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Development of the Ionic Lattice Model Theory for Concentrated Aqueous Electrolytes[†]

Moonis R. Ally*

Energy and Transportation Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

In their landmark paper published in 1948, Stokes and Robinson (*J. Am. Chem. Soc.* **1948**, *70*, 1870−1878) proposed a modified form of the Brunauer−Emmett−Teller (BET) adsorption isotherm to explain the water activity of various concentrated 1:1 and 2:1 aqueous electrolytes. Their pioneering idea of viewing such solutions as an irregular ionic lattice structure inspired much of the author's work from the mid 1980s to the present time. This paper, written in celebration of Prof. Stokes' 90th birthday anniversary, briefly describes the author's contribution toward further development of the theory, its capabilities, and future directions.

Introduction

The author's career at Oak Ridge National Laboratory began at a time when there was renewed interest in waste heat recovery from industrial processes using physisorption and chemisorption processes. After partially successful attempts to extend existing theories of dilute aqueous solutions to higher concentrations of practical interest, the author began to wonder why the region of extremely high concentration remained so intractable. Maurice Abraham[1] also pondered along similar lines when he stated that one major reason why concentrated aqueous electrolytes had been less studied than dilute solutions could be due to the difficulties of extending concepts from dilute solutions to concentrated ones. Gradually, researchers realized that more progress in understanding concentrated aqueous electrolytes could come from studying molten salts which may be considered an extreme case of very concentrated aqueous electrolytes. First, it is important to establish the link between the BET[2] model and what Stokes and Robinson may have contemplated in their earlier work published in 1948,[3] before describing subsequent progress.

The interesting questions concerning Stokes and Robinson's idea of treating concentrated aqueous electrolytes as an irregular ionic-lattice structure (supported by X-ray data) were as follows: Besides the BET-type of equation for the water activity, could the same theory yield a similar BET-type of equation for the solute activity as well? What other thermodynamic properties could be obtained? What is the minimum information required to predict the properties of concentrated solutions? What would be the limits of concentrations over which this theory is valid? How could multicomponent systems be handled? Substantial progress has been made since the preliminary work of Stokes and Robinson[1] as shown in some of the author's work[4] done in the 1990s.

Modified BET Adsorption Isotherm

The typical form of the BET adsorption isotherm depicting the multilayer adsorption of a gas (e.g., water) onto active sites on a solid substrate is given by

$$\frac{p}{v(p^{\mathrm{o}}-p)} = \frac{1}{v_{\mathrm{m}}c} + \frac{(c-1)}{v_{\mathrm{m}}c}\left(\frac{p}{p^{\mathrm{o}}}\right) \tag{1}$$

where v is the total volume of gases (e.g., water) adsorbed on all layers; v_{m} is the volume of water adsorbed when the surface is covered by a complete monolayer; and c is a measure of the adsorption energy of bound water to the adsorption site.

Factoring p^{o} from the left-hand side of eq 1 with the water activity, $a_{\mathrm{w}} = p/p^{\mathrm{o}}$ (by definition, assuming ideal gas behavior), and rearranging gives

$$\frac{a_{\mathrm{w}}}{(1-a_{\mathrm{w}})} = \frac{v}{v_{\mathrm{m}}c} + \frac{v(c-1)}{v_{\mathrm{m}}c}a_{\mathrm{w}} \tag{2}$$

In terms of moles of water

$$v = n_{\mathrm{t}}\bar{v}_{\mathrm{w}} \quad v_{\mathrm{m}} = n_{\mathrm{m}}\bar{v}_{\mathrm{w}} \quad \frac{v}{v_{\mathrm{m}}} = \frac{n_{\mathrm{t}}}{n_{\mathrm{m}}} \tag{3}$$

where n_{t} and n_{m} are the total number of moles of water and those adsorbed in a monolayer, respectively, and $\bar{v}_{\mathrm{w}}$ is the partial molar volume of water.

