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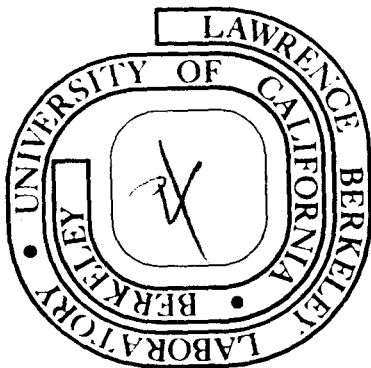
Kenneth S. Pitzer

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THERMODYNAMICS OF ELECTROLYTES. V. EFFECTS OF
HIGHER ORDER ELECTROSTATIC TERMS

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(ABSTRACT)

The contribution of higher order electrostatic terms (beyond the Debye-Hückel approximation) to the thermodynamic properties of mixed and pure electrolytes is investigated. It is found that these effects are important for cases of unsymmetrical mixing-especially when one ion has a charge of three units or more. The appropriate correction can be made by a purely electrostatic function since the mutual repulsion of ions of the same sign keeps them far enough apart that short range forces have little effect. This function is evaluated, and several convenient approximations are also given. Application is made to various systems mixing ions of the type 1-2 and 1-3. Higher order limiting laws exist for symmetrical mixtures and for pure, unsymmetrical solutes, but these effects were not found to be significant in relationship to existing activity or osmotic coefficient data.

At finite concentration the properties of an electrolyte solution depend in a very complex way on short-range forces between solute ions, both direct and as modified by the solvent, in addition to the long-range electrostatic forces. However, knowledge of the limiting or idealized behavior arising purely from electrostatic forces, with the solvent as a dielectric, is extremely valuable in the form of the limiting law of Debye and Hückel.

The Debye-Hückel limiting law arises from a mathematical approximation, and various authors have pointed out that, in at least three cases, higher terms in the mathematical expansion yield "higher order" limiting laws of the same sort, i.e., arising purely from electrostatic effects. In this paper these higher-order electrostatic effects will be explored in connection with the general equations presented in Part I⁽¹⁾ of this series and applied extensively to most pure and mixed electrolytes in Parts II,⁽²⁾ III,⁽³⁾ and IV⁽⁴⁾ (hereafter cited as I, II, etc.). Insofar as possible, however, we shall consider the entire electrostatic effect (in excess of the Debye-Hückel limiting law), rather than merely the next term in the series expansion.

One case arises with unsymmetrical pure electrolytes, e.g., MgCl_2 or AlCl_3 , where the existence of a higher-order term was noted by Gronwall, LaMer, and Sandved⁽⁵⁾ in 1928. This effect has never been found to be distinguishable from the effects of short-range forces; although there is no reason to doubt its theoretical existence. Recent freezing-

point-lowering data for a 6-1 electrolyte⁽⁶⁾ allows us to make a more searching test than heretofore, but the result is similarly negative.

The other cases relate to mixed electrolytes. If ions of different charges of the same sign are mixed, e.g., HCl with $AlCl_3$, there is a higher-order electrostatic function⁽⁷⁾ which we shall find to be significant and useful. Most of the paper will be concerned with this effect which is small for 2-1 mixing and can be omitted without large error but which must be included to deal with 3-1 or more unsymmetrical types of mixing.

Even for the mixing of ions of the same charge, but with different short-range interactions, Friedman⁽⁷⁾ has shown that there is a higher-order limiting law; but in this case as in the first, its effect is too small to be of practical importance.⁽⁸⁾

Theory for Unsymmetrical Mixing

The mixing of ions of different charge of the same sign is best discussed theoretically by the cluster-integral method introduced for electrolytes by Mayer⁽⁹⁾ and applied with generality by Friedman.⁽⁷⁾ 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 free energy.

$$\frac{G^{ex}}{VKT} = -\frac{\kappa^3}{12\pi} + \sum_i \sum_j c_i c_j \left[\frac{2\pi z_i z_j \ell}{\kappa^2} J_{ij}(\kappa, z_i, z_j, \dots) \right] \quad (1)$$

$$\ell = e^2/DkT. \quad (2)$$

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 i -th ion, D is the dielectric constant, and e , k , and T have familiar meanings. The function J depends on the interionic potential and κ . If the potential is

$$v_{ij} = u_{ij} + z_i z_j \ell / r \quad (3)$$

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

$$J_{ij} = -\frac{\kappa^2}{z_i z_j \ell} \int_0^\infty [\exp(q_{ij} - u_{ij}/kT) - 1 - q_{ij} - \frac{1}{2} q_{ij}^2] r^2 dr \quad (4)$$

with

$$q_{ij} = -(z_i z_j \ell / r) e^{-\kappa r}. \quad (5)$$

In general the integral and J cannot be evaluated without explicit knowledge of the short-range potential u_{ij} , but for our particular purposes a simplification is possible as will be shown below.

Since we wish to work in macroscopic units, in particular molalities, these equations are restated below. We omit the secondary terms which arise from differences between concentration and molality, etc., since these can be accommodated within the virial coefficients we add for the effects of all short-range forces.

$$G^{ex}/RT = -4A_\phi I^{3/2} + \sum_i \sum_j m_i m_j (z_i z_j / 4I) J_{ij} \quad (6)$$

$$A_\phi = 1/3(2\pi N_0 d_w / 1000)^{1/2} \ell^{3/2}. \quad (7)$$

Here A_ϕ is the Debye-Hückel coefficient for the osmotic coefficient, G^{ex} is for a solution containing one kilogram of solvent of density d_w and m_i is the molality of the i -th species. The ionic strength I is, of course, $\frac{1}{2} \sum m_i z_i^2$.

The corresponding general equation adopted in I is

$$G^{ex}/RT = f(I) + \sum_i \sum_j m_i m_j \lambda_{ij}(I) \quad (8)$$

where

$$f(I) = -A_\phi (4I/b) \ln(1+b I^{1/2}). \quad (9)$$

Here A_ϕ is the same Debye-Hückel constant defined above and b was chosen to be 1.2 for all solutions. The second virial coefficients λ_{ij} are functions of ionic strength as indicated.

