A Unified Approach for Prediction of Thermodynamic Properties of Aqueous Mixed-Electrolyte Solutions

Part II: Volume, Thermal, and Other Properties

The overall reduced ionic activity coefficient Γ^* is useful in characterizing the overall nonideality of an aqueous mixed-electrolyte solution. It has been shown in Part I that Γ^* can be simply related to Γ of single-electrolyte solutions containing the component electrolytes without using empirical constants. This basic relationship is used in this paper for deriving predictive equations for several properties in terms of corresponding properties of single-electrolyte solutions containing the component electrolytes. The predictive equations need no empirical constants. The properties covered include volume properties such as density and adiabatic compressibility, thermal properties such as enthalpy and specific heats, and others such as free energy, expansibility, and depression in freezing point. Comparison with experimental data shows that the predictive equations have an accuracy varying from 0.03% for density to 2% for freezing point depression, and are valid for the entire range of concentrations encountered in practice.

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SCOPE

The thermodynamic properties of aqueous mixed-electrolyte solutions play an important role in several areas of chemical engineering. These properties have been reported extensively in the literature for aqueous solutions of single electrolytes. Predictive methods that can make use of this information and predict the properties of mixed solutions even for concentrated solutions (up to an ionic strength of 20 or above) obviously have a tremendous practical utility. The present study was aimed at developing simple but sufficiently accurate predictive equations for the thermodynamic properties of aqueous mixed-electrolyte solutions. The properties include volume properties such as density and compressibility, thermal properties such as enthalpy and specific heat, free energy, and freezing point depression.

It has been shown in Part I that the overall nonideality of an aqueous mixed-electrolyte solution can be expressed in terms of the nonidealities of single-electrolyte solutions of component electrolytes. The thermodynamic properties mentioned above can be related to the nonideality of a solution using well-known thermodynamic equations. This framework enables us to derive a consistent set of predictive equations for all these properties, starting from a single basic relationship.

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CONCLUSIONS AND SIGNIFICANCE

The overall nonideality of an aqueous mixed-electrolyte solution is related to those of single-electrolyte solutions through Eq. 5, as shown in Part I. Using this and the well-established thermodynamic relationships between the nonideality and various properties, predictive equations have been derived for several properties of mixed-electrolyte solutions. They cover the prediction of density, adiabatic compressibility, enthalpy, specific heat, expansibility, freezing point depression, and free energy, via Eqs. 15, 18, 28, 29, 34, 36, and 39, respectively. Comparison with the experimental data listed in Table 1 indicates the predictive accuracy to be within 0.03% for density and 2% for freezing point depression. In the case of density, experimental data were available for six systems, some of which are multicomponent systems. For freezing point depression, data on eight two-component systems were available, though they are all three-ion systems. On the other hand, for expansibility, data for only one system was available. Experimental data involving solutions of more than two electrolytes are very scanty.

A unique feature of the predictive equations presented here and in Part I is that they have all been derived from a single relationship, i.e., Eq. 5, using well-known thermodynamic equations. In this sense they represent a consistent set of predictive equations. The comparisons with experimental data for different predictive equations can thus be considered to validate the entire set of predictive equations and the basic relationship in Eq. 5. All of them require only the knowledge of properties of single-electrolyte solutions; no empirical constants are required.

Introduction

The nonideality of an aqueous solutions of a single electrolyte is conventionally represented in terms of the mean ionic activity coefficient, $\gamma_\pm$, which accounts for the combined effects arising out of positive and negative ions. It has been shown in Part I that the total nonideality of an aqueous solution of several electrolytes can conveniently be represented in terms of the overall ionic activity coefficient, γ^* defined by

$$\log \gamma^* = \sum_i x_i \log \gamma_i \qquad (1)$$

Similarly, the overall ionic molality and the overall ionic activity can be defined as

$$\log m^* = \sum_i x_i \log m_i \qquad (2)$$

and

$$\log a^* = \sum_i x_i \log a_i \qquad (3)$$

With these definitions, a^* becomes equal to $m^* \gamma^*$, and also, γ^* reduces to the usual definition of $\gamma_\pm$ for solutions of single electrolytes. It may be noted here that γ_i in Eq. 1 represents the ionic activity coefficient of the ith ionic species in the mixed electrolyte solution. It has been shown by Meissner and Tester (1972) that single-electrolyte solutions for different electrolytes give an ordered family of curves on the log Γ vs. μ plot, where $\log \Gamma = (\log \gamma_\pm)/(z_+ z_-)$. A similar parameter for mixed electrolyte solutions is defined as

$$\log \Gamma^* = (\log \gamma^*) \Big/ \sum_i (x_i z_i^2) \qquad (4)$$

It has been shown in Part I that the following relationship holds good, i.e.,

$$\log \Gamma^* = \sum_J y_J \log \Gamma_J^0 \qquad (5)$$

This relationship forms the basis for evolving predictive equations for several thermodynamic properties of mixed-electrolyte solutions in terms of those of the corresponding single-electrolyte solutions. In this part, predictive equations are developed and their accuracy is tested with available experimental data as listed in Table 1.

