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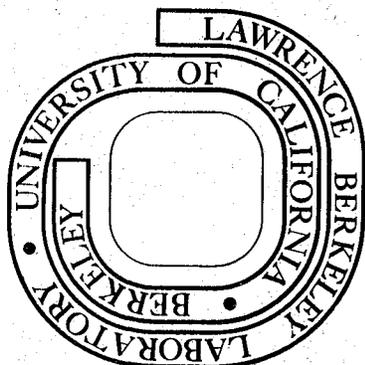
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THERMODYNAMICS OF ELECTROLYTES. XI. PROPERTIES OF
3-2, 4-2, AND OTHER HIGH-VALENCE TYPES

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Abstract

Various thermodynamic properties are considered for very high-valence 3-2 and 4-2 electrolytes in water at room temperature. These solutions show the behavior described by Davies in which ion pairing arises as the concentration increases follow by re-dissociation at still higher concentrations. Heat of dilution data, which extend below 10^{-4} M, are interpreted with the same form of equation used earlier for 2-2 electrolytes. Activity and osmotic coefficient data do not extend to low enough concentration for independent interpretation, but they are treated with the aid of conductance data in the more dilute range. Parameters are reported for $\text{Al}_2(\text{SO}_4)_3$, $\text{La}_2(\text{SO}_4)_3$, $\text{In}_2(\text{SO}_4)_3$, and several cyanoferrates.

High-valence electrolytes show a special behavior at very low concentrations which was recognized by Bjerrum¹ who showed in 1926 that purely electrostatic forces would yield an ion association. Davies² showed that this association commonly reached a maximum at an intermediate concentration above which there was a re-dissociation. From one viewpoint, this ion association is an artifact of the linearization approximation in the Debye-Hückel theory since a more exact statistical treatment³⁻⁵ yields agreement with experiment without assuming a separate associated species. If an association equilibrium is assumed for these electrolytes, it is found that the value of the association constant depends on the assumptions about the activity coefficients of the ions.

To the extent that these effects are important for 2-2 electrolytes, they are discussed in paper III⁶ of this series. While in 3-2 and 4-2 electrolytes the effects are of the same nature as those in the 2-2 solutes, they occur at much lower concentration in the higher-valence solutes; consequently new problems arise in treating experimental data. Indeed, it is only the conductance and heat-of-dilution measurements, which extend down to 10^{-5} M, that show clearly these effects for the 3-2 and 4-2 electrolytes in water. Thus it was not possible to give an adequate treatment of osmotic and activity coefficients for such solutes without considering these other properties which can be measured at lower concentrations.

While conductance data have been reasonably interpreted following Davies² and others,⁷ the reports of enthalpy data for very high valence electrolytes left the behavior as apparently anomalous. Thus Nathan, Wallace, and Robinson⁸ stated that the heat of dilution of $\text{La}_2(\text{SO}_4)_3$ solutions fails to approach the Debye-Hückel limiting law even at 2×10^{-5} M and Lange and Miederer⁹ reported similar conclusions for several 3-2 and 4-2 solutes. We shall show that these data may be given a reasonable interpretation consistent with the limiting law and that these results assist in estimating activity coefficients for high-valence electrolytes.

Enthalpy of Dilution

In view of the fact that the heat of dilution can be measured with useful accuracy down to very low concentration (less than 10^{-4} M), we first treat these data. We use the same form of equation which was successful for 2-2 electrolytes for both activity and osmotic coefficients⁶ and for heat of dilution.¹⁰ This equation does not distinguish a separate species of ion-pairs but instead adds a special term to the second virial coefficient to describe this effect. For the osmotic and activity coefficients the equations for a pure electrolyte $M_{\nu_M} X_{\nu_X}$ are

$$\phi - 1 = |z_M z_X| f^\phi + m \left(\frac{2\nu_M \nu_X}{\nu} \right) B_{MX}^\phi + m^2 \frac{2(\nu_M \nu_X)^{3/2}}{\nu} C_{MX}^\phi \quad (1)$$