Clearly there is a close analogy between the first term on the right in (6) and (8), each of which contain the Debye-Hückel limiting law. Also each of the second virial coefficients λ_{ij} in (8) is analogous to the corresponding terms involving J_{ij} in (6).

It is possible to divide $f(I)$ into two terms: one is identical with the corresponding term in (6) while the remainder can be further divided into terms which can be combined with the λ 's. Indeed, this was done in exploratory calculations, but it was found to offer no practical advantage. It seems preferable to assume that these terms based on the difference of our $f(I)$ from the first term in (6) are combined with effects of short-range forces and of the use of molalities instead of concentrations in the virial coefficients.

If we proceed now to the experimentally observable combinations of λ 's as defined in I, the properties of a pure electrolyte MX are related to

$$B_{MX} = \lambda_{MX} + |z_X/2z_M| \lambda_{MM} + |z_M/2z_X| \lambda_{XX}. \quad (10)$$

In mixtures the properties depend also on quantities of the type

$$\theta_{MN} = \lambda_{MN} - (z_N/2z_M) \lambda_{MM} - (z_M/2z_N) \lambda_{NN} \quad (11)$$

These same combinations of the J 's will yield the corresponding quantities for the cluster-integral theory.

In order to proceed further in general one must have the expression for u_{ij} , the potential for short-range interionic interaction. But for pairs of ions of the same sign, if the electrostatic repulsion is strong enough, the ions will seldom approach one another closely; hence the short-range potential should have little or no effect. This can be seen mathematically in equation (4). 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 throughout 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 electrostatic forces on the difference terms θ_{MN} or θ_{XY} without making any detailed assumption about short-range forces. Let us write

$$\theta_{MN} = S_{\theta_{MN}} + E_{\theta_{MN}} \quad (12)$$

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 equation (8) from that in (6). 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

$$E_{\theta_{MN}} = E_{\lambda_{MN}}^{-z_N/2z_M} E_{\lambda_{MM}}^{-z_M/2z_N} E_{\lambda_{NN}} \quad (13)$$

$$E_{\lambda_{ij}} = (z_i z_j / 4I) J_{ij} \quad \text{with } u_{ij} = 0 \quad (14)$$

$$J_{ij} = \frac{\kappa^2}{z_i z_j \ell} \int_0^{\infty} (1 + q_{ij} + \frac{1}{2} q_{ij}^2 - e^{q_{ij}}) r^2 dr. \quad (15)$$

With the substitutions

$$y = \kappa r \quad (16)$$

$$x = z_i z_j \ell \kappa \quad (17)$$

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

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

The integrals of the second and third terms within the parentheses are straightforward and yield

$$J(x) = \frac{1}{4} x^{-1} + J_2(x) \quad (20)$$

$$J_2(x) = x^{-1} \int_0^{\infty} (1 - e^q) y^2 dy. \quad (21)$$

There is no simple integral for J_2 , but this function is readily evaluated by direct numerical integration on modern computers.

For very large x one finds that J_2 is small, and the first two terms of equation (20) give a limiting approximation. For very small x an alternate expansion is possible yielding a series whose leading term is

$$J(x) = -\frac{1}{6} x^2 (\ln x + 0.419711). \quad (22)$$

From equation (22) one notes the limiting form (omitting the 0.419711) for very small x which has been stated⁽⁷⁾ previously as a "limiting law". We find, however, that this limiting form is not a good approximation in the range of practical application and use the full expression for J in all of our work.

The derivative of J is also readily computed by numerical integration. The resulting curves for J and J' are shown in Figure 1. For practical calculations it is convenient to use simpler approximate expressions for J and J' ; several examples are given in the Appendix together with further discussion of the evaluation of these functions and a table of numerical values. In our working units

$$x_{ij} = 6z_i z_j A_\phi I^{1/2} \quad (23)$$

and

$$E_{\theta_{MN}} = (z_M z_N / 4I) [J(x_{MN}) - \frac{1}{2} J(x_{MM}) - \frac{1}{2} J(x_{NN})] \quad (24)$$

$$E_{\theta'_{MN}} = -(E_{\theta_{MN}} / I) + (z_M z_N / 8I^2) [x_{MN} J'(x_{MN}) - \frac{1}{2} x_{MM} J'(x_{MM}) - \frac{1}{2} x_{NN} J'(x_{NN})]. \quad (25)$$

It should be emphasized that these results apply over the full range of ionic strength, and therefore have much greater applicability than an expression which applies only in the limit at low concentration.

Figure 2 shows the values of $(E_{\theta} + I E_{\theta}')$ for mixing ions of charge types 2-1, 3-1, and 4-1. This quantity may be compared with θ or S_{θ} values to judge the magnitude of the effect we are discussing. Since typical θ values range up to about 0.1, it is clear that the effect is significant for 2-1 mixing and large for 3-1 or 4-1 systems. Also note the marked increase of $(E_{\theta} + I E_{\theta}')$ as ionic strength decreases.

Data for Unsymmetrical Mixing

The most interesting systems for application of these equations are those of the types $\text{HCl} - \text{AlCl}_3$ and $\text{HCl} - \text{BaCl}_2$ where the activity coefficient of HCl is measured. For the type $\text{HX} - \text{NX}_z$ the activity coefficient of HX is given by equation (15) of IV which reduces to:

$$\begin{aligned} \ln \gamma_{\text{HX}} = & f^Y + (m_{\text{H}} + m_{\text{X}})(B_{\text{HX}} + m_{\text{X}} C_{\text{HX}}) \\ & + m_{\text{N}}(B_{\text{NX}} + m_{\text{X}} C_{\text{NX}} + S_{\theta_{\text{HN}}} + E_{\theta_{\text{HN}}}) \\ & + m_{\text{H}}m_{\text{X}}(B'_{\text{HX}} + C_{\text{HX}}) + m_{\text{N}}m_{\text{X}}(B'_{\text{NX}} + C_{\text{NX}} + \frac{1}{2} \psi_{\text{HNX}}) \\ & + m_{\text{H}}m_{\text{N}}(E_{\theta'_{\text{HN}}} + \frac{1}{2} \psi_{\text{HNX}}) \end{aligned} \quad (26)$$

$$f^Y = -A_{\phi} [I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2) \ln (1 + 1.2I^{1/2})] \quad (27)$$

$$B_{ij} = \beta_{ij}^{(0)} + (2\beta_{ij}^{(1)}/\alpha^2 I) [1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})] \quad (28)$$

$$B'_{ij} = (2\beta_{ij}^{(1)}/\alpha^2 I^2) [-1 + (1 + \alpha I^{1/2} + \frac{1}{2} \alpha^2 I) \exp(-\alpha I^{1/2})] \quad (29)$$

$$C_{\text{HX}} = C_{\text{HX}}^{\phi}/2, \quad C_{\text{MX}} = C_{\text{MX}}^{\phi}/2z^{1/2}. \quad (30)$$

