UC Davis
UC Davis Previously Published Works

Title

Raoult Was Right After All

Permalink

https://escholarship.org/uc/item/9rf0d182

Journal

ACS Omega, 4(7)

ISSN

2470-1343

Author

Wexler, Anthony S

Publication Date

2019-07-31

DOI

10.1021/acsomega.9b01707

Peer reviewed

Raoult Was Right After All

Anthony S. Wexler*

Air Quality Research Center and Departments of Mechanical and Aerospace Engineering, Civil and Environmental Engineering and Land, Air and Water Resources, University of California, Davis, California 95616, United States

ABSTRACT: Raoult's law, published in 1887, is taught in chemistry and chemical engineering fields as a first approximation to the vapor pressure and activity of solutes and solvents in mixtures. In ideal solutions, it is exact but many solutions are known to have substantial deviations from Raoult's law as conventionally interpreted. In 1908, Callendar showed that water hydrated to the solute can explain some of the departures from Raoult's law in aqueous solution. Here, we show that by simply assuming equilibria between the free water in solution and its hydrated forms, Raoult's law and Callendar's extension are valid over the full range of concentrations, while also showing how water and solutes interact in solution. This model of solutions has importance in highly concentrated solutions common in atmosphere aerosols relevant to climate change and air quality, and in numerous industrial processes.
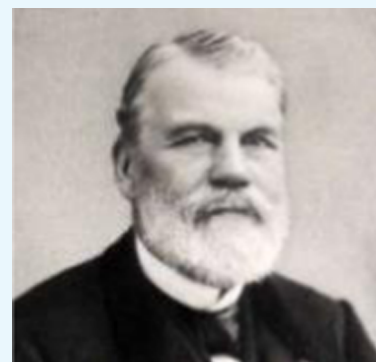
INTRODUCTION

Highly concentrated solutions occur in a wide range of industrial and natural processes including brines, carbon capture, atmospheric aerosols, and food drying. These solutions are typically labeled as exhibiting nonideal behavior because the vapor pressures of the solute and solvent and their corresponding activities in solution are not proportional to their mole fraction. Raoult first proposed this linear mole fraction−vapor pressure relationship in 1887[5] and Raoult's law has become a paradigm in chemistry and chemical engineering. For dilute solutions, this relation holds but deviations grow as the solution becomes more concentrated. In 1908, Callendar[6] explained some of the deviations from Raoult's model by positing that in aqueous solutions, solute molecules are hydrated such that some of the water is bound to the solute, so it does not contribute to the vapor pressure. That is, only the so-called "free water" contributes to the vapor pressure. This paradigm extended the validity of Raoult's law to higher concentrations but it still failed at yet higher concentrations. In 1973, Stokes and Robinson[7] extended this paradigm further by assuming that for electrolytes there is an equilibrium between the free and bound water and a power law relationship between the equilibrium constants. As the concentration of the solution increases, the water activity decreases and some of the bound water falls off the solute and becomes free water.

Starting in 2011, we published a series of papers that used statistical mechanical techniques to describe solutions over the full range from the infinitely dilute limit to the pure solute limit.[8−10] These models were successful at describing solutions of organics and electrolytes in water by assuming that one water was bound to the solute or ion, the next water bound to that water, and so on. Although a huge step forward, this model has a shortcoming of not necessarily capturing hydration the way we understand it. From the prior work of Callendar,[6] Stokes and Robinson,[7] and many others, we know

that multiple waters can bind to solute molecules. They may also bind to each other in a secondary layer, but the single stacked water model of Dutcher and colleagues does not capture what is known from the physics and chemistry of these solutions. For instance, raffinose is thought to have a hydration number (the average number of water molecules bound to the solute molecule in dilute solutions) in excess of 10 but we do not expect 10 waters to be stacked on top of each other to hydrate raffinose.

RESULTS AND DISCUSSION

Here, we apply two assumptions to derive equations that describe the "nonideality" of solutions to show that they are actually ideal and fit Raoult's law:

Assumption 1: Raoult's law applies rigorously. That is, the ratio of partial pressure to vapor pressure, the activity of all constituents, a_i, be they pure solute, hydrated solute, or free water, is simply their mole fraction given by

$$a_i = \frac{\text{moles of } i}{\text{total moles of all distinct constituents}} = \frac{n_i}{n_t} \quad (1)$$

where n_i is the number of moles of constituent i in solution and n_t is the total number of moles of all of the constituents in solution. These constituents consist of free water, bare solute, and hydrated solute.

