Thermodynamic Modeling of Concentrated Aqueous Electrolyte and Nonelectrolyte Solutions

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A new approach is presented for calculation of activity coefficients in aqueous electrolyte solutions. This approach requires only standard thermodynamic properties for the pure components and for the solutes at infinite dilution. No adjustable mixture parameters are necessary. This new procedure has been applied to calculate: (1) the solubility of salts and the activity of water in binary aqueous solutions; (2) the temperature dependence of the solubility of salts; (3) the azeotropic composition of a system containing a volatile electrolyte, (H_2O-HNO_3); (4) the solubility of carbon dioxide in water at elevated pressures and at different temperatures.

Introduction

Electrolyte solutions are ubiquitous in engineering practice. In spite of several decades of research, however, engineering methods for prediction of the thermodynamic properties of complex multicomponent aqueous systems containing both electrolytes and nonelectrolytes are scarce. The main problem that needs to be addressed is that of calculating the activity coefficients of all species within a consistent molecular thermodynamic framework. Over the years, several methods have been suggested for calculating activity coefficients of salts in aqueous phases, most notably by Bromley, by Meissner, and by Pitzer (Zemaitis et al., 1988; Pitzer, 1991). These methods have proved to be very useful for calculation of the properties of electrolyte solutions. Unfortunately, they require a number of empirical adjustable parameters that must be determined in advance from extensive binary and ternary experimental data. Their predictive capabilities are therefore limited. In some cases, different theoretical models can lead to drastically different predictions, even when the same sources of experimental data are employed for calculations (Corti et al., 1990; Barta and Bradley, 1985).

In this article we describe a method that offers the possibility of calculating the thermodynamic properties of solutions of both electrolytes and nonelectrolytes in water using nonelectrolyte-type expressions for the activity coefficients. The suggested procedure, which is based on the ideas of Renon and Prausnitz (1968), does not require adjustable mixture parameters; only pure components and infinite dilution experimental data are necessary. Furthermore, the constants appearing in the model discussed here have a well-defined physical interpretation.

Binary Electrolyte Solutions: Theoretical Framework

The excess Gibbs energy of a solution g^E arises from inequalities between interparticle forces. At very low electrolyte concentrations, the long-range nature of ionic interactions has to be taken into account. This can be done by means of Debye–Huckel theory (Cruz and Renon, 1978; Chen et al., 1982; Liu and Gren, 1989; Pitzer, 1991). The total excess Gibbs energy of a solution then comprises short-range-force contributions (primarily ion–solvent and solvent–solvent interactions), g_s^E, and long-range (Debye–Huckel) contributions (from ion–ion interactions), g_{DH}^E,

$$g^E = g_S^E + g_{DH}^E. \tag{1}$$

However, at moderate to high ionic concentrations, interionic forces are effectively screened from long range to short range. Interionic forces can then be treated on the same basis as all other interparticle interactions. We therefore assume that the same type of expression for g^E used for nonelectrolytes (Pitzer and Simonson, 1986; Pitzer, 1980) can be used to describe ionic interactions. Furthermore, at such concentrations Debye–Huckel contributions to the excess Gibbs free energy become negligible; as shown by Simonson and Pitzer (1986), in practice the Debye–Huckel term is only important for electrolyte concentrations in the range $x_2 \ll 0.1$, where the screening effect is lost and an almost random distribution of ions is encountered.

The Debye–Huckel contribution to the excess Gibbs energy is given by (Pitzer and Simonson, 1986)

$$g^E_{DH} = -(4A_x I_x/\rho)\ln\left[\left(1+\rho\sqrt{I_x}\right)\Big/\left(1+\rho\sqrt{I^0_x}\right)\right] \quad (2)$$

where I_x is the ionic strength on a mole fraction basis. For a pure fused salt the ionic strength is denoted by I^0_x and it is equal to 1/2 for singly charged ions. Constant A_x is equal to 2.91 at 298.16 K, and parameter ρ defines a hard-core collision diameter for the ions.

For the short-range contributions to the excess Gibbs energy, g^E_s, we use the NRTL local composition model (Renon and Prausnitz, 1968):

$$g^E_s = x_1x_2[A_{21}\tau_{21}/(x_2A_{21}+x_1) + A_{12}\tau_{12}/(x_1A_{12}+x_2)] \quad (3)$$

where

$$A_{21} = \exp(\tau_{21}/\alpha_{21}) \qquad A_{12} = \exp(\tau_{12}/\alpha_{12})$$
$$\tau_{21} = g_{21} - g_{11} \qquad \tau_{12} = g_{12} - g_{22}$$
$$\alpha_{21} = n_{21} + n_{11} \qquad \alpha_{12} = n_{12} + n_{22}$$

and where x_i is the mole fraction of component i ($i = 1,2$).

Most applications of the NRTL model to date have treated the quantities g_{ij} and α_{ij} appearing in Eq. 3 as adjustable mixture parameters. Our work is different in that we adhere to the original derivation of the model and regard the g_{ij} as Gibbs free energies (in units of RT) that can be expressed in terms of thermodynamic information for the pure components and the same components at infinite dilution. Similarly, we treat the n_{ij} as the average numbers of nearest neighbors of type i that interact with a central species of type j in the mixture (with i, $j = 1,2$). These numbers can be inferred from molecular information. Note that g_{12} is not necessarily equal to g_{21} (Reid et al., 1987) and α_{12} is not equal to α_{21}.

