

A LATTICE MODEL OF ELECTROLYTES FOR THE WHOLE CONCENTRATION RANGE

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Based on the quasi-lattice concept, a simple model is proposed for calculating the quantities of mixing of strong electrolyte solutions over the whole concentration range from pure solvent to pure salt. This model is analogous to the regular solution model for non-electrolyte systems. Relationships for the activity coefficients of the solvent and salt have been derived, and the behaviour of the model in the limit of infinite dilution is discussed by comparison with the Debye-Hückel theory. The adequacy of equations derived from the proposed model has been tested by fitting published experimental data for the activities of water in the systems $(\text{Li, K})\text{NO}_3\text{-H}_2\text{O}$ and $(\text{Ag, Tl})\text{NO}_3\text{-H}_2\text{O}$, which have been measured over the whole concentration range.

In analyzing experimentally determined phase diagrams¹, complications arise if one component is a polar solvent and the other a salt which dissociates in the system into the ions. In this case, the regular solution model is not applicable, and the Debye-Hückel theory, which was derived for this type of system, is limited to dilute solutions.

The aim of this paper is to propose a simple model analogous to the model of regular solutions, but taking into account the nature of the species present in the system and permitting extrapolation over the whole concentration range, *i.e.* from the pure solvent to pure salt.

The problem has been treated by several workers, but no satisfactory solution has been obtained. Pitzer² used the simple equation of van Laar and modified it by adding the Debye-Hückel term in seeking to obtain a better agreement in the region of dilute solutions. Another approach has its origin in the fundamental work of Stokes and Robinson³, who started from a model of multilayer hydration of ions and proposed an equation for the activity of water strongly resembling the BET adsorption isotherm (see p. 1876 of ref.³). Unfortunately, their equation is not capable of describing the behaviour of systems over the whole concentration range.

THEORETICAL

Basic Assumptions of the Model

For simplicity, we shall consider systems of completely dissociating salts made up of singly charged ions:



where R denotes the polar solvent and MA represents the salt dissociating into M^+ and A^- ions.

The system composition will be expressed exclusively in the mole fraction terms. Molalities or other concentration units cannot be used if one aims at extending the validity of the model up to pure salts.

We also consider as inconsistent the use of the term the mole fraction "on an ionized basis", introduced by some workers. In our approach we replace it by the concept of the activity in an ideal mixture⁴ (see below), which appears to be more appropriate and rigorous from the thermodynamic point of view.

Let us consider N ion pairs M^+A^- ($N_{\text{S}} = N_{\text{M}} = N_{\text{A}}$) and N_{R} particles of solvent, *i.e.* a total of $N = N_{\text{S}} + N_{\text{R}}$. The mole fraction of the salt is then $x = N_{\text{S}}/N$ and the mole fraction of the solvent, $1 - x = N_{\text{R}}/N$.

To proceed further, we need to express the energy of all interactions between the species in the system. In principal, the interaction energy is composed of contributions from the RR, MR, AR, MA, AA, and MM pairs. Thus, it is necessary to determine the numbers of the various pairs. Here the concept of the quasi-lattice model with two interpenetrating sublattices, one for cations and one for anions, has proved useful. As previously⁴, we consider that the solvent particles enter the two sublattices in the ratio of the stoichiometric coefficients of the ions, in the present case in the ratio 1 : 1.

The numbers of sites of the cationic and anionic sublattices are thus $N_{\text{M}} + N_{\text{R}}/2$ and $N_{\text{A}} + N_{\text{R}}/2$, respectively. The probability of finding a particle M at a site of the cationic sublattice is then

$$p_{\text{M}} = \frac{N_{\text{M}}}{N_{\text{M}} + N_{\text{R}}/2} = \frac{x}{x + (1-x)/2} = \frac{2x}{1+x}. \quad (1)$$

The probability of finding a particle R at a site is

$$p_{\text{R}} = \frac{N_{\text{R}}/2}{N_{\text{M}} + N_{\text{R}}/2} = \frac{(1-x)/2}{x + (1-x)/2} = \frac{1-x}{1+x}. \quad (2)$$

The relationships for the other sublattice are obtained in an analogous manner, and we find that $p_{\text{A}} = p_{\text{M}}$.