In the Stokes−Robinson model, all water is either bonded (monolayer adsorption) to adsorption sites provided by the electrolyte or piled on top of the bonded water molecules in multilayer adsorption. The number, n_{m}, of water molecules that can be adsorbed to form a complete monolayer is proportional to the number of adsorption sites, n_{s}, provided by the electrolyte; thus, $n_{\mathrm{m}} = \alpha n_{\mathrm{s}}$, where n_{s} corresponds to the moles of electrolyte and α is a proportionality constant. Therefore, the last term of eq 3 may be rewritten as

$$\frac{v}{v_{\mathrm{m}}} = \frac{n_{\mathrm{t}}}{\alpha n_{\mathrm{s}}} = \frac{55.51}{\alpha m} \tag{4}$$

where m is molality (mol·kg^{-1}) of the electrolyte in aqueous solution. Substituting eq 4 in eq 2 gives $a_{\mathrm{w}}/(1-a_{\mathrm{w}}) = (55.51/\alpha mc) + (55.51/\alpha m)[c - 1/c]a_{\mathrm{w}}$ which on further rearrangement yields

$$\frac{ma_{\mathrm{w}}}{55.51(1-a_{\mathrm{w}})} = \frac{1}{\alpha c} + \frac{(c-1)}{\alpha c}a_{\mathrm{w}} \tag{5}$$

where $\alpha = r$ is the average number of adsorption sites per *molecule*of electrolyte.

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* Corresponding author. E-mail: allymr@ornl.gov.

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Equation 5 is the familiar Stokes−Robinson modification of the BET adsorption isotherm as represented in ref 3.

Stokes and Robinson observed a surprisingly good fit of eq 5 to data on 1:1 and 2:1 electrolytes but noted an "unsatisfactory" feature in eq 5 in that it demanded nonintegral r values. They further commented that, "These can scarcely correspond to any physical reality, and have more likely arisen as a result of approximations in the BET theory and its application to this case. The most drastic of these approximations is that of treating all water molecules beyond the first layer as held by ordinary liquid forces, with a heat of liquefaction E_L." The parameter c which represents the liquefaction energy is defined as $c = \exp[(E - E_L)/RT]$ where E is the energy of adsorption released when a water molecule adheres to a site on the electrolyte in monolayer adsorption; E_L is the energy of liquefaction of pure water; and R and T are the universal gas constant and absolute temperature, respectively. Though Stokes and Robinson[3] utilized a further modification of the BET equation deduced by Anderson[5] to take into account the diminishing adsorption energy with additional layers of water beyond the first, this only extended the applicability of the modified BET model up to $a_w = 0.5$. In the author's development of the theory of multilayer adsorption, the influence of successively diminishing adsorption energy with additional layers of adsorbed water has been ignored.

Statistical Mechanical View of the BET Adsorption Isotherm

If the irregular ionic lattice model can yield an expression for the water activity of concentrated electrolyte solutions in the form of a BET-type equation, then it should also be possible to obtain a BET-type equation for the solute activity from the same model. In fact, the entire thermodynamics of concentrated aqueous electrolytes could be formulated from this viewpoint.

Hydrated melts such as $CaCl_2 \cdot 2H_2O$ yield a molality of $m = 27.7\ \text{mol} \cdot \text{kg}^{-1}$ corresponding to an ionic molality of $3m = 3(27.7\ \text{mol} \cdot \text{kg}^{-1}) = 83.1\ \text{mol} \cdot \text{kg}^{-1}$, or 0.668 water molecules per ion. Evidently, at such a high molality, there is insufficient water to satisfy the hydration needs of the individual ions, and the basic assumptions of the Debye−Hückel based electrostatic models become invalid. Stokes and Robinson[1] reasoned that highly concentrated aqueous salt solutions might be treated as a somewhat irregular ionic lattice in which water is distributed in a manner such that some ions have multiple layers of water, some have complete or incomplete hydration shells, and some have unbound or "free" water molecules. Hence, some adsorption sites have multilayer adsorption and some have monolayer adsorption, while others are vacant. A highly concentrated aqueous solution will have more vacant and monolayer sites and fewer sites with multilayer adsorption because of low water content than solutions that are dilute. Imagine a "string" arbitrarily run through seven random sites in this irregular lattice as shown in Figure 1. Those seven sites along with their arbitrarily assigned 13 adsorbed water particles are shown separately to the right in Figure 1. The dashed horizontal line demarcates water particles in monolayer adsorption from those in multilayer adsorption. This arrangement is not unique. Instead, these same seven adsorption sites with 13 adsorbed water particles could have many different distributions of which only *three* possible distributions are shown in Figure 2. How many possible distributions can there be for the 13 particles, nine of which are "free" (i.e., unbound) and four are adsorbed as monolayers (bound) among seven available sites? All water particles are considered indistinguishable, and so are the salt sites. In other words, there are no preferred adsorption sites. Under these circumstances, the total number of distinguishable arrangements are $(9 + 3)!/9!3! = 220$, of which only three possible distributions are shown in Figure 2. In an aqueous electrolyte, the numbers of adsorption sites, particles in monolayer adsorption, and those of "free" (unbound) water are of the order of Avogadro's number, and therefore, the number of arrangements are very, very large but nonetheless may be computed as in the simpler example described above.