Activity coefficients based on these expressions for g^E provide thermodynamic information relative to the reference state of a "pure supercooled fused salt":

$$\ln\gamma_1 = \ln\gamma^\#_1 + \ln\gamma_{1DH} \quad (4)$$

$$\ln\gamma_2 = \ln\gamma^\#_2 + \ln\gamma_{2DH} \quad (5)$$

where

$$\ln\gamma^\#_1 = -\left[\tau_{12}(A_{12}+A'_{12}x_1x_2)/(x_1A_{12}+x_2)^2 + \tau_{21}(A^2_{21}+x^2_1A'_{21})/(x_2A_{21}+x_1)^2\right]x^2_2$$

$$\ln\gamma^\#_2 = -\left[\tau_{12}(A^2_{12}-A'_{12}x^2_2)/(x_1A_{12}+x_2)^2 + \tau_{21}(A_{21}-x_1x_2A'_{21})/(x_2A_{21}+x_1)^2\right]x^2_1$$

and where $\ln\gamma_{1DH}$ and $\ln\gamma_{2DH}$ are the Debye–Huckel contributions to the activity coefficient of water and that of the electrolyte, respectively (these expressions have been given explicitly by Pitzer and Simonson, 1986). The prime indicates a derivative with respect to x_1.

The value of $\ln\gamma_{1DH}$ is significant (compared to $\ln\gamma^\#_1$) only for $x_2 \ll 0.1$ and its contribution is neglected for $x_2 > 0.1$. The contribution of $\ln\gamma_{2DH}$ is also significant (compared to $\ln\gamma^\#_2$) only in this range; at infinite dilution we have the following limiting behavior:

$$\lim_{x_2\to 0}[\ln\gamma_{2DH}] = \ln\gamma^\infty_{2DH} = 2A_x/\rho\,\ln(1+\rho/\sqrt{2})$$

For ρ, Pitzer and Simonson (1986) recommend the value $\rho = 2{,}150(d/DT)^{1/2}$ (where d is the density of the solvent and D its dielectric constant). For water at 298.16 K we have $\rho = 14.05$. These authors recommend that a fixed value of ρ be used for a wide variety of aqueous systems and over a relatively narrow range of temperature. The values $\rho = 14.08$ and $A_x = 2.9$ give $\ln\gamma^\infty_{2DH} = 0.99$, or $RT\ln\gamma^\infty_{2DH} = 0.58$ kcal/mol at the standard temperature of 25°C. As shown later, this value is relatively small compared to the other terms in the righthand side of Eq. 10b (see next section) for most salts (see Table 2). Even at infinite dilution, the Debye–Huckel contribution is only appreciable for poorly hydrated and low-melting salts.

Calculation of Constants for Activity Coefficients

We now suggest a procedure for calculating the free energies g_{ij} appearing in Eqs. 4 and 5 from experimental data for the Gibbs free energy of formation of the pure components and data for the Gibbs free energy of formation of the same components at infinite dilution.

The absolute value of the chemical potential of a component does not depend on the reference state (unlike the activity coefficient and the standard chemical potential). We can therefore express it in terms of molalities or mole fractions. For the solute we write

$$\mu_2 = \mu^*_{2m} + RT\ln m_2\gamma_{2m} = \mu^0_{2x} + RT\ln\gamma_2x_2 \quad (6)$$

where μ^*_{2m} and γ_{2m} are the standard chemical potential and the activity coefficient of the solute in the molal scale (γ_{2m} is normalized unsymmetrically, that is, $\gamma_{2m}\to 1$ as $m_2\to 0$); μ^0_{2x} and γ_2 are the standard chemical potential and the activity coefficient of the solute in the mole fraction scale (γ_2 is normalized symmetrically, that is, $\gamma_2\to 1$ as $x_2\to 1$). At infinite dilution $m_2\to 0$ and $x_2\to 0$ while $\gamma_{2m}\to 1$ and $\gamma_2\to\gamma^\infty_2$. Therefore,

$$RT\ln\gamma^\infty_2 = \mu^*_{2m} - \mu^0_{2x} + RT\ln m_W = \Delta G^*_{2m}(T) - \Delta G^0_2(T) + RT\ln m_W \quad (7)$$

where m_W is the molality of water (= 55.51). Here, $\Delta G^*_{2m}(T)$ is the Gibbs energy of formation of the salt at infinite dilution in the molal scale at the temperature of the system, and $\Delta G^0_2(T)$ is the Gibbs free energy of formation of the pure salt at the temperature of the system. Note that the reference state we use here is that of a pure "supercooled fused salt." Even if the temperature of an electrolyte solution is well below the melting point of the corresponding pure salt, it may be useful to take the supercooled liquid as the reference state (Pitzer and Simonson, 1986). The relation between $\Delta G^0_2(T)$ and the more readily available Gibbs free energy of formation of a pure solid salt, $\Delta G^0_{2,s}(T)$, is given by

$$\Delta G_2^0(T) = \Delta G_{2,s}^0(T) + \Delta H_0(1 - T/T_0) - \Delta c_p[T_0 - T(1 + \ln T_0/T)] + \sum_k \Delta H_k(1 - T/T_k) \quad (8)$$

where ΔH_0 and T_0 are the salt's enthalpy and temperature of fusion, and where Δc_p is the change of heat capacity upon fusion. If k phase transitions occur in the crystal structure of a salt, each with enthalpy change ΔH_k at temperature T_k, the term $\Sigma_k \Delta H_k(1 - T/T_k)$ must be added to the righthand side of Eq. 8. Values for $\Delta G_{2,s}^0$, ΔG_{2m}^*, ΔH_0, ΔH_k, T_0, T_k, and Δc_p for many salts can be found in the literature (Rossini et al., 1952; Glushko, 1962–1981; Weast, 1986).