Density

Let us consider the process of preparing a mixed-electrolyte solution from the pure electrolytes and water. The volume change on mixing the pure components, per 1,000 g water, is given by

$$\Delta V = \frac{1{,}000}{M_w}(\bar{V}_w - V_w) + \sum_J m_J(\bar{V} - V_J) \qquad (6)$$

Writing $\bar{V}$ in terms of derivatives of the activity, and using Eq. 10 of Part I, we get

$$\Delta V = \frac{1{,}000}{M_w} RT \left(\frac{\partial \ln a_w}{\partial P}\right)_{T,N} + RT\left(\sum_J m_J \nu_J\right)\left(\frac{\partial \ln a^*}{\partial P}\right)_{T,N} - \left(\frac{1{,}000}{M_w} V_w + \sum_J m_J V_J\right) \qquad (7)$$

Let us now consider the process of preparing a solution of the Jth salt alone, from pure components, such that the solution has

Table 1. Experimental Data Used to Test the Accuracy of the Proposed Predictive Equations

Systems	μ_{max}	Composition (Ionic % Strength of Second Component)	No. of Data Points	References
Density				
$NaCl$-$CaCl_2$	5	5–95	59	Kumar et al. (1982); Kumar and Atkinson (1983)
$NaCl$-$MgCl_2$	5	20–80	12	Atkinson et al. (1984)
$NaCl$-$CaCl_2$-$MgCl_2$	5	5–95	76	Atkinson et al. (1984)
$NaCl$-KBr	4	5–95	25	Kumar (1985)
$CaCl_2$-$MgCl_2$	5	20–80	12	Atkinson et al. (1984)
$NaCl$-KCl-$MgCl_2$-$CaCl_2$	9, 8	—	6	Krumgalz and Millero (1982)
Compressibility				
$NaCl$-$CaCl_2$	5	5–95	83	Kumar et al. (1982); Kumar and Atkinson (1983)
$NaCl$-$MgCl_2$	5	20–80	12	Atkinson et al. (1984)
$CaCl_2$-$MgCl_2$	5	20–80	12	Atkinson et al. (1984)
Enthalpy				
$NaCl$-Na_2SO_4	1	20–90	12	Duer et al. (1976)
$MgCl_2$-Na_2SO_4	1	20–80	11	Duer et al. (1976)
$NaCl$-$MgCl_2$	1	20–80	7	Duer et al. (1976)
$NaCl$-KCl	1	50	6	Bazlova et al. (1965)
Specific Heat				
$NaCl$-KCl	4.5	50	6	Stakhanova and Vasilev (1960)
$NaCl$-$CsCl$	4.5	50	7	Stakhanova and Vasilev (1963)
$NaCl$-$NaClO_4$	5	50	5	Epikhin and Stakhanova (1967)
$NaCl$-$NaNO_3$	6	50	11	Epikhin and Stakhanova (1967)
KCl-KBr	4.5	50	11	Stakhanova et al. (1963)
KCl-KNO_3	3	50	8	Epikhin and Stakhanova (1964)
Expansibility				
$NaCl$-$CaCl_2$	5	5–95	27	Kumar and Atkinson (1983)
Depression in Freezing Point				
$NaCl$-KCl	3	50	12	Vilcu and Stanciu (1965); Vilcu et al. (1984)
$LiCl$-$NaCl$	3	50	5	Vilcu et al. (1984)
$LiCl$-KCl	3	50	5	Vilcu et al. (1984)
$LiCl$-$CsCl$	3	50	5	Vilcu et al. (1984)
$NaBr$-KBr	3.4	50	9	Vilcu and Stanciu (1968)
$NaCl$-$MgCl_2$	3	40–75	24	Gibbard and Gossmann (1974)
KIO_3-$NaIO_3$	0.1	50	4	*Int. Crit. Tables* (1928)
KNO_3-KCl	0.2	50	5	*Int. Crit. Tables* (1928)

the same ionic strength as that of the mixed solution. For such a solution, we get

$$\Delta V_J^\circ = \frac{1{,}000}{M_w} RT \left(\frac{\partial \ln a_{w,J}^\circ}{\partial P}\right)_{T,N} + RT\, m_J^\circ \nu_J \left(\frac{\partial \ln a_{\pm J}^\circ}{\partial P}\right)_{T,N} - \frac{1{,}000}{M_w} V_w - m_J^\circ V_J \tag{8}$$

Let us now see how a^* is related to $a_{\pm J}^\circ$. Using Eq. 4 for the mixed- as well as single-electrolyte solutions, we get

$$\left(\sum_J m_J \nu_J\right) \log \gamma^* = \sum_J m_J \nu_J \log \gamma_{\pm J}^\circ \tag{9}$$

By definition, m^* can be written as

$$\left(\sum_J m_J \nu_J\right) \log m^* = \sum_J m_J \nu_J \log m_{\pm J} = \sum_J m_J \nu_J \log (y_J m_J^\circ) \tag{10}$$

Adding Eqs. 9 and 10

$$\left(\sum_J m_J \nu_J\right) \log a^* = \sum_J y_J m_J^\circ \nu_J \log a_{\pm J}^\circ + \sum_J m_J \nu_J \log y_J \tag{11}$$