Here the $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} values are those determined from the respective pure electrolytes and $\alpha = 2$ for all cases of type under consideration. Also equation (12) for θ has been introduced; but the term S_{θ}' has been omitted since in IV it was found that such terms were negligible. The term E_{θ}' , on the contrary, is quite important.

Next we define $\Delta \ln \gamma_{HX}$ as the difference between the experimental value of $\ln \gamma_{HX}$ and that calculated from equation (26) with all pure electrolyte terms included, with S_{θ} and ψ zero, and, alternatively with or without E_{θ} and E_{θ}' . The relationship

$$(\Delta \ln \gamma_{HX})/m_N = S_{\theta_{HN}} + \frac{1}{2} (m_H + m_X) \psi_{HNX} \quad (31)$$

shows that a plot of the left side of this equation against $1/2(m_H + m_X)$ should give a straight line with intercept S_{θ} and slope ψ .

The results for the systems $HCl - SrCl_2$ ^(10,11) and $HCl - AlCl_3$ ^(12,13) are shown on Figure 3 where the open circles and triangles indicate results including E_{θ} and E_{θ}' and the solid circles and triangles indicate values excluding those terms. The estimated effect of experimental uncertainty is shown by error bars where it is significant.

It is apparent from Figure 3 that the inclusion of the additional electrostatic terms E_{θ} and E_{θ}' is essential in order to treat $HCl - AlCl_3$ satisfactorily. For $HCl - SrCl_2$ the discrepancy without those terms is somewhat greater than the experimental uncertainty whereas by including those terms the agreement is excellent. Similar results are obtained for the system $HCl - BaCl_2$ ^(14,15). For other systems of these types, the data are much less extensive, but in all cases examined there is no difficulty fitting the results when E_{θ} and E_{θ}' are included.

The results shown in Figure 3 clearly confirm the correctness of the higher-order electrostatic contribution

to the interaction of H^+ and N^{+z} ions in these systems. Also they show that this effect is of a significant magnitude and should be included in practical calculations, especially when z is 3 or greater.

Mixtures of singly and doubly charged ions were treated in IV with considerable success without the inclusion of E_θ and $E_{\theta'}$. Most of these calculations were repeated with E_θ and $E_{\theta'}$ included, and the results for mixtures with a common ion are shown in Table 1. It is apparent that the inclusion of these terms improves the fit significantly for several systems, most notably the first three, while it makes little difference in other cases. The values of S_θ are increased over the values of θ (without E_θ and $E_{\theta'}$) by about 0.07 while the new values of ψ are decreased by about 0.01 from those reported before.

Two systems of mixing without a common ion were also recalculated with E_θ and $E_{\theta'}$ and with the other parameters determined from the data for mixing with a common ion. The resulting fits for $NaCl - MgSO_4$ and for $Na_2SO_4 - MgCl_2$ yielded the same σ values as were obtained without E_θ and $E_{\theta'}$.

One may conclude that the E_θ and $E_{\theta'}$ terms should be included for systems mixing singly and doubly charged if maximum accuracy is desired. But in most practical cases of this type, these terms may be omitted provided the appropriate θ and ψ values are used. It is essential, however, to maintain consistency, i.e., if E_θ and $E_{\theta'}$ are included

Table 1
Systems Mixing Doubly and Singly Charged Ions

System	with E_{θ} and E_{θ}'			without E_{θ} and E_{θ}'			Ref.
	θ	ψ	σ	θ	ψ	σ	
HCl - SrCl ₂	.065	.003	.002	-.020	0.018	0.010	10, 11
HCl - BaCl ₂	.072	.000	.003	-.036	.024	.005	14, 15
HCl - MnCl ₂	.075	-.007	.002	.000	.000	.008	16
LiCl - BaCl ₂	.000	.009	.002	-.070	.019	.002	17
NaCl - MgCl ₂	.070	-.010	.001	.000	.000	.002	18
Na ₂ SO ₄ - MgSO ₄	.070	-.023	.003	.000	.000	.005	18
NaCl - CaCl ₂	.070	-.007	.003	.000	.000	.004	19
NaCl - BaCl ₂	.067	-.012	.001	-.003	.000	.001	20
NaCl - MnCl ₂	.082	-.017 ₄	.002	.000	-.003	.003	21
KCl - CaCl ₂	.032	-.025	.004	-.040	-.015	.003	22
KCl - BaCl ₂	.010	-.017	.002	-.072	.000	.001	23
CsCl - BaCl ₂	-.070	-.015	.002 ₅	-.150	.000	.003	17
NaCl - Na ₂ SO ₄	.020	.0014	.002	-.035	.007	.002	18
KCl - K ₂ SO ₄	.020	.000	.002	-.035	.000	.002	24
MgCl ₂ - MgSO ₄	.020	-.014	.002	-.035	.000	.002	18

the values of S_θ and ψ must be those derived on that basis whereas if E_θ and $E_{\theta'}$ are omitted the corresponding θ and ψ must be used.

