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NMR Evidence of Weak Continuous Transitions in Water and Aqueous Electrolyte Solutions

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Nuclear magnetic resonance chemical shifts are used to examine the perturbations in water structure that occur with concentration changes in aqueous KF, KCl, and LiOH solutions. Changes in the slope of ion chemical shifts as a function of solute concentration can be explained by changes in water structure. The equilibrium shift in water structure occurs as a result of changes in the hydrogen bond strength. The changes in hydrogen bond strength are a result of changes in electrolyte concentration and electron delocalization throughout the liquid. The location of the changes in slope with concentration is temperature dependent. A correlation of the changes in slope of chemical shifts to minima in specific heat capacity suggests the occurrence of a weak continuous transition in the solution structure at the critical concentration corresponding to the specific heat capacity minimum. By extrapolation the experiments reported here imply that there is a weak continuous transition associated with the heat capacity minimum for pure water. There must also be a structural relaxation time in the liquid associated with this transition. The results of these experiments provide confirmation for the model of aqueous solutions we recently proposed in which the solution is composed of regions of pure water and regions of liquid crystalline electrolyte hydrates. The subphase composed of structurally perturbed water is the part of the system that participates in the weak continuous phase transition that is evidenced by the NMR chemical shifts. In complete agreement with earlier Raman experiments it appears that the entire solution is a single electronic whole with exquisite electronic delocalization between the water and liquid crystalline subphases so that the ionic nuclei experience the electronic effects of the transition in the water subphase.

1. Introduction

Nuclear magnetic resonance (NMR) chemical shifts are a traditional probe of the phase behavior of solids, liquids, and liquid crystals.[1] Discontinuous changes in chemical shifts are indicative of first-order phase transitions; abrupt changes in slope for, e.g., chemical shifts as a function of concentration, are generally indicative of continuous (second-order) transitions.[1]

Raman OH stretch spectra of aqueous electrolytes suggest that these solutions are composed of two components: pure water and liquid crystalline clusters of hydrated ion pairs.[2] In this model there are two distinct environments for hydrating water: water that is in the interior of the liquid crystalline hydrate cluster and water that is on the surface of the liquid crystalline cluster, and in contact with "bulk" water. The proportion of these two subenvironments will change with electrolyte concentration, but the nature of the two chemical environments will be approximately constant. One feature that will change with electrolyte concentration is the equilibrium structure of the "bulk" water.[3]

If the ions are localized within liquid crystalline hydrated arrays, the impact of the water of hydration on the ion chemical shift should be a nearly constant function of concentration. This is because the chemical environment of the hydration water should be approximately the same as a function of electrolyte concentration. Water that is on the surface of the liquid crystalline clusters can makecontact with both "bulk" water and hydrated ions.

It is known that there are shifts in the equilibrium structure of the "bulk" water in electrolyte solutions from evaluation of solution density as a function of concentration.[4] Hydrating water on the surface of liquid crystalline clusters of ions can communicate these small shifts to the ion nuclei and be reflected in changes in chemical shift.

Shifts in the equilibrium structure of the bulk liquid with concentration, caused by changes in hydrogen bond strength, will be expected to shift the position of the specific heat minimum for the solution. It is these small shifts in the location of the specific heat minimum for electrolyte solutions that we are interested in detecting by the use of an NMR probe.

Previous NMR studies of aqueous electrolyte solutions have resulted "not quite linear" relationships between chemical shifts and concentration.[5−7] Deverell and Richards reported cation and anion shifts over the solubility range for most of the alkali halide salts.[5,6] They reported[5,6] changes in the slope of chemical shifts with concentration similar to the results presented below. Due to the small number of samples per electrolyte and the broad concentration ranges, their plots of chemical shift against electrolyte concentration did not pinpoint the transitions.[5,6]

2. Materials and Methods

Chemicals were purchased from Aldrich and were of the highest purity available. Solutions were prepared by serial dilution from stock. NMR sample tubes were sealed after one freeze−pump−thaw cycle. Spectra were measured with a Bruker AC300 spectrometer. All experiments were run at 298 K. A 10 mm ^{39}K probe was used for KCl. A 5 mm ^{19}F probe was used

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in the case of KF. Four scans per set were taken for each KCl sample over a sweep width of 20 kHz. A single scan over the same sweep width was taken for KF samples. Due to the small deviations in the chemical shifts, experiments were repeated until the standard deviation in the chemical shift measurements were a factor of 10 below the magnitude of the chemical shift deviation. Spectra presented are averages of a minimum of three or more separate experiments. Chemical shifts for each ion were determined by use of an external standard in a concentric tube inside the sample tube. ^{39}K shifts for KCl were measured from a saturated sample of KNO_3 in D_2O. ^{19}F shifts for KF were measured from a 2.0 mol/L sample of trifluoroacetic acid in D_2O. All peaks were baseline resolved.

