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Biophysical Chemistry 105 (2003) 269–278

Biophysical Chemistry

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Analysis of excess Gibbs energy of electrolyte solutions: a new model for aqueous solutions[☆]

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Received 9 October 2002; accepted 1 November 2002

Abstract

This paper presents an analysis of the excess Gibbs free energy of aqueous electrolytes. The analysis of experimental data leads to the conclusion that the equilibrium state for dilute univalent electrolytes in water involves an intercalation of water and ionic liquid crystal domains. Excess free energy of the solution is determined by the Madelung energy of hydrated ion-pair liquid crystals, and the energy associated with a shift in the structural equilibrium of water. The data that point to such a model include: molecular orbital–molecular dynamics applied to electrolyte water systems; Raman spectra; infrared spectra; magnetic resonance spectra of ions; the apparent density of water; and the excess free energy of electrolytes in aqueous solutions. Molecular orbital–molecular dynamics calculations of relatively large water clusters containing a molecule of sodium iodide show that the solvent separated ion pair exists in a substantial potential well compared to other possible structures. Raman spectra of univalent electrolyte solutions as a function of concentration can be quantitatively modeled using only the spectra of pure water and electrolyte solution at the concentration of the solvent separated ion pair. The other observations are consistent with the structures proposed from the Raman spectral study. The new model provides a satisfactory account of the fact that the excess free energy of dilute (<0.2 mol/l) solutions is generally more negative than anticipated on the basis of Debye–Hückel theory, and that the equilibrium evidence points to the same functional behavior at very low concentrations as is seen at 0.05 mol/l. We present a testable hypothesis that the excess free energy, and other thermodynamic properties of the solutions do not follow the Debye–Hückel limiting law. The tests of this hypothesis must involve only equilibrium measurements at concentrations between 0.05 and 0.0005 mol/l. This hypothesis concerning the structure of aqueous electrolyte solutions is not in conflict in any way with the Debye–Hückel–Onsager theory of electrical conductivity.

Keywords: Gibbs energy; Electrolyte solutions; Aqueous solutions; Solution structure

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[☆] It is an honor and a great pleasure to participate in a project organised to recognize and honor the work of Walter Kauzmann. Prof. Kauzmann's leading contributions to the study of water and aqueous solutions dominated this area of science in the 20th century. His signal contributions have been exceptionally diverse, spanning the range from the Kauzmann temperature to solvation of proteins.

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0301-4622/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0301-4622(03)00077-2

1. Introduction

Conceptual scientific models are exceptionally important to the development of new ideas and experiments. Increases in knowledge of physical reality occasionally call for significant changes in our conceptual models. We are convinced that this is the case for aqueous solutions of electrolytes.

This paper proposes a model for aqueous electrolyte solutions that is based on two primary building blocks: water, with a mildly perturbed structure subsequent to ion–water–ion and water–water electron delocalization; and domains made up of clusters of the solvent separated ion pairs. These two building blocks form intercalated sub-phase regions of water and liquid crystalline ion-pair hydrates. As the concentrations increase, intimate ion pairs will also be present in the liquid crystalline portion of the solution. The partition between the various species will be determined, as usual, by a Boltzman distribution.

The evidence that supports this model for aqueous electrolyte solutions is reviewed below. The evidence includes molecular dynamics–molecular orbital theory simulations [1,2]; Raman spectroscopy [3–6]; attenuated total reflectance infrared spectroscopy [7–14]; NMR chemical shifts of electrolytes and the specific heats of solutions [15]; the apparent density of water in aqueous solutions [16]; and data on the excess free energy of electrolytes in aqueous solutions [17,18]. The evidence that was used to establish the validity of the classical models for dilute solutions of aqueous electrolytes [19,20] will also be considered. We shall present the outlines of a theoretical model and an empirical model for treating excess free energy of electrolytes.