Similarly, for component 1 (water) we write

$$RT \ln \gamma_1^\infty = \mu_1^* - \mu_1^0 = \Delta G_1^*(T) - \Delta G_1^0(T) \quad (9)$$

where γ_1^∞ is the value of γ_1 as $x_1 \to 0$, and where $\Delta G_1^*(T)$ and $\Delta G_1^0(T)$ are the Gibbs free energies of formation of component 1 (water) at infinite dilution in component 2 (salt) and in the pure state (pure liquid water), respectively, also at the temperature of the system. (For notational simplicity, in the remainder of this article we write ΔG_i as opposed to $\Delta G_i(T)$.)

To derive expressions for $\ln \gamma_1^\infty$ and $\ln \gamma_2^\infty$ we take the limits of Eqs. 4 and 5 as $x_1 \to 0$ and $x_2 \to 0$, respectively. The resulting equations are inserted into 9 and 7 to give

$$\tau_{12} \exp(\tau_{12}/n_{22}^0) + \tau_{21} = (\Delta G_1^0 - \Delta G_1^*)/RT \quad (10a)$$

and

$$\tau_{21} \exp(\tau_{21}/n_{11}^0) + \tau_{12} = (\Delta G_{2,s}^0 - \Delta G_{2m}^*)/RT - \ln m_W + \left\{\Delta H_0(1 - T/T_0) - \Delta c_p[T_0 - T(1 + \ln T_0/T)] + \sum_k \Delta H_k(1 - T/T_k)\right\}/RT + \frac{2A_x}{\rho} \ln\left(1 + \frac{\rho}{\sqrt{2}}\right). \quad (10b)$$

Here n_{11}^0 is the value of n_{11} as $x_2 \to 0$ (considered to be the average number of nearest neighbors of pure component 1) and n_{22}^0 is the value of n_{22} as $x_1 \to 0$ (considered to be the average number of nearest neighbors of pure component 2).

Equations 10 contain the following, still unspecified quantities: n_{11}^0, n_{22}^0, g_{11}, g_{12}, g_{21}, and g_{22}. For n_{11}^0, the average number of nearest neighbors for pure water, we use the value ~ 4.6 at 25°C (Harned and Owen, 1950; Robinson and Stokes, 1965). For n_{22}^0, the average number of nearest neighbors for pure salt, we use the approximate values suggested by Petrucci (1971) (see Table 2).

The righthand side of Eq. 10b corresponds to the free energy required to bring species 2 from a condensed pure phase (in the standard state) to an infinitely dilute solution, where solute molecules do not interact with each other. We define this free energy as g_{22} and we write

$$\tau_{21} \exp(\tau_{21}/n_{11}^0) + \tau_{12} = g_{22}. \quad (11)$$

Since all the quantities appearing on the righthand side of Eq. 10b can be found in the literature, the value of g_{22} can be determined.

Similarly, the righthand side of Eq. 10a corresponds to the free energy required to bring species 1 from a condensed pure phase to an infinitely dilute solution. We define this free energy as g_{11} and we write

$$\tau_{12} \exp(\tau_{12}/n_{22}^0) + \tau_{21} = g_{11}. \quad (12)$$

Unfortunately, we are unable to determine the numerical value of g_{11} because ΔG_1^* appearing in Eq. 10a, the Gibbs free energy of formation of component 1 (water) at infinite dilution in component 2 (salt), is not an experimentally accessible quantity. Having specified n_{11}^0, n_{22}^0, g_{22} three constants remain to be determined, namely g_{21}, g_{12}, and g_{11}.

At this point we invoke the concept of local composition. The basic idea behind this concept is that, on the average, a molecule of species 1 will be surrounded by n_{11} molecules of species 1 and n_{21} molecules of species 2, thereby forming a cell of type a. Similarly, a molecule of species 2 will be surrounded by n_{12} molecules of species 1 and n_{22} molecules of species 2, thereby forming a cell of type b. Renon and Prausnitz (1968) originally proposed the equations:

$$\frac{n_{12}}{n_{22}} = \exp(\tau_{12}/\alpha_{12}) \frac{x_1}{x_2} \quad (13a)$$

$$\frac{n_{21}}{n_{11}} = \exp(\tau_{21}/\alpha_{21}) \frac{x_2}{x_1}. \quad (13b)$$

In the spirit of two-liquid theory (Prausnitz et al., 1986), we propose two additional equations. First, we write an expression for the "distribution ratio" of molecules of species 1 between a cell of type a and a cell of type b:

$$\frac{n_{12}}{n_{11}} = \exp(g_{12}/\alpha_{12} - g_{11}/\alpha_{21}). \quad (14)$$

Second, we write an expression for the local conservation of the number of molecules contained in cells a and b

$$\frac{(n_{11} + n_{12})}{(n_{22} + n_{21})} = \frac{x_1}{2x_2}. \quad (15)$$

In the limit as $x_2 \to 0$, Eq. 14 can be written as

$$\frac{n_{12}^0}{n_{11}^0} = \exp(g_{12}/n_{12}^0 - g_{11}/n_{11}^0). \quad (16)$$

Next, we take the limits of Eqs. 13a, 13b and 15 as $x_2 \to 0$. By use of L'hopital's rule for indeterminate forms and subsequent rearrangement of these limits, we arrive at

$$n_{11}^0[\exp(\tau_{21}/n_{11}^0) - 2] + n_{12}^0[\exp(-\tau_{12}/n_{12}^0) - 2] = 0. \quad (17)$$

(Note that as $x_2 \to 0$, $n_{11} \to n_{11}^0$, $n_{12} \to n_{12}^0$, $n_{22} \to 0$, and $n_{21} \to 0$.)