Using Eqs. 7, 8, 11, Eq. 31 of Part I, and the fact that $m_J = y_J m_J^\circ$, we get

$$\Delta V = \sum_J y_J \Delta V_J^\circ \tag{12}$$

If d, d_o, and d_{oJ} are the densities of the mixed solution, pure water, and pure electrolyte, respectively, then

$$\Delta V = \frac{1{,}000 + \sum_J m_J M_J}{d} - \frac{1{,}000}{d_o} - \sum_J \frac{m_J M_J}{d_{oJ}} \tag{13}$$

Similarly,

$$\Delta V_J^o = \frac{1{,}000 + \sum_J m_J^o M_J}{d_J^o} - \frac{1{,}000}{d_o} - \frac{m_J^o M_J}{d_{oJ}} \tag{14}$$

Substituting in Eq. 12 and rearranging, we get

$$d = \frac{\sum_J \psi_J}{\sum_J (\psi_J / d_J^o)} \tag{15}$$

where

$$\psi_J = (1{,}000\, y_J + m_J M_J) \tag{16}$$

Equation 15 is the predictive equation for density of a mixed-electrolyte solution from d_J^o values.

We now utilize Eq. 15 for analyzing various systems at different conditions, listed in Table 1. Figure 1 depicts the experimental and calculated $(d - d_o) \times 10^3$ for various systems. The data analyzed include two different cations with common anion, three different cations with common anion, four different cations with common anion, and four different cation and anion systems at high ionic strengths. The predictions are accurate within 0.03%.

The semiempirical approach of Brønsted-Guggenheim has been used by Kumar (1984) to predict the density of the aqueous NaCl—$CaCl_2$ system up to $\mu = 1.0$ with an average deviation of 0.005%. This approach is limited to an ionic strength of 1 and fails beyond this, as the interactions arising in concentrated solution become important. The more recent approach of Pitzer (1973) has been further developed by Kumar et al. (1982) and Kumar and Atkinson (1983). The latter authors reported densities of aqueous NaCl—$CaCl_2$ mixtures at $\mu = 0.3$ to 20 in the temperature range of 5 to 35°C. Using the Pitzer approach they could predict the density of aqueous NaCl—$CaCl_2$—H_2O system up to $\mu = 5$ to 0.003%. They also used the mixing terms recognizing explicitly the like charge interactions, and predictions were improved, with an average deviation of 0.001%. The improved accuracy of these approaches arises out of the fact that they are based on several empirical constants. Equation 15, however, uses no empirical constants and has the accuracy required by most practical applications.

Adiabatic compressibility

The adiabatic compressibility β is given by

$$\beta = \frac{1}{d}\left(\frac{\partial d}{\partial P}\right)_T \tag{17}$$

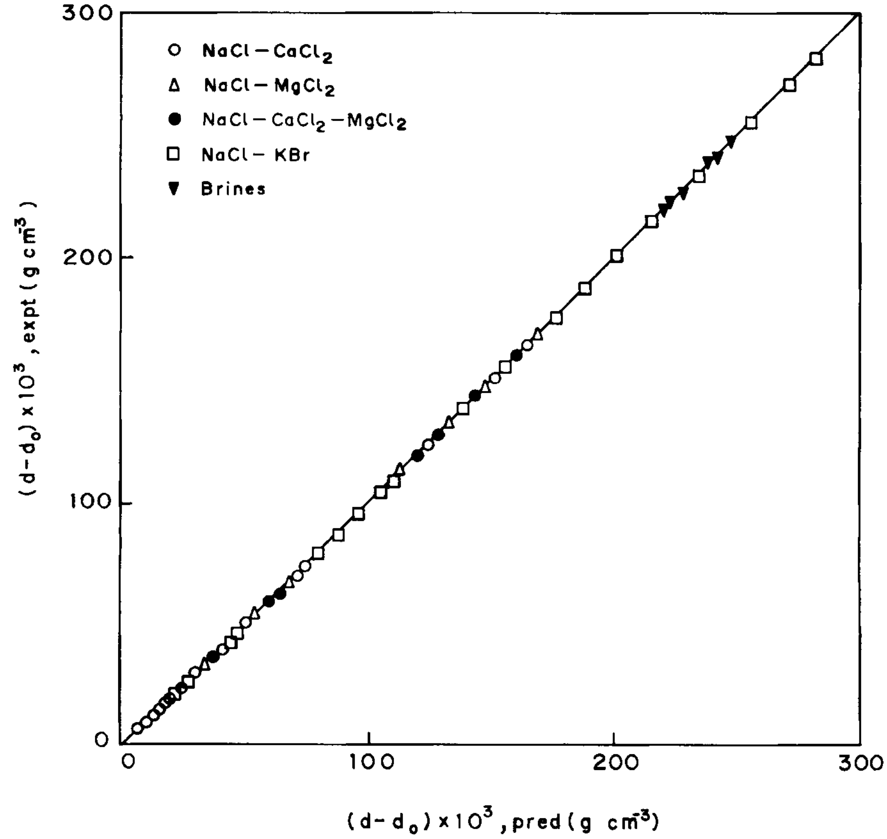

Figure 1. Experimental and predicted densities for various systems.