Assumption 2: Each solute may be hydrated and this hydration is governed by the following equilibria

$$a_{i1w} = K_{i1w} a_w a_i \quad (2.1)$$

$$a_{i2w} = K_{i2w} a_w a_{i1w} \quad (2.2)$$

$$a_{i3w} = K_{i3w} a_w a_{i2w} \qquad (2.3)$$

...

$$a_{ijw} = K_{ijw} a_w a_{i(j-1)w} \qquad (2.4)$$

where a_w is the activity of water, a_{ijw} is the activity of solute i hydrated with j water molecules, and K_{ijw} is the equilibrium constant between the solute hydrated with j water molecules and $(j - 1)$ water molecules. All activities are given by eq 1. We will now use eqs 1 and 2.1–2.4 to calculate the water associated with each solute.

First, we multiply all of these equilibria in eqs 2.1–2.4 by each other, so that the activities of the hydrated solutes cancel, except for the most hydrated solute, giving

$$a_{ijw} = a_i a_w^j \prod_{q=1}^{j} K_{iqw} \qquad (3)$$

Multiply both sides by n_t and applying eq 1, we obtain the number moles of each hydrated solute in terms of the number of moles of free solute, water activity, and the equilibrium constants

$$n_{ijw} = n_i a_w^j \prod_{q=1}^{j} K_{iqw} \qquad (4)$$

where the number of moles of each constituent, n_{ijw}, contains one mole of solute i and j moles of water.

By adding all of these together plus the number of moles of bare solute, we obtain the total number of moles of solute i in solution

$$n_{iT} = n_i \left(1 + \sum_{j} a_w^j \prod_{q=1}^{j} K_{iqw} \right) = n_i S_i(a_w) \qquad (5)$$

where S_i is the total number of moles of solute i per mole of unhydrated solute i and is only a function of water activity. Similarly, the total amount of water hydrated to solute i is given by

$$n_{iwT} = n_i \sum_{j} j a_w^j \prod_{q=1}^{j} K_{iqw} = n_i W_i(a_w) \qquad (6)$$

where W_i is the total number of moles of water hydrated to solute i per mole of bare solute i and like S_i is only a function of water activity. Dividing eq 6 by eq 5 gives the hydration number as a function of water activity

$$H_i(a_w) = \frac{n_{iwT}}{n_{iT}} = \frac{W_i(a_w)}{S_i(a_w)} \qquad (7)$$

That is, $H_i(a_w)$ is the total number of water molecules hydrated to all of the hydrated forms of solute i per total number of moles of solute i. The hydration number defined by Callendar (1908) is the value of H_i at the limit of infinite dilution, $H_i(a_w = 1)$. Marcus[11] used isothermal compressibility to deduce how hydration number depends on concentration fitting a linear curve through his data.

Equation 7 is the number of bound water molecules per solute molecule. We also need to know the number of free waters in solution. Starting with the definition of water activity from eq 1

$$a_w = \frac{n_w}{n_t} = \frac{n_w}{n_w + \sum_i n_{iT}} \qquad (8)$$

where $\sum_i n_{iT}$ is the total number of all solutes in solution regardless of their hydration state. Remember that n_t is the total number of moles of free water, free solute, and hydrated solute in solution. Solving eq 8 for the number of moles of free water gives

$$n_w = \frac{a_w}{1 - a_w} \sum_i n_{iT} \qquad (9)$$

The term $a_w/(1 - a_w)$ appears in other derivations of the thermodynamics of solutions, such as that by Dutcher and co-workers.[8–10] Here, we see that it represents the number of moles of free water per mole of solute.

