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

Part I: Vapor Pressure and Heat of Vaporization

The overall nonideality of an aqueous mixed electrolyte solution is characterized in terms of a newly defined parameter Γ^*, called the overall reduced ionic activity coefficient. It is shown that Γ^* for the mixed solution is simply related to the properties of single-electrolyte solutions. Γ^* is related to the vapor pressure of a mixed-electrolyte solution through well-known thermodynamic equations. This leads to a predictive equation for the vapor pressure of a mixed-electrolyte solution in terms of the vapor pressures of single-electrolyte solutions of the components. This equation is valid over the entire concentration range encountered in practice, without any empirical constants, and has a predictive accuracy of 2%. A predictive equation for the latent heat of vaporization is also developed and tested against experimental data.

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SCOPE

The thermodynamic properties of aqueous mixed-electrolyte solutions play an important role in several areas, such as design of absorption heat pumps, general-purpose property packages for process simulators, water desalination, and oil recovery. Such properties include the vapor pressure, latent heat of vaporization, volume properties such as density and compressibility, thermal properties such as enthalpy and specific heat, and free energy. These properties have been extensively reported 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 obviously have tremendous practical utility.

Theoretical approaches available for understanding aqueous electrolyte solutions are usually limited to rather dilute solutions and are cumbersome for numerical calculations. Semiempirical approaches overcome these limitations, but need several adjustable parameters based on specific experimental data. The present study was aimed at developing simple but sufficiently accurate predictive equations for the thermodynamic properties of aqueous mixed-electrolyte solutions. In this paper, we restrict our attention to vapor pressures and heats of vaporization. In the case of a single electrolyte solution, the nonideality is represented in terms of the mean ionic activity coefficient, which is related to the vapor pressure. A generalization of this for mixed-electrolyte solutions leads to the newly defined overall ionic activity coefficient, which is related to the vapor pressure of such solutions. Making use of these, and a proposed relationship between the overall ionic activity coefficient and the mean ionic activity coefficients for single-electrolyte solutions, predictive equations are derived for the vapor pressure and the heat of vaporization for mixed-electrolyte solutions.

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CONCLUSIONS AND SIGNIFICANCE

The overall nonideality of an aqueous mixed electrolyte solution is represented by Γ^*, the overall reduced ionic activity coefficient. A relationship between Γ^* and the nonidealities of single-electrolyte solutions is proposed through Eq. 16. Comparison with experimental data on the seven systems listed in Table 1 indicates that Eq. 16 has an accuracy better than 2%. The nonideality of an aqueous electrolyte solution is related to several properties through well-known thermodynamic equations. Therefore, Eq. 16 becomes a starting point from which predictive equations for several properties of mixed solutions can be derived. The thermodynamic significance of this relationship lies in its implication that when two aqueous electrolyte solutions of equal ionic strength are mixed together, the change in free energy is exclusively due to the process of mixing. This is considered in further detail in Part II.

Predictive equations have been derived for the vapor pressure and the heat of vaporization of mixed aqueous electrolyte solutions, which have an accuracy of 2% and 4% respectively. The experimental data used for testing these equations, i.e. Eqs. 31 and 37, are listed in Table 1. The twelve systems include three-ion systems, four-ion systems, and multicomponent systems such as brines, some of which refer to high temperatures. Testing of the vapor pressure equation has been done quite extensively. For the heat of vaporization equation, the experimental data available are very scanty. Additional justification of this equation lies in the fact that it has been derived analytically from the vapor pressure equation. Both these predictive equations require only the knowledge of properties of single electrolyte solutions. No system-specific empirical constants are involved.

Introduction

In the past decade there has been a growing interest in the *a priori* prediction of thermodynamic properties of aqueous solutions of mixed electrolytes. These properties for aqueous solutions of single electrolytes, determined experimentally, have been reported extensively in the thermodynamic literature. However, experimental determination of these properties for mixed solutions has received attention only relatively recently. Debye and Hückel (1923, 1924) developed the theory for activity coefficient of very dilute electrolyte solutions by considering the long-range electrostatic forces. Major theoretical advances in understanding the mixed electrolyte solutions are mainly based on the statistical mechanical and semiempirical theories. The statistical mechanical theory is largely due to the development of integral equations of the hypernetted chain (HNC) and of Percus-Yevick (P-Y). Friedman (1962) and Rasaih (1970) applied the HNC equation up to a one molar solution. The method is mathematically quite complicated and is cumbersome for practical applications. The Monte Carlo simulations of Card and Valleau (1970) are quite significant in the development of these treatments. Kondo and Eckart (1983) recently developed expressions from statistical mechanics for activity and osmotic coefficients, based on a unique parameter d_{+-}, known as depth of the square-well potential. The predictions for activity and osmotic coefficients up to an ionic strength of 3 mol · kg^{-1} of water are accurate within ±0.03.