For the system $\text{HCl} - \text{AlCl}_3$ the parameters are $S_\theta = 0.185$, $\psi = 0.013$ which yield a good fit, $\sigma = 0.006$. There are no other systems involving 3-1 mixing for which comparably accurate and extensive data are available. The results for $\text{HCl} - \text{LaCl}_3$ ⁽²⁵⁻²⁷⁾ and for $\text{HCl} - \text{CeCl}_3$ ⁽²⁸⁾ show behavior similar to that of $\text{HCl} - \text{AlCl}_3$ in the dilute range which fully confirms the need for the additional electrostatic terms E_θ and $E_{\theta'}$. In the more concentrated range, however, the data are sufficiently scattered that I hesitate to recommend specific values of S_θ and ψ . One can use either zero values for these quantities or the values for $\text{HCl} - \text{AlCl}_3$ if estimates are desired.

Symmetrical Mixing

The higher order electrostatic terms considered above for unsymmetrical mixtures vanish if the ions mixed have the same charge. Friedman⁽⁷⁾ has shown, however, that there is a different and more subtle limiting law applicable to symmetrical mixtures. In terms of our parameters this is

$$\lim_{I \rightarrow 0} \frac{\partial \ln |\theta_{MN}|}{\partial I^{1/2}} = 6z^2 A_\phi \quad (32)$$

where z is the number of charges on the ions mixed and A_ϕ is the Debye-Hückel coefficient for the osmotic coefficient. Robinson, Wood, and Reilly⁽⁸⁾ gave an alternate derivation of this limiting law in simple terms but were unable to find experimental confirmation of it with isopiestic data. This was not surprising since Friedman's sample calculations indicated an approach to equation (32) only below an ionic strength of 0.01.

The physical basis of this law may be related to the change with ionic strength of the radial distribution function at repulsive contact for ions of the same sign of charge. This is shown in Figure 3 of paper I. It is this change with ionic strength of the radial distribution functions that leads to the ionic strength dependence of the second virial coefficients for pure electrolytes. Thus it seems reasonable to assume the same mathematical form for θ_{MN} as for B_{MX} .

For the combination appearing in the osmotic coefficient this yields

$$\theta + I\theta' = \theta^{(0)} + \theta^{(1)} e^{-\alpha I^{1/2}}.$$

Then one obtains

$$\theta = \theta^{(0)} \{1 + (2\theta^{(1)}/\alpha^2 I \theta^{(0)}) [1 - (1 + \alpha I^{1/2}) e^{-\alpha I^{1/2}}]\} \quad (33)$$

$$\lim_{I \rightarrow 0} \frac{\partial \ln |\theta|}{\partial I^{1/2}} = - \frac{2/3 \alpha (\theta^{(1)}/\theta^{(0)})}{1 + (\theta^{(1)}/\theta^{(0)})} = 6z^2 A_\phi \quad (34)$$

$$\theta^{(1)}/\theta^{(0)} = -9z^2 A_\phi / (\alpha + 9z^2 A_\phi).$$

One may now make the reasonable assumption that α retains the same value 2.0 for these expressions as for the second virial coefficients of most pure electrolytes; then the numerical relationship of $\theta^{(1)}$ to $\theta^{(0)}$ is determined.

Equations (33) and (34) thus yield a plausible function for θ at all concentrations which is consistent with the limiting law. These equations were applied to the systems HCl - KCl⁽²⁹⁾ and HCl - CsCl⁽³⁰⁾ for which the activity coefficient measurements appeared most likely to yield confirmation of this effect. While no contradiction was observed, the use of equations (33) and (34) gave so little improvement over the use of constant θ 's that the complexity is unjustified.

There is a corresponding limiting law for heats of mixing, and Falcone, Levine, and Wood⁽³¹⁾ have presented experimental data on mixing for the systems LiCl - CsCl and n-Bu₄NCl - KCl

which tend to confirm that law. While the concepts behind equations (33) and (34) could be applied to the enthalpy, this approach will not be carried further at present.

Unsymmetrical Pure Electrolytes

The theory for a higher-order limiting law for unsymmetrical pure electrolytes has been well established by several authors. (5,7) It can be expressed for the osmotic coefficient by the equation

$$\lim_{m \rightarrow 0} \left(\frac{\phi - 1 - \text{DHLL}}{I} \right) = \frac{3}{2} \frac{n_3^2}{n_2} A_\phi^2 \ln I \quad (35)$$

with similar expressions for the activity coefficient and the excess Gibbs energy. Here DHLL refers to the appropriate expression for the Debye-Hückel limiting law, A_ϕ is the coefficient in that law for the osmotic coefficient and n_3 and n_2 are, respectively, the third and second moments of concentration of charge types. In contrast to the case discussed above for unsymmetrical mixing, it is not possible to extend this law over a finite range of concentration without making some assumption concerning short-range forces.

Friedman⁽⁷⁾ showed that the experimental data available in 1962 did not extend to low enough concentration with high enough precision to confirm this law, although there was no conflict with the law. Recently Stock and Plewinsky⁽⁶⁾ presented data for an even more unsymmetrical electrolyte of the 6-1 type $\text{Na}_6(\text{H}_2\text{W}_{12}\text{O}_{40})$. Their freezing-point measurements were shown to be consistent with the Debye-Hückel limiting law for that charge type, but the higher-order law was not considered.

First the experimental data are fitted to the equation employed throughout this series of papers. For a $z-1$ charge type of pure electrolyte MX_z of molality m it becomes

$$\begin{aligned} \phi-1 = z f^\phi + m[2z/(z+1)] B_{\text{MX}}^\phi \\ + m^2 [2z^{3/2}/(z+1)] C_{\text{MX}}^\phi \end{aligned} \quad (36)$$

$$B_{\text{MX}}^\phi = \beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)} \exp(-\alpha I^{1/2}) \quad (37)$$

$$I = mz(z+1)/2. \quad (38)$$

The experimental data range from $8 \times 10^{-5} \text{M}$ to $1.2 \times 10^{-2} \text{M}$. Below 0.001M , however, the freezing-point depression becomes so small that the data do not contribute to the determination of these constants nor to the detection of the higher-order limiting law. Since the highest concentration is relatively low, the third virial coefficient C^ϕ was omitted. A good fit is obtained with the following values

$$(12/7) \beta^{(0)} = -11.$$

$$(12/7) \beta^{(1)} = 112.$$

$$\sigma = 0.005.$$

While the above treatment showed no discrepancies suggestive of the higher-order limiting law, the original data are also presented in Figure 4 in a form suggested by Friedman. The higher order limiting law requires the slope to approach that of the dashed line eventually as $\log I$ becomes more negative.