Using Eq. 15 and rearranging, we get

$$\beta = \frac{\sum_J \left(\frac{\psi_J \beta_J^o}{d_J^o}\right)}{\sum_J (\psi_J / d_J^o)} \tag{18}$$

Equation 18 was used to predict the adiabatic compressibility of aqueous NaCl—$CaCl_2$, NaCl—$MgCl_2$, and aqueous $CaCl_2$—$MgCl_2$ systems at various temperatures. Figure 2 shows the accuracy to be better than 1%. The sound velocities calculated from β were found to be accurate within 0.5%. Kumar (1984a, b) predicted the compressibility of aqueous NaCl—$CaCl_2$ system up to $\mu = 1$ using the Brønsted-Guggenheim approach within about 1% and sound velocities within 2%. Equations developed by Kumar and Atkinson (1983) based on the Pitzer approach predicted the compressibility of aqueous NaCl—$CaCl_2$ mixture up to $\mu = 5$ within 0.4%. The accuracy of predictions was further improved to 0.1% by including the mixing terms.

Thermal Properties

Enthalpy

Let us consider the heat change accompanying the dissolution of an electrolyte in 1,000 g of water. The heat change ΔH_s can be written as

$$\Delta H_s = \frac{1{,}000}{M_w}(\overline{H}_w - H_w) + \sum_J m_J(\overline{H}_J - \overline{H}'_J) + \sum_J m_J(\overline{H}'_J - H_J) \tag{19}$$

Using temperature derivatives of activities, and Eq. 10 of Part I, we get

$$\Delta H_s = -\frac{RT^2\,1{,}000}{M_w}\left(\frac{\partial \ln a_w}{\partial T}\right)_{P,N} - RT^2\left(\sum_J m_J\nu_J\right)\left(\frac{\partial \ln a^*}{\partial T}\right)_{P,N} + \sum m_J(\overline{H}'_J - H_J) \tag{20}$$

Now, considering the process of preparing the solution of Jth electrolyte alone at the same μ as that of mixture, we get

$$\Delta H^o_{s,J} = -\frac{RT^2\,1{,}000}{M_w}\left(\frac{\partial \ln a^o_{w,J}}{\partial T}\right)_{P,N} - RT^2 m^o_J\left(\frac{\partial \ln a^o_J}{\partial T}\right)_{P,N} + m^o_J(\overline{H}'_J - H_J) \tag{21}$$

Proceeding along the same lines as for volume properties, we get

$$\Delta H_s = \sum_J y_J \Delta H^o_{s,J} \tag{22}$$

Equation 22 can be used to estimate the heat of solution of the mixtures. It can also be used to generate the enthalpy-concentration diagram for mixed-electrolyte solutions from those of single-electrolyte solutions.

The relative apparent molar enthalpy can be written as (Glasstone, 1960)

$$\phi_L = \frac{H - n_1\overline{H}'_1 - n_2\overline{H}'_2}{n_2} \tag{23}$$

Equation 23 can be written on a 1,000 g water basis for a single-electrolyte solution as

$$\phi^o_{L,J} = \frac{H^o_J - \frac{1{,}000}{M_w}\overline{H}'_1 - m^o_J\overline{H}'_J}{m^o_J} \tag{24}$$

A similar equation for a mixture becomes

$$\phi_L = \frac{H - \frac{1{,}000}{M_w}\overline{H}'_1 - \sum_J m_J\overline{H}'_J}{\sum_J m_J} \tag{25}$$

The heats of solution for such solutions can be written as

$$\Delta H_s = H - \frac{1{,}000}{M_w}\overline{H}'_w - \sum_J m_J H_J \tag{26}$$

and

$$\Delta H^o_{s,J} = H^o_J - \frac{1{,}000}{M_w}\overline{H}'_w - m^o_J H_J \tag{27}$$

Using Eqs. 26 and 27, and substituting the values of H^o_J and H from Eqs. 24 and 25 in terms of $\phi^o_{L,J}$ and ϕ_L, Eq. 22 gives

$$\phi_L = \frac{\sum_J m_J \phi^o_{L,J}}{\sum_J m_J} \tag{28}$$

There is only a limited amount of experimental data reported in literature that can be used for testing Eqs. 22 and 28. Duer et al. (1976) have reported heats of mixing for NaCl—Na_2SO_4, $MgCl_2$—Na_2SO_4, and NaCl—$MgCl_2$ systems. From their experimental data, the ϕ_L values for these systems can be calculated using their equations. These, along with ϕ_L values predicted using Eq. 28, are presented in Figure 3. The predicted and experimental values match within 2%.

Heat of solution (ΔH_s) data of Bazlova et al. (1965) on aqueous NaCl—KCl at 25°C were used for testing Eq. 22. Predicted values match with the experimental data within 0.4%, as shown in Table 2.