3. Results and Discussion

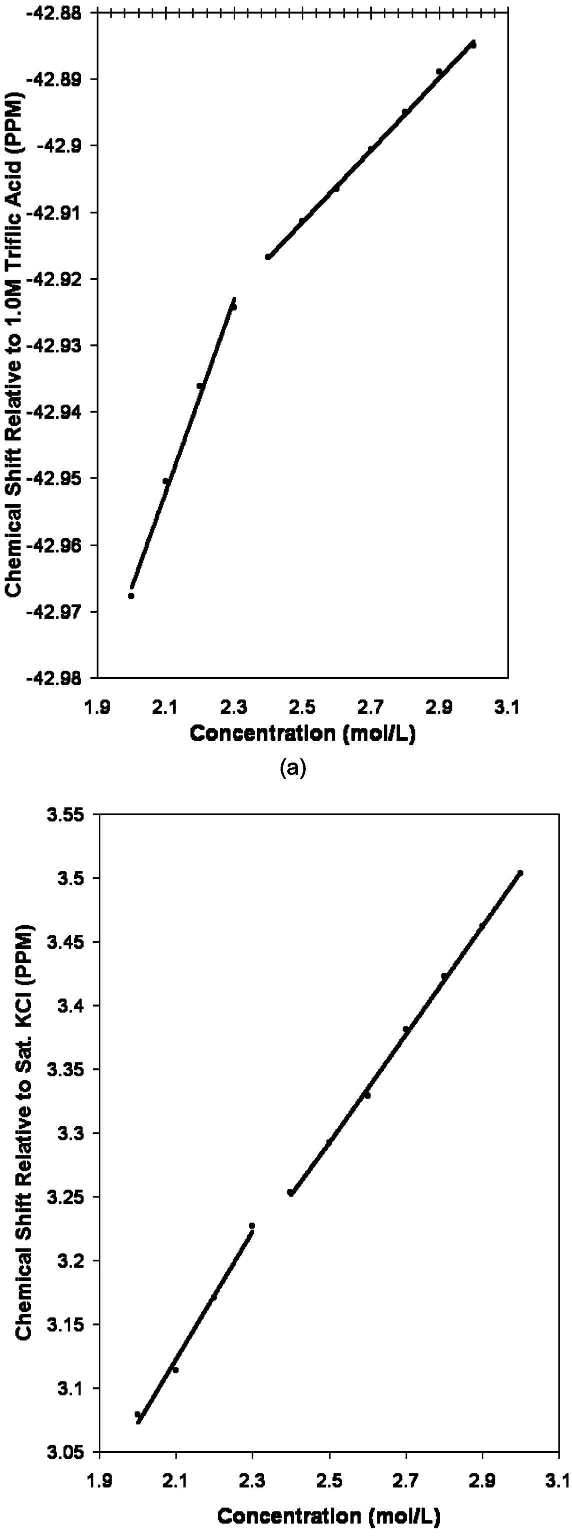
Variations in chemical shifts for potassium in ^{19}F and ^{39}K in KF solutions are shown in Figure 1a,b as a function of electrolyte concentration. The ^{19}F chemical shift for aqueous KF (Figure 1a) shows a change in slope at ~2.4 mol/L KF (slope 0.145 ± 0.002 to 0.054 ± 0.0005 δL/mol; maximum standard deviation in chemical shift measurement 0.005 ppm). The ^{39}K chemical shift for aqueous KF has an analogous change in slope at the same concentration (Figure 1b, slope 0.500 ± 0.007 to 0.422 ± 0.003 δL/mol; maximum standard deviation in chemical shift measurement 0.0013 ppm). The specific heat for 2.4 M KF[6] shows a minimum at 298 K, the temperature of the NMR experiment.

The chemical shift of ^{39}K in aqueous KCl (Figure 2a) shows a change in slope near 1.7 mol/L (1.36 ± 0.008 δL/mol, 0.1−1.5 M, and 0.601 ± 0.001 δL/mol, 1.8−2.2 M KCl; maximum standard deviation in chemical shift measurement 0.00008 ppm). The chemical shift of ^{7}Li in aqueous LiOH (Figure 2b) shows a change in slope near 3.0 M (−0.0197 ± 0.0002 δL/mol, 2.5−3.0 M, and −0.0191 ± 0.0002 δL/mol, 3.0−3.5 M; maximum standard deviation in chemical shift measurement 0.0004 ppm).