The presently accepted model for the structure of aqueous solutions essentially began with the Ph.D. thesis of Svante Arrhenius in 1883 [21]. Arrhenius' thesis was so controversial that he only obtained a fourth class pass, the lowest possible [21]. Prior to Arrhenius it was thought that salts dissolved as neutral entities, e.g. NaCl, not $\mathrm{Na}^{+}_{\mathrm{hydrate}}$:$\mathrm{Cl}^{-}_{\mathrm{hydrate}}$, as we now understand ionic solutions. It is interesting that the hypothesis presented here is congruent with the ideas originally presented by Arrhenius.

2. Evidence supporting the development of a new model for aqueous electrolyte solutions

2.1. Molecular dynamics–molecular orbital theory calculations

Molecular dynamics modeling using quantum mechanical potentials $(6-31+G^{**}/\mathrm{MP}\ 2)$ shows that the solvent separated ion pair (SSIP) is quite stable compared to free solvated ions in a cluster of 2000 water molecules [$\Delta G_{\mathrm{solv\ SSIP}}$ $(-418.4\ \mathrm{kJ/mol})$] [1,2]. The contact ion pair (CIP) is significantly less stable [$\Delta G_{\mathrm{solv\ CIP}}$ $(-171.5\ \mathrm{kJ/mol})$] [1,2]. These results suggest that for the same concentration of NaI in water with 4000 water molecules there would be either two solvent separated ion pairs, or a liquid crystalline tetrad of hydrated ions. The salt concentration we are discussing here is approximately 0.03 mol/l. The asymptotic behavior of the solvation free energy for NaI, with reference to the size of the water cluster, strongly suggests that the energy per mol of NaI would not change significantly if the concentration were reduced by 1 or 2 orders of magnitude. A solution model constructed using these results would be quite different from the ionic atmosphere model that is the limiting case in Debye–Hückel theory.

2.2. Raman spectra of aqueous electrolytes

Raman spectra of glassy states of lithium chloride solutions were interpreted by Suzuki and Mishima [22] as indicating the presence of two distinct glassy states of water in dilute LiCl solution at low temperature. The cooling rates in the splat cooling procedure used by Suzuki and Mishima [22] are thought to exceed 10^6 K/s, so only minimal structural reorganization would be expected.

Aliotta et al. were the first to report strong evidence for the segregation of water and hydrated ion pairs in electrolyte solutions into distinct subphases [23]. They used Raman spectra of electrolyte solutions to infer the existence of separate