R-R Interactions

Because of short-range forces between the solvent particles, the predominant interactions are those between nearest neighbours R and these are particles belonging to different sublattices. The number of pairs of neighbouring particles R is given by the product of the number of all sites of a sublattice, the coordination number z , and both the probabilities of finding the particles R at the sites of the sublattices:

$$n_{RR} = z(N_S + N_R/2) (p_R)^2 = \frac{zN}{2} \frac{(1-x)^2}{1+x}. \quad (3)$$

M-R and A-R Interactions

Owing to the nature of the forces between the ions and the polar molecules of the solvent, the predominant interactions are again those between nearest neighbours, *i.e.* between an ion from one sublattice and a solvent molecule from the other sublattice. The number of pairs is given by

$$n_{MR} = z(N_S + N_R/2) p_M p_R = \frac{zN}{2} \frac{2x(1-x)}{1+x}$$

$$n_{MR} = n_{AR} = zN \frac{x(1-x)}{1+x}. \quad (4)$$

M-A, M-M, and A-A Interactions

These are Coulomb interactions between ions. In the case of the MA interactions, we must take into account the repulsion between the electron shells of the ions in intimate contact. The main problem here is that the Coulomb forces are long-range in nature and it is therefore necessary to consider a large number of interactions. For a pure crystal (here for $x = 1$), the Coulomb interaction energy is calculated as a series whose sum is called the Madelung constant, A_M , its value depending on the type of the lattice:

$$U = -e^2/r(6 - 12/\sqrt{2} + 8/\sqrt{3} - \dots) = -e^2/rA_M, \quad (5)$$

where r is the shortest distance between M^+ and A^- .

In our case where the ionic lattice is diluted by particles R, we may invoke a picture in which randomly distributed ions are again arranged in a regular lattice but with a proportionately larger spacing r' . The proportionality constant k ($r' = kr$) is apparently related to the density of the ions,

$$k = \frac{1}{(p_M)^{1/3}} = \left(\frac{1+x}{2x} \right)^{1/3}. \quad (6)$$

If the energy of the Coulomb interactions between the ions of the ionic crystal lattice is

$$\varepsilon_1 = N_S e^2 A_M / r = \varepsilon_{MA} N_S, \quad (7)$$

the energy of the "dilute" lattice may be estimated as

$$\varepsilon_x = N_S e^2 A_M / r' = \varepsilon_1 / k = \varepsilon_{MA} N_S [2x / (1+x)]^{1/3}. \quad (8)$$

To make sure that the concept of regularly disposed ions in the so-called "dilute quasi-lattice" does not introduce an error into the model (especially as regards the magnitude of the exponent in Eq. (8)), we made a test by the Monte Carlo method. For a given number of particles in the lattice, we generated random configurations and averaged the values of the potential energy. The obtained dependence of the average energy on x confirmed the correctness of the exponent in Eq. (8).

The Quantities of Mixing

In deriving the quantities of mixing, we start from the following simple relationship for the zero approximation to the partition function Q of regular solutions⁵:

$$Q = W \exp(-E/kT), \quad (9)$$

where W is the number of possible configurations, and E is the energy of all interactions between the particles in the system. In the classical manner, we obtain

$$F = -kT \ln Q = -kT \ln W + E. \quad (10)$$

The free energy of mixing is

$$\Delta F = F - F_R(1-x) - F_S x = -kT \ln W + E - F_R(1-x) - F_S x. \quad (11)$$

Identifying the term $-kT \ln W$ with the ideal free energy of mixing, ΔF^* , and putting $G = F$ while neglecting the volume changes, we get

$$\Delta F^E = \Delta G^E = E - F_R(1-x) - F_S x, \quad (12)$$

where

$$E = \varepsilon_{RR} n_{RR} + \varepsilon_{MR} n_{MR} + \varepsilon_{AR} n_{AR} + \varepsilon_{MA} n_{MA}. \quad (13)$$

Substituting $F_R = \varepsilon_{RR}zN/2$ and $F_S = \varepsilon_{MA}N$ and using the relationships derived in the preceding section for the number of pairs n_{ii} , we obtain

$$\begin{aligned} \Delta G^E &= \varepsilon_{RR}zN/2[(1-x)^2/(1+x) - (1-x)] + (\varepsilon_{MR} + \varepsilon_{AR}) \cdot \\ &\quad \cdot zNx(1-x)/(1+x) + \varepsilon_{MA}Nx\{[2x/(1+x)]^{1/3} - 1\} = \\ &= zN(\varepsilon_{MR} + \varepsilon_{AR} - \varepsilon_{RR})x(1-x)/(1+x) + N\varepsilon_{MA}x\{[2x/(1+x)]^{1/3} - 1\}. \quad (14) \end{aligned}$$