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

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha_1 I^{1/2}} + \beta_{MX}^{(2)} e^{-\alpha_2 I^{1/2}} \quad (3)$$

$$\ln \gamma_{\pm} = |z_M z_X| f^{\phi} + m \left(\frac{2v_M v_X}{v} \right) B_{MX}^Y + m^2 \frac{2(v_M v_X)^{3/2}}{v} C_{MX}^Y \quad (4)$$

$$f^Y = -A_{\phi} [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] \quad (5)$$

$$B_{MX}^Y = 2\beta_{MX}^{(0)} + (2\beta_{MX}^{(1)} / \alpha_1^2 I) [1 - (1 + \alpha_1 I^{1/2} - \frac{1}{2} \alpha_1^2 I) \exp(-\alpha_1 I^{1/2})] + (2\beta^{(2)} / \alpha_2^2 I) \times [1 - (1 + \alpha_2 I^{1/2} - \frac{1}{2} \alpha_2^2 I) \exp(-\alpha_2 I^{1/2})] \quad (6)$$

$$C_{MX}^Y = 3/2 C_{MX}^{\phi} \quad (7)$$

Here z_M and z_X are the charges on the ions M, X, A_{ϕ} is the Debye-Hückel parameter. $v = v_M + v_X$, and b is a constant given the value 1.2 for all electrolytes. For low-valence electrolytes α_1 is given the value 2.0 and the terms in $\beta^{(2)}$ are omitted. The parameters $\beta^{(0)}$ and $\beta^{(1)}$ describe short-range interactions of pairs of ions, while C^{ϕ} relates to triple interactions. For high-valence electrolytes $\beta^{(2)}$ has a large negative value related to the apparent association constant while α_2 has a large positive value which removes the effect of this term at higher concentration in a manner corresponding to the re-dissociation phenomenon noted by Davies. For all 2-2 electrolytes the parameters are $\alpha_1 = 1.4$ and $\alpha_2 = 12$. For higher valence types we expect α_2 to be substantially larger and will evaluate it empirically. The results may not be sensitive to the exact value of α_1 hence we return to the choice $\alpha_1 = 2.0$ used for all except 2-2 solutes.

In deriving the equation for heat of dilution we note that the excess Gibbs energy for a solution with one kg of solvent is

$$G^{\text{ex}} = \nu mRT(1 - \phi + \ln \gamma_{\pm}) \quad (8)$$

where $\nu = \nu_M + \nu_X$ is the number of ions in the formula. After the appropriate temperature differentiation and other steps one finds for the apparent molal enthalpy

$$\begin{aligned} \phi_L = \nu |z_M z_X| (A_H/3b) \ln(1 + bI^{1/2}) - \\ 2\nu_M \nu_X RT^2 [mB_{MX}^L + m^2 (\nu_M z_M) C_{MX}^L] \end{aligned} \quad (9)$$

$$\begin{aligned} B_{MX}^L = (\partial \beta_{MX}^{(0)}/\partial T) + (\partial \beta_{MX}^{(1)}/\partial T) (2/\alpha_1^2 I) \times \\ [1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})] + (\partial \beta_{MX}^{(2)}/\partial T) \times \\ (2/\alpha_2^2 I) [1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})] \end{aligned} \quad (10)$$

$$C_{MX}^L = (\partial C_{MX}^{\phi}/\partial T)_P / 2 |z_M z_X|^{1/2}. \quad (11)$$

This derivation, which is given in more detail elsewhere,¹⁰ assumes b , α_1 , and α_2 to be constant; also A_H is the Debye-Hückel parameter for enthalpy with the value for water at 25°C of $A_H/RT = 1.1773$.