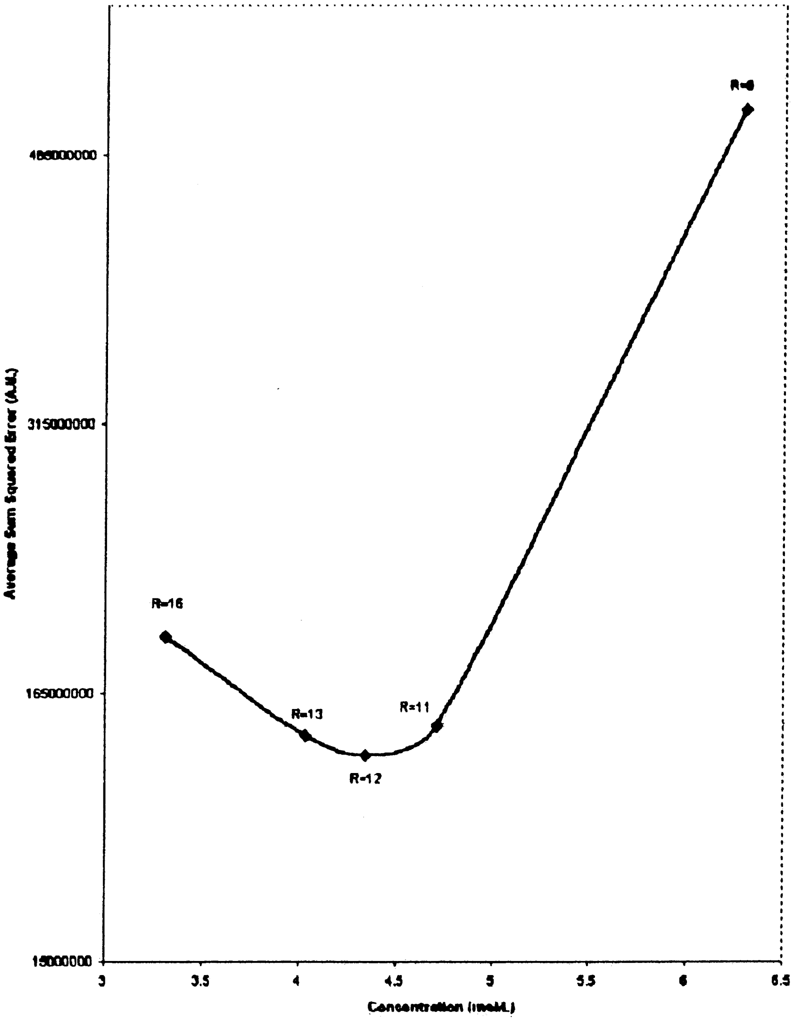

Fig. 1. Absolute sum-squared error for fitting KF Raman spectra as a function of concentration [6]. The minimum occurs at approximately 4.4 mol/l, the concentration of the solvent separated ion pair as the only solution component.

water and hydrated-electrolyte sub-phases in these solutions. The impact of this discovery on our understanding of the structure of aqueous solutions has been slow in developing (more than 20 years) because the theoretical treatments needed to understand these observations in detail is not straightforward.

We have reported the results of analysis of a two sub-phase model for aqueous electrolyte solutions showing that fitting error was minimized when the concentration of the solution selected to be the 'high electrolyte concentration' standard corresponded to the concentration of the solvent separated ion pair as the only solution component (Fig. 1) [6]. One of the remarkable observations of this report is the fact that the refractive index of both of the sub-phases, one composed of water and the other composed of hydrated ions, was identical [6].

The identity of the refractive index in the water sub-phase with that of the hydrated electrolyte sub-phase, can be inferred from the changes in the intensity parameter for this curve fitting exercise. The equation used in the fitting procedure [6] follows:

$$I_{\text{soln}} = \beta\{\alpha I_{\text{water}} + (1-\alpha) I_{\text{electrolyte}}\} \qquad (1)$$

I_{water} is the Raman spectrum of pure water. $I_{\text{electrolyte}}$ is the spectrum of the electrolyte at the concentration of the hydrated ion pair. The procedure for determining this concentration is based on minimization of the overall fitting error as a function of concentration. α Is a parameter that scales the proportion of the two 'standard' spectra. β is an intensity parameter; it accounts for the influence of the structure of the solution on the Raman intensities of the components of the solution. The value of β in Eq. (1) was the same for both the water and the electrolyte hydrate liquid crystal sub-phase. This would happen if the electronic communication between the two sub-phases was exquisite, and that the change in polarizability with vibrational excitation was the same for both of the sub-phases.

2.3. Factor analysis of attenuated total reflection infrared spectra

Chapados and colleagues used factor analysis of attenuated total reflectance infrared spectra [7–14] to develop a clearer picture of the structure of solutions of aqueous electrolytes. Solutions of lithium chloride and nine other electrolytes indicated the presence of two principal species in the solutions: pure water; and salt solvated water.