Denoting the constants involving so far unknown contributions from individual interactions as interaction parameters L_1 and L_2 , we obtain the final form for the excess Gibbs energy

$$\Delta G^E = L_1x(1-x)/(1+x) + L_2x\{[2x/(1+x)]^{1/3} - 1\}. \quad (15)$$

The first term is similar in form to the ΔG^E of regular solutions $[Lx(1-x)]$. It can readily be seen that Eq. (15) becomes zero at the boundary points ($x = 0$ and $x = 1$). The dependences of the functions contained in the final expression on the mole fraction are shown in Fig. 1, along with the dependence of the function $x(1-x)$ which constitutes ΔG^E of regular solutions.

An analogous approach was used to derive a more general relationship for the excess Gibbs energy of a salt system with an arbitrary number of ions, $R-M_pA_q$,

$$\Delta G^E = L_1x(1-x)/(vx + 1 - x) + L_2x\{[vx/(vx + 1 - x)]^{1/3} - 1\}, \quad (16)$$

where

$$v = p + q.$$

Activity Coefficients

From Eq. (15) for the excess Gibbs energy satisfying at the boundary points, we obtain in a straightforward manner the activity coefficients for the two components:

$$\ln \gamma_R = L_12x^2/(1+x)^2 - L_2[2x/(1+x)]^{4/3}/6 \quad (17)$$

$$\ln \gamma_S = L_1(1-x)^2/(1+x)^2 + L_2\{[2x/(1+x)]^{1/3}(4+2x)/(3+3x) - 1\}. \quad (18)$$

The dependences of the component functions contained in the two equations on the mole fraction are represented in Figs 2 and 3, along with those for regular solutions. The shape of the function corresponding to the electrostatic contribution explains the typical shape of the activity coefficient against concentration plot for electrolyte systems, with sign reversal in the region of dilute solutions.

If the limit as $x \rightarrow 0$, i.e. as pure solvent is approached, is taken of the expression for the activity coefficient of water, a polynomial with the powers x^2 and $x^{4/3}$ is

obtained. This explains the previously observed empirical paradox that, when activity coefficients of water obtained from phase diagrams are fitted to empirical polynomials, the term in x^1 is statistically significant, though from the physical point of view its occurrence in the polynomial is ruled out (it has no counterpart in the expression for ΔG^E). This is due to the existence of the term in $x^{4/3}$, which is close to x^1 .

Taking the limit as $x \rightarrow 0$ of the equation for the activity coefficient of the other component, the salt, the second term becomes an expression containing $x^{1/3}$. This may seem to be in conflict with the generally accepted " $x^{1/2}$ -power law" derived from the Debye-Hückel theory. This contradiction may be discussed as follows. Besides the Debye-Hückel theory of strong electrolyte solutions, there are others based on different assumptions which in the limit of $x \rightarrow 0$ lead to the dependence on $x^{1/3}$ (ref. 6). An attempt to resolve this problem on the basis of experimental data reveals that the exponents $1/3$ and $1/2$ are statistically indistinguishable owing to errors in the data.

Verification of the Model

A check of the applicability of the proposed equation (17) to actual experimental data was made for two systems which are liquid over the whole concentration range from the pure solvent to pure salt, namely for (Li, K)NO₃-H₂O at 100°C (ref. 7) and

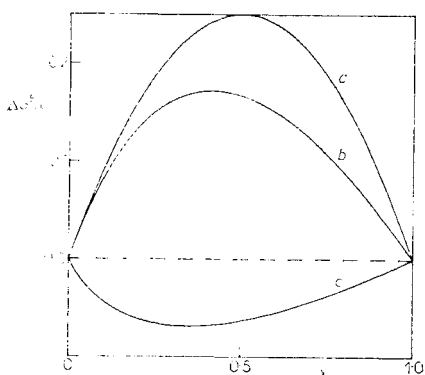


FIG. 1

The excess Gibbs energy and its contributions as a function of the mole fraction of salt; *a* regular solutions, $y = x(1 - x)$; *b* Eq. (15), $y = x(1 - x)/(1 + x)$; *c* Eq. (15), $y = x\{[2x/(1 + x)]^{1/3} - 1\}$