Now, we have the tools that we need to derive the relationship between molality and water activity. The simplest case is an aqueous solution containing a single solute A that does not dissociate or associate. Many alcohols and sugars fit this description. The total amount of water, n_{wTot}, in a solution containing solute A, its hydrated forms, and free water is

$$n_{wTot} = n_w + n_{AwT} \qquad (10)$$

Combining this with eqs 7 and 9 gives

$$n_{wTot} = \frac{a_w}{1 - a_w} n_{AT} + H_A(a_w) n_{AT} \qquad (11)$$

Noting that the molality of solute in solution is given by $M_w m = n_{AT}/n_{wTot}$, where M_w is the molar mass of water, yields an equation for the molality as a function of water activity

$$m_A = \frac{1/M_w}{\frac{a_w}{1 - a_w} + H_A(a_w)} \qquad (12)$$

The denominator is the amount of free water per total solute plus the amount of water bound in hydrates per total solute. The solute activity is obtained by taking the total number of constituents in solution

$$n_w + n_{AT} = n_t \qquad (13)$$

Dividing both sides by n_t and combining with eq 5 to obtain

$$a_A = \frac{1 - a_w}{S_A(a_w)} \qquad (14)$$

which can also be obtained using the Gibbs–Duhem equation, eq 12, and noting that $W_A = a_w dS_A/da_w$.

The values of the equilibrium constants, K_{iqw}, govern the performance of eqs 12 and 14 via the functions $H_A(a_w)$ and $S_A(a_w)$. For each water hydrated to each solute, there is a K_{iqw} so that say for raffinose that has a hydration number of about 12, at least 12 K_{iqw} values are needed. For organic solutes, we expect that roughly one water molecule will hydrogen bond to each of the OH moieties and that the equilibrium constant will be roughly the same for each hydrogen bond. As a result, the K_{iqw} values should be roughly the same until q (the number of hydrated waters) reaches a value, where all of the bonding locations are taken, then it should precipitously drop in value to zero. The logistic function neatly captures this behavior

$$K_{iqw} = \frac{K_{iw}^x}{1 + \exp(q - q_0)/\Delta q} \qquad (15)$$

where K_{iw}^x is the equilibrium constant for each water hydrogen bonded to the solute, q_0 is the number of bound waters where the value of K_{iqw} is half K_{iw}^x, and Δq governs how rapidly K_{iqw} drops to zero as q increases. Since we expect the value of K_{iqw} to drop precipitously to zero when q becomes larger than the number of hydrogen bonding sites, q_0, we set $\Delta q = 0.1$, an arbitrary but small value. We now have only two fit parameters, K_{iw}^x and q_0, instead of the 12 or more equilibrium constants needed for say raffinose. Figure 1 shows the fit for raffinose.
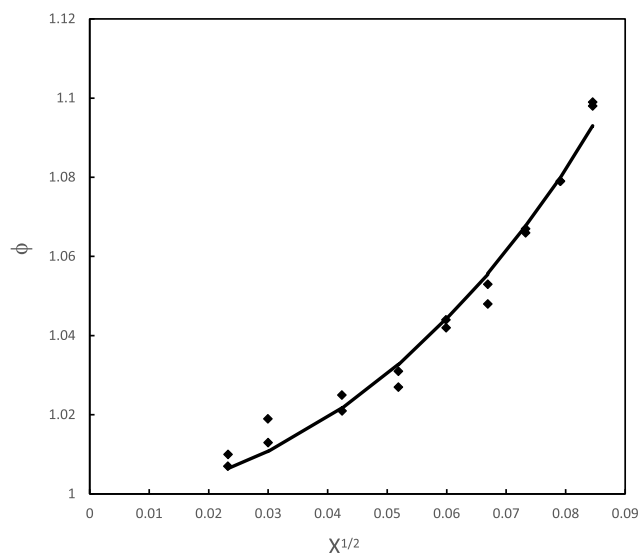

Figure 1. Osmotic coefficient as a function of solute mole fraction for raffinose in water. Freezing point depression data from ref 2. K_{iw}^x was fixed at 2, the fit value for q_0 is 13.8, and the resulting hydration number is 12.3.

For this and subsequent solutes, osmotic coefficient defined as $\varphi = -\ln(a_w)/(M_w m)$ is displayed on the y-axis because it is a very sensitive indicator of deviations between activity data and fits to these data. The square root of the solute mole fraction is displayed on the x-axis to better show the behavior at low concentration, which is not relevant for raffinose but is for other more-soluble solutes.