2.4. Apparent density of liquid water in electrolyte solutions

The apparent density of water can be obtained from the density of a solution, the concentration and the ionic radii and masses of the ions. When we looked at the apparent density of water in a series of univalent electrolytes [16] there were a number of cases in which the apparent density of water decreased with increasing electrolyte concentration, e.g. NaF, KF, NaOH and KOH. Expansion of the apparent volume of water with increasing electrolyte concentration is a result of shifts in the structural equilibrium for water as a result of increases in hydrogen bond strength caused by electron delocalization between water and the ions. The Raman results mentioned above suggest that electron delocalization is responsible for changes in hydrogen bond strength, and shifts in the water equilibrium. Results for both apparent density and nuclear magnetic resonance shifts suggest that the water structure (in the water sub-phase) is only mildly perturbed from ordinary water. The shapes of the curves for apparent density of water against electrolyte concentration look very much like the density, temperature profile for pure water. The largest perturbation appears to be an increase in hydrogen bond strength and a subsequent shift in the water structural equilibrium. Equilibrium shifts in structure for water that are directly analogous to structural changes in pure

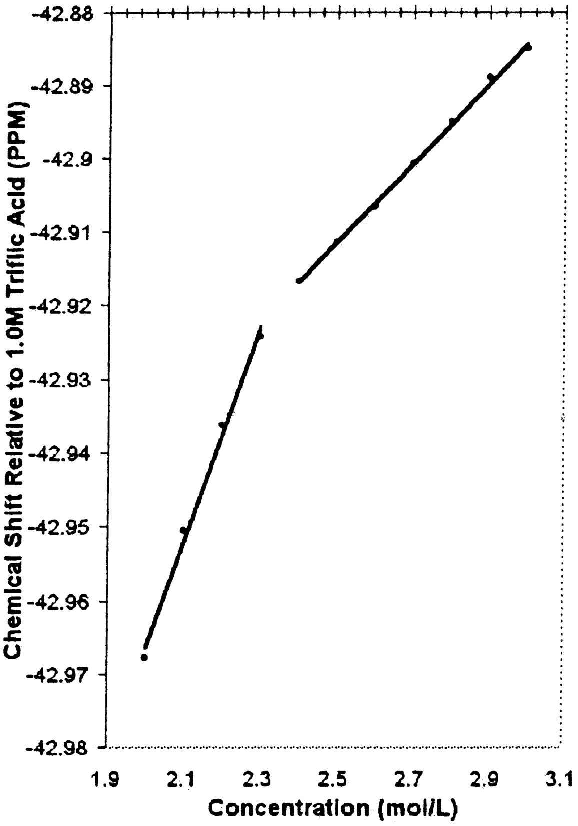

Fig. 2. [^{19}F] Chemical shift vs. KF concentration, 298 K [15].

water, e.g. the occurrence of an apparent density maximum, would seem very unlikely if something other than pure water domains were involved in the solution structure.

2.5. Correspondence between minima in electrolyte solution specific heats, and changes in the slope of NMR shifts as a function of concentration

We have examined both the anion and cation NMR spectra of KF, KCl and LiOH and have compared the results with those for specific heat as a function of concentration and temperature [15].

Previous NMR studies of aqueous electrolyte solutions have reported 'not quite linear' relationships between chemical shifts and concentration [24–26]. Deverell and Richards reported cation and anion shifts over the solubility range for most of the alkali halide salts [24–26]. They reported [24–26] changes in the slope of chemical shifts with concentration similar to the results shown in Fig. 2. As a result of the small number of samples per electrolyte and the broad concentration ranges their plots of chemical shift against electrolyte concentration appeared to be smooth curves and did not associate the transitions with a specific concentration [25–27].

Variations in chemical shifts for ^{19}F in KF solutions from our recent experiments [15] are shown in Fig. 2 as a function of electrolyte concentration. The ^{19}F chemical shift for aqueous KF shows a change in slope at ∼2.4 mol/l KF (slope 0.145 ± 0.002 to 0.054 ± 0.0005 δl/mol). The ^{39}K chemical shift for aqueous KF has an analogous change in slope at the same concentration (slope 0.500 ± 0.007 to 0.422 ± 0.003 δl/mol). The specific heat for 2.4 M KF [25,26] shows a minimum at 298 K, the temperature of the NMR experiment. The influence of K^+ on the specific heat of an aqueous solution has been the subject of molecular dynamics modeling [27]. The results in this case were qualitatively in agreement with the experiment. The foundation for the theoretical model was provided by the careful studies of Henn and Kauzmann on heat capacity (equation of state) modeling using random network models [28].