Simultaneous solution of Eqs. 11, 12, 16 and 17 leads to values for g_{21}, g_{12}, g_{11} and an additional unknown, n_{12}^0, which we interpret as the average number of molecules of type 1 surrounding a molecule of type 2 at infinite dilution.

The last step in the calculation of constants for the activity coefficients is that of determining α_{12} and α_{21}. These two quantities depend on n_{ij} and must depend on composition. Note that up to this point we have assigned values to n_{ij} only at infinite dilution, but not for arbitrary compositions. To do so, we use Eqs. 13a, 13b, 14 and 15; after some algebraic manipulations, we arrive at

$$\alpha_{12}(x_2A_{21}+x_1)-\alpha_{21}(x_1A_{12}+x_2)A=0$$

$$A(A_{12}-0.5)-0.5A_{21}+1=0 \qquad (18)$$

where

$$A=\exp\left(g_{12}/\alpha_{12}-g_{11}/\alpha_{21}\right).$$

Equations 18 can be solved to determine α_{12} and α_{21} as a function of composition.

At this point it is instructive to outline the main features of the approach proposed here. Experimental data for the Gibbs free energy of formation of the pure solute and for the solute at infinite dilution in the solvent are used to determine the g_{ij} appearing in Eqs. 4 and 5 for the activity coefficients. This calculation requires that n_{11}^0 and n_{22}^0 be specified. These constants are subsequently used to calculate α_{12} and α_{21} for any given composition of the solution. Activity coefficients can then be calculated.

Solubility of Salts in Water

Using Eqs. 4 and 5, we can now proceed to calculate thermodynamic properties of engineering interest. It is important to test these equations for calculation of the properties of concentrated solutions. We therefore begin by applying them to calculate the solubility of salts and the activity of water in saturated electrolyte solutions.

The solubility of salts that do not form a crystal hydrate in the solid state is described by the equation (Reid et al., 1987)

$$RT\ln\gamma_2x_2=-\Delta H_0(1-T/T_0)-\sum_k\Delta H_k(1-T/T_k)$$
$$+\Delta c_p[T_0-T(1+\ln T_0/T)] \qquad (19)$$

Table 1 gives experimental data as well as the results of our solubility calculations for a number of salts. Table 1 also gives the activity of water in the corresponding saturated solutions. The agreement between theory and experiment is reasonable. However, it is important to point out that the results of our calculations depend to a large extent on the values assumed for the thermodynamic functions of the pure salt and the Gibbs free energies of formation at infinite dilution. Unfortunately, for a number of salts, different authors report significantly different data for the Gibbs free energies of formation. In Table 2 we provide a collection of such data and also the actual values (the lines marked by the asterisk,*) that we have used for our calculations. (The T_0 found in different sources coincide within 3–5 K and, therefore, are not included in this table). These values were selected on the basis of the agreement between calculated and experimental solubilities. Analysis of the results obtained shows that, for many salts, direct use of handbook data leads to satisfactory results. It is important to recognize, however, that for some salts (such as KNO_3) satisfactory results can only be obtained for thermodynamic constants that differ markedly from those given in the abovementioned sources.

Table 1. Solubility of Salts m (mol/kg) and Water Activity a_1 in Saturated Solutions at 25°C

	NaF	NaCl	NaI	$NaNO_3$	KCl	KBr	KI	KNO_3
m	0.99	6.12	12.41	10.73	4.84	5.71	8.98	3.88
m_{exp}	0.99	6.14	12.3	10.83	4.83	5.74	8.96	3.84
a_1	0.979	0.767	0.374	0.746	0.854	0.820	0.667	0.940
a_{1exp}	0.969	0.758	0.380	0.738	0.843	0.808	0.686	0.924

	CsCl	CsF	CsBr	CsI	$CsNO_3$	$NaClO_3$	$AgNO_3$	NH_4Cl
m	11.34	35.63	5.81	3.36	1.38	9.99	15.23	7.42
m_{exp}	11.37	35.6	5.80	3.33	1.4	9.94	15.12	7.39
a_1	0.664	0.041	0.842	0.915	0.974	0.763	0.772	0.774
a_{1exp}	0.658	0.040	0.826	0.906	0.965	0.751	0.828	0.771

Note that in practice it could prove useful to use solubility data and the formalism proposed here to determine some of the least accurately known or not-known-at-all thermodynamic constants of salts.

Partial Vapor Pressures and Azeotropic Composition for Systems Containing a Volatile Electrolyte (H_2O-HNO_3)

In contrast to the electrolyte solutions discussed in the previous section, where only the solvent has a measurable vapor pressure, in the system H_2O-HNO_3 the dissolved electrolyte also has an appreciable vapor pressure over a broad concentration range. This makes possible a direct comparison of the values calculated for the activity of the electrolyte with experiment. Note that for electrolyte solutions, we have so far compared calculated electrolyte activities with experimental data only indirectly, through calculation of solubilities via Eq. 19.