The data of Nathan, Wallace, and Robinson⁸ for $\text{La}_2(\text{SO}_4)_3$ and those of Lange and Miederer⁹ for $\text{Ca}_3(\text{Fe}(\text{CN})_6)_2$, $\text{Sr}_3(\text{Fe}(\text{CN})_6)_2$, $\text{Ba}_3(\text{Fe}(\text{CN})_6)_2$, $\text{Mg}_2\text{Fe}(\text{CN})_6$, $\text{Ca}_2\text{Fe}(\text{CN})_6$, and $\text{Sr}_2\text{Fe}(\text{CN})_6$ were fitted to equation (9) with $(\partial \beta^{(0)}/\partial T)$, $(\partial \beta^{(1)}/\partial T)$, and $(\partial \beta^{(2)}/\partial T)$ adjusted by least-squares individually for each

solute while α_2 was assigned various values. The third virial coefficient was omitted since all solutions are dilute. The data reported by Lange and Miederer⁹ for $\text{LaFe}(\text{CN})_6$ do not extend to low enough molality to be useful. Also an inconsistency, possibly of typographical origin, was noted in the data for $\text{Sr}_3(\text{Fe}(\text{CN})_6)_2$ and no further consideration was given to them.

While one might expect a somewhat higher value of α_2 for the 4-2 than for the 3-2 electrolytes, the value $\alpha_2 = 50$ was nearly optimum for each type. With this value of α_2 , the other parameters shown in Table 1 were obtained. The standard deviations of fit, given in the last column, seem large but are not unreasonable for dilutions which extend below 10^{-4} M and involve heats as large as $5000 \text{ cal mole}^{-1}$ for $\text{La}_2(\text{SO}_4)_3$.

Figure 1 shows the experimental data for $\text{La}_2(\text{SO}_4)_3$ as horizontal chords giving $\Delta\phi_L/\Delta m^{1/2}$. In one case several experiments were combined in order to obtain a relatively small dilution ratio. The limiting law is indicated by the arrow marked L.L. Our curve is shown as a solid line while the empirical equation chosen by Nathan, et al, is given by the dashed line. The peak with a maximum at about 0.00003 M is very apparent. Figure 1 shows only the more dilute range of the data fitted; hence it is understandable that the fit seems less than ideal over this partial range. The curves for the various cyanoferrate salts are qualitatively similar but less extreme than that on Figure 1.

Table 1. Parameters for the Enthalpy of 3-2 and 4-2 Electrolytes in Water at 25°C. ($b=1.2$, $\alpha_1=2.0$, $\alpha_2=50$ throughout)

Electrolyte	$\frac{\partial \beta^{(0)}}{\partial T}$	$\frac{\partial \beta^{(1)}}{\partial T}$	$\frac{\partial \beta^{(2)}}{\partial T}$	Max. m	σ/cal
$\text{Ca}_3(\text{Fe}(\text{CN})_6)_2$	-0.0052	0.087	- 2.13 ₅	0.04	26
$\text{Ba}_3(\text{Fe}(\text{CN})_6)_2$	0.0008	0.065 ₆	- 3.54 ₅	0.04	35
$\text{La}_2(\text{SO}_4)_3$	0.082 ₉	-0.202	-51.3	0.024	187
$\text{Mg}_2\text{Fe}(\text{CN})_6$	0.016 ₂	0.041 ₈	-23.9	0.04	83
$\text{Ca}_2\text{Fe}(\text{CN})_6$	0.0016	0.158 ₅	- 7.47	0.04	55
$\text{Sr}_2\text{Fe}(\text{CN})_6$	0.0052	0.118 ₃	-19.5	0.04	34

Osmotic and Activity Coefficients

There are no osmotic or activity coefficient data for 3-2 or 4-2 electrolytes which extend to low enough molality (less than 10^{-4}) to yield reliable interpretation standing alone. But as we shall note below the parameter $\beta^{(2)}$ is related to the association constant determined from conductance measurements. Thus one can estimate values of $\beta^{(2)}$ which can be used with the α_2 value determined from heats of dilution. With $\beta^{(2)}$ and α_2 determined, the remaining parameters in equations (1) or (4) can be evaluated from osmotic or activity coefficients at higher concentration.