The observation that aqueous solutions behave like perturbed water in terms of specific heat, suggests that the aqueous solutions contain perturbed water that participates in water structures analogous to those of unperturbed water at a different temperature. The most reasonable way for this to happen is through the existence of sub-phase regions of perturbed water and sub-phase regions of hydrated electrolyte.

3. Excess Gibbs energy of aqueous electrolyte solutions

3.1. Experimental data

Data on the excess Gibbs energy of electrolyte solutions is primarily derived from isopiestic, isobaric, measurements of activity and osmotic coefficients [17,18]. These measurements, which are based on gravimetric evaluation of solution concentrations, are robust and highly reproducible at concentrations above 0.05 mol/l. A plot of the excess Gibbs energy for NaF, KCl and RbBr is shown in Fig. 3 along with expectations based on the Debye–Hückel theory [19,20]. The details of plots of excess Gibbs energy differ from one univalent electrolyte to another; however, the general features of the plots in Fig. 3 are representative. For the vast majority of univalent electrolytes the slope of the plot at 0.05 mol/l is significantly larger than would be anticipated on the basis of a square root law, and the excess Gibbs energy is more negative than the value anticipated by Debye–Hückel theory. We cannot imagine a physical cause for an inflection in the excess Gibbs energy curve that would cause the curve to have a limit along the path of a square root law.

Careful examination of the data supporting the limiting law shows that the data are obtained from activity coefficients determined by conductivity at concentrations at or below 0.01 mol/l [19,20]. The determination of activity coefficients by conductivity measurements is the result of the fact that classical equilibrium methods are generally not reliable for very low concentrations. Unfortunately, the electric fields that are essential for conductivity measurements will very substantially perturb the thermodynamic equilibrium of the solu-

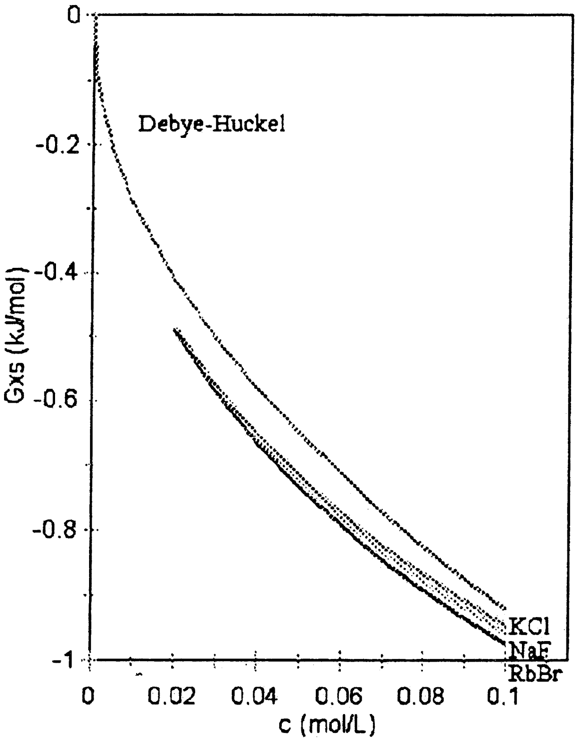

Fig. 3. Excess Gibbs energy of NaF, KCl and RbBr [17] compared with the expectation based on Debye–Hückel theory [18,19].

tion. Any electric field that is large enough to allow for a conductivity measurement, is phenomenonologically large enough to separate charge in the solution. Should the thermodynamic equilibrium state involve association of charge, as the evidence regarding the stability of solvent separated ion pairs above suggests, activity coefficients obtained by conductivity will not reflect the equilibrium state.