Again it is apparent that the data above $0.001M$, $\log I = -1.7$, show no confirmation of the higher-order limiting law. Below this concentration the effect of experimental error becomes so great that nothing can be concluded. Thus the higher-order law, although undoubtedly valid as $I \rightarrow 0$, is not useful at experimentally accessible concentrations and its effect on measureable properties is negligible by present standards.

Discussion

While there seems no doubt about the theoretical validity of the higher-order limiting laws, and there is good experimental confirmation in the case of unsymmetrical mixing, it is difficult to offer any simple physical picture. Mathematically these laws arise from additional terms in the expansion in series of the Boltzmann factor after the separation of the first terms which yield the Debye-Hückel limiting law (or are zero by electrical neutrality). The physical concept of a statistical distribution governed by the Boltzmann expression is clear enough, but it is not easy to picture the meaning of individual terms in the series expansion of the exponential. One can say that these effects arise from modifications of the radial distribution function from its linearized (Debye-Hückel) approximation. Possibly future statistical calculations of distribution functions for appropriate examples will clarify this matter.

Acknowledgements

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APPENDIX

The evaluation of the function $J(x)$

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

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

was discussed briefly in the text. Additional details including empirical equations for convenient, approximate calculations are presented here.

The corresponding function for an ionic model with a hard-core potential was evaluated by Friedman⁽⁷⁾ and his numerical results can be extrapolated to zero core diameter to yield our $J(x)$ over a considerable range of x . His methods of calculation appear to be less convenient, however, than the direct numerical integration suggested above for the expression

$$J_2(x) = x^{-1} \int_0^{\infty} (1 - e^q) y^2 dy. \quad (21)$$

The other terms in (19) are simply integrated to yield

$$J(x) = \frac{1}{4} x^{-1} + J_2(x). \quad (20)$$

The same method is readily applied to the calculation of the derivative of J .

$$J' = dJ/dx = \frac{1}{4} x^{-2} - (J_2/x) + J_3 \quad (39)$$

$$J_3 = x^{-1} \int_0^{\infty} e^{-y} e^q y dy. \quad (40)$$

Some numerical values of J and J' calculated by this method are given in Table II.

It is also possible to obtain a series expression for J valid for small x . One may break the integration into two ranges and use different expansions of equation (19) for each range. It is convenient to divide the ranges at $y = x/L$ where L is a constant and $L \gg x$. Then one has

$$J = J_4 + J_5 + J_6 \quad (41)$$

$$\begin{aligned} J_4 &= x^{-1} \int_0^{x/L} (1 + q + \frac{1}{2} q^2) y^2 dy \\ &= x^2/3L^3 - 1 + e^{-x/L}(1+x/L) + (x/4)(1-e^{-2x/L}) \end{aligned} \quad (42)$$

$$\begin{aligned} J_5 &= -x^{-1} \int_0^{x/L} e^q y^2 dy \\ &= -x^{-1} \int_0^{x/L} y^2 dy (e^{-x/y}) (e^x) (e^{-xy/2}) (e^{xy^2/6}) \dots \\ &= -x^2 e^x [L^{-3} E_4(L) - \frac{1}{2} x^2 L^{-4} E_5(L) + (\frac{1}{6} x^3 + \frac{1}{8} x^4) L^{-5} E_6(L) \dots] \end{aligned} \quad (43)$$

$$\begin{aligned} J_6 &= x^{-1} \int_{x/L}^{\infty} (1 + q + \frac{1}{2} q^2 - e^q) y^2 dy \\ &= x^2 \sum_{p=3}^{\infty} (L^{p-3}/p!) E_{p-2}(px/L). \end{aligned} \quad (44)$$

One may now insert the series expressions for the exponential integrals and collect all terms by powers of x . Terms involving L cancel, and there results:

Table II
Values of the Functions J and J'

x	J	J'
0.01	0.0000706	0.0127
0.02	0.0002387	0.0207
0.03	0.0004806	0.0275
0.04	0.0007850	0.0333
0.05	0.0011443	0.0385
0.06	0.0015529	0.0432
0.07	0.0020063	0.0475
0.08	0.0025010	0.0514
0.09	0.0030340	0.0551
0.10	0.0036028	0.0586
0.12	0.0048393	0.0649
0.14	0.0061961	0.0706
0.16	0.0076615	0.0758
0.18	0.0092260	0.0806
0.20	0.010882	0.0850
0.24	0.014441	0.0928
0.28	0.018295	0.0997
0.32	0.022409	0.1059
0.36	0.026755	0.1114
0.40	0.031313	0.1164
0.44	0.036061	0.1210
0.48	0.040985	0.1252
0.52	0.046070	0.1291

Table II (continued)

x	J	J'
0.56	0.051306	0.1327
0.60	0.056680	0.1360
0.80	0.085346	0.1499
1.00	0.11644	0.1605
1.20	0.14941	0.1689
1.40	0.18390	0.1758
1.60	0.21965	0.1815
1.80	0.25645	0.1864
2.00	0.29416	0.1906
3.00	0.49283	0.2053
4.00	0.70293	0.2142
5.00	0.92035	0.2202
6.00	1.14288	0.2246
7.00	1.36918	0.2279
8.00	1.59839	0.2304
9.00	1.82990	0.2325
10.00	2.06328	0.2342
12.00	2.53446	0.2368
16.00	3.48916	0.2402
20.00	4.45453	0.2423
24.00	5.57865	0.2374
28.00	6.40378	0.2447
32.00	7.38429	0.2455

Table II (continued)

36.00	8.36745	0.2461
40.00	9.35270	0.2465
50.00	11.82248	0.2474
60.00	14.29890	0.2479
70.00	16.77979	0.2483
80.00	19.26387	0.2485
90.00	21.75033	0.2487
100.00	24.23861	0.2489
200.00	49.17099	0.2496
400.00	99.11907	0.2498
600.00	149.09520	0.2499
800.00	199.08083	0.2499
1000.00	249.07101	0.2500
2000.00	499.04682	0.2500
4000.00	999.03028	0.2500
6000.00	1499.02328	0.2500
8000.00	1999.01925	0.2500
10000.00	2499.01659	0.2500

$$J = - \sum_{p=3}^{\infty} [x^{p-1} p^{p-3} / p!(p-3)!] (\ln x + K_p) \quad (45)$$

The quantities K_p are constants given as sums involving Euler's constant, $\ln p$, and integral fractions; the first few values are: $K_3 = 0.419710$, $K_4 = -0.292608$, $K_5 = -0.369464$, $K_6 = -3.00381$.