The specific heat capacity of aqueous solutions includes contributions from the water and from the hydrated electrolyte. As electrolyte is added to the solution, the specific heat capacity decreases monotonically. Plots of the specific heat capacity of electrolyte solutions as a function of temperature are similar to the corresponding plot for pure water; however, the perturbation of the bulk water structure by the electrolyte results in a shift in the location of the minimum as well as subtle changes in curve shape (Figure 3).

Figure 3a shows a plot of the specific heat capacity of a solution of 2.4 M KF and that of pure water. The minimum value for each of the specific heat capacities was subtracted to present the two graphs on the same scale. Figure 3b is a corresponding plot of the specific heat capacities of 1.6 M KCl and pure water. The concentration at which the minimum in the specific heat capacity of LiOH solution corresponds to 298 K is 2.95 M.

The solution concentration at which the specific heat minimum corresponds to 298 K, the temperature of the NMR experiment, is the same as the concentration at which the slope of the chemical shift changes for KF, KCl, and LiOH solutions. The change in the slope of the chemical shift with concentration points to the existence of a weak continuous transition at the concentration where the slope changes. The correspondence between this concentration and the concentration at which the specific heat capacity has a minimum at the same temperature is consistent with the occurrence of a weak continuous transition in the structure of the liquid.



(a)

(b)

Figure 1. (a) Concentration dependence of ^{19}F chemical shift of aqueous KF relative to 1 M trifluoromethanesulfonic acid (triflic acid). (b) Concentration dependence of ^{39}K chemical shift of aqueous KF relative to saturated KCl.

The plots in Figures 1 and 2 show a linear relationship between chemical shift and temperature both before and after a presumed transition. The slopes of the two straight line segments are in all cases statistically significantly different from each other. The plots are very similar to the variation of the Mössbauer center shift measured with ^{57}Co as a function of temperature in a ferroelectric lead titanate lattice.[8] The original plot shows a straight line dependence on the center shift both

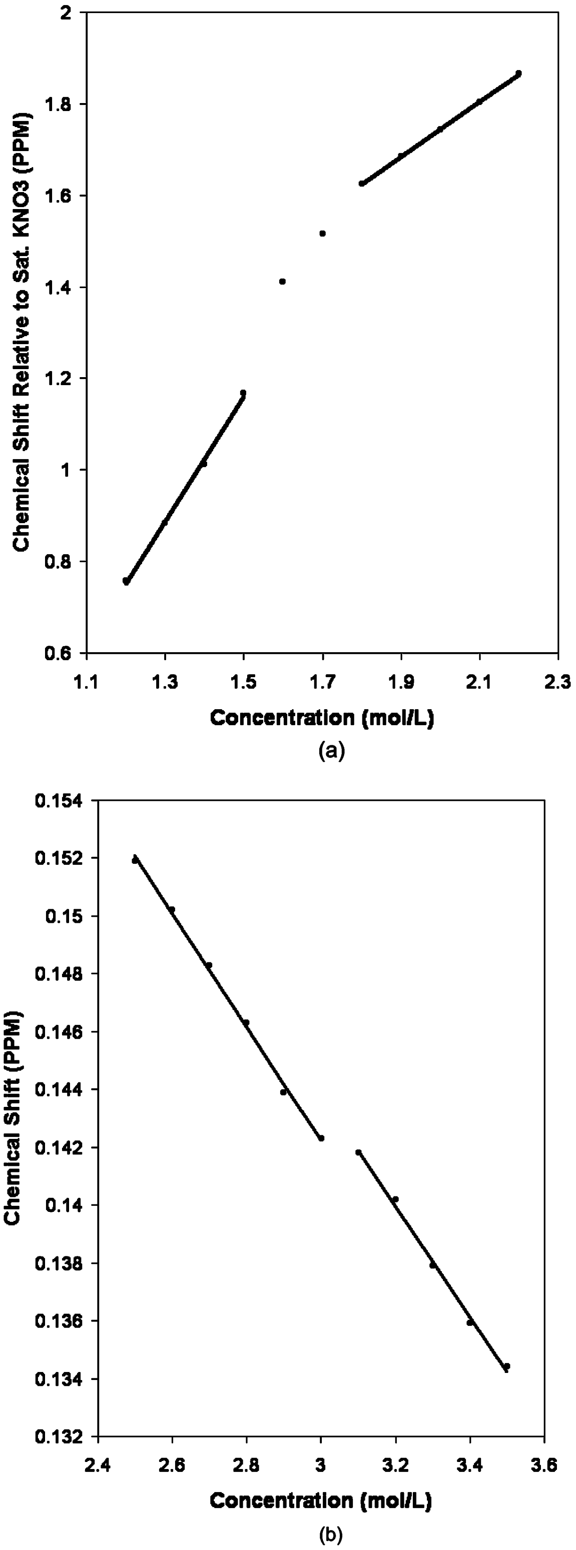


Figure 2. (a) ^{39}K chemical shift (ppm) of KCl relative to saturated KNO_3. (b) ^{7}Li chemical shift (ppm) of LiOH relative to 2.0 M LiI.