The partial pressure of nitric acid, P_1^{sat}, is determined by the activity of molecular (nonionized) nitric acid, a_{2M}, through $P_2^{sat}=P_2^{sat,0}a_{2M}$, where $a_{2M}=\gamma_{2M}x_{2M}$. Here, $P_2^{sat,0}$ is the vapor pressure of pure nitric acid, and γ_{2M} and x_{2M} are the activity coefficient and the mole fraction of molecular solute. The latter two quantities are determined by the degree of ionization of nitric acid in solution, α. To obtain an expression for γ_{2M} in terms of the total activity coefficient, γ_2, we can write

$$x_2\ln\gamma_2=x_{2D}\ln\gamma_{2D}+x_{2M}\ln\gamma_{2M} \qquad (20)$$

where x_2 and x_{2D} are the total molal fraction of nitric acid and the molal fraction of its ionic form, and γ_{2D} is the activity coefficient of the ionic form.

Since ionic and molecular nitric acid are in the equilibrium, their chemical potentials are equal to each other; their activities are consequently also equal (we use the same standard state for both the ionic and molecular forms):

Table 2. Thermodynamic Constants of Salts at 298.16 K, kcal · mol $^{-1}$

Salt	ΔH_0	ΔH_k	ΔC_p	$\Delta G_2^0 - \Delta G_{2m}^*$	n_{22}^0	Source
NaF	8.0 ± 0.05	—	—	−0.66 ± 0.3	—	1
	7.8	—	0.65	−0.63	—	2
	—	—	—	—	4.1	3
	7.8	—	0.65	−0.35	3.0	*
NaCl	6.74	—	—	2.15 ± 0.69	—	1
	6.80	—	0.8	2.15	—	2
	—	—	—	—	4.7	3
	6.80	—	0.8	2.3	3.0	*
NaI	5.67 ± 0.05	—	—	6.92 ± 0.05	—	1
	5.2	—	—	—	—	2
	—	—	—	—	—	3
	6.0	—	0.1	6.0	4.5	*
$NaNO_3$	3.6	1.0	—	1.52 ± 0.14	—	1
	3.8	—	0.3	1.47	—	2
	—	—	—	—	—	3
	3.6	1.0	0.3	1.55	3.0	*
$NaClO_3$	5.08	—	—	1.7 ± 0.5		1
	5.4	—	4.9	1.81	—	2
	—	—	—	—	—	3
	5.4	—	4.5	1.5	4.5	*
KCl	6.29	—	—	1.23 ± 0.3	—	1
	6.1	—	0.61	1.28	—	2
	—	—	—	—	3.6	3
	6.1	—	0.61	1.38	3.0	*
KBr	6.1 ± 0.1	—	—	1.55 ± 0.14	—	1
	7.0	—	—	1.57	—	2
	—	—	—	—	—	3
	6.1	—	1.0	1.65	3.0	*
KI	5.74 ± 0.1	—	—	2.73 ± 0.05	—	1
	—	—	—	2.38	—	2
	—	—	—	—	—	3
	5.7	—	1.0	2.75	3.0	*
KNO_3	2.34	1.2	—	−0.12 ± 0.1	—	1
	2.8	1.3	0.7	−0.08	—	2
	—	—	—	—	—	3
	3.6	1.2	1.13	0.05	3.0	*
CsF	5.19 ± 0.1	—	—	10.42 ± 0.62	—	1
	2.45	—	—	10.83	—	2
	—	—	—	—	—	3
	3.1	—	1.0	10.6	3.0	*
CsCl	4.85	0.9 ± 0.1	—	2.1 ± 0.4	—	1
	3.6	1.8	—	2.08	—	2
	—	—	—	—	4.6	3
	3.6	1.0	1.5	2.30	3.0	*
CsBr	5.64 ± 0.1	—	—	1.08 ± 0.16	—	1
	1.7	—	—	1.09	—	2
	—	—	—	—	4.6	3
	5.4	—	1.0	1.3	3.0	*
CsI	6.1 ± 0.5	—	—	0.72 ± 0.1	—	1
	—	—	—	0.72	—	2
	—	—	—	—	4.5	3
	6.15	—	0.1	0.72	3.0	*
NH_4Cl	—	1.06	—	—	—	1
	—	1.0	—	1.83	—	2
	—	—	—	—	—	3
	4.5	1.0	0.1	1.83	3.0	*
HNO_3	—	—	—	7.35	—	1
	—	—	—	7.30	—	2
	—	—	—	—	—	3
	—	—	—	7.40	3.0	*
$AgNO_3$	2.9 ± 0.1	0.59	—	0.2 ± 0.2	—	1
	2.76	0.66	4.5	0.18	—	1
	—	—	—	—	—	3
	2.85	0.55	4.5	0.78	3.0	*
CO_2	6.03	1.99	—	−1.99	—	1
	6.28	2.07	—	—	—	4
	6.16	2.0	25	—	—	5
	6.2	2.0	25	−2.05	8	*

1. For NH_4Cl the heat of melting has been estimated on the empirical formula: $\Delta H_0 \approx 6.10^{-3} T_0$.

2. The value of ΔC_p for CO_2 is obtained by extrapolation of data (Vukalovich and Altunin, 1968).

3. Source: 1—Glushko, 1962–1981; 2—Rossini et al., 1952; Wagman et al., 1981; 3—Petrucci, 1971; 4—Angus et al., 1976; 5—Vukalovich and Altunin, 1968.

4. Assumed values are represented in the lines marked by the *.

$$x_{2D}\gamma_{2D} = x_{2M}\gamma_{2M}. \tag{21}$$

Combining Eqs. 20 and 21, and taking into account that $x_{2D} = x_2\alpha$ and $x_{2M} = x_2(1-\alpha)$, we arrive at the following expression for $\ln \gamma_{2M}$:

$$\ln \gamma_{2M} = \ln \gamma_2 - \alpha \ln \frac{1-\alpha}{\alpha}. \tag{22}$$

Note that in the absence of ionization, $\alpha \to 0$ and $\ln \gamma_{2M} \to \ln \gamma_2$.