Equation (45) shows the limiting behavior of J for very small x , but it is convenient for numerical calculation only up to about $x = 0.10$.

Since only approximate values of J are needed for use with experimental data, simpler expressions were developed for convenience in practical calculations. The two most useful expressions are

$$J = - \frac{1}{6} x^2 (\ln x) e^{-10x^2} + \left(\sum_{k=1}^6 C_k x^{-k} \right)^{-1} \quad (46)$$

$$J = x [4 + C_1 x^{-C_2} \exp(-C_3 x^{C_4})]^{-1} \quad (47)$$

with the parameters given in Table III. Either equation (46) or (47) is fully adequate for practical calculations with experimental data of presently available accuracy. Equation (46) includes the correct limiting law for low x and is accurate to 2% or better over the important range $0.1 \leq x \leq 80$. It does deviate by as much as 10% near $x = .02$. Equation (47) includes the correct limiting form for large x and is accurate to 2% or better for x greater than 0.05 and its maximum deviation for smaller x is 6×10^{-6} .

Since this function and its derivative are used only for relatively small terms in the expressions for thermodynamic functions, this accuracy is adequate.

Table III
Parameters for Equations (46) and (47)

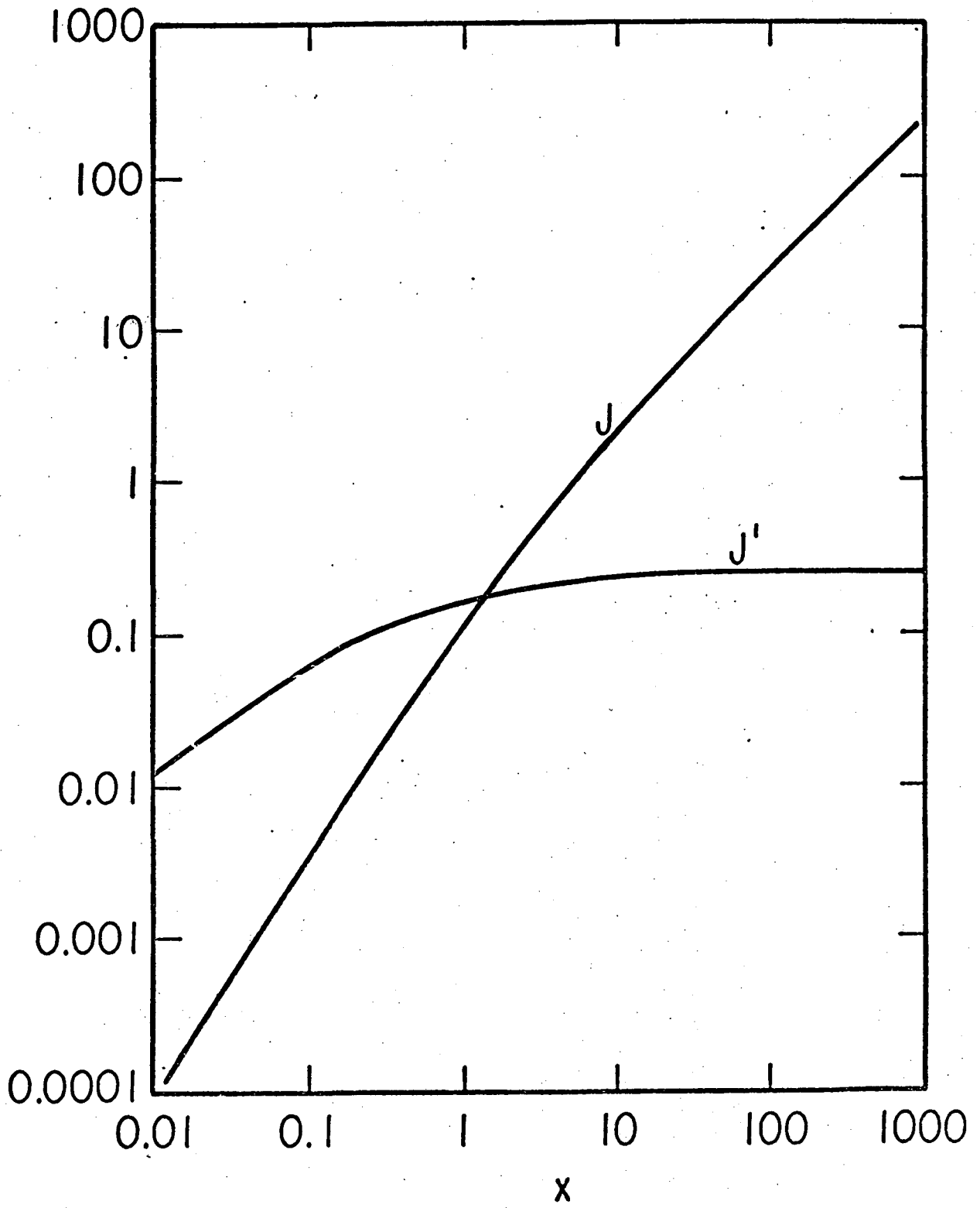
	Eq. (46)	Eq. (47)
C_1	4.118	4.581
C_2	7.247	0.7237
C_3	-4.408	0.0120
C_4	1.837	0.528
C_5	-0.251	-
C_6	0.0164	-