The quantum mechanical–molecular dynamics evidence for the thermodynamic stability of the solvent separated ion pair [1] reflects the importance of electron delocalization of the detailed structure of solutions of electrolytes [16]. When electron delocalization is substantially decreased by insignificant overlap of the appropriate molecular wave functions, the structure of the solution will certainly change. Electron delocalization involving ions can be inhibited by constructing ions with exterior insulators, e.g. tetraphenyl borate anion, or by using ions with very low energy wave functions, e.g. hexafluorophosphate anion.

KPF_6 appears to be a classical Debye–Hückel ionic system [17]. The excess free energy for this system fits a power law with a 0.494 exponent for the total excess free energy, and a 0.494 exponent for the partial molal excess free energy of the KPF_6 salt. The plot in Fig. 4 illustrates the closeness of fit to the Debye–Hückel model.

3.2. Energy components from theory

Henry's Law qualitatively describes the free energy of aqueous electrolytes as a function of electrolyte concentration. The Henry's Law line is not strictly straight. The deviation from linearity, expressed as experimental free energy—Henry's Law value, has been called the excess Gibbs (free) energy [18]. This deviation has the potential to inform us concerning the alterations in the struc-

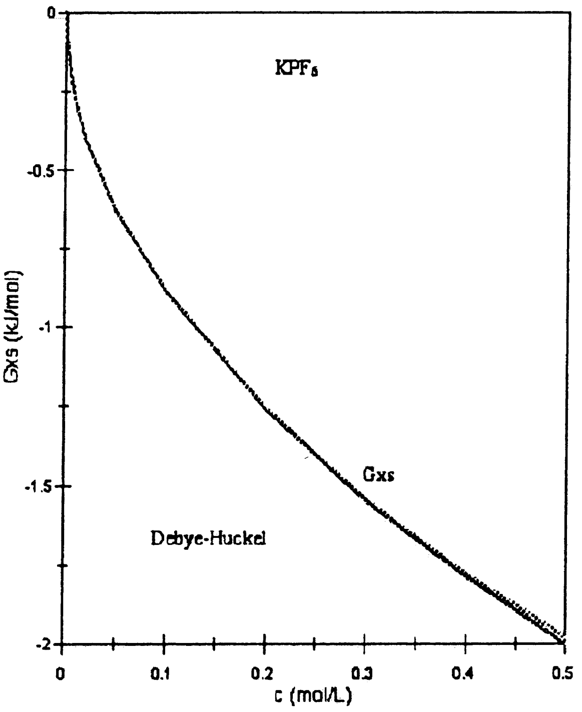

Fig. 4. Experimental [17] and Debye–Hückel excess free energies for KPF_6.

ture of liquid water subsequent to introduction of electrolytes and the energy of interaction of the electrolytes. In Section 3.2 we introduce the terms that should be components of a model of the excess Gibbs energy of aqueous solutions. The terms are based on the physical observations above that suggest that aqueous solutions are composed of intercalating regions of slightly perturbed water and liquid crystalline hydrated electrolyte.

The excess free energy as a function of shell number, n, for lattice-like arrays of solvated ion pairs in water is the sum of the excess enthalpy, $H_{xs}(n)$, and $-T\Delta S_{xs}$. The first term has a relatively straightforward solution:

$$H_{xs}(n) = -\frac{q^2 N_A(n)}{4\pi\varepsilon_o\varepsilon_r R} \tag{2}$$

$M(n)$ is the apparent Madelung constant which converges to a fixed value at high n. R is the time-averaged distance between ions in the hydrated lattice. ε_r is the relative permitivity, apparent dielectric constant for the hydrating water. ε_o is the permitivity of free space. The Madelung function for the cluster, $M(n)$, converges as $1/n$ for $n>5$ to a value fixed by the geometry of the lattice. For sodium chloride (cubic lattice) this value is 1.7476. The fitting constants for $M(n)$ for $n=$ 6–14 for addition of ion pairs to the lattice were: $1.7476-0.20489/n$ (S.D. $=9.7\times10^{-5}$, sum square error $=6.0\times10^{-7}$).