Data for the degree of ionization of nitric acid as a function of its concentration at 25°C are obtained by comparing the Raman spectra of nitric acid to that of fully ionized sodium nitrate (Harned and Owen, 1950).

Figure 1 shows the calculated and experimental (Yakimov and Mishin, 1964) composition dependence of the partial pressure of water $P_1 = P_{01}a_1$ and that of nitric acid $P_2 = P_{02}a_{2M}$. Since the reference state for nitric acid is pure liquid

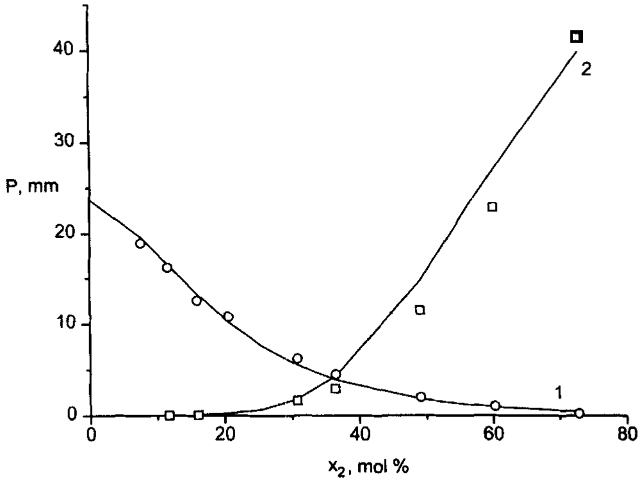

Figure 1. Partial pressure of water (1) and nitric acid (2) in the binary system.

The points show experimental data (Yakimov and Mishin, 1964). The lines show the results of our calculations.

acid, ΔH_0 and Δc_p are taken to be zero. Agreement with experiment is satisfactory.

The azeotropic composition is determined here by the condition

$$P_{02}/P_{01} = \gamma_1/[\gamma_{2M}(1-\alpha)]$$

(we assume that the vapor phase is ideal and that nitric acid is partially ionized in the liquid phase). Our calculations yield an azeotropic composition of $x_2 = 0.327$ (at 298.6 K and 0.01 atm); the experimental value is approximately 0.355 (Sander et al., 1986).

Temperature Dependence of the Solubility of Salts and their Enthalpy of Solution

In this section we show how to apply the method proposed in this article to calculation of the temperature dependence of the solubility of salts and their heats of solution in saturated solutions. The prediction of the temperature dependence of these properties poses a stringent test of a model's physical significance.

To calculate such a dependence we evaluate the functions $\ln \gamma_1(T)$, $\ln \gamma_2(T)$, and their derivatives with respect to temperature. Expressions for $(\partial \ln \gamma_1/\partial T)_{x_2}$ and $(\partial \ln \gamma_2/\partial T)_{x_2}$ can be obtained by direct differentiation of Eqs. 4 and 5. These expressions include the functions $g_{ij}(T)$, $n_{ij}(T)$, $\alpha_{ij}(T)$, and their derivatives with respect to T.

Differentiation of g_{22} gives

$$dg_{22}/dT = d(\Delta G_h/RT)/dT - \left[\Delta H_0 + \sum_k \Delta H_k - \Delta c_p(T_0 - T)\right]\Big/RT^2 \quad (23)$$

where $\Delta G_h = \Delta G^*_{2m} - \Delta G^0_2$. From the Gibbs-Helmholtz equation it follows that

$$d(\Delta G_h/RT)/dT = -\Delta H_h/RT^2 \quad (24)$$

where

$$\Delta H_h = \Delta H_{hr} + \int_{T_r}^{T} \Delta c_{ps}\, dT.$$

Here T_r is the reference temperature 298.16 K and $\Delta H_h = \Delta H^0 - \Delta H^*$ is the difference between the enthalpy of formation of the pure solute and that for an infinitely dilute solution. Subscript r denotes the corresponding value at the reference temperature T_r, and $\Delta c_{ps} = c^0_p - c^*_p$ is the difference between the heat capacity of the solute in the pure state and that for an infinitely dilute solution. If Δc_{ps} is approximately constant (it generally is), it can be shown that

$$dg_{22}/dT = -\left[\Delta H_{hr} + \Delta c_{ps}(T - T_r) + \Delta H_0 + \sum_k \Delta H_k - \Delta c_p(T_0 - T)\right]\Big/RT^2. \quad (25)$$

Experimental data for ΔH_r and for Δc_{ps} can be found in handbooks of thermodynamic properties (Parker, 1965).

With the aid of the equations given before we can calculate the temperature dependence of the solubility of salts and the heat of solution of solutes in their saturated solutions. Note that in spite of their practical importance, these values could not be estimated by previously available models. Differentiation of Eq. 14 with respect to T gives

$$RT^2 dx_2/dT = x_2\left[\Delta H_0 + \sum_k \Delta H_k - \Delta c_p(T_0 - T) - RT^2(\partial \ln \gamma_2/\partial T)_{x_2}\right]\Big/[1 + x_2(\partial \ln \gamma_2/\partial x_2)_T]. \quad (26)$$

Transformation to concentration in wt. %, and molality, m_s, gives, respectively,

$$dw/dT = 100\, M_s/(m_s + M_s)^2 dm_s/dT$$

and

$$dm_s/dT = m_W/x_1^2(dx_2/dT)$$

where $w = 100 m_s/(m_s + M_s)$, $m_s = m_W x_2/x_1$, $M_s = 1{,}000/M_2$, and where M_2 is the molecular weight of the solute.