Due to scatter in the raffinose data, many combinations of K_{iw}^x and q_0 fit the data well, so here we picked $K_{iw}^x = 2$ and just fit q_0. For glycerol and NaCl, the values were simple fits to the data. The fits minimized the sum of the squared error in osmotic coefficient between the model and the data.

Figure 2a shows the fit for glycerol that is miscible in water, so data exist for the full range of solute mole fractions. For both raffinose and glycerol, the hydration number deduced from these fits agrees well with the values reported in the literature. Figure 2b shows the change in hydration as a function of water activity for glycerol. The corresponding figure for raffinose and NaCl is not shown because the change over the water activity range is extremely small.

For two or more solutes in solutions A and B, what kind of mixing rule applies? The total amount of water in solution is now

$$n_{wTot} = n_w + n_{AwT} + n_{BwT}$$

$$= \left(\frac{a_w}{1 - a_w} + H_A\right)n_{AT} + \left(\frac{a_w}{1 - a_w} + H_B\right)n_{BT} \quad (16)$$

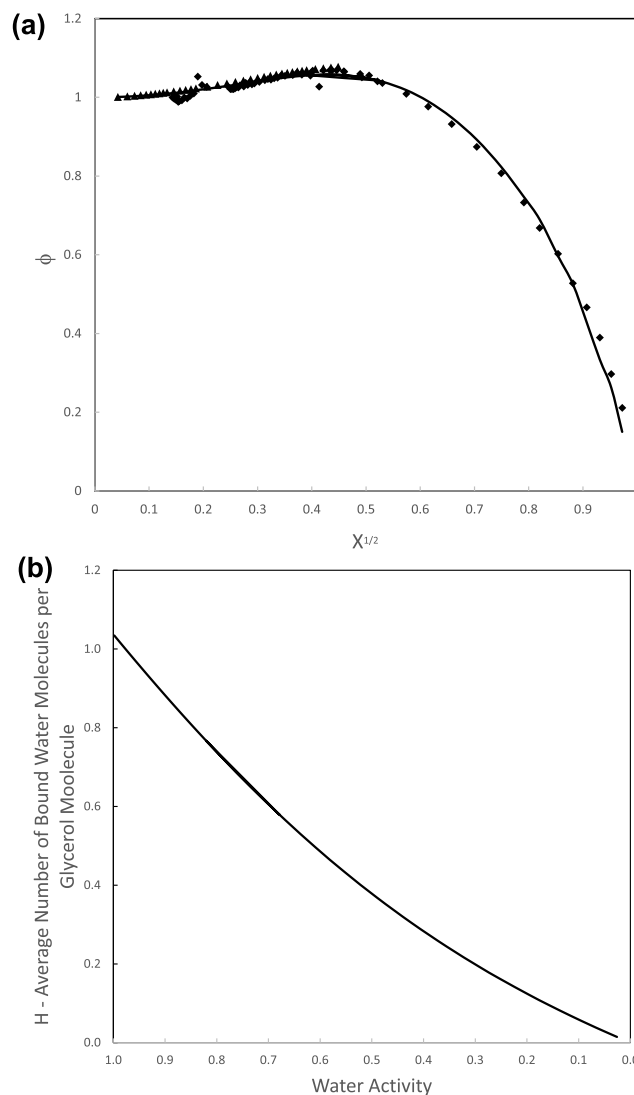Dividing both sides by n_{wTot} and rearranging gives

Figure 2. (a) Osmotic coefficient as a function of solute mole fraction for glycerol in water. Data from triangle,[3] diamond.[4] Parameter values are $K_{iw}^x = 0.553$ and $q_0 = 5.1$; the resulting hydration number is 1.0. (b) Predicted hydration as a function of water activity for glycerol using the same parameters as in (a).

$$\frac{m_A}{\left[\dfrac{1/M_w}{\frac{a_w}{1-a_w} + H_A(a_w)}\right]} + \frac{m_B}{\left[\dfrac{1/M_w}{\frac{a_w}{1-a_w} + H_B(a_w)}\right]} = 1 \quad (17)$$

Comparing this to eq 12, we see that the square-bracketed quantities in the denominator are simply the single-solute molalities; that is, the numerator in each term is the molality in the solution mixture, whereas the denominator is the molality in the single-solute solution. This is the ZSR mixing rule posited independently by Zdanovski[12] and Stokes and Robinson,[13] which has been shown to be valid for a wide range of solutes that do not associate in solution. It also shows the role that free water $a_w/(1 - a_w)$ and hydrated water H_A play. In the work of Dutcher and colleagues,[9] free water was assumed to be associated with each solute. Here, we obtain the same result without assumption.