The relationship between relative permitivity and the polarizability, of a given ion cluster is given by a relationship presented by Debye in 1912 [29]:

$$\frac{(\varepsilon_r-1)M}{\rho} = \frac{N_A}{\varepsilon_o}\left(\alpha + \frac{\mu_e^2}{3kT}\right) \tag{3}$$

M is the molecular mass of the fluid molecule. N_A is Avogadro's constant. ρ is the density and μ_e is the dipole moment of the fluid molecule.

The polarizability of a cluster of hydrated ions should scale as the cube root of the volume of the cluster, or n, the shell number. It should also be a function of the electron exchange between the electrolyte and the water, and the water with itself, caused by hydration of the ions, f(2nd order interaction energy).

The change in energy per ion pair as a function of cluster size has the following form:

$$E(n) = \chi\frac{M(n)}{\varepsilon_r(n)} \tag{4}$$

where χ is a constant.

Including the dependence of $M(n)$ and $\varepsilon_r(n)$ on n gives:

$$E(n) = \frac{1.7476}{a+bn} - \frac{0.20489}{an+bn^2} \tag{5}$$

a and b are constants that depend on the solvent and solute.

$$a = \frac{4\pi\varepsilon_o\varepsilon_{ro}R}{q_1q_2N_A}$$
$$b = \frac{4\pi\varepsilon_o Rp}{q_1q_2N_A} \tag{6}$$

ε_o is the permivivity of free space. ε_{ro} is the dielectric constant of the solvent. R is the average distance between ions in the lattice-like cluster. Q_1 and q_2 are the charges on the cation and anion, respectively. N_A is Avagadro's number. P is a constant that depends on the electronic properties of the ion pair.

The change in energy with cluster size is the derivative of $E(n)$ with respect to n.

$$E'(n) = -\frac{1.7476b}{(a+bn)^2} + \frac{0.20489(a+2bn)}{(an+bn^2)^2} \tag{7}$$

The term in Eq. (7) must be convolved with a partition function for the distribution of energy as a function of a number of properties. Among these properties are: the size of the liquid crystalline electrolyte hydrate cluster; and the hydration level within the cluster. As the concentration of the electrolyte increases, the abundance of contact ion pairs will increase within the liquid crystalline cluster. The presence of contact ion pairs will

