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LETTERS

Raman Studies of the Solution Structure of Univalent Electrolytes in Water

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This paper reports results of analysis of the OH stretch Raman spectra of aqueous solutions of electrolytes. Error analysis supports the view that the environment of the electrolyte in the liquid is that of a liquid crystalline hydrate. Fitting error analysis for a two-state model further suggests that the presence of the hydrated electrolyte perturbs the structure of the bulk water in the solution. This perturbation is consistent with the results of previous studies of the apparent density of water in aqueous solutions of electrolytes. The previous studies showed that electrolytes increase the hydrogen bond strength of the bulk water and thereby cause a shift in the water equilibrium, which results in a change of the apparent density of water in the solution.

Introduction

Raman spectra of glassy states of lithium chloride solutions have been interpreted as indicating the presence of two distinct glassy states of water in dilute LiCl solution at low temperature.[1] The transfer of the solution from the gas-phase liquid droplet to the solid, low-temperature glass must have involved only minimal changes in the chemical environment of the ions. The cooling rates in the splat cooling procedure used by Suzuki and Mishima[1] are thought to exceed 10^6 K/s, so only minimal structural reorganization would be expected.

Aliotta et al.[2] were among the first to study the coexistence of bulk water clusters and hydrated-electrolyte clusters using Raman spectra of electrolyte solutions. Factor analysis of attenuated total reflection infrared spectra of solutions of lithium chloride and nine other electrolytes indicated the presence of two principal species in the solutions: pure water and salt-solvated water[3]. Preliminary infrared studies included solutions of the chlorides of sodium, potassium, and cesium.[4−7]

Max and Chapados[8] used extrapolation beyond the maximum obtainable salt concentration to obtain "pure salt-solvated water spectra". This approach gave hydration numbers for NaCl, KCl, NaBr, KBr, and CsI as 5, KI and $MgCl_2$ 4, NaI 3.5, CsCl 3, and LiCl 2. These hydration numbers indicate the presence of very substantial numbers of intimate ion pairs in the hypothetical "pure salt-solvated water" phase. Our approach to this problem has been quite different in that we have used fitting error analysis as an indicator of the state of hydration of the electrolyte in the hydrated electrolyte subphase.

It has been proposed that ionic amorphous hydrates of HCl nucleate as distinct phases during the conversion of ice to HCl hydrates.[9] This apparent phase nucleation may be closely related to the behavior of the amorphous liquid and solid phases mentioned above.

Results reported here are consistent with the earlier reports and suggest that the electrolyte species present in 1 M solutions are liquid crystalline clusters of hydrated ion pairs.

Experimental Section

All Raman spectra were recorded on a Jobin Yvon Horiba LabRam Spectrograph. The spectrometer is equipped with an 1800 gr/mm holographic grating. Excitation for normal Raman studies was provided by a 632 nm Helium/Neon laser. The detector is an ISA air-cooled CCD. All spectra were collected at 298 ± 1 K maintained by a circulating isopropyl alcohol

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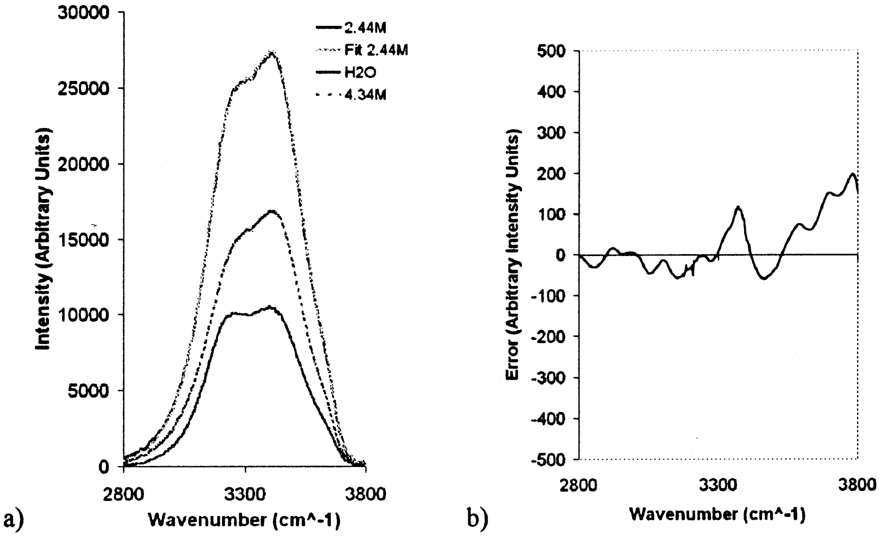