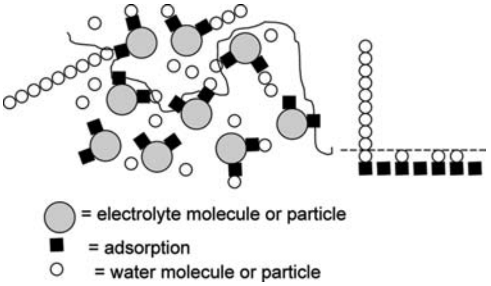

Figure 1. Irregular ionic lattice model of concentrated aqueous electrolytes with monolayer and multilayer adsorption.

If the number of electrolyte (undissociated salt, for example) particles are designated by s, with r sites per particle, then the total number of available sites for adsorption are (rs). Let the total number of water particles in the aqueous electrolyte solution be designated by h, of which x particles partake in monolayer adsorption. Then, the free or unbound water particles are $(h - x)$ and the number of vacant sites where no adsorption occurs is given by $(rs - x)$. Under this scenario, the total number of distinguishable arrangements of (x) bound water particles on (rs) available sites are

$$\Omega_{\text{monolayer}} = \frac{(rs)(rs-1)(rs-2)(rs-3)..........(rs-x+1)}{x!}$$

$$= \frac{(rs)!}{(x!)(rs-x)!} \tag{6}$$

and the total number of distinguishable arrangements of the $(h - x)$ "free" water particles on x bound (monolayer) occupied sites is given by

$$\Omega_{\text{multilayer}} = \frac{[h - x + (x-1)]!}{(h-x)!\,(x-1)!} = \frac{(h-1)!}{(h-x)!\,(x-1)!}$$

which reduces to

$$\Omega_{\text{multilayer}} = \frac{(h)!}{(h-x)!\,(x)!} \tag{7}$$

because h and $x \gg 1$.

The combinatorial statistics of multilayer adsorption of water molecules on solute sites is given by

$$\Omega = \Omega_{\text{monolayer}} \cdot \Omega_{\text{multilayer}} = \frac{(rs)!}{(x)!\,(rs-x)!} \cdot \frac{h!}{(h-x)!\,(x)!} \tag{8}$$

The entropy of the mixture of solute and water may be written as

$$S = k \ln \Omega = k \ln \frac{(rs)!}{(x)!\,(rs-x)!} \cdot \frac{(h)!}{(h-x)!\,x!} \tag{9}$$