Electrolytes can be thought of as multicomponent solutions, wherein the salt dissociates into its ionic components and each of these ions comprises a solute in solution. In contrast to

mixtures of nonionic solutes, the ions project their electrostatic fields beyond the vicinity of the ion altering the thermodynamics of the solution. This effect was first recognized by Debye and Hückel in 1923.[14,15] Pitzer[16] evaluated a number of forms for representing these long range forces and found that it is well represented by

$$K_w^{DH} = \exp\left(-\frac{2A_x I^{3/2}}{1 + \rho I^{1/2}}\right)$$

(18)

where I is the ionic strength, $A_x = 2.917$ at 298 K and ρ is a fit parameter related to the ion size and charge. The factor K_w^{DH} modifies the water activity in the equations derived here. Employing the stoichiometry of the electrolyte, the equations derived above and this Debye−Huckel term yield an expression for the molality as a function of water activity for electrolytes

$$m = \frac{1/M_w}{\nu_A\left(\frac{K_w^{DH} a_w}{1 - K_w^{DH} a_w} + H_A(K_w^{DH} a_w)\right) + \nu_B\left(\frac{K_w^{DH} a_w}{1 - K_w^{DH} a_w} + H_B(K_w^{DH} a_w)\right)}$$

(19)

where ν_A and ν_B are the number of cations and anions in the electrolyte, respectively, assuming that the electrolyte is only comprised of one type of cation and one type of anion. More complex electrolytes are an easy extension. Figure 3 shows the fit for NaCl to saturation.

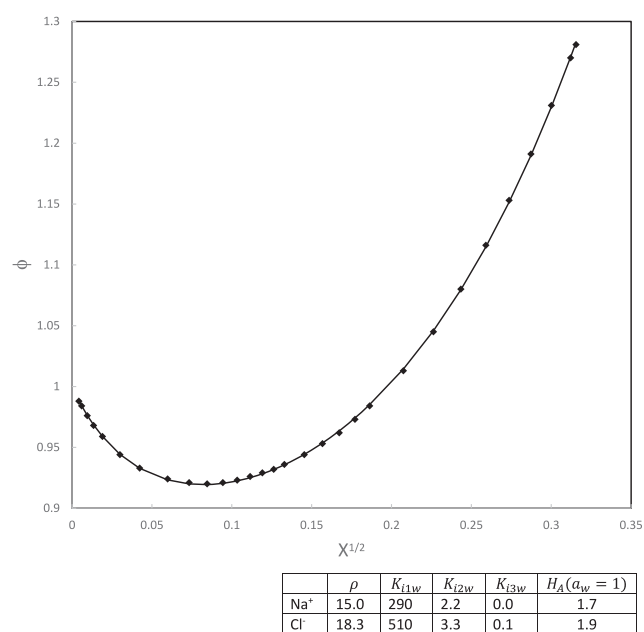|	ρ	K_{i1w}	K_{i2w}	K_{i3w}	$H_A(a_w = 1)$
Na$^+$	15.0	290	2.2	0.0	1.7
Cl$^-$	18.3	510	3.3	0.1	1.9

Figure 3. Osmotic coefficient as a function of solute mole fraction for sodium chloride in water. Data from ref 1. Parameter values are given in the table.

CONCLUSIONS

In summary, the theory presented here shows that Raoult's original idea, that the activity of solutes in solution is proportional to the mole fraction, needs no correction if we consider the hydrated forms of the solute in solution as Callendar suggested and employ simple equilibria between the hydrated forms.