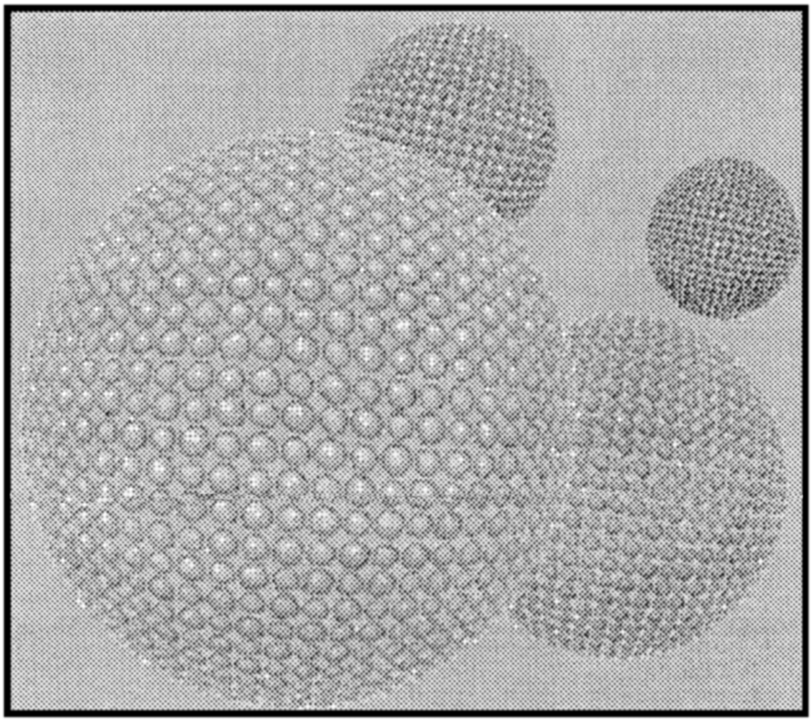

Fig. 5. An artist's view of the hydrated ion pair clusters in aqueous electrolyte solution, for clarity neither the bulk water, nor the water molecules that coordinate the ions have been shown.

increase the amount of 'free' water in the system. The partition function for this system, which has numerous environments, each with an intrinsic size-related stability will be exceptionally complex. Max and Chapados [9] showed that a virtual sodium chloride concentration of 8.85 mol/l (substantially above the saturation concentration of 6.14 $\mathrm{mol/kg_{water}}$ [17]) was required to obtain an infrared spectrum that was free of 'free' water thus proving the need for this level of complexity.

The excess free energy, $G_{xs\ \mathrm{ions}}$, is the excess free energy per ion pair times the number of ion pairs per unit volume. Assuming that the partition function, $\Xi(n)$, can be obtained in analytical form, it should be possible to obtain a numerical solution for the excess free energy. Unfortunately, the equations involving energy above do not explicitly treat the effect of electron delocalization between the electrolyte and water on the structure of the 'free' water and its free energy [16]. The level of complexity of the problem is such that a physically satisfying quantitative picture may be elusive outside the realm of quantum mechanical molecular dynamics and Monte Carlo simulations.

The body of evidence presented above does, however, present a qualitative physical model that may be of some use in the study of electrolyte solutions. Water intercalated with liquid crystalline arrays of electrolyte hydrates is an interesting picture of aqueous solution (Fig. 5) that manages to qualitatively account for the observations of both the excess Gibbs energy, and the spectroscopy of the solutions. The artist's view of aqueous electrolyte solutions in Fig. 5 does not show any water, so the drawing is a 'negative' of a Swiss cheese structure. The hydrated electrolyte liquid crystals will certainly be irregular; however, they will tend to minimize their surface area which will lead to the Swiss cheese-like structure. The magnitude of the surface area minimization will vary from electrolyte to electrolyte, and will vanish in electrolytes such as KPF_6 that closely approximate a Debye–Hückel model.

The variation in excess free energy curve shape with electrolyte (Fig. 3) can be qualitatively accounted for by the combination of the Madelung convergence to different values and the increase in free energy subsequent to increases in water hydrogen bond strength caused by electron delocalization involving the electrolyte. Since electron delocalization is an intimate part of the structure of the solution, it will be necessary to utilize quantum mechanical models for a proper molecular dynamic or Monte Carlo description of the system.

The clear hypothesis from this work is that equilibrium measurement of the excess free energy limiting behavior of univalent electrolytes will show variations from one electrolyte to the next. Furthermore, for most electrolytes the limiting behavior ($c < 0.01$ mol/l) will follow a power law closer to 0.42 than 0.5. The value of 0.42 is a close approximation to the initial curvature of the Madelung convergence for arbitrary liquid crystal lattice parameters.

4. Summary

Molecular dynamics–molecular orbital theory computations [1], Raman spectra [5,6], infrared spectra [7–14], nuclear magnetic resonance spectra [5,15], the apparent density of water [16] and the excess Gibbs energy of solutions of aqueous univalent electrolytes are all consistent with a model of these solutions containing sub-phases of structurally perturbed liquid water and of liquid crystalline arrays of electrolyte hydrates.

Acknowledgments

It is a pleasure to thank Irving M. Klotz for his encouragement and thoughtful corrections as this work proceeded. Thanks are due to Stephanie R. Dillon for inspiring conversations, and considerable help with the literature and to C. Austen Angell for insight building discussions.

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