Specific heat

Differentiation of Eq. 22 with respect to temperature gives, after simplification,

$$C_p = \Sigma y_J C^o_{p,J} \tag{29}$$

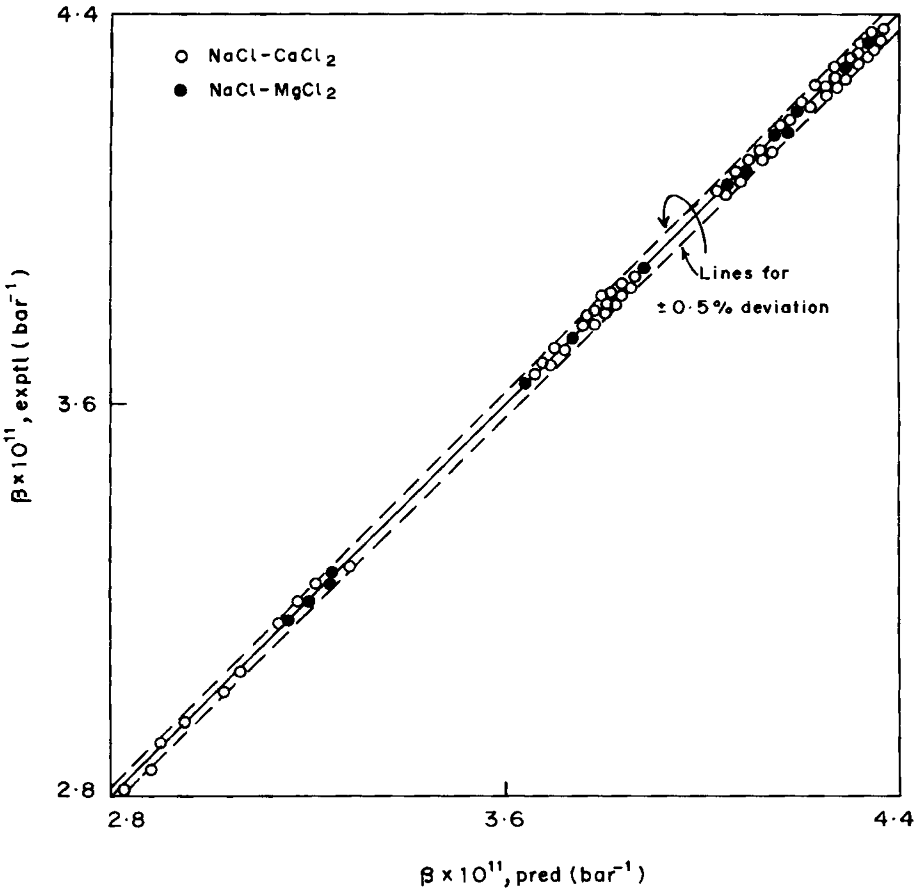

Figure 2. Experimental and predicted adiabatic compressibilities β for two systems.

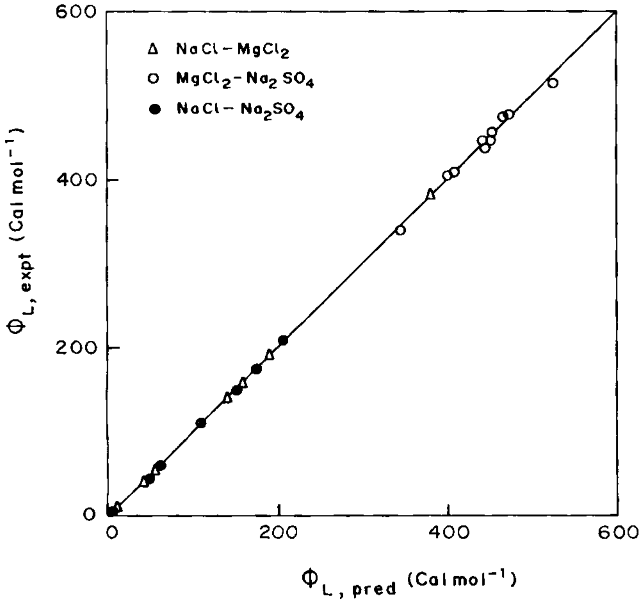

Figure 3. Experimental and predicted ϕ_L for various systems.

Figure 4 shows a comparison of the experimental and predicted C_p values. The limited data available show that C_p can be predicted within 0.06%. The Zdanovskii rule (Stakhanova and Vasilev, 1960, 1963) has frequently been used for estimating the heat capacities of mixed aqueous solutions of two electrolytes and may be stated as

$$C_p = \sum_J m_J C^o_{p,J} \Big/ \sum_J m_J \qquad (30)$$

This rule has only been tested for equimolal mixtures of 1-1 electrolyte solutions. This rule and our Eq. 29 are the same for such mixtures.