The semiempirical approach, easier to compute, was first developed by Guggenheim (1935) and Guggenheim and Turgeon (1955). The use of a specific interaction parameter predicted the thermodynamic properties with reasonable accuracy in moderately concentrated solutions of 1 ionic strength. More recently, Pitzer and his group developed semiempirical expressions for electrolyte solutions (Pitzer, 1973; Pitzer and Kim, 1974). The Pitzer formalism for predicting the thermodynamic properties is based on the virial coefficients for cation-anion

Table 1. Literature Data Used to Test Eqs. 16 and 31

System	Property	μ_{max}	% Composition (y of Second Component)	No. of Data Points	Reference
$CaCl_2$—$MgCl_2$	$\log \Gamma^*$, $\log a_w$	12	40, 84	9, 9	Robinson and Bower (1966a)
$NaCl$—$CaCl_2$	$\log \Gamma^*$, $\log a_w$	5.5	10–90	15, 44	Ananthaswamy and Atkinson (1982); Robinson and Bower (1966b)
KCl—$CaCl_2$	$\log \Gamma^*$, $\log a_w$	5	20–80	20, 20	Robinson and Covington (1968)
HCl—$CoCl_2$	$\log \Gamma^*$	3	10–90	10	Khoo and Chen (1978)
$HClO_4$—$UO_2(ClO_4)_2$	$\log \Gamma^*$, $\log a_w$	6, 13	10–90	9, 60	Rush and Johnson (1971)
$NaClO_4$—$UO_2(ClO_4)_2$	$\log \Gamma^*$, $\log a_w$	6, 14	10–90	9, 60	Rush and Johnson (1971)
$MgCl_2$—$Ca(NO_3)_2$	$\log a_w$	20	10–85	21	Platford (1971)
$MgCl_2$—$Mg(NO_3)_2$	$\log a_w$	15	10–90	23	Platford (1971)
$Mg(NO_3)_2$—$Ca(NO_3)_2$	$\log a_w$	17	20–80	15	Platford (1971)
$CaCl_2$—$Ca(NO_3)_2$	$\log a_w$	21	20–85	16	Platford (1971)
KCl—$NaBr$	$\log a_w$	4		4	Covington et al. (1968)
$LiNO_3$—KNO_3	$\log a_w$,† λ‡	57, 27	50	2, 1	Braunstein and Braunstein (1971); Tripp and Braunstein (1969)
Brines	$\log \Gamma^*$, $\log a_w$	9.8	—	2, 2	Krumgalz and Millero (1982)

† at 100°C, ‡ at 135°C

pairs and on explicit recognition in the mixing terms of the short-range interaction forces in very concentrated solutions. The method needs three adjustable parameters from pure salts, and binary and ternary difference parameters evaluated from mixtures. These parameters are specific to the electrolytes and their mixtures.

The theories discussed above refer to specific properties and are limited to certain concentration ranges. No simple and unified approach is currently available that can be used for the prediction of all the properties over the entire range of concentrations of practical importance. In this work, theoretical development is presented which relates the overall nonideality of a mixed-electrolyte solution to that of the corresponding single-electrolyte solutions. Using well-known thermodynamic relationships, predictive equations for the thermodynamic properties of aqueous mixed-electrolyte solutions are derived from this theoretical development. The predictive equations are tested extensively with experimental data and are shown to lead to accurate predictions.

Theory

The nonideality of an aqueous solution 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 the positive and negative ions. Here we define new parameters that account for the nonideality arising out of the presence of several different ions, both positive and negative, which characterize aqueous solutions of mixed electrolytes. The derivations presented closely follow those used for aqueous solutions of single electrolytes, which can be found in standard texts such as Glasstone (1960). Let us define the overall ionic activity coefficient, γ^*, by the following equation.

$$\log \gamma^* = \sum_i x_i \log \gamma_i \tag{1}$$

The overall ionic molality, m^*, is defined by

$$\log m^* = \sum_i x_i \log m_i \tag{2}$$

The overall ionic activity, a^*, is similarly defined by

$$\log a^* = \sum_i x_i \log a_i \tag{3}$$

Since $a_i = m_i \gamma_i$ by definition, Eq. 3 can be rewritten as

$$a^* = m^* \gamma^* \tag{4}$$

In Eqs. 1–3, the summations are carried out over all the ionic species in solution. The utility of defining overall ionic properties, as in these equations, will become clear later. Let us consider the aqueous solution of a single electrolyte $M_{\nu+} A_{\nu-}$ (of molality m) which dissociates as

$$M_{\nu+} A_{\nu-} \longrightarrow \nu_+ M^{z+} + \nu_- A^{z-} \tag{5}$$

Equation 1 gives

$$\log \gamma^* = (\nu_+ \log \gamma_+ + \nu_- \log \gamma_-)/\nu \tag{6}$$

where $\nu = \nu_+ + \nu_-$. Therefore,

$$\gamma^* = (\gamma_+^{\nu+} \gamma_-^{\nu-})^{1/\nu} = \gamma_\pm \tag{7}$$

Thus, for the solution of a single electrolyte, γ^* reduces to $\gamma_\pm$ defined in the conventional manner. Similarly, m^* and a^* also reduce to $m_\pm$ and $a_\pm$, respectively, when Eqs. 2 and 3 are applied to solutions of a single electrolyte.