The energy accompanying adsorption is

$$U = x\varepsilon \tag{10}$$

where $\varepsilon = (U - U_l)$; U is the (negative) internal energy of monolayer adsorption of water on to the salt; and U_l is the (negative) internal energy of liquefaction of pure water. Since U and U_1 are negative and $|U| > |U_1|$, ε is negative for monolayer adsorption and abruptly becomes zero for adsorption of water beyond the first layer, further emphasizing that the diminishing adsorption energy with additional layers of water beyond the first is ignored. Thus, the model described here is a two-state model, with water molecules either on a salt sorption site ("bound"; first layer) or in contact with other water molecules only ("free", second layer and beyond). The excess internal energy of a "bound" water molecule relative to the internal energy of a "free" molecule is denoted by ε. Before adsorption occurs, all the water (h particles) is present as pure liquid. Similarly, all the salt particles are considered present as a molten mass (hypothetical state). The standard states are pure liquid water and molten salt, the latter clearly being a hypothetical state unrealizable in practice under ordinary conditions. The internal energies of the two (water and molten salt) standard states are arbitrarily assigned a value of zero, and eq 10 only considers the change in internal energy occurring on account of monolayer adsorption. The differences in internal energy and enthalpy are also considered negligible for the condensed phases. Maximizing the entropy of the system given by eq 9 under the energy constraint specified by eq 10 is carried out in the usual manner[1,4,6] to ultimately yield (after extensive algebra) the most probable distribution of the "bound" and "free" water as

$$\frac{x^2}{(rs-x)(h-x)} = e^{-\varepsilon/kT} \tag{11}$$

with water and electrolyte activities a_w and a_s given by

$$a_w = \frac{(h-x)}{h} \tag{12}$$

$$a_s = \left(\frac{rs-x}{rs}\right)^r \tag{13}$$

In eqs 12 and 13, we see a simple interpretation of the water activity as the ratio of the "free" water to the total water and of the salt activity as a function of the ratio of the number of sites on which multilayer adsorption occurs to the total number of available sites offered by the salt.

Solving eqs 11 and 12 simultaneously, with rearrangement and some algebraic manipulation yields the expression for the BET adsorption isotherm

$$\frac{ma_w}{55.51(1-a_w)} = \frac{1}{rc} + \frac{(c-1)}{rc}a_w \tag{14}$$

where eq 14 is the same as eq 5 if $\alpha = r$.

Similarly, solving eqs 11 and 13 with rearrangement and manipulation yields the expression for the BET adsorption isotherm in terms of the salt activity a_s and mole fraction x_s of solute[1]

$$\frac{55.51\lambda}{m(1-\lambda)} = \frac{\lambda(1-x_s)}{x_s(1-\lambda)} = \frac{r}{c} + \frac{r(c-1)}{c} \tag{15}$$

where $\lambda = a_s^{(1/r)}$.

Equations 14 and 15 embody the BET-type adsorption isotherms for the solvent (water) and solute (salt).

Mixed Electrolytes

When applying eqs 14 and 15 to mixed electrolyte solutions, the BET parameters r and ε pertain to the specific proportion of mixed electrolytes used in the aqueous solution under investigation.[7] Another aqueous solution of the same molality and containing the same salts, but in different proportions, will yield a different set of the BET parameters. Realizing that in practical applications there may be a need to obtain water activity data for mixed electrolytes not yet studied experimentally, Ally and Braunstein[8] generalized the additivity rules proposed by Sangster[9] and Abraham[1] for two-salt mixtures with a common ion and tested it for two- and three-salt mixtures with a common ion. The r and ε parameters for mixed salts are related empirically to their pure component parameters by

$$r_m = \sum r_i x_i \tag{16}$$

where i represents each salt component in the mixed salt; r_m is the parameter for the mixed salt; r_i is the parameter r for salt component i in the mixed salt (not the same as the mole fraction of salt component i in solution). The mixing rule to evaluate the parameter ε for mixed salts is

$$\varepsilon_m = \sum x_i(r_i\varepsilon_i)/r_m \tag{17}$$

Both r_m and ε_m retain the same physical significance as their parent terms r and ε, respectively. When applying eq 15 to a salt mixture, it should be noted that the value of the salt activity obtained from it represents some averaged value for the mixed salts and that the nature of the averaging remains unknown. Subsequently, Ally and Braunstein[4] showed that explicit analytical expressions for the activities of individual species in a mixed electrolyte system can be developed from the statistical mechanical viewpoint, thus showing that there is no fundamental restriction of this treatment or the interpretation of the species activity to multiple-electrolyte systems. The major hurdle in the statistical mechanical treatment of multiple electrolytes is the complexity of the expression for the most probable configuration and the degree of algebra that is involved.