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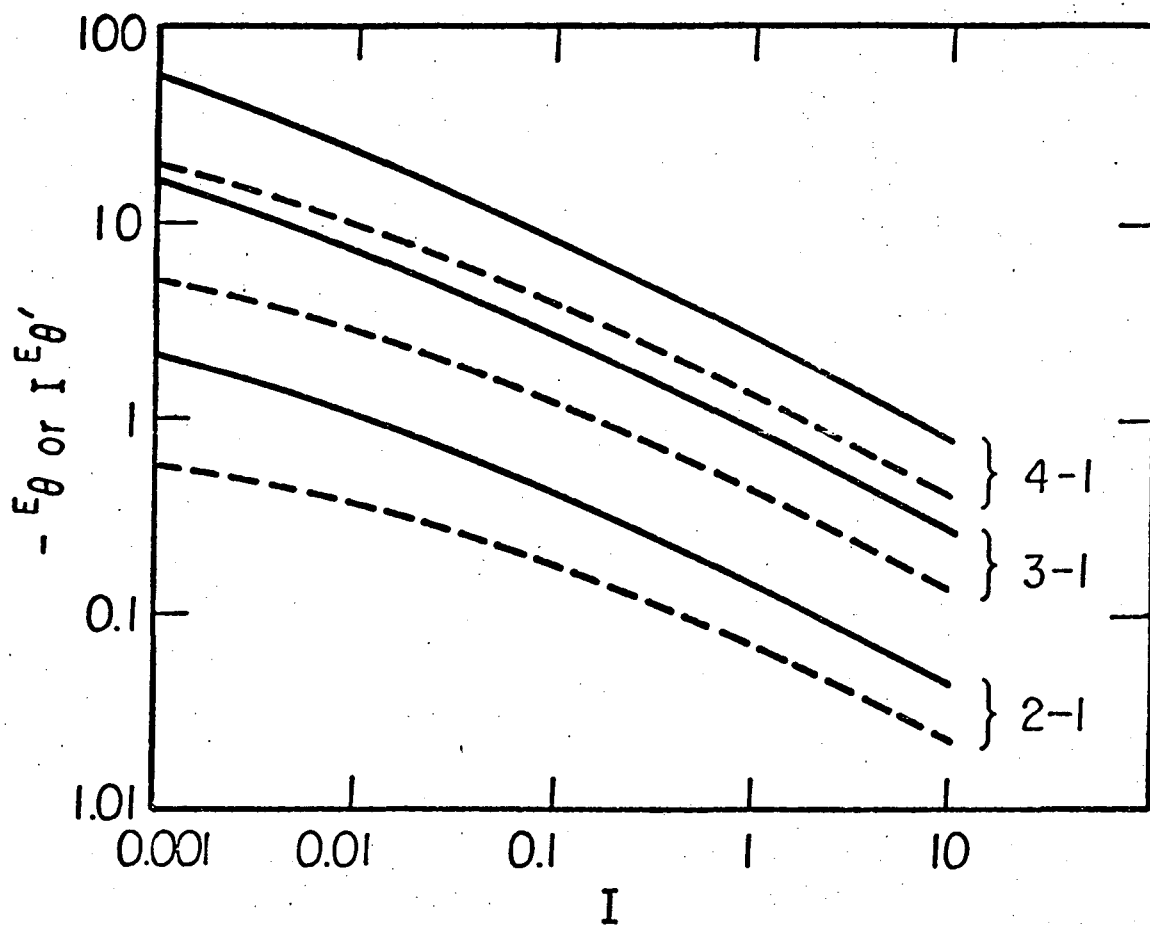
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XBL 746-6613

Figure 1. The functions J and J'.



XBL747-6672

Figure 2. The functions $-E_{\theta}$ (solid curves) and $I E_{\theta}'$ (dashed curves) for mixing ions of charge types 2-1, 3-1, and 4-1.

