 3.

This falsely negative distribution implied by the Debye-Hückel limiting law can yield false predictions of phase separation in highly unsymmetrical electrolytes and plasmas. This was discussed recently on a somewhat different basis.[20]

The contribution of this higher order electrostatic effect to the heat capacity of unsymmetrical mixed electrolytes is probably no more than the experimental uncertainty with current calorimetry. Thus for $I = 1.6$ mol kg^{-1} and equal mixing of 1-1 and 2-1 salts, the contribution to $^\phi C_p/R$ is 0.12 at 298 K or 0.7 at 473 K for a solution with 1 kg of water. Since the θ^J and ψ^J values can be adjusted to include a linear contribution from $^E\theta^J$, it seems unlikely that the $^E\theta^J$ term is needed for

results at the present level of precision. This effect might be detectable, however, by heat capacity measurements especially designed to reveal it.

Acknowledgments

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TABLE I. Heat of Mixing Parameters

System	$\dfrac{10^4 \; S_\theta{}^L_{MN}}{\text{kg mol}^{-1} \text{ K}^{-1}}$	$\dfrac{10^4 \; \psi^L_{MNX}}{\text{kg}^2 \text{ mol}^{-2} \text{ K}^{-1}}$	Reference
$NaCl-BaCl_2$	-2.5	2.4	4,16
$NaCl-Na_2SO_4$	0.6	-0.7	4,18
$LiCl-MgCl_2$	0.5	0.1	15
$LiCl-CaCl_2$	0.3	0.2	16
$NaCl-MgCl_2$	-6.4	3.0	15,18
$NaCl-CaCl_2$	-5.7	3.1	16
$KCl-MgCl_2$	0.7	3.4	15