Figure 1. (a) Experimental and curve fit spectra for 2.44 M KF. (b) Fitting error for panel a as a function of wavelength.

bath. Each spectrum is the result of four 20 s exposures which were ensemble averaged.

Spectral quantitation was made possible by use of an external standard. Both the standard and the sample were illuminated simultaneously by means of a split cell cuvette. $CDCl_3$ was used as the standard. The fiber optic probe is configured in a backscattering geometry. The probe was centered flush to the side of the cuvette.

Chemicals were purchased from Aldrich and were of the highest purity available. Solutions were prepared by serial dilution from stock. Concentrations were checked by comparing refractive indices to literature values.[10,11]

Results and Discussion

The O−H stretch of the Raman spectra of the series of solutions are quantitatively fit using a linear model based on the approach used by Suzuki and Mishima[1], with the addition of an intensity parameter, β:

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

I_{water} is the Raman spectrum of pure water. $I_{\mathrm{electrolyte}}$ is the spectrum of the electrolyte at the concentration of the hydrated ion pair. The procedure for determining this concentration is discussed below. 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.

In fitting spectra for a series of electrolytes, we found minima in the fitting error per spectrum when the $I_{\mathrm{electrolyte}}$ solution had R, the electrolyte concentration [(mol H_2O)/(mol electrolyte)], corresponding to the hydration number of the electrolyte (see Table 1). The solution at this concentration is a liquid crystalline array of hydrated ion pairs. We have assumed that the concentrated standard spectrum corresponds to this concentration. These solutions must contain small populations of intimate ion pairs and small islands of water. The concentration of both of these species with reference to the hydrated ion pair subphase is determined by a Boltzman distribution.

The quality of the curve fitting in this series was high. Figure 1a illustrates the experimental and curve fit spectra for 2.44 M KF. The intensities of the curves for water ($\alpha I_{\mathrm{water}}$) and 4.34 M KF($(1-\alpha)I_{\mathrm{electrolyte}}$) are scaled using the calculated α values for the fit. The differences between the experimental and the fitted spectrum in this case are less than the noise-to-signal ratio. Figure 1b presents the fitting error for the graphic in Figure 1a as a function of wavelength. The fitting error ($I_{\mathrm{soln}} - I_{\mathrm{expt}}$) for the 2.44 M spectrum is near the maximum error in the series of KF spectra. A major source of the fitting error is small shifts in the equilibrium structure of the bulk water after an increase in hydrogen bond strength in the bulk water due to the presence of the electrolyte.[12] 2.44 M is the concentration of the specific heat minimum in KF solution as a function of concentration at 298 K.[13] The locus of the specific heat minimum may correspond to a weak continuous transition in the structure of the liquid.[14]

TABLE 1: Comparison Values for Ion Hydration and Experimental Fit Minima

electrolyte	concentration (mol/L) at error min (*R* value)	cation hydration number	anion hydration number	average fit error (%)	average noise/signal (%)
LiCl	3.95 (12)	4[15]	6[16]	0.255	0.090
LiBr	~4.0 (~14)	4[14]	6[17]	0.247	0.440
NaCl	5.45 (9)	6[18]	6[15]	0.609	0.153
NaBr	3.95 (~15)	6[17]	6[16]	0.262	0.078
NaI	6.10 (12)	6[17]	6[19]	0.353	0.449
KF	4.34 (12)	6[20]	6[21,22]	0.209	0.143
RbF	5.30 (12)	6[23]	6[20,21]	0.102	0.308