Electrolyte Activity Coefficients from the BET Model

For comparisons of the electrolyte activity coefficients based on the BET model against experimental data, it is essential to take into consideration the differences in standard states. In the

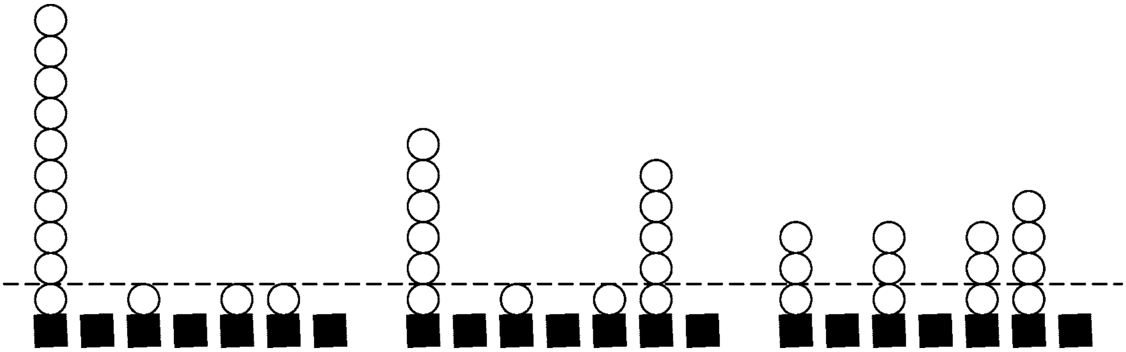

Figure 2. Three of several possible distributions of 13 water particles on seven discrete adsorption sites.

dilute solution, the reference state is an infinitely dilute solution of the electrolyte in water so that the standard states are pure liquid water and, for the electrolyte, the hypothetical ideal solution of the electrolyte at unit molality. In the BET model, however, the reference state is the pure anhydrous liquid (hypothetical) electrolyte. For the component water, the standard state is pure liquid water, as for dilute solutions, so there is no difficulty in comparing water activities or the water activity coefficients. For the electrolyte component, however, comparison of activity coefficients requires a knowledge of the hypothetical free energy of transfer of electrolyte from anhydrous liquid electrolyte (molten salt:hypothetical) to the hypothetical ideal solution at unit activity. Ideally, the required experimental data would be activity measurements over the complete range of concentrations between pure water and pure molten salt, but such data are difficult to come by. Ally and Braunstein[10] developed a method to overcome this difficulty. The procedure adopted was to designate a range of concentrations (arbitrarily between molalities of (6 and 10) mol·kg^{-1}) where the BET model would reasonably apply. By comparing the mean ionic activity coefficients calculated from the BET model and from experimental data at any one molality between (6 and 10) mol·kg^{-1}, the proportionality factor between the activity coefficients on the two scales can be determined over the entire concentration range (except at the two extremes of nearly pure water and nearly pure electrolyte) from which the predictions at different molalities can be made to check against experimental data.

The chemical potential, μ_s^{BET} of the electrolyte (solute) in the BET model at mole fraction x_s and temperature T may be written as

$$\mu_s^{BET}(x_s, T) = \mu_s^{*,liq}(x_s = 1, T) + RT \ln \frac{a_s(x_s, T)}{a_s^{*,liq}(x_s = 1, T)} \tag{18}$$

where, $\mu_s^{*,liq}$ is the chemical potential of solute in the hypothetical pure liquid standard state at the same temperature. The solute mole fraction x_s is defined on an undissociated electrolyte basis with a_s and $a_s^{*,liq} = 1$, the solute activities at mole fraction x_s, and in the standard state (hypothetical), respectively. For experimental data on the molality scale, the chemical potential of the solute at molality m is given by

$$\mu_s(m, T) = \mu_s^{\oplus}(m^{\oplus}, T) + RT \ln(\gamma_{\pm})^{\nu} + RT \ln(\nu_+^{\nu+}\nu_-^{\nu-})m^{\nu} \tag{19}$$

where $\mu_s(m,T)$ is the chemical potential of solute at molality m and $\mu^{\oplus}(m^{\oplus},T)$ is the chemical potential of solute in the standard state (hypothetical ideal solution at $m = 1$ mol·kg^{-1}; $\gamma_{\pm}$ is the usual mean ionic activity coefficient; m is the mean ionic molality of solute ($m = m_{\pm}$); and $\nu = \nu_+ + \nu_-$ is the number of moles of ions per mole of salt. Since the chemical potential of solute at any given concentration must be independent of the standard states, equating eqs 18 and 19 and rearranging gives an expression (defined as Φ) that is a measure of the difference in the chemical potentials of the respective standard states. Note that Φ is not to be confused with osmotic coefficient.