For aluminum sulfate we use the association constant determined by Nishide and Tsuchiya¹¹ to be 5400 at 25°C.

Since $\beta^{(2)} = -K/2$, we estimate $\beta^{(2)} = -2700$. Then the osmotic data of Burge¹² and of Robinson¹³ yield $\beta^{(0)} = 1.219$, $\beta^{(1)} = 14.901$, $C^\phi = -0.4287$ for $\text{Al}_2(\text{SO}_4)_3$. The standard deviation of fit is 0.007.

For $\text{La}_2(\text{SO}_4)_3$ the freezing point data of Hovorka and Rodebush¹⁴ can be considered. Even though these data extend down to 0.001 M they show no anomaly and were extrapolated smoothly to the Debye-Hückel slope. Probably this is misleading, however. At 25° the conductance data⁷ for $\text{La}_2(\text{SO}_4)_3$ yield $K = 4170$ or $\beta^{(2)} = -2085$. From the value -51.3 in Table 1 for $\partial\beta^{(2)}/\partial T$ this yields at 0°C, $\beta^{(2)} = -803$. Since the data extend only to 0.01 M, we neglect $\beta^{(0)}$ and C^ϕ . Then for lanthanum sulfate at 0°C, $\beta^{(1)} = 13.0$. The standard deviation in the osmotic coefficient is 0.010.

In the case of indium sulfate a different approach is possible. Here the metal can be used as an electrode in a Galvanic cell with its potential determined from indium chloride solutions in the cell $\text{In}|\text{InCl}_3(m)|\text{AgCl}, \text{Ag}$. For the $\text{In}/\text{In}^{+++}$ electrode the value $E_o = 0.3382$ v was given by Covington, Hakeem, and Wynne-Jones¹⁵ while a recalculation in paper II¹⁶ of this series yielded 0.3376 v. For determination of the activity coefficient of $\text{In}_2(\text{SO}_4)_3$ the cell $\text{In}|\text{In}_2(\text{SO}_4)_3(m)|\text{Hg}, \text{Hg}_2\text{SO}_4$ is appropriate. The standard potential of the $\text{Hg}, \text{Hg}_2\text{SO}_4$ electrode was given as 0.612₅ v by Covington, Dobson, and Wynne-Jones.¹⁷ The various calculations for sulfuric acid in paper VII¹⁸ of this series yielded 0.612₄ v for this quantity.

The indium sulfate cell was measured by Hattox and DeVries¹⁹ and by Covington, Hakeem, Wynne-Jones.¹⁵ There is no disagreement between the two investigations but both sets of data show an unreasonable trend below 0.05 M which has been attributed to hydrolysis of the mercurous sulfate.^{15,20} We chose $E^\circ = 0.9500$ V and fitted the data above 0.05 M with the results $\beta^{(0)} = 2.014_5$, $\beta^{(1)} = 48.36$, and $\beta^{(2)} = -21513$. The large negative value of $\beta^{(2)}$ indicates relatively strong ion association.

Discussion

The behavior in very dilute solutions of high-valence electrolytes, which can be described as ion association with re-dissociation at higher concentration, has been discussed and verified from conductance data by Davies.² For our purposes let us discuss a very simple model with an association equilibrium $M + X = MX$ and with all activity coefficients following the Debye-Hückel limiting law.

$$K = \left[\frac{\alpha}{(v_M^{-\alpha})(v_X^{-\alpha})} \right] \left[\frac{\gamma_{MX}}{m\gamma_M\gamma_X} \right] \quad (12)$$

$$\ln(\gamma_{MX}/\gamma_M\gamma_X) = 6|z_M z_X| A_\phi I^{1/2} \quad (13)$$

Here the proportion of association α clearly increases with m at very low m where other factors are nearly constant. But for highly charged ions, as m increases further, the second bracketed factor reaches a minimum and then increases because the activity coefficients γ_M and γ_X decrease very rapidly.