The trends in both α and β with concentration for KF solutions are representative of other electrolytes and are shown in Figure 2. Figure 2a includes the straight line that reflects α as a strictly linear function of concentration. The plot of β as a function of concentration (Figure 2b) shows that adding electrolyte to water increases the Raman intensities of both the water and the hydrated ion pair subphase. Raman intensity is proportional to the polarizability change on vibrational excitation. The initial increase in the value of β parameter followed by the sharp decrease indicates that the introduction of KF initially increases the change in polarizability on vibrational excitation. Above ~1.0 M, the trend reverses, and increases in KF concentration decrease the overall intensity of the spectra which is reflected in the decrease in β. These changes are consistent with changes in the apparent density of water in KF solution[12]. The changes in apparent density of water show that the structure of the water subphase changes with increasing KF concentration. The values of β as a function of KF concentration show those changes.

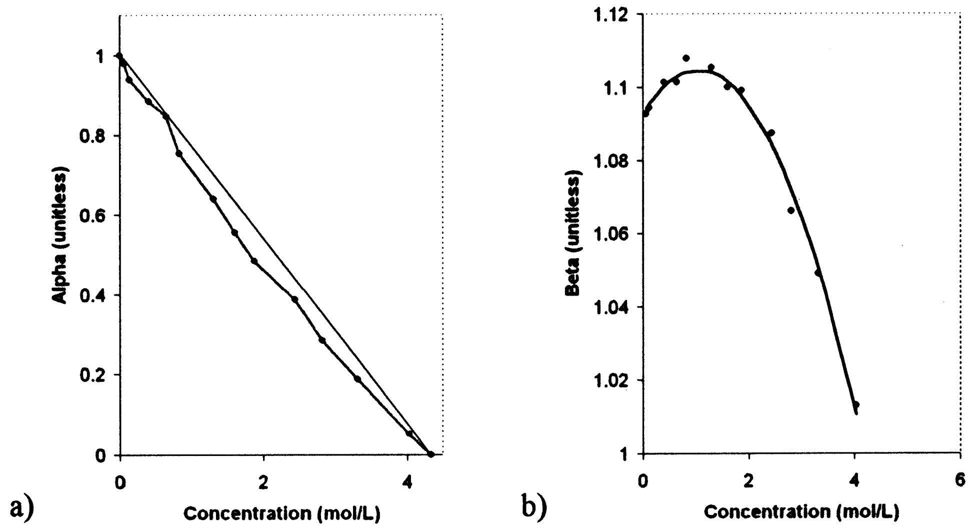

Figure 2. (a) α values for KF solution fits with concentration. (b) β values for KF solution fits with concentration.

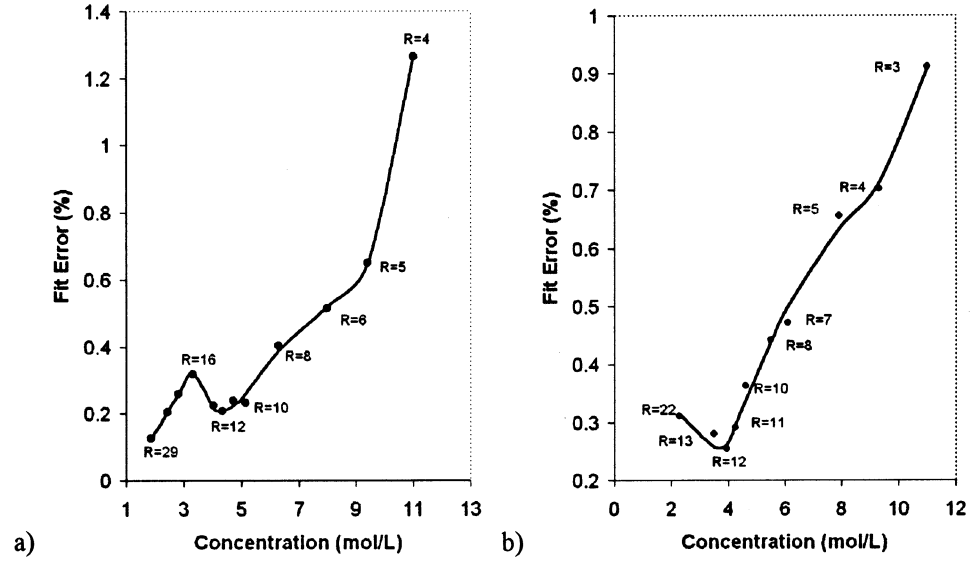

Figure 3. Minimum in the fit error for (a) KF spectra and (b) LiCl spectra.