$$\Phi \equiv \left[\frac{\mu_s^{\oplus}(m^{\oplus}, T) - \mu_s^{*,liq}(x_s = 1, T)}{RT}\right] = \frac{a_s(x_s, T)}{(Qm\gamma_{\pm})^{\nu}} \tag{20}$$

where $Q = (\nu_+^{\nu+}\nu_-^{\nu-})^{1/\nu}$.

The technique of calculating Φ is discussed extensively by Ally and Braunstein[10] and tested against experimental data for NaOH, HCl, KOH, $CaCl_2$, and Ca $(NO_3)_2$. Comparisons of experimental mean ionic activity coefficients of $CaCl_2$, LiBr, LiCl, HCl, NaOH and KOH with those predicted by the BET model have also been shown[10,11] to be in very good agreement over the range of validity of the BET model. Here it suffices to mention that the measure of the validity of the BET model is indicated by the constancy of Φ over the concentration range in question as shown in Figure 3. A discussion on mean ionic activity coefficients calculated from the BET model by selecting different molalities, m for the reference state are discussed in detail elsewhere.[10]

Excess and Molar Properties of Concentrated Aqueous Electrolytes

Recognizing the simplicity of the BET model and the fact that closed form equations for the water and electrolyte activities may be obtained from the statistical mechanical viewpoint, Ally and Braunstein[8] applied the general relationships of thermodynamics to show how partial molar excess volumes, partial molar excess enthalpies, the molar volume, and integral enthalpies of solution may be obtained for multicomponent salt mixtures and solid−liquid equilibria in single salt solutions. Further evidence of the viability of this theory was independently confirmed by Abraham who successfully applied it to nitrate + water systems from fused salts to dilute solution[12] and to explain properties of bridging electrolyte solutions.[13] The equations describing the partial molar, excess, and integral properties are too extensive to present here, but the usefulness of the technique for predicting the liquidus curve, eutectics, and metastable phases is presented briefly for which the equations for the partial molar excess enthalpies are needed and shall be presented in closed form.

Liquidus Curves

The differential equation governing solid−liquid equilibria developed from first principles in an earlier paper[8] given as

$$R \ln a_s a_w^j = [-L_{SH_j}(T) + \bar{H}_s^E(T_j) + \bar{H}_w^E(T_j)]d(1/T) \tag{21}$$

is exact at the melting temperature of the particular hydrate. $\bar{H}_w^E$ and $\bar{H}_s^E$ are the partial molar excess enthalpies of water and of salt, respectively, as defined by eqs 22 and 23. Water and solute activities are denoted by a_w and by a_s, respectively. The notation for the jth solid hydrate of a salt S is S·jH$_2$O with j = 0,1,2,3,... for the zeroth hydrate (anhydrous salt) or $j > 0$ for successive hydrates. Fractional hydrates are represented by fractional values of j (j = 1/2, 7/2, 1/3,..., etc.).[8] For eq 21 to be exact over the entire temperature range in the integration, it

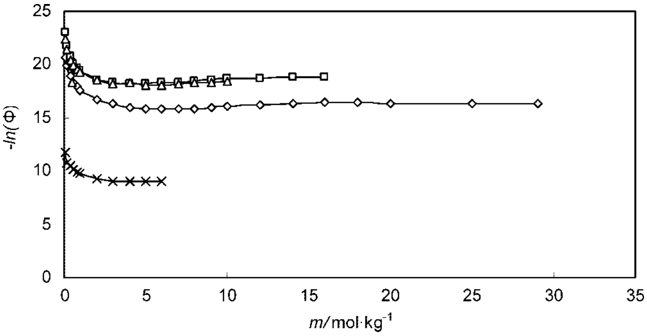

Figure 3. Constancy in the difference of chemical potentials at the two discrete standard states, represented as $-\ln \Phi = \ln[\mu_s^{\oplus}(m^{\oplus},T) - \mu_s^{*,liq}\cdot(x_s = 1,T)]/(RT)$, is a measure of the applicability of the BET model over molalities m greater than about 5 mol·kg^{-1}. ◇, NaOH; □,HCl; Δ, $CaCl_2$;x, Ca$(NO_3)_2$.