Table 2. Experimental and Predicted ΔH_s for Aqueous NaCl-KCl System at Equimolal Mixtures

	ΔH_s	
μ	Exp.* cal · mol^{-1}	Pred.** cal · mol^{-1}
1.1101	2518	2501
0.5550	2595	2583
0.2775	2622	2613
0.1388	2628	2617
0.0694	2609	2604
0.0347	2599	2595

*Bazlova et al. (1965)
**Eq. 22

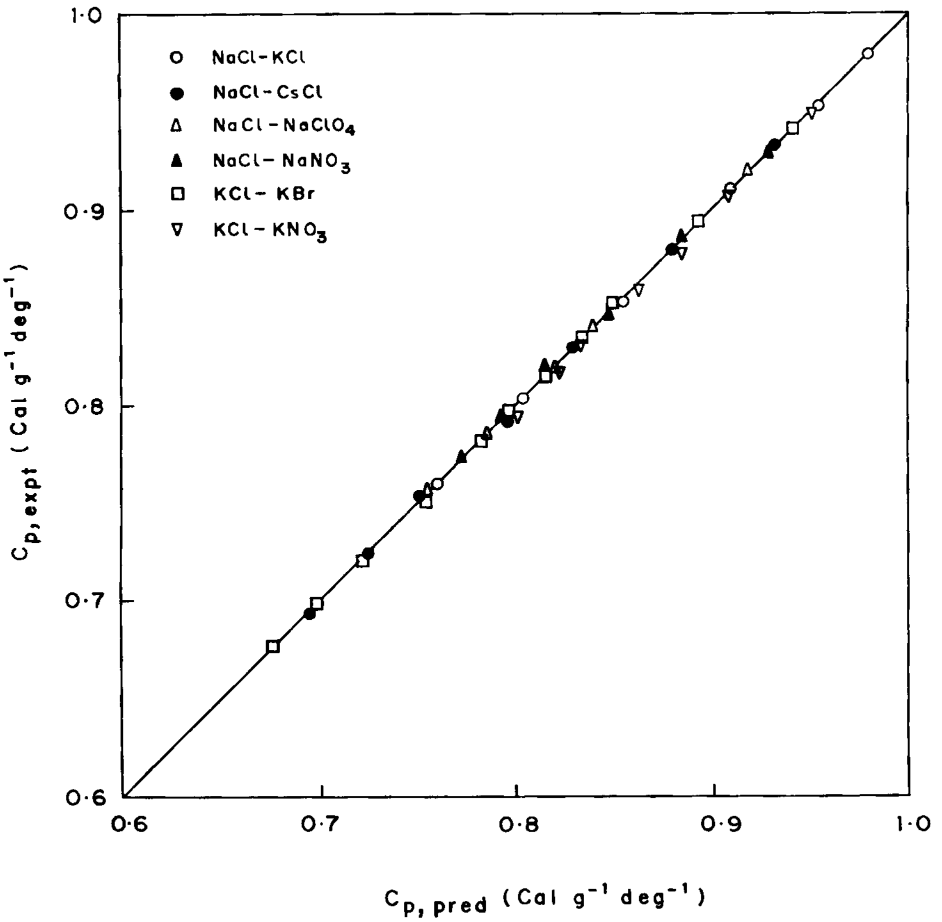

Figure 4. Experimental and predicted specific heats C_p for various systems.

Expansibility

The thermal expansion of an electrolyte solution is given by

$$\alpha = -\frac{1}{d}\left(\frac{\partial d}{\partial T}\right)_P \tag{31}$$

Using Eq. 15 for d, we get

$$\alpha = \sum_J\left(\frac{\psi_J\alpha^o_J}{d^o_J}\right)\Big/\sum_J\left(\frac{\psi_J}{d^o_J}\right) \tag{32}$$

The apparent molal expansibility ϕ_E is given by (Millero, 1979)

$$\phi^o_{EJ} = \frac{1{,}000}{m^o_J d^o_J d_o}\left(d_o\alpha^o_J - d^o_J\alpha_o\right) + \frac{M_J}{d^o_J}\alpha^o_J \tag{33}$$

ϕ_E for the mixed-electrolyte solution is defined similarly. Substituting for α from this equation and for α^o_J from Eq. 33 into Eq. 32 and using Eq. 15, we get

$$\phi_E = \frac{\sum_J m_J\phi^o_{E,J}}{\sum_J m_J} \tag{34}$$

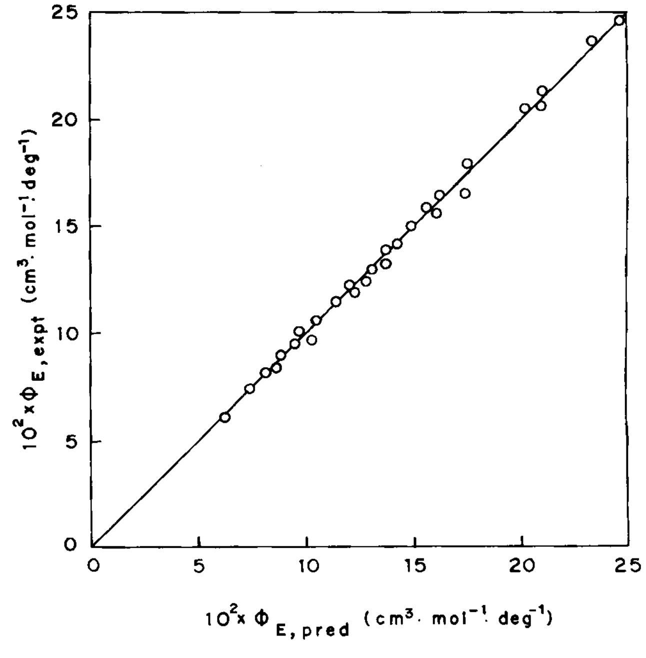

Figure 5. Experimental and predicted ϕ_E for aqueous NaCl—CaCl$_2$ system.