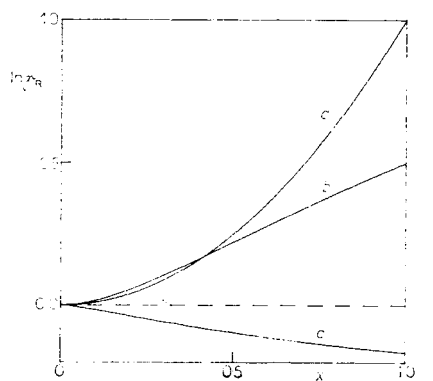


FIG. 2

The activity coefficient of solvent and its contributions as a function of the mole fraction of salt; *a* regular solutions, $y = x^2$; *b* Eq. (17), $y = 2x^2/(1 + x)^2$; *c* Eq. (17), $y = -[2x/(1 + x)]^{4/3}/6$

119°C (ref.⁸), and (Ag, Tl)NO₃-H₂O at 98°C (ref.⁹). For purely practical reasons (depression of the salt melting point), salt mixtures were employed so that, strictly speaking, the systems were not binary but only pseudobinary. Our interest is, however, centred mainly on the activity of water determined from vapour pressure measurements.

Published data on water activity were first converted to activity coefficients by means of the relationship $\gamma = a/a^*$, with the water activity in the ideal mixture, a^* , calculated from the general equation⁴ ($\nu = 2$)

$$a^* = (1 - x)/(vx + 1 - x) = (1 - x)/(1 + x),$$

where x is the stoichiometric mole fraction of salt. A regression method was then used to adjust the interaction parameters in Eq. (17). The results were as follows.

$$(\text{Li, K})\text{NO}_3\text{-H}_2\text{O: } L_1 = -1.086 \quad L_2 = -1.268$$

$$(\text{Ag, Tl})\text{NO}_3\text{-H}_2\text{O: } L_1 = 3.615 \quad L_2 = -2.364$$

The interaction parameter L_2 , which represents the electrostatic contribution to the total energy, is of negative sign in both cases, whereas L_1 , which incorporates

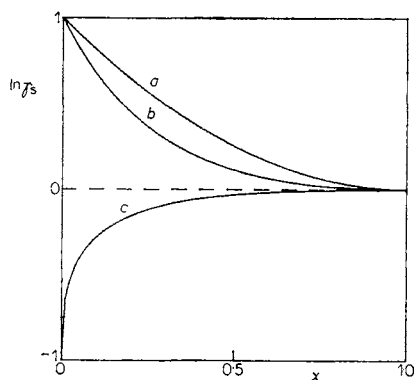


FIG. 3

The activity coefficient of salt and its contributions as a function of the mole fraction of salt; *a* regular solutions, $y = (1 - x)^2$; *b* Eq. (18), $y = (1 - x)^2/(1 + x)^2$; *c* Eq. (18), $y = [2x/(1 + x)]^{1/3} (4 + 2x)/(3 + 3x) - 1$

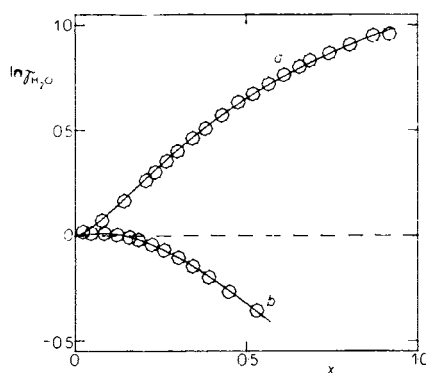


FIG. 4

A plot of activity coefficients of water, calculated from experimentally determined activities of water in the systems *a* (Ag, Tl) NO₃-H₂O (ref.⁹) and *b* (Li, K)NO₃-H₂O (refs^{7,8}), against the mole fraction of salt. Comparison with regression curves according to Eq. (17)

the sum of all contributions from short-range forces, is positive in one case and negative in the other, in accord with the observation that the two systems behave in the opposite way as far as deviations from Raoult's law are concerned.

The fit of experimental data to the regression curve (Fig. 4) is very good considering the simplicity of the starting assumptions and the comparability with the regular solution model, which has not proved to be very accurate in practical use. It should be noted that for the system (Ag, Tl)NO₃-H₂O, for example, the BET equation is only adequate over the range of x from 0.1 to 0.7.

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