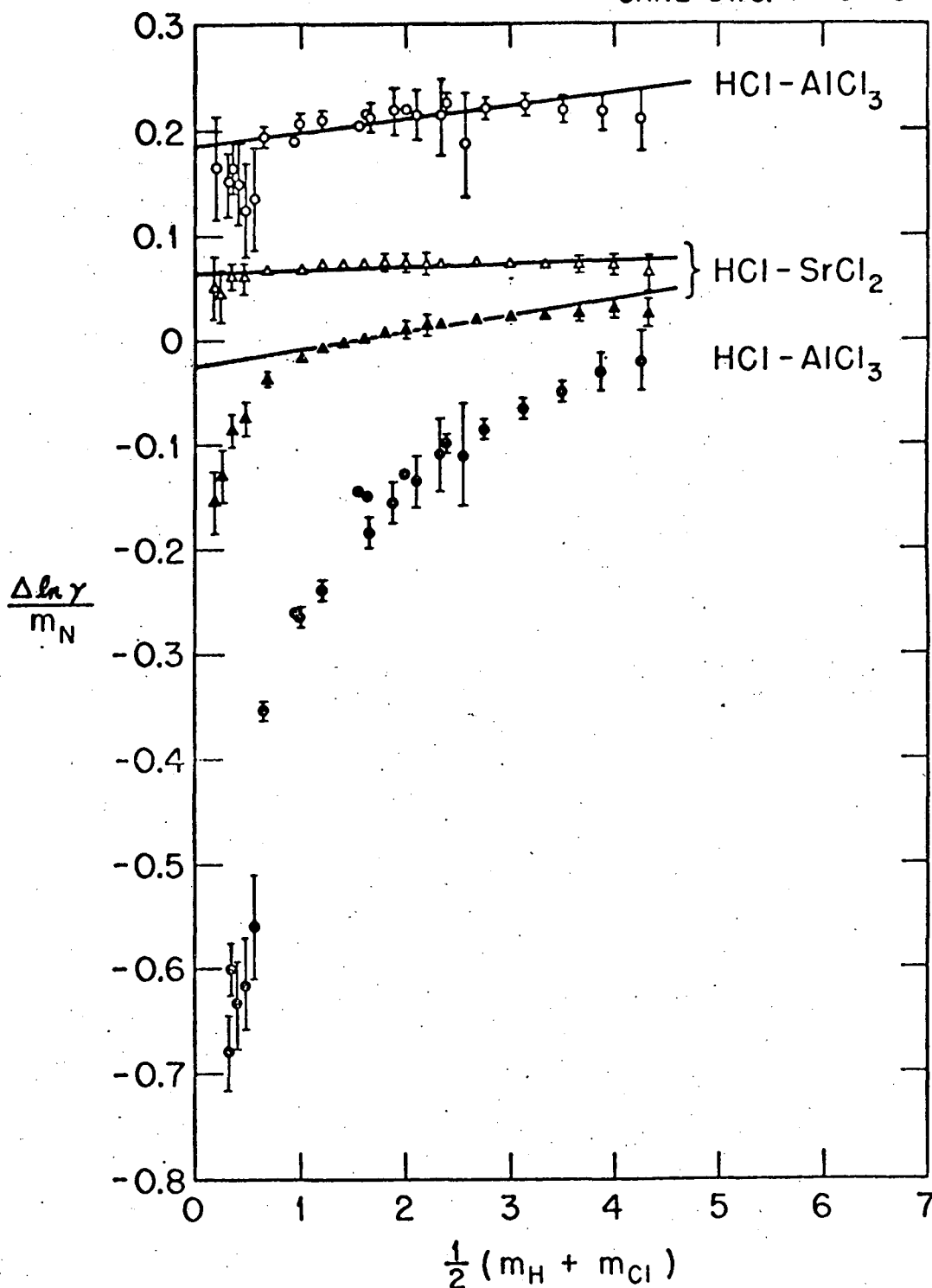
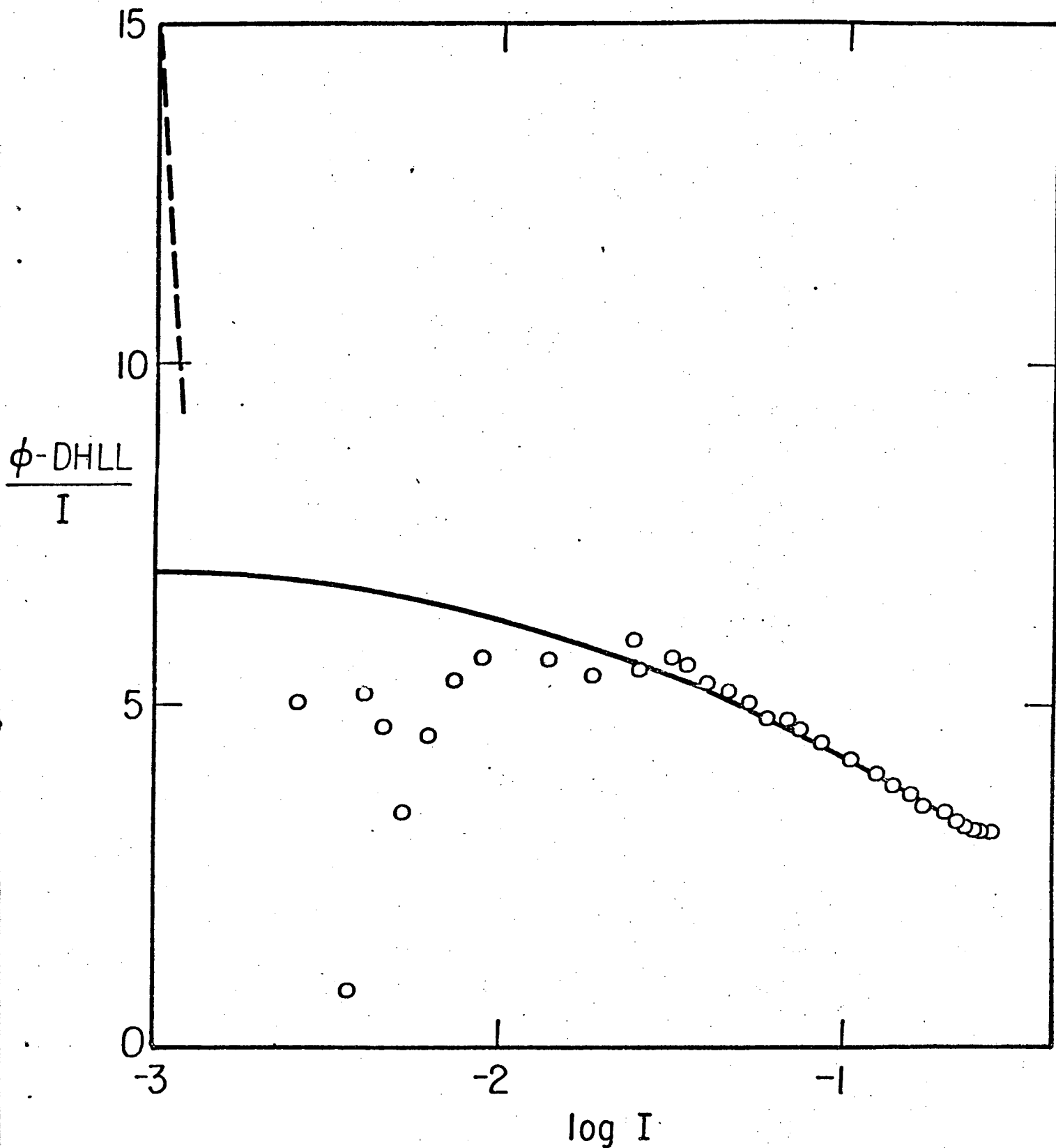


Figure 3. Fits of equation (31) to the activity coefficient of HCl in HCl-SrCl₂ and HCl-AlCl₃ solutions. Open circles and triangles show results calculated including E_{θ} and E_{θ}' while solid circles and triangles show results without those terms.



XBL 747-6671

Figure 4. Freezing point data for $\text{Na}_6(\text{H}_2\text{W}_{12}\text{O}_{40})$ presented as deviations from the Debye-Hückel limiting law. The dashed line shows the slope of the higher order limiting law which must be approached at large negative values of $\log I$. The solid curve is defined in the text.

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