Calculation of γ^* and m^*

Although Eqs. 1 and 2 serve as useful definitions of γ^* and m^*, they are not convenient for numerical calculations. Experimental data available in literature on solutions of mixed electrolytes are usually in the form of $\gamma_\pm$ values for individual electrolytes determined in mixed solutions. For such cases, algebraic manipulation of Eqs. 1–3 gives

$$\log \gamma^* = \sum_J \nu_J m_J \log \gamma_{\pm,J} \Big/ \sum_J \nu_J m_J \tag{8}$$

$$\log m^* = \sum_J \nu_J m_J \log m_{\pm,J} \Big/ \sum_J \nu_J m_J \tag{9}$$

$$\log a^* = \sum_J \nu_J m_J \log a_{\pm,J} \Big/ \sum_J \nu_J m_J \tag{10}$$

Graphical representation

It has been shown by Meissner and Tester (1972) that experimental data for solutions of single electrolytes fail to show much order on a log $\gamma_\pm$ vs. μ plot. However, if one defines a new variable Γ by

$$\log \Gamma = (\log \gamma_\pm)/(z_+ z_-) \tag{11}$$

then the same experimental data fall into a single family of curves on the log Γ vs. μ plot, irrespective of the ionic charges involved. The transformation given by Eq. 11 has its roots in the classical Debye-Hückel theory for dilute solutions of electrolytes. According to this theory, the ionic activity coefficient for a single ion in dilute solutions may be written as

$$\log \gamma_i = -A z_i^2 \sqrt{\mu} \tag{12}$$

where A is a constant for the solvent at the specific temperature (Glasstone, 1960). Applying this to both the ions present in the solution of a single electrolyte and using the definition of $\gamma_\pm$, we can write Eq. 11 as

$$\log \Gamma = \log \gamma_\pm/(z_+ z_-) = -A \sqrt{\mu} \tag{13}$$

which is strictly valid only for dilute solutions. The observations of Meissner and Tester regarding the log Γ vs. μ plots indicate that for a given salt, log Γ is a function of μ alone even for highly concentrated solutions, although the functionality is quite different from that in Eq. 13. This is hardly surprising, since Eq. 13, valid only for dilute solutions, does not account for those ionic interactions that play a dominant role in concentrated solutions.

It is very interesting to see if experimental values of γ^* for solutions of mixed electrolytes for various ionic strengths can be represented so as to fit into the family of curves of log Γ vs. μ for solutions of single electrolytes. For this purpose, the transformation of Eq. 11 needs to be generalized for mixed-electrolyte solutions. Using Eqs. 1 and 12 for dilute solutions, we get

$$\log \gamma^* = -A\sqrt{\mu}\sum_i x_i z_i^2 \qquad (14)$$

We therefore define Γ* by

$$\log \Gamma^* = \log \gamma^* \Big/ \sum_i x_i z_i^2 \qquad (15)$$

It is very easily seen that for a solution of a single salt, Γ* reduces to Γ as defined for a single-electrolyte solution by Meissner and Tester [1972]. Figure 1 shows the log Γ* vs. μ plots for several aqueous electrolyte systems. The solid lines refer to single-electrolyte solutions and are calculated from experimental data reported by Robinson and Stokes (1959). They indeed give a family of curves as observed by Meissner and Tester. The dashed line refers to aqueous solutions of mixtures of KCl and $CaCl_2$, based on the $\gamma_\pm$ values of individual electrolytes in mixed solutions as reported by Robinson and Covington (1968). It is clearly seen that log Γ* values for the mixed solutions fall in between those for single-electrolyte solutions of the component electrolytes for the same total ionic strength μ. Moreover, it appears that the log Γ* values change almost linearly as the mixed-electrolyte composition is changed, keeping μ constant. Similar observations can be made for the $CaCl_2$-$MgCl_2$ system, shown in Figure 1 by dotted lines. These calculations are based on the experimental data of Robinson and Bower (1966a).

The linear dependence of log Γ* on the composition of the $CaCl_2$-KCl system at various ionic strengths is more clearly seen from Figure 2. A similar dependence for the ternary systems involving $HClO_4$-$UO_2(ClO_4)_2$ and $NaClO_4$-$UO_2(ClO_4)_2$ at $\mu = 6$ is seen in Figure 3, which is based on the experimental