This behavior is exemplified on Figure 2 for a 3-2 electrolyte with $K = 1000$ and $A_\phi = 0.377$ (for water at 0°C). The bottom curve shows that the fraction associated reaches a maximum near 0.001 M. The upper curve shows that by 0.01 M the excess Gibbs energy has essentially returned to the value calculated without association. The form of the term in $\beta^{(2)}$ in equations (3), (6), and (10) is qualitatively correct for the deviation between the two curves for G^{ex} in that its effect is proportional to m at very small m and then decreases exponentially with further increase in m . The initial proportionality can be shown to yield the equations

$$\beta^{(2)} = -K/2 \quad (14)$$

$$\partial\beta^{(2)}/\partial T = -K\Delta H/2RT^2 \quad (15)$$

where ΔH is the heat of association.

For $\text{La}_2(\text{SO}_4)_3$ the heat of association has been reported²¹ to be 18.45 kJ while K is 4170 . Equation (15) then yields for $\partial\beta^{(2)}/\partial T$ the value -52 which is in fortuitously good agreement with the value -51.3 in Table 1.

We have demonstrated that it is possible to represent the thermodynamic properties of 3-2 and 4-2 electrolytes by the same methods used for 2-2 electrolytes and without explicit consideration of an association equilibrium. For the higher valence types, however, data are required at extremely low concentration (below 10^{-4} M) and these are difficult to obtain. It is possible to use data of one type in this very dilute range to assist in treating data of another type at higher

concentration. The re-dissociation phenomenon at higher concentration is such that data for these electrolytes above 0.001 M may seem quite normal provided the very strong effect of the Debye-Hückel limiting law is recognized.

Acknowledgement

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Figure Captions

Figure 1. The heat of dilution of $\text{La}_2(\text{SO}_4)_3$, shown as $(\Delta\phi_L/\Delta m^{1/2}) \times 10^5$ in $\text{cal kg}^{1/2} \text{ mol}^{-1/2}$, as a function of $m^{1/2}$. See text for details.

Figure 2. The excess Gibbs energy and the fraction associated for a simple model for a 3-2 electrolyte.