Figure 2 shows the results of our calculations for the temperature dependence of the solubility of various salts. Ex-

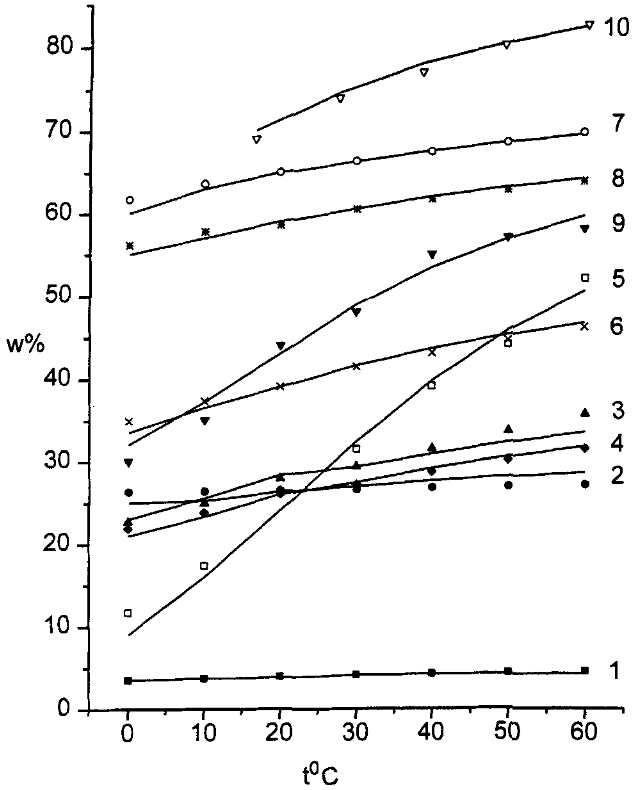

Figure 2. Temperature dependence of the solubility of salts, wt. %.

The solid curves are calculated results; the points show experimental data (Linke and Seidell, 1965). 1—NaF, ■; 2—NaCl, ●; 3—NH_4Cl, ▲; 4—KCl, ◆; 5—KNO_3, □; 6—KBr, ×; 7—KI, ○; 8—CsCl, ∗; 9—CsI, ▼; 10—$AgNO_3$, ∇.

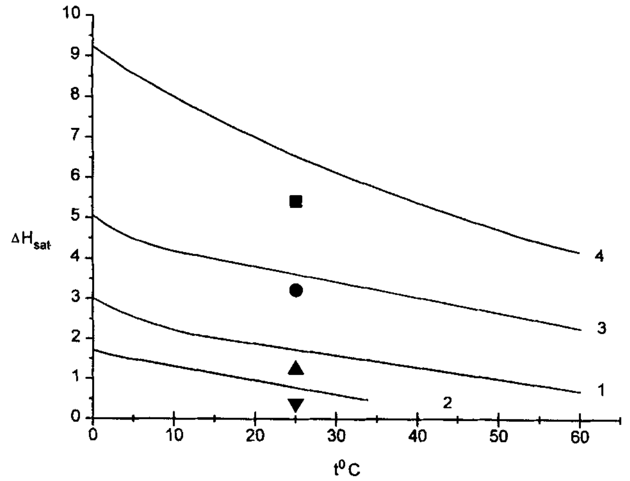

Figure 3. Temperature dependence of the heat solution of various salts, ΔH_{sat} (kcal·mol^{-1}), in their saturated solutions.

The lines show our calculated results. The symbols show experimental data (Nakajama, 1970). 1—NaF, ●; 2—NaCl, ▲; 3—KCl, ▼; 4—KNO_3, ■.

perimental data from (Linke and Seidell, 1965) are also represented in Figure 2. The calculations are in good agreement with experiment, indicating that the model does have some physical significance and could therefore be used to estimate a number of other characteristics of electrolyte solutions.

The electrolyte's enthalpy change of solution at saturation, ΔH_{sat}, is given by

$$\Delta H_{sat} = \Delta H_0 + \sum_k \Delta H_k - \Delta c_p(T_0 - T) - RT^2(\partial \ln \gamma_2/\partial T)_{x_2}.$$

Calculated values for ΔH_{sat} are shown in Figure 3. These values, at the reference temperature 298.16 K, have also been reported by Nakajama (Nakajama, 1970) and are represented in Figure 3. The uncertainties in the data reported by this author are high because he used a graphical procedure to determine the derivatives of nonlinear functions (for the experimental solubility as a function of temperature and for the activity coefficients of the salts as a function of concentration). Nevertheless, the values of ΔH_{sat} obtained by these two different methods are consistent with each other (note that our model shows an important temperature dependence of ΔH_{sat}).

Solubility of CO_2 in Water

Vapor–liquid equilibria are determined by requiring that the chemical potentials of all components in the vapor phase be equal to those in the liquid phase, that is,

$$\begin{aligned} &\mu^0_{2,v} + RT \ln Py_2\varphi_2 = \mu^0_{2,\text{liq}} + RT \ln \gamma_2 x_2 \qquad (\text{for } CO_2) \\ &\mu_{1,v} + RT \ln P(1-y_2)\varphi_1 = \mu^0_{1,\text{liq}} + RT \ln a_1 \qquad (\text{for water}) \end{aligned} \tag{27}$$

where P is the total pressure, φ_1 and φ_2 are the fugacity coefficients, and x_2 and y_2 are the mole fractions of carbon dioxide in water and in the vapor, respectively. The standard chemical potentials for the liquid and the vapor phases are denoted by subscripts liq and v, respectively.