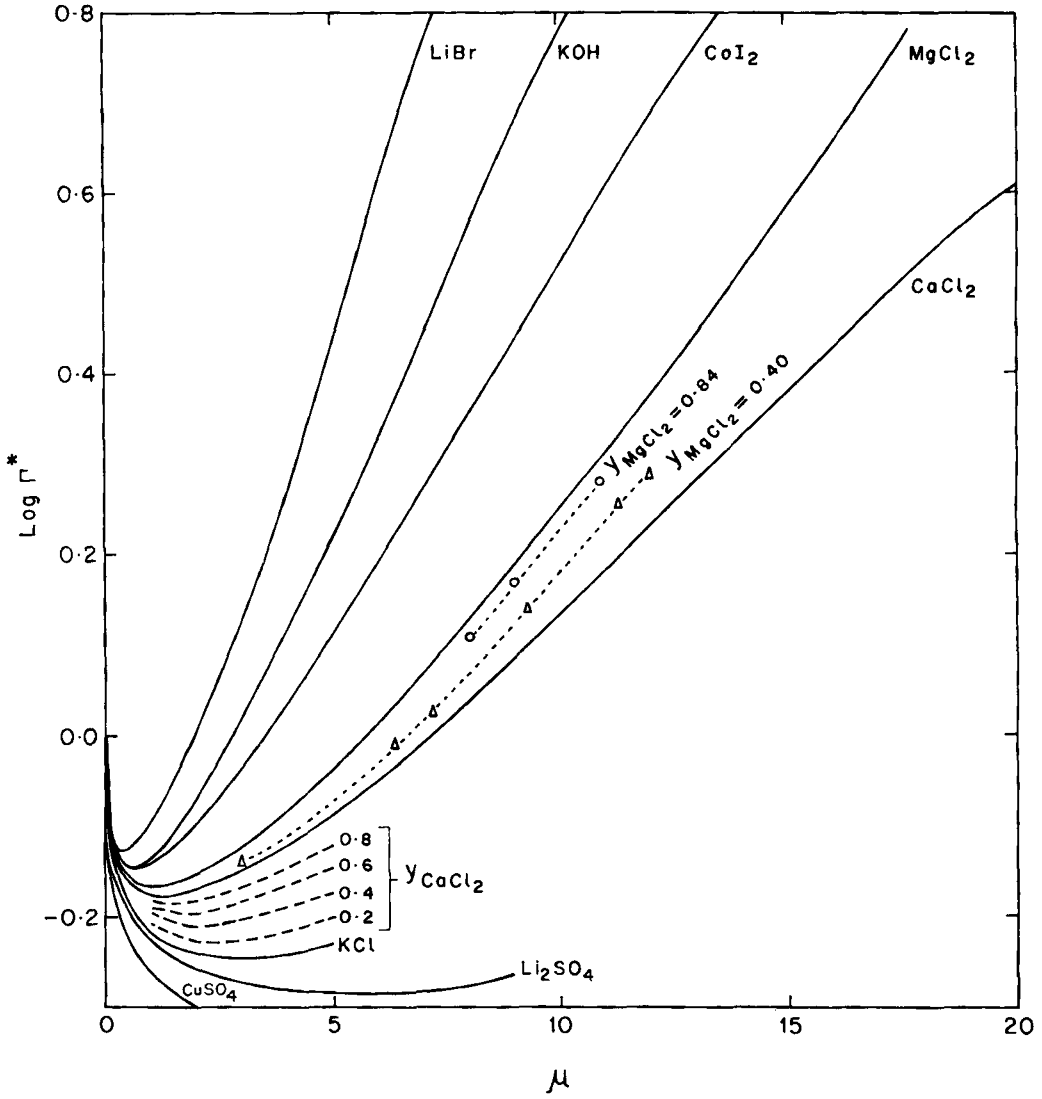

Figure 1. Log Γ* vs. μ for aqueous solutions of single and mixed electrolytes.

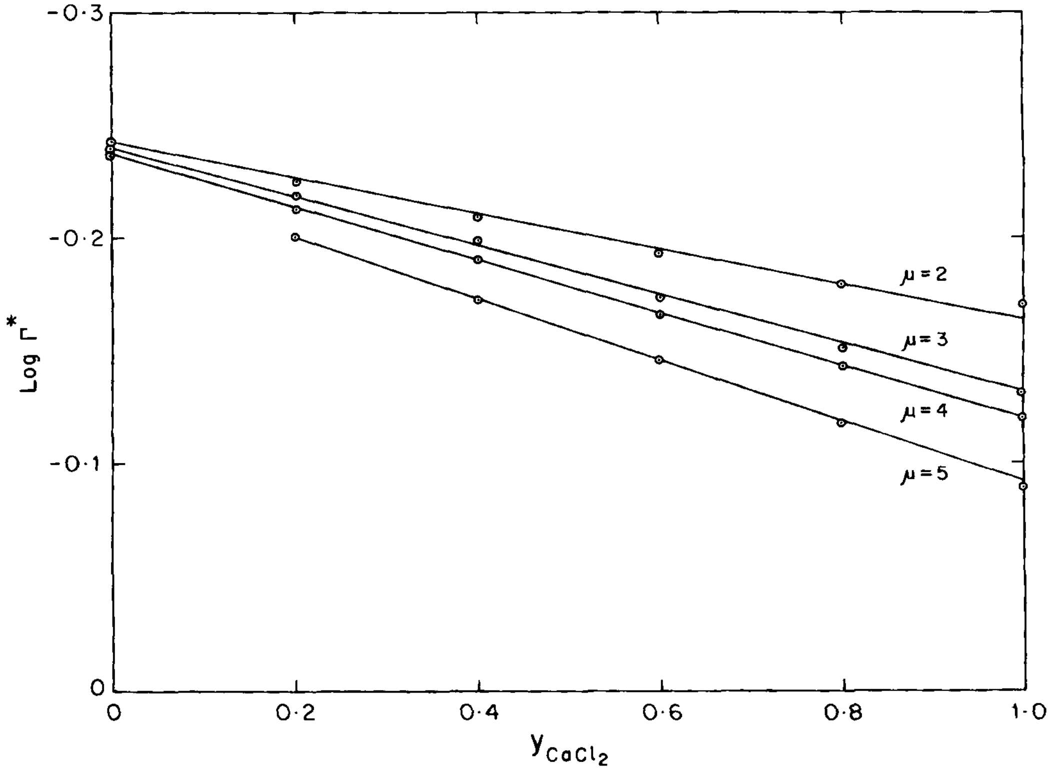

Figure 2. Variation of log Γ* with composition at various ionic strengths for KCl—CaCl₂ system.

data reported by Rush and Johnson (1971). It is therefore proposed that Γ* can be expressed as

$$\log \Gamma^* = \sum_j y_j \log \Gamma_j^o \tag{16}$$

Experimental data on activity coefficients in mixed-electrolyte solutions are available in literature for several systems as listed in Table 1. For these systems, log Γ* was calculated using Eqs. 8 and 15 and the experimental values of $\gamma_\pm$ in mixed solutions. The predictions of log Γ* were obtained using Eq. 16 and the experimental data for single-electrolyte solutions reported by Robinson and Stokes (1959). A comparison between the predicted and experimental values of log Γ* for these systems is presented in Figure 4. It is seen that Eq. 16 predicts Γ* within 2% even for highly concentrated solutions. Equation 16 was also tested for brines (which are multicomponent solutions) at μ = 7.9 and 9.8, and was found to give an accuracy of 1% or better. The thermodynamic significance of Eq. 16 is discussed in Part II, where free energy of mixed-electrolyte solutions is considered.