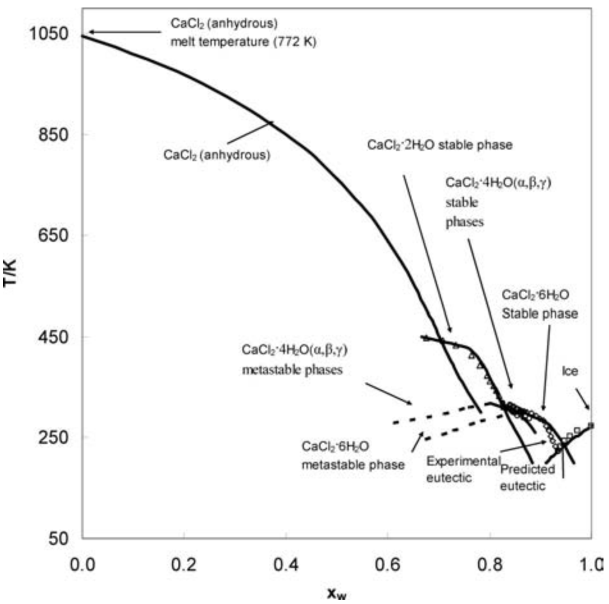

Figure 4. Some crystalline phases in the $CaCl_2 + H_2O$ system as a function of the mole fraction of water, x_w: −, prediction of stable phases from the BET model; - - -, prediction of metastable phases from the BET model. Symbols represent experimental data. Redrawn from ref 15.

would be necessary to incorporate the temperature dependence of the heat of fusion, via the heat capacities. Since the variation in enthalpy of fusion with temperature is not well-known, they are omitted with nominal loss of accuracy over the limited temperature range over which the hydrate exists (in the stable or in the metastable form). The partial molar excess enthalpy terms required in eq 21 were originally derived by Ally and Braunstein.[8] The partial molar excess enthalpy of water relative to pure liquid water as the standard state is

$$\bar{H}_w^E = \frac{-c\varepsilon(1 - rs - a_w)}{c(1 - rs) - 2a_w(c - 1) - 2} \tag{22}$$

The partial molar excess enthalpy of the undissociated salt relative to anhydrous liquid salt (hypothetical) as the standard state is

$$\bar{H}_S^E = \frac{-c\varepsilon r[rs(\lambda - 1) + 1]}{[rs(c - 2) + 2rs(1 - c) - c]} \tag{23}$$

Integrating eq 21 between the limits T_j, x_j, and T, x (the liquidus points) gives[8]

$$R \ln a_S(T, x_w)a_w^j(T, x_w) - R \ln a_S(T_j, x_j)a_w^j(T_j, x_j) = [L_{SH_j} - \bar{H}_S^E(T_j, x_j) - j\bar{H}_w^E(T_j, x_j)][T_j^{-1} - T^{-1}] \tag{24}$$

where L_{SH_j} is the enthalpy of fusion of the jth hydrate at its melting temperature T_j and $\bar{H}_w^E$ and $\bar{H}_S^E$ are the partial molar excess enthalpies of water and of solute in the hydrate melt, to be evaluated from eqs 22 and 23, respectively. Examination of eqs 22 and 23 shows that the adsorption theory of electrolytes quantifies the excess enthalpy terms in terms of palpable variables, *r*, *c*, and *s*, which have a clear physical meaning.