Addition of the β parameter allows for observation of the trends in spectral intensity which would be lost if the spectra were normalized (i.e., scaled to 100%.) The fact that the β parameter applies to both the spectra of the water subphase and the hydrated electrolyte subphase shows that the solution has only one refractive index, and there should be no light scattering from the subphases.

Figure 3a shows the average error per spectrum as the % area under the curve versus the concentration of the solution that was used as the "standard" for the concentrated spectrum for KF. The average error passes through a minimum at the concentration corresponding to the hydration number of the hydrated ion pair.

In addition to stochastic errors associated with experimental uncertainties, there are two systematic sources of error in plots such as those in Figure 3. It is known from studies of the apparent density of water in salt solutions that the structural equilibrium in water is shifted by the presence of electrolytes.[12] This means that there will be small shifts in the Raman OH stretch for the water as the concentration of electrolyte changes. Fitting errors associated with these shifts will increase with electrolyte concentration. The second systematic source of error comes from the concentration associated with the "standard" spectrum of the hydrated electrolyte. The fitting error associated with this source should minimize at the concentration associated with the liquid crystalline electrolyte in the dilute solutions.

For KF the minimum in the average error per spectrum occurs at $R \approx 12$, which corresponds to the sum of the hydration numbers for fluoride ($6^{20,21}$) and potassium (6^{19}). The spectrum of $R = 12$ KF was used as the concentrated "standard" solution in eq 1 for KF. At this concentration the solution corresponds to a liquid crystalline array of solvent-separated ion pairs, with low concentrations of both intimate ion pairs and electrolyte free water. The fact that the error per spectrum minimizes at the concentration corresponding to the water separated ion pair suggests that the ion environment in solution, like that in the low-temperature glassy state,[1] is that of packed hydrated ion pairs.

Figure 3b shows the average error per spectrum as the % area under the curve versus the concentration of the solution that was used as the "standard" for the concentrated spectrum for LiCl. The minimum in the fit occurs when the spectrum for 3.95 M ($R = 12$) is used as the "standard".

A plot like those in Figure 3 for KBr solutions did not show an error minimum. This is presumably because the solubility limit for KBr at room temperature is below the concentration associated with the hydrated liquid crystalline subphase. The solubility of KBr is lower than the *R* value corresponding to the sum of the hydration numbers.[16,19]

Table 1 presents data on the concentration locus of the minimum in fitting error using eq 1 and the hydration numbers of the ions in the electrolyte. The correlation of the best fit to the sum of the hydration values of the individual ions for the electrolytes in Table 1 supports the conclusions reached by Max et al.,[2] that the ions form hydrated clusters in aqueous solutions.

The Raman spectra of the solutions in Table 1 can be quantitatively reproduced with the spectra of pure water and a concentrated hydrated ion pair standard. This suggests that the structure of aqueous electrolyte solutions has the ions isolated as clusters of hydrated ion pairs. The size of the liquid crystalline clusters is subject to a Boltzman distribution. The bulk of the water, at electrolyte concentrations below 1 M, is dispersed through the solution as interconnected pools of pure water. This picture is consistent with the observation of two distinct glassy states for water in hyperquenched glasses formed from electrolyte solutions.[1] The Raman spectrum of hyperquenched glassy water[1,15−17] is significantly more distinct from the Raman spectrum of hyperquenched concentrated lithium chloride solution[1] than the corresponding difference in the room-temperature Raman spectra of the liquids (see, e.g., Figure 1a). If there were significant amounts of either isolated ions or hydrated ion pairs in the water regions of the hyperquenched glass, it would have degraded any attempt at curve fitting[1] using just the Raman spectra of hyperquenched glassy water and hyperquenched concentrated electrolyte solution. The pure water/clustered ion pair hydrate structure for aqueous electrolyte solutions is further supported by the fact that the intermolecular and intramolecular water structure in 1 M LiCl is not distinguishable from pure water by neutron scattering measurements.[27]

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