Vapor Pressures of Mixed Aqueous Electrolyte Solutions

The vapor pressure of water over an electrolyte solution is related to a_w simply as

$$a_w = p/p_w \tag{17}$$

which is valid at pressures up to several atmospheres.

The activities of different components in a homogeneous mixture at equilibrium at a constant pressure and temperature are related by the well known Gibbs-Duhem equations, which can be written as

$$\sum_k n_k \, d\mu_k' = 0 \tag{18}$$

where the summation is carried out over all constituents of the solution. For an aqueous solution of mixed electrolytes containing 1,000 g water, this equation can be rewritten, using $\mu' = \mu_o' + RT \ln a$, as

$$\frac{1{,}000}{M_w} d \log a_w + m_T \sum_i x_i \, d \log a_i = 0 \tag{19}$$

Let us now consider a process whereby a given solution is merely diluted or concentrated, i.e., m_T is changed, keeping x_i's constant. Equation 3 gives

$$d \log a^* = \sum_i x_i \, d \log a_i \tag{20}$$

The osmotic coefficient, ϕ, is defined by

$$\log a_w = -\frac{M_w \phi \, m_T}{2{,}303} \tag{21}$$

Using Eqs. 20 and 21, Eq. 19 becomes

$$d \log a^* = \frac{d\phi}{2.303} + \phi \, d \log m_T \tag{22}$$

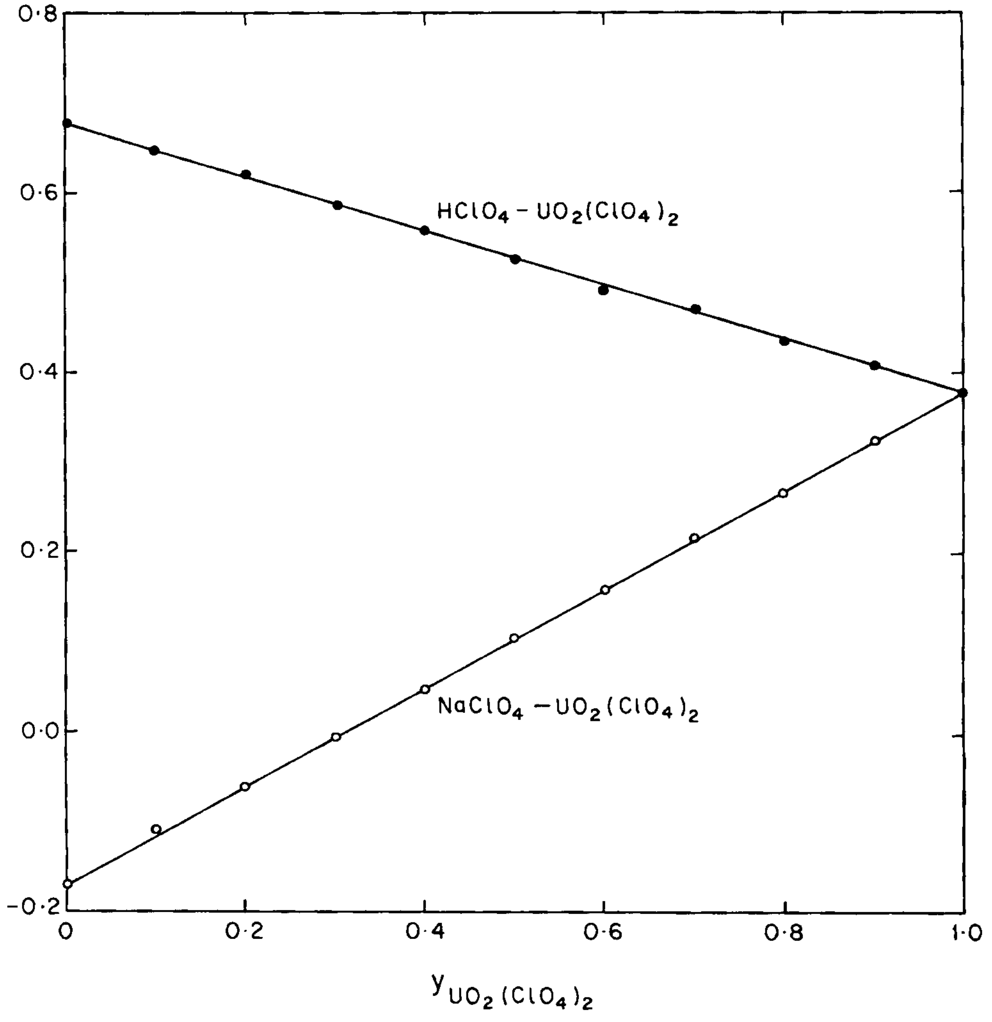

Figure 3. Variation of log Γ^* with composition for two systems at $\mu = 6$.

Since $a^* = \gamma^* m^*$ and since $d \log m_T = d \log m^*$ (for constant x_i's), we get

$$d\log\gamma^* = \frac{d\phi}{2.303} + (\phi - 1)\, d\log m_T \tag{23}$$

This equation gives γ^* at the total ionic molality m_T in terms of ϕ, and is very similar to the corresponding equation for single-electrolyte solutions available in standard texts (Glasstone, 1960).