The methodology of using eq 24 in conjunction with eqs 14, 15, and 22 are described in detail[8] and used extensively to predict the liquidus curve for $NaNO_3$,[14] of $CaCl_2$,[15] $LiNO_3$(aq),[16] NH_4NO_3(aq),[17] and calculation of liquidus temperatures of common-ion binary salt hydrate mixtures.[18,19] Figure 4 shows the phase diagram of the binary $CaCl_2 + H_2O$ system including the eutectic point and stable and metastable phases from the melting point of ice to the melting point of pure anhydrous $CaCl_2$ exemplifying the capability of this two-parameter model.

Discussion

Application of the general properties of solutions to extensions of the Stokes−Robinson applications of the BET adsorption isotherm has led to a comprehensive treatment of moderately to highly concentrated (up to molten salt regime) aqueous electrolytes with as few as two parameters. Multicomponent aqueous solutions may be treated as a pseudobinary if desired, by invoking the proposed mixing rules. If the configurational entropy of multicomponent electrolytes can be constructed, then in principle the activities of individual species can be obtained in closed-form expression, obviating the need for treating such a system as a pseudobinary. The statistical mechanical approach has enabled extensions of the original approach of Stokes and Robinson in ways that were not fully anticipated about a decade ago. The real advantage of the method lies in the use of a minimal number of parameters to represent a wide variety of thermodynamic properties with reasonable accuracy over relatively wide temperature and composition ranges. Of special use is the ability to predict properties of solutions for which no data exist (especially at high concentrations and temperatures). Among other applications, this model has been used to calculate the thermodynamic activities and osmotic coefficients of supersaturated solutions of $(NH_4)_2SO_4$(aq) and NaCl(aq) which are among manmade aerosols of atmospheric importance.[20] The range of concentrations, temperatures, and salt species for which this two-parameter model can provide an adequate description testifies for its viability and breadth of applications.

Future Research

Extension of the ionic lattice theory by the statistical mechanical approach paves the way for examining, explaining, predicting, and extending the information on the properties of multicomponent concentrated aqueous electrolytes with sparse data. It has been shown that there is no fundamental restriction in the number of solutes and solvents that may be considered in the statistical mechanical approach, if the degree of algebra can be tolerated. The present state of development allows treatment of electrolytes with common anions or common cations but does not yet include reciprocal salt mixtures. The framework for a unified theory of adsorption has been laid down by the statistical mechanical approach. Since the Langmuir adsorption (monolayer) isotherm is a subset of the BET adsorption (multilayer), the approach described here may potentially provide a common theoretical framework of other types of adsorption (Freundlich, Tempkin) as well as providing a common approach to the theory of adsorption and concentrated aqueous electrolytes.

Acknowledgment

My correspondence with Prof. Stokes dates back to 1995, following publication of the first comprehensive paper with Jerry Braunstein in 1993.[8] In numerous subsequent correspondences, Prof. Stokes' critique inspired me to expand the scope of the irregular ionic lattice theory beyond what seemed to be possible earlier. Despite the excruciating algebra, the veracity of our results[4] through satisfaction of the Gibbs−Dühem consistency criteria seemed rather elegant to Prof. Stokes. His questions on the standard states were the driving force behind the paper published in Fluid Phase Equilibria[10] on activity coefficients calculated from the BET model, explored in Figure 3 in this paper. An important conclusion that I drew from our mutual correspondence is to maintain a healthy dose of

skepticism and let the facts dictate where the theory goes. I also admired the way in which Prof. Stokes characterized his personal contribution to the theory published in 1948. In an e-mail in 2004, he wrote, “I must say I am pleased by the way this 50-year-old idea (mainly Robinson’s in fact, my contribution in that 1948 paper being mainly the combination of D−H theory and hydration) has continued to attract interest”. In the same spirit, I also recognize Jerry Braunstein’s contribution and his patience to work alongside with me. My contact with Prof. Stokes was initiated and facilitated by Prof. Kenneth Marsh sometime in 1994, and his invitation to me to contribute an article in celebration of Prof. Stokes’ 90th birthday is especially meaningful. Prof. Stokes’ contribution to thermodynamics more than 50 years ago had a significant impact on my career. I thank Dr. Abdi Zaltash and Dr. Dave DePaoli and Mr. Bill Craddick from Oak Ridge National Laboratory for reviewing the manuscript and Prof. Kenneth Marsh for offering suggestions to improve on it.

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