Figure 5 shows the experimental and predicted values of ϕ_E for aqueous NaCl—CaCl$_2$ system at several values of μ. The predictions are accurate within 0.8%. These are probably the only data available in literature on expansibilities of mixed aqueous electrolyte solutions. Kumar and Atkinson (1983) developed Pitzer equations for estimating the ϕ_E in mixed solutions. Their equations predicted ϕ_E within 1.7, 0.7, and 0.25% at $\mu = 5, 2,$ and 1, respectively.

Other Properties

Depression in freezing point

The activity of water in an electrolyte solution is related to the depression in freezing point T_θ as (Glasstone, 1960)

$$-\ln a_w = \frac{L_o T_\theta}{RT_o^2} + \frac{T_\theta^2}{RT_o^2}\left(\frac{L_o}{T_o} - \frac{\Delta C_p}{2}\right) + \cdots \qquad (35)$$

Since T_θ in general is small in magnitude, one can neglect the second term. Substituting Eq. 35 in Eq. 31 of Part I leads to

$$T_\theta = \sum_J y_J T^\circ_{\theta J} \qquad (36)$$

Comparison with experimental data on the seven different systems listed in Table 1 shows that the predictions of Eq. 36 have an accuracy of 2%. The second term in Eq. 35 was found to be very small in relation to the first term. Figure 6 presents the experimental and predicted T_θ values.

Free energy

Let us consider the process of preparing a mixed-electrolyte solution from pure water and electrolytes at constant temperature and pressure. The free energy change accompanying the process, per 1,000 g water, is given by

$$\Delta G = (1{,}000/M_w)\, RT \ln a_w + RT \sum_J m_J \nu_J \ln a^* \qquad (37)$$

If a solution of a single electrolyte of the same μ is prepared, we have

$$\Delta G^\circ_J = (1{,}000/M_w)\, RT \ln a^\circ_{w,J} + RT m^\circ_J \ln a^\circ_{\pm J} \qquad (38)$$

Proceeding along the same lines as for volume and thermal properties, we get

$$\Delta G = \sum_J y_J \Delta G^\circ_J + RT \sum_J m_J \nu_J \ln y_J \qquad (39)$$

The first term on the righthand side indicates the additive contribution from different component electrolytes, while the second term indicates the contribution due to mixing of the components. In view of the experimental data presented by Whitefield (1979), one can expect Eq. 39 to be accurate within 1%. Thus, Eq. 39 very clearly brings out the thermodynamic significance of Eq. 5, which was the starting point for predicting various properties of mixed-electrolyte solutions. It may be noted that Eq. 39 does not amount to neglecting ion-ion interactions in mixed-electrolyte solutions. It merely states that such interac-

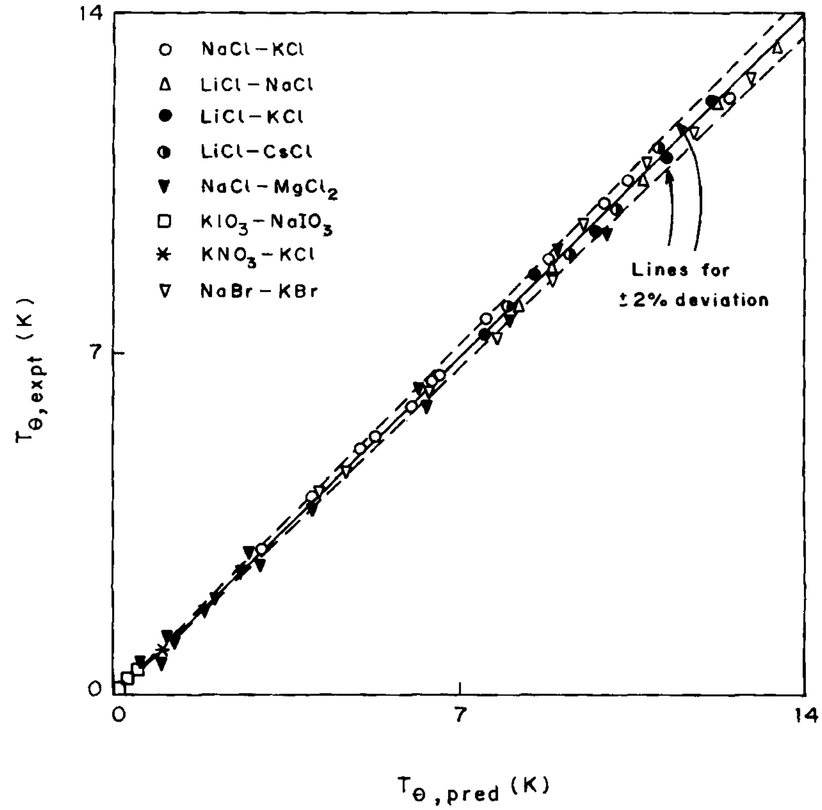

Figure 6. Experimental and predicted T_θ for various systems.

tions can be adequately accounted for in terms of those existing in single-electrolyte solutions with an acceptable degree of accuracy.