Following the approach outlined in previous sections, we chose the standard state of carbon dioxide in water to be that of a hypothetical superheated pure liquid CO_2 at the temperature and pressure of the system. This standard state (compared to a standard state at infinite dilution) has the advantage of being independent of the presence of other solutes.

Equations 27 lead to the following expression for the solubility of the gas

$$\ln \gamma_2 x_2 = \left(\mu^0_{2,v} - \mu^0_{2,\text{liq}}\right)/RT + \ln P\varphi_2 y_2 \tag{28}$$

where

$$\begin{aligned} y_2 &= 1 - \exp\left[\left(\mu^0_{1,\text{liq}} - \mu^0_{1,v}\right)/RT\right] a_1/P\varphi_1 \\ &\approx 1 - \exp\left[\left(\Delta G^0_{1,\text{liq}} - \Delta G^0_{1,v}\right)/RT\right]/P. \end{aligned}$$

For simplicity we assume that $a_1/\varphi_1 \approx 1$ (the mole fraction of water in the vapor phase is very small at elevated pressures of carbon dioxide and the activity of water in the binary system CO_2–H_2O is close to unity).

The difference between the chemical potentials of gaseous and superheated liquid CO_2 on the righthand side of Eq. 28 is equal to

$$\begin{aligned} \mu^0_{2,v} - \mu^0_{2,\text{liq}} &= \Delta G^0_{2,v} - \Delta G^0_{2,\text{liq}} \\ &= \Delta H_0(1 - T/T_0) - \Delta H_p(1 - T/T_p) \\ &\quad - \Delta c_p[T_0 - T(1 + \ln T_0/T)] - v^0_2(P - P_0). \end{aligned} \tag{29}$$

Here $\Delta G^0_{2,v}$ and $\Delta G^0_{2,\text{liq}}$ are the Gibbs free energies of formation in the gaseous phase and in the superheated liquid state, ΔH_0 and ΔH_p are the heats of sublimation and melting of solid carbon dioxide, Δc_p is the difference between the heat capacities of liquid and gaseous carbon dioxide, T_0 and T_p are sublimation and melting temperatures, v^0_2 is the molar volume of liquid carbon dioxide, and P_0 is the reference pressure (usually 1 atm).

The activity coefficient of the solute is given by Eq. 5. At elevated pressures a poynting correction must be taken into account:

$$\ln \gamma_2 = \ln \gamma_2(P_0) + \frac{\bar{v}_2 - v^0_2}{RT}(P - P_0)$$

where $\bar{v}_2$ is the partial molar volume of carbon dioxide in water.

To calculate the fugacity coefficient of carbon dioxide in the vapor phase we use the equation of state proposed by Nakamura et al. (1976). Values for ΔH_0, ΔH_p, T_0, T_p, and Δc_p for CO_2 are taken from the compilations of Angus et al. (1976) and Vukalovich and Altunin (1968) (Table 2).

Note that for the calculations of CO_2 solubility reported

Table 3. Solubility of CO_2 (m, mol/kg H_2O) in Water at Different Pressures and Temperatures

	P, atm			
t°C	25	30	75	100
12	1.086	2.152	1.821	1.804
	(0.973)*	(1.59)	(1.63)	(1.65)
25	0.777	1.471	1.604	1.604
	(—)	(1.22)	(1.4)	(1.43)
50	0.460	0.849	1.134	1.245
	(0.44)	(0.774)	(1.01)	(1.15)
75	0.297	0.549	0.746	0.885
	(0.306)	(0.565)	(0.765)	(0.925)

*The data in the parenthesis are experimental ones taken from the compilation (Linke and Seidell, 1965).

here we did not take into account the formation of ions due to the reaction

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^-$$

The equilibrium constant for this reaction is rather small and for molalities greater than 10^{-4} the effect of dissociation disappears (Edwards et al., 1978), thereby causing the Debye–Huckel contributions to Eq. 5 to be negligible.

Our results for the solubility of CO_2 in water at different pressures and temperatures are given in Table 3. Experimental data are also given in Table 3. The agreement between theory and experiment is satisfactory, and could be further improved by eliminating some of the approximations employed in this work. Note that our results for the solubility of CO_2 at 12°C go through a maximum at 50 atm. According to the equation of state of Nakamura et al. (1976), which has been used for our calculations, at 12°C carbon dioxide condenses at a pressure of 55 atm. Once carbon dioxide has condensed, the effect of pressure on its solubility is different from that for the gaseous state, thereby giving rise to the aforementioned maximum.

Conclusions

We have proposed a semi-empirical formalism that leads to quantitative predictions for the equilibrium thermodynamic properties of binary electrolyte solutions. To illustrate the usefulness of such a formalism, we have presented results for the solubility of a variety of salts in water, we have examined the temperature dependence of various thermodynamic quantities, we have determined the azeotropic composition of water–nitric acid solutions, and we have estimated the solubility of a gas (carbon dioxide) in water at elevated pressures.

In all cases, the predictions appear to be in reasonable agreement with experiment. The advantage of the methods discussed here over other available techniques for estimation of the properties of electrolyte solutions is that only pure component data and infinite dilution data for binary mixtures are necessary. Furthermore, the constants appearing in the model used here have a well-defined physical significance. For estimation of the properties of multicomponent solutions, we expect our method to provide a useful tool for engineering thermodynamic predictions. Preliminary results for multicomponent systems are encouraging; these are reported elsewhere (Kolker and de Pablo, 1995).

Acknowledgments

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