Calculation of activity of water

Here we derive an equation relating the activity of water in a mixed-electrolyte solution to the activities of water in single-electrolyte solutions at the same ionic strength. Using Eqs. 4 and 20, Eq. 19 can be written as

$$d\log a_w = -\frac{m_T M_w}{1{,}000}\, d\log m^* - \frac{m_T M_w}{1{,}000}\, d\log\gamma^* \tag{24}$$

For constant x_i's, Eq. 15 gives

$$d\log\gamma^* = 2\mu\, d\log\Gamma^*/m_T \tag{25}$$

and Eq. 2 gives

$$d\log m^* = d\, m_T/(2.303\, m_T) \tag{26}$$

Substitution from Eqs. 25 and 26 in Eq. 24 followed by integration gives

$$\log a_w = -\frac{M_w m_T}{2{,}303} - \frac{M_w\mu\log\Gamma^*}{500} + \frac{M_w}{500}\int_o^\mu \log\Gamma^*\, d\mu \tag{27}$$

Consider the solution of mixed electrolytes consisting of several different electrolyte species. Let m_J^o be the molality of a solution containing only electrolyte J, which has the same ionic strength as that of the mixed-electrolyte solution. Let $a_{w,J}^o$ be the water activity in this single-electrolyte solution. We can then write

$$\log a_{w,J}^o = -\frac{M_w m_J^o \nu_J}{2{,}303} - \frac{M_w\mu\log\Gamma_J^o}{500} + \frac{M_w}{500}\int_o^\mu \log\Gamma_J^o\, d\mu \tag{28}$$

Let m_J be the molality of electrolyte J in the mixed-electrolyte

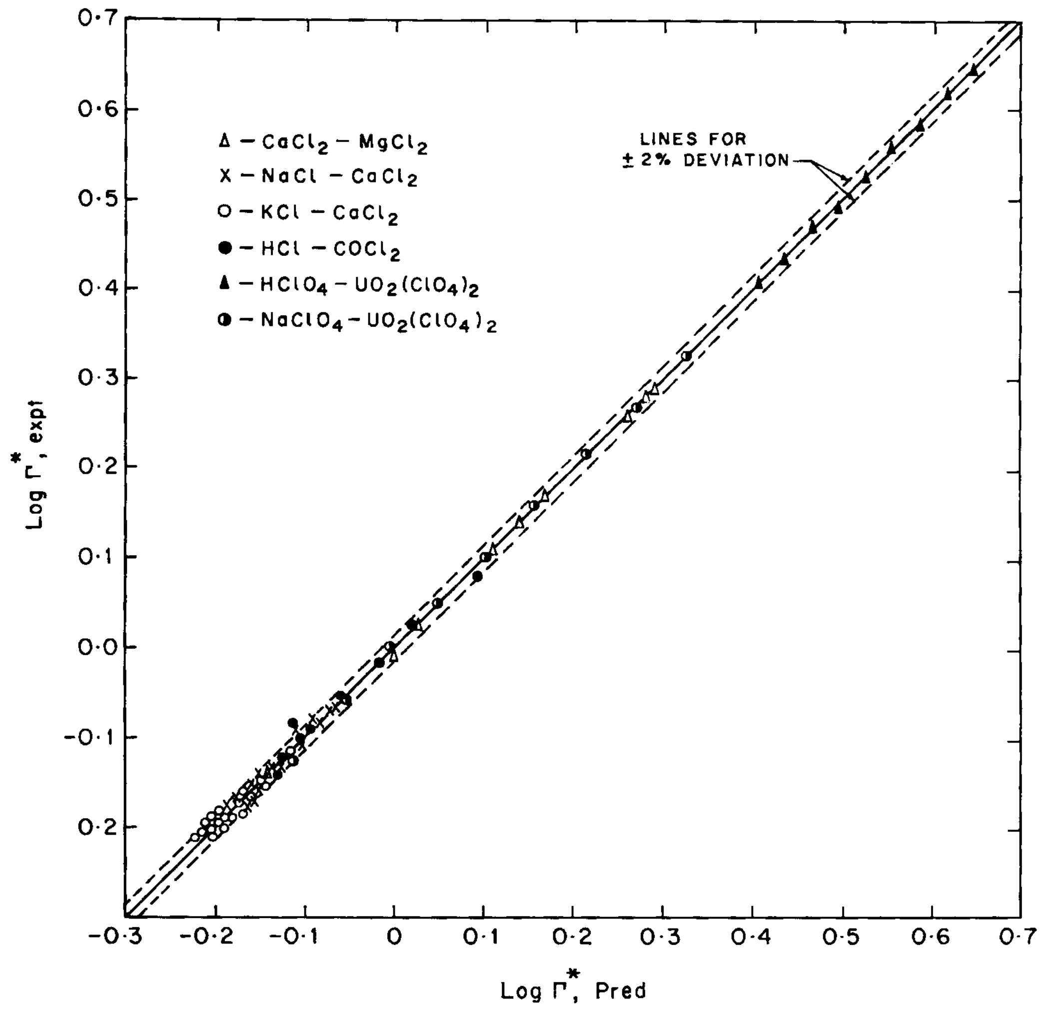

Figure 4. Experimental and predicted log Γ* for various systems.

solution. Therefore,

$$\mu = \sum_J m_J\theta_J = m_J^o\theta_J \text{ for all } J \tag{29}$$

and

$$m_J = y_J\, m_J^o \tag{30}$$

It is now easily seen from Eqs. 16 and 27–30 that

$$\log a_w = \sum_J y_J \log a_{w,J}^o \tag{31}$$

This predictive equation gives a simple relationship between the activity of water in a mixed-electrolyte solution and that in single-electrolyte solutions of the same ionic strength. It is noteworthy that Eq. 31 does not contain any empirical constants.