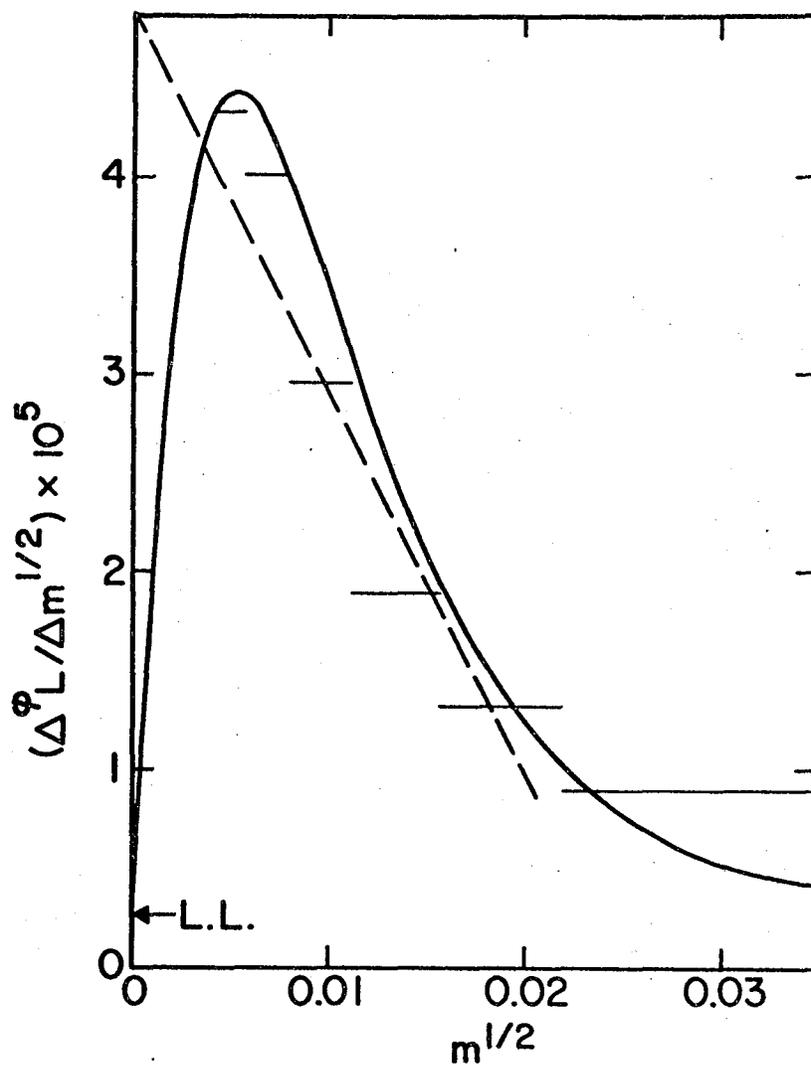


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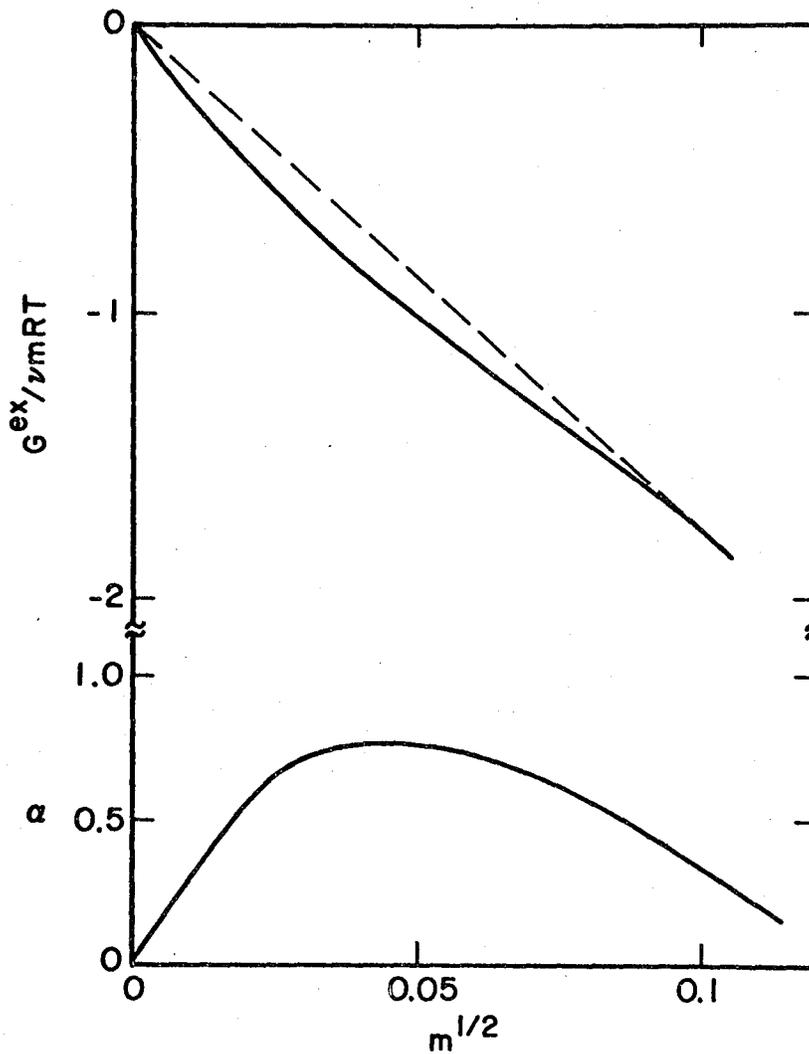


Figure 2. The excess Gibbs energy and the fraction associated for a simple model for a 3-2 electrolyte.

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