$KCl-CaCl_2$	2.0	3.4	16
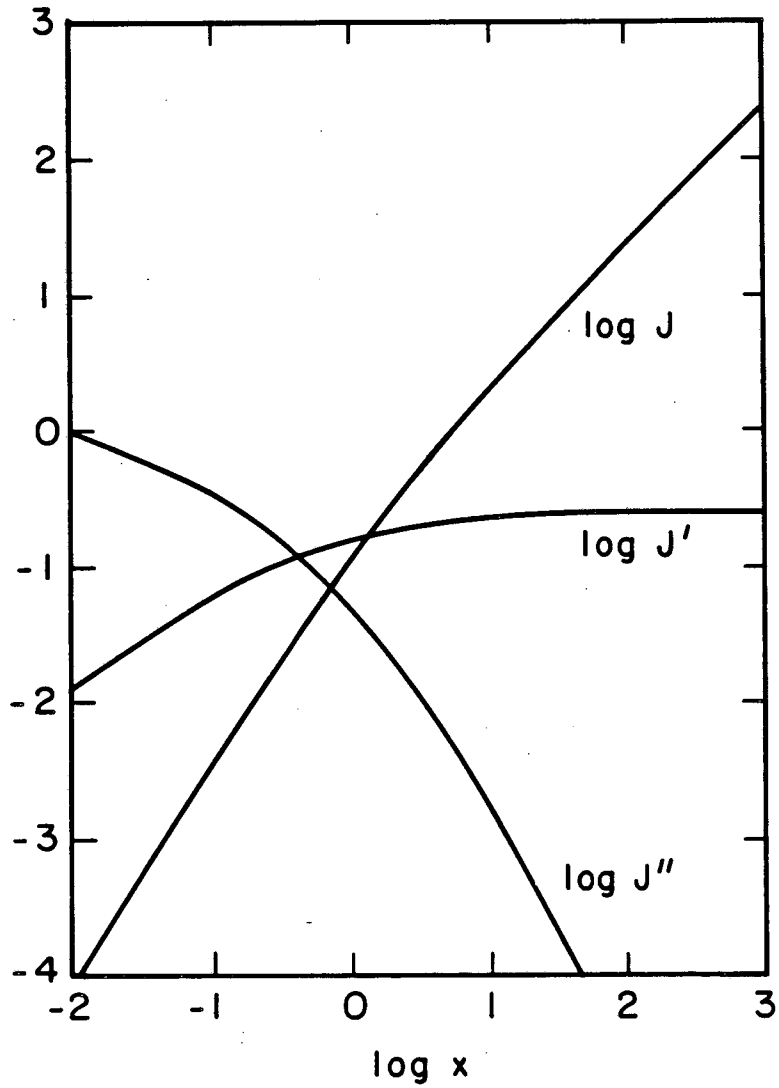
Figure 1. The functions J, J', and J".
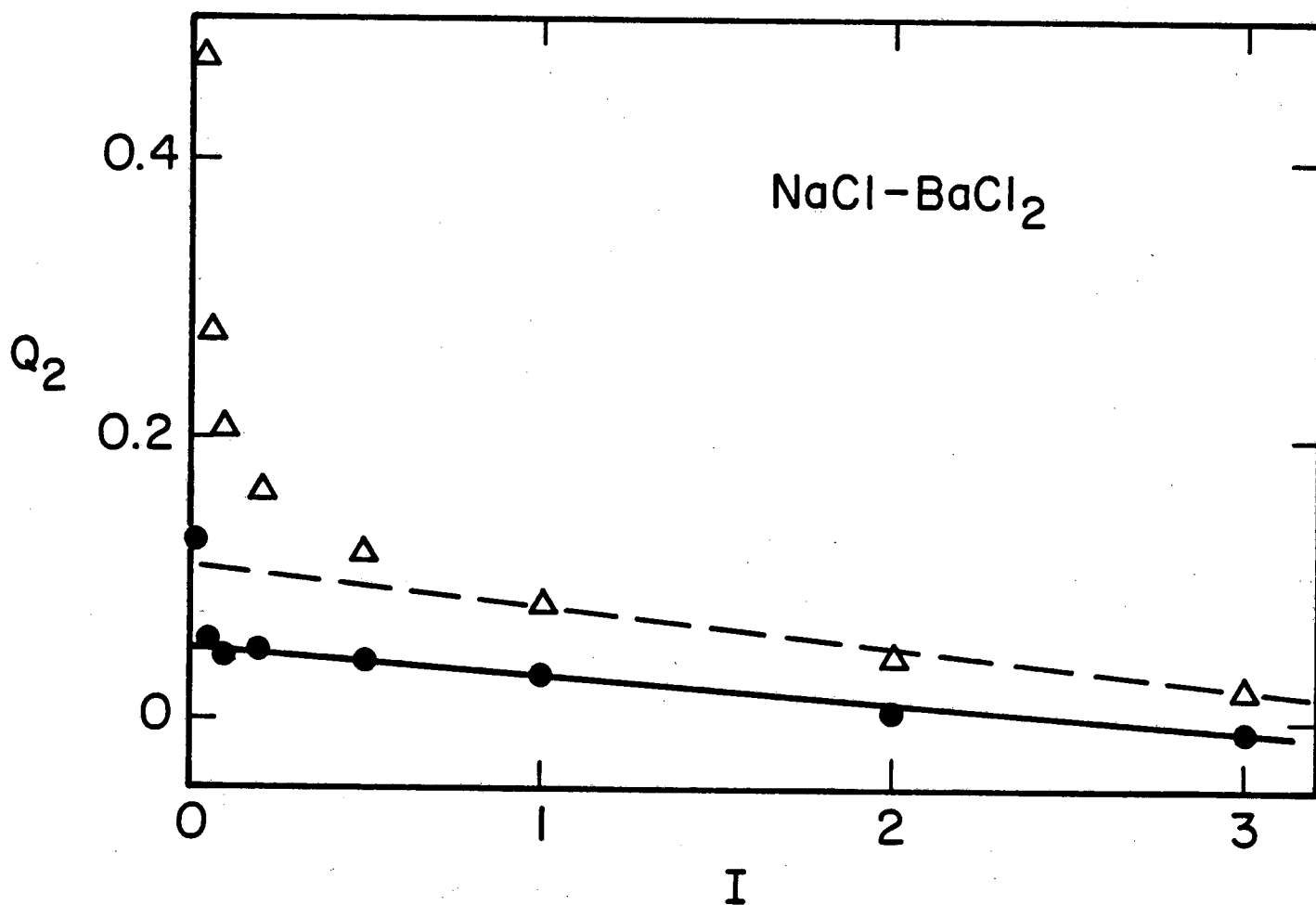
Figure 2. The interaction from short-range-forces for mixing ions of the same sign, Q_2 of eq (42), calculated including (circles) and excluding (triangles) the higher order unsymmetrical mixing term for electrostatic forces. The system is $NaCl-BaCl_2$.
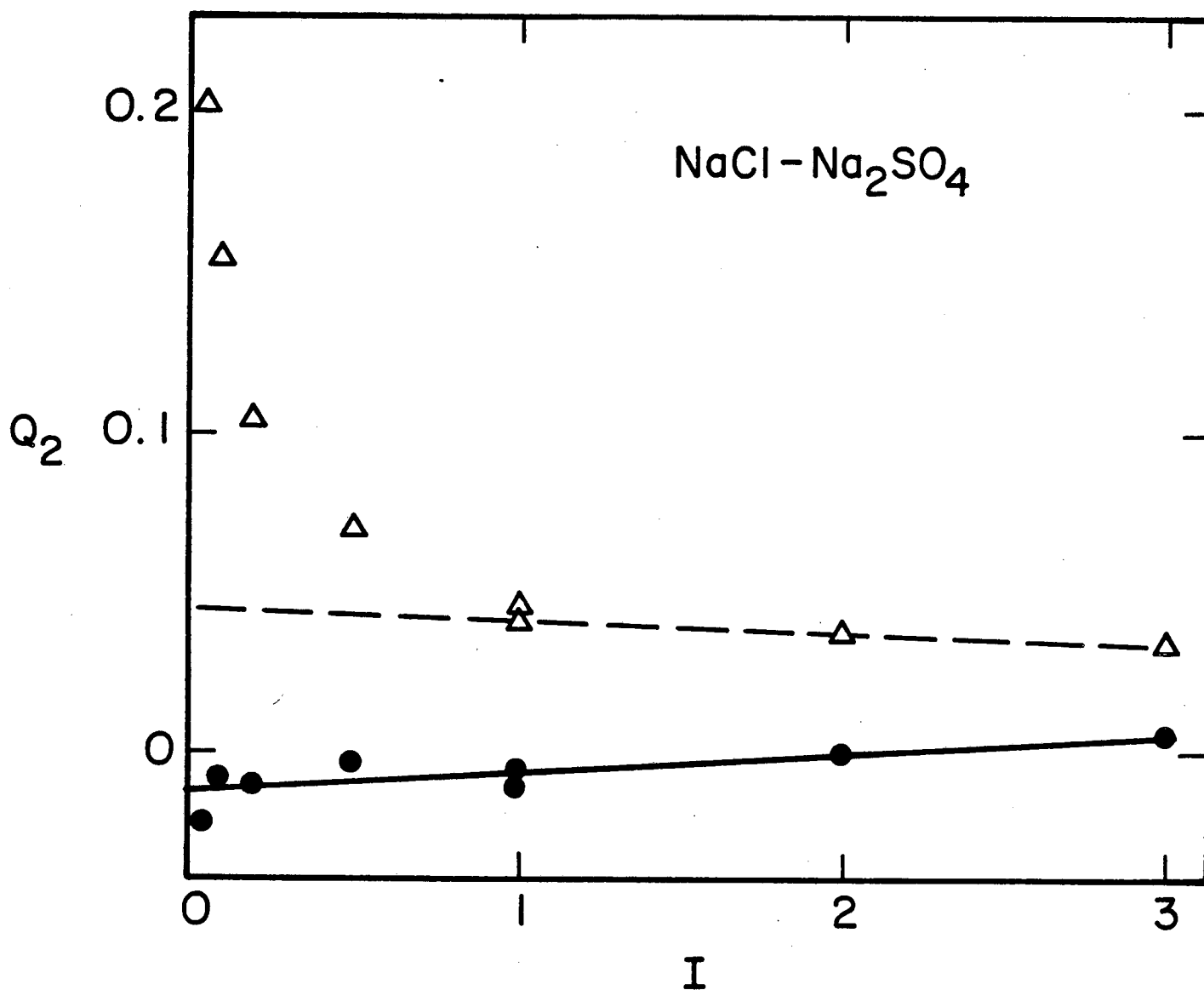
Figure 3. The interaction from short-range forces for mixing ions of the same sign, Q_2 of eq (42), calculated including (circles) and excluding (triangles) the higher order unsymmetrical mixing term for electrostatic forces. The system is $NaCl-Na_2SO_4$.