Comparison with earlier prediction methods

Additivity Rule of Robinson and Bower (1965). This rule may be stated as

$$\Delta = \sum_J (m_J\, \Delta_J^o / m_J^o) \tag{32}$$

where Δ is the vapor pressure lowering for the mixed-electrolyte solution. This rule was found to give satisfactory predictions in solutions where the maximum Δ was about 5.2 mm Hg (0.7kPa). Since $a_w = 1 - \Delta/p_w$, we can simplify Eq. 31 for $\Delta \ll p_w$ as

$$\Delta = \sum_J y_J\, \Delta_J^o \tag{33}$$

Since $y_J = m_J\theta_J/\mu = m_J/m_J^o$, Eqs. 32 and 33 are identical. Thus Eq. 31 simplifies to the additivity rule for systems where the vapor pressure lowering is much less than the vapor pressure of pure water.

Method Proposed by Meissner and Kusik. For a mixed-electrolyte solution containing cations 1, 3, 5 . . . and anions 2, 4, 6 . . . , the following predictive equation was proposed by Meissner and Kusik (1973):

$$\begin{aligned}\log a_w = {} & X_1Y_2 \log (a_w^o)_{12} + X_1Y_4 \log (a_w^o)_{14} \\ & + X_1Y_6 \log (a_w^o)_{16} \cdot \cdot \cdot + X_3Y_2 \log (a_w^o)_{32} \\ & + X_3Y_4 \log (a_w^o)_{34} + X_3Y_6 \log (a_w^o)_{36} \cdot \cdot \cdot \\ & + X_5Y_2 \log (a_w^o)_{52} + X_5Y_4 \log (a_w^o)_{54} \\ & + X_5Y_6 \log (a_w^o)_{56} \ldots \end{aligned} \tag{34}$$

where X and Y are the cationic and anionic strength fractions, respectively, and a_w^o's are the activity of water in various single-electrolyte solutions. It is easy to see that for systems with a common anion (or cation) and with cations (or anions) of equal charges, this equation is identical to our Eq. 31. However, for systems where different electrolytes have dissimilar charges, they are different. Table 1 contains four such systems for which experimental a_w values are available: $NaCl—CaCl_2$; $KCl—CaCl_2$; $HClO_4—UO_2(ClO_4)_2$; and $NaClO_4—UO_2(ClO_4)_2$. Equation 31, developed in the present work, predicts a_w for these systems with an average deviation of less than 1% from experimental values. Equation 34, developed by Meissner and Kusik (1973), gives an average deviation of 3.5%. It may also be noted that for a four-ion system such as NaBr and KCl, our Eq. 31 is based on the single-electrolyte solution data for NaBr and KCl only, while the method of Meissner and Kusik requires, in addition, the single-electrolyte solution data for NaCl and KBr as well. This need for additional single-electrolyte solution data becomes all the more inconvenient as the numbers of different ionic species involved increases.

Comparison with experimental data

Table 1 summarizes the systems analyzed using Eq. 31. The predicted values of a_w up to $\mu = 21$ are plotted in Figure 5 along with the experimental points. It is clear that Eq. 31 can predict the vapor pressure of such solutions even at high ionic strength with an accuracy of 2%. The systems represented in Figure 5 include common ion systems as well as four-ion systems. They encompass wide ranges of concentration up to saturation points. They also involve multielectrolyte systems such as brines of ionic strengths 7.9 and 9.8, and also a binary system at a temperature of 100°C. Thus, Eq. 31 is seen to give accurate predictions of the vapor pressure over wide ranges of experimental conditions. This equation holds good even at high temperatures. For example, the predicted vapor pressure of an equimolar $LiNO_3—KNO_3$ mixture of $\mu = 10.5$ ($a_{w,pred} = 0.70$) and 57.69 ($a_{w,pred} = 0.205$) are within approximately 2% of the experimental values ($a_w = 0.71$ and 0.200, respectively) of Braunstein and Braunstein (1971).

Latent Heat of Vaporization

The latent heat of vaporization of water from an aqueous solution of electrolytes can be related to the vapor pressure by using the Clayperon equation:

$$\frac{dp}{dT} = \frac{\lambda}{T \Delta V} \tag{35}$$

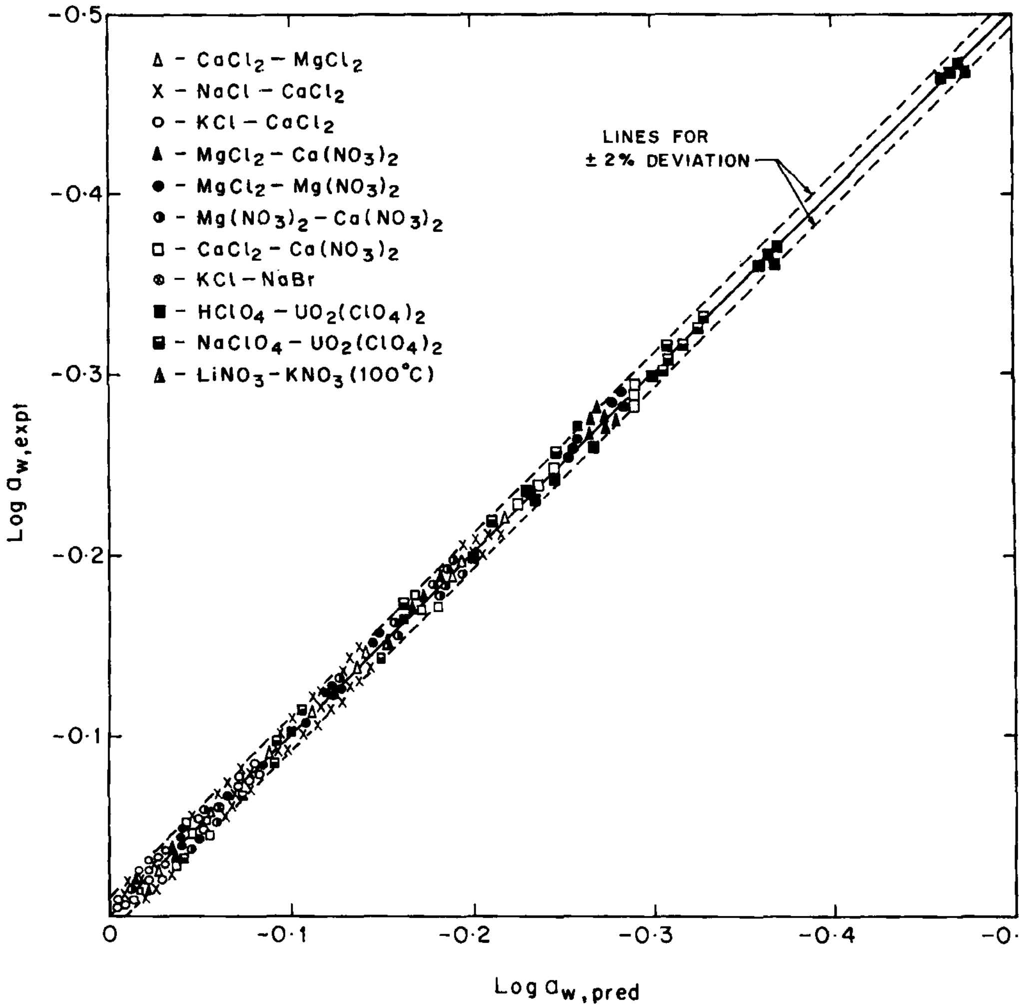

Figure 5. Experimental and predicted log a_w for various systems.

where ΔV is the volume change accompanying vaporization. Neglecting the liquid volume compared to the water vapor volume V_v, this can be rewritten as

$$\frac{dp}{dT} = \frac{\lambda}{T V_v} \tag{36}$$

Differentiating Eq. 31 with respect to temperature, and using Eq. 36, we get

$$\lambda = p \sum_J y_J (\lambda_J^o / p_J^o) \tag{37}$$

The vapor pressure data for the $LiNO_3$—KNO_3 solutions in water (for ionic strength = 27.75) at 135°C have been reported by Tripp and Braunstein (1969), giving $\lambda = 10.4 \pm 0.1$ kcal/mol (43.6 ± 0.4 kJ/mol) for their mixed-electrolyte solution. λ for the single-salt solutions of the component electrolytes at the same temperature and ionic strength are available in literature (Braunstein and Braunstein, 1971; *International Critical Tables*, 1928). Equation 37 gives a predicted value of λ for the mixed-electrolyte solution = 10.8 kcal/mol (45.3 kJ/mol), which matches the experimental value of 10.4 kcal/mol within 4%.

Conclusions

The overall nonideality of an aqueous mixed-electrolyte solution can be expressed conveniently in terms of the nonideality of single-electrolyte solutions using Eq. 16. This leads to Eq. 31, which is a predictive equation for the vapor pressure of aqueous mixed-electrolyte solutions with an accuracy of 2%. The latent heat of vaporization can be predicted with Eq. 37. These equations do not involve any empirical constants.

Notation

a = activity of an electrolyte in solution
a^* = overall ionic activity in solution
a_w^o = 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 of mixed electrolytes
A = constant, Eq. 12
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
p = vapor pressure of solution
p_w = vapor pressure of water
x_i = mole fraction of ionic species i on water-free basis (m_i/m_T)
X = cationic strength fraction
y_J = ionic strength fraction of electrolyte J
Y = anionic strength fraction
z_i = charge on ionic species i

Greek letters

$\gamma_{\pm,J}$ = mean ionic activity coefficient of Jth electrolyte
γ_i = activity coefficient of ith ionic species
γ^* = overall ionic activity coefficient
ν_+, ν_- = stoichiometric factors, Eq. 5
$\nu = \nu_+ + \nu_-$
Γ = reduced ionic activity coefficient, Eq. 11
Γ^* = overall reduced ionic activity coefficient, Eq. 15
μ = ionic strength = $\frac{1}{2} \Sigma_i m_i z_i^2$
μ' = chemical potential
Δ = vapor pressure lowering for the mixed-electrolyte solution
$\theta_J = (\nu_+ z_+^2 + \nu_- z_-^2)/2$
ϕ = osmotic coefficient
λ = latent heat of vaporization

Subscripts

i = ion
J = electrolyte
$\pm$ = mean ionic property

Superscript

$*$ = overall property
o = pure salt property at same μ as that of mixture

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