Conclusions

The relationship between Γ^* and Γ^o_J given by Eq. 5 can be used along with well-known thermodynamic equations to evolve simple but accurate predictive equations for several properties of aqueous mixed electrolyte solutions. Predictive equations for density, adiabatic compressibility, enthalpy, specific heat, expansibility, and freezing point depression are presented in the text, and have been successfully tested with available experimental data. The predictive accuracy lies between 0.03% for density and 2% for freezing point depression. These equations involve no empirical constants.

Notation

a = activity of an electrolyte in solution
a^* = overall ionic activity in solution
a^o_w = activity of water in a single-electrolyte solution of the same ionic strength as that of a mixed-electrolyte solution
a_w = activity of water in solution
C_p = specific heat of aqueous mixed-electrolyte solution
$C^o_{p,J}$ = specific heat of single-electrolyte solution at the same ionic strength as that of a mixture
d = density of aqueous mixed-electrolyte solution
d^o_J = density of a single-electrolyte solution of the same ionic strength as that of a mixed-electrolyte solution
d_o = density of pure water
$\overline{G}_m$ = relative chemical potential of mixed solution
H = solution enthalpy per 1,000 g water
$\underline{H}_J$ = molar enthalpy of pure electrolyte
$\overline{H}_J$ = partial molar enthalpy in solution
$\overline{H}'_J$ = partial molar enthalpy of an electrolyte at infinite dilution
ΔH_s = enthalpy of solution for aqueous mixed-electrolyte solution
$\Delta H^o_{s,J}$ = enthalpy of solution for a single-electrolyte solution of the same ionic strength as that of a mixed-electrolyte solution
$\underline{H}_w$ = molar enthalpy of water
$\overline{H}_w$ = partial molar enthalpy of water
$\overline{H}'_1$ = partial molar enthalpy of pure water at infinite dilution
$\overline{H}'_2$ = partial molar enthalpy of an electrolyte at infinite dilution
M_J = molecular weight of an electrolyte
m_i = molality of ith ionic species
m_J = molality of electrolyte J
$m_T = \Sigma_i m_i$
m^* = overall ionic molality
M_w = molecular weight of water
n_1 = number of moles of water
n_2 = number of moles of salt
$Q_J = [\nu_{+J}^{\nu_{+J}} \nu_{-J}^{\nu_{-J}}]^{1/\nu_J}$
R = gas constant
T = absolute temperature
T_θ = depression in freezing point in an aqueous mixed-electrolyte solution
$T^o_{\theta,J}$ = depression in freezing point in a single-electrolyte solution at the same ionic strength as that of a mixture
ΔV = volume change on mixing the pure components on 1,000 g water basis
ΔV^o_J = volume change accompanied during preparation of a solution of Jth salt alone with the same ionic strength as that of a mixture
$\overline{V}_w$ = partial molar volume of water
V = molar volume of pure component
x_i = mole fraction of ionic species i
y_J = ionic strength fraction of electrolyte J
z_i = charge on ionic species i

Greek letters

α = thermal expansion of an electrolyte solution
α_o = thermal expansion of water
β = adiabatic compressibility of an aqueous solution of mixed electrolytes
β^o_J = adiabatic compressibility of a single-electrolyte solution at the same ionic strength as that of a mixture
β_o = adiabatic compressibility of pure water
$\gamma_{\pm,J}$ = mean ionic activity coefficient of electrolyte J
γ_i = activity coefficient of ith ionic species
γ^* = overall ionic activity coefficient
ν_+, ν_- = stoichiometric factors
$\nu = \nu_+ + \nu_-$
$\psi_J = (1{,}000\, y_J + m_J M_J)$
Γ = reduced ionic activity coefficient
Γ^* = overall reduced ionic activity coefficient
μ = ionic strength $= \frac{1}{2} \Sigma_i m_i z_i^2$
$\theta_J = (\nu_{+J} z^2_{+J} + \nu_{-J} z^2_{-J})/2$
ϕ = osmotic coefficient
ϕ_E = apparent molal expansibility of aqueous mixed-electrolyte solution
$\phi^o_{E,J}$ = apparent molal expansibility of single-electrolyte solution at the same ionic strength as that of a mixture
ϕ_H = apparent molar enthalpy of solute
ϕ_L = relative apparent molar enthalpy of aqueous mixed-electrolyte solution
$\phi^o_{L,J}$ = relative apparent molar enthalpy of a single-electrolyte solution at the same ionic strength as that of a mixture

Subscript

i = ion
J = electrolyte

Superscript

$*$ = overall property
o = pure salt property at same ionic strength as that of mixture
$'$ = property at infinite dilution

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