Most models of solutes in solution use one of the forms derived by Pitzer[17] because they accurately model the molality−activity relationship over a wide range of conditions. For instance, the Clegg and Pitzer formulation is employed by E-AIM, our popular model of aerosol thermodynamics that performs about 100 000 calculations annually for scientists worldwide working in the fields of air pollution and climate change. The shortcoming of the Pitzer family of models is that they do not extrapolate well to concentrations higher than the available data because they are semiempirical. In fact, beyond the physical data, they can give unphysical results. The formulation by Dutcher and co-workers[8−10] extrapolates well at concentrations beyond the available data but does not capture conceptually how we understand that solutes hydrate in solution. The model presented here, based on the work published more than 100 years ago, extrapolates well to concentrations higher than the available data, represents hydration of the solute realistically, covers both organic and electrolyte solutes in water, and due to its simplicity shows the role of free and bound water in solution.

AUTHOR INFORMATION

Corresponding Author

*E-mail: aswexler@ucdavis.edu.

ORCID

Anthony S. Wexler: 0000-0003-1565-814X

Notes

The author declares no competing financial interest.

REFERENCES

(1) Hamer, W. J.; Wu, Y. C. Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25° C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047−1100.

(2) Kiyosawa, K. The volumes of hydrated glucose, sucrose and raffinose molecules, and the osmotic pressures of these aqueous saccharide solutions as measured by the freezing-point-depression method. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 633−642.

(3) Scatchard, G.; Hamer, W.; Wood, S. Isotonic solutions. I. The chemical potential of water in aqueous solutions of sodium chloride, potassium chloride, sulfuric acid, sucrose, urea and glycerol at 25. *J. Am. Chem. Soc.* **1938**, *60*, 3061−3070.

(4) To, E. C.; Davies, J. V.; Tucker, M.; Westh, P.; Trandum, C.; Suh, K. S.; Koga, Y. Excess chemical potentials, excess partial molar enthalpies, entropies, volumes, and isobaric thermal expansitivies of aqueous glycerol at 25 C. *J. Solution Chem.* **1999**, *28*, 1137−1157.

(5) Raoult, F.-M. Loi générale des tensions de vapeur des dissolvants. *C. R. Hebd. Seances Acad. Sci.* **1887**, *104*, 1430−1433.

(6) Callendar, H. L. On vapour-pressure and osmotic pressure of strong solutions. *Proc. R. Soc. A* **1908**, *80*, 466−500.

(7) Stokes, R.; Robinson, R. Solvation equilibria in very concentrated electrolyte solutions. In *The Physical Chemistry of Aqueous System*; Springer, 1973; pp 75−93.

(8) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. Statistical mechanics of multilayer sorption: extension of the Brunauer−Emmett−Teller (BET) and Guggenheim−Anderson−de Boer (GAB) adsorption isotherms. *J. Phys. Chem. C* **2011**, *115*, 16474−16487.

(9) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. Statistical mechanics of multilayer sorption: 2. Systems containing multiple solutes. *J. Phys. Chem. C* **2012**, *116*, 1850−1864.

(10) Dutcher, C. S.; Ge, X.; Wexler, A. S.; Clegg, S. L. An isotherm-based thermodynamic model of multicomponent aqueous solutions, applicable over the entire concentration range. *J. Phys. Chem. A* **2013**, *117*, 3198−3213.

(11) Marcus, Y. Concentration dependence of ionic hydration numbers. *J. Phys. Chem. B* **2014**, *118*, 10471−10476.

(12) Zdanovskii, A. Fundamental Aspects of Variation of Properties of Mixed Solutions: Works of Salt Laboratory. *Tr. Solyanoi Lab., Vses. Inst. Galurgii, Akad. Nauk SSSR* **1936**, *6*, 5−70.

(13) Stokes, R.; Robinson, R. Interactions in aqueous nonelectrolyte solutions. I. Solute-solvent equilibria. *J. Phys. Chem. A* **1966**, *70*, 2126−2131.

(14) Debye, P.; Hückel, E.; Zur Theorie der Elektrolyte, I. I. Das Grenzgesetz für die elektrische Leitfähigkeit. *Phys. Z* **1923**, *24*, 305.

(15) Debye, P. J. W. The Collected Papers of Peter J. W. Debye, Interscience Publishers, Inc.: New York; 1954.

(16) Pitzer, K. S. Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem. A* **1973**, *77*, 268−277.

(17) Clegg, S. L.; Pitzer, K. S. Thermodynamics of multicomponent, miscible, ionic solutions: generalized equations for symmetrical electrolytes. *J. Phys. Chem. A* **1992**, *96*, 3513−3520.