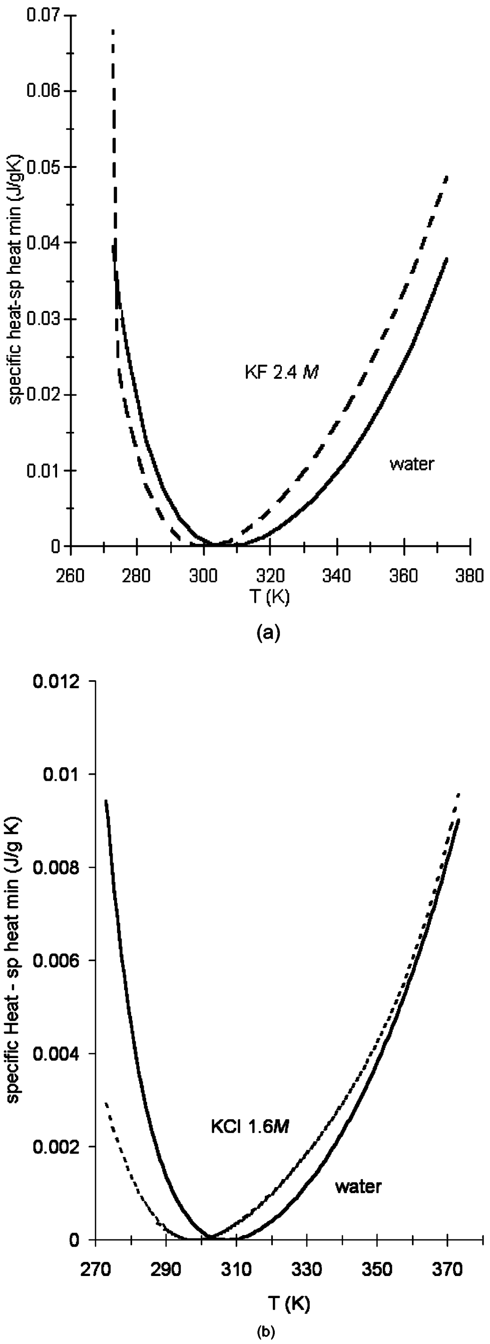


Figure 3. (a) Specific heat minimum of water and 2.4 M KF. (b) Specific heat minimum of water and 1.6 M KCl. (The minimum value for each of the specific heat capacities was subtracted to present the two graphs on the same scale.)

prior to and after the critical temperature. The two lines have distinct slopes and intercepts.

The addition of electrolytes to water perturbs hydrogen bond strength and liquid structure through electron delocalization between the electrolyte and water.[4] This perturbation of the water structure shifts the location of the specific heat minimum in the liquid.

A maximum in the heat capacity, C_P, of a liquid is recognized at the locus of a continuous phase transition. Probably the best-known example of this is the so-called λ transition in helium.[9] The helium λ transition is associated with a sharply peaked heat capacity. A plot of heat capacity with temperature that showed a correspondingly sharp minimum would be directly recognized as indicating a continuous phase transition. In the case of the heat capacity of water (Figure 3) the minimum is very broad, so the continuous transition must be weak. The change in slope of the chemical shifts of electrolytes at the concentration corresponding to the specific heat minimum at the same temperature points to the occurrence of a weak continuous transition in the electrolyte solutions. Because the effect of the electrolyte is to produce a small perturbation in the specific heat capacity of water, the corresponding minimum in the heat capacity of water should also correspond to a weak continuous transition in the structure of the liquid. The nearly flat curve for the heat capacity at constant pressure as a function of temperature suggests that the precise location of the minimum will strongly depend on the absolute pressure.

The observation of a weak continuous transition in aqueous solutions of electrolytes gives substantial support to the new model for the equilibrium structure of aqueous solutions of electrolytes.[10] The existence of a phase transition in the liquid structure that can be extrapolated back to the minimum in the heat capacity at 1 atm indicates the presence of a structural change at the transition in both pure water and the electrolyte solution. Presumably both of these structural changes are the same, which means that in the aqueous solution there must be regions of the liquid that have the same local and globally averaged chemical structure as is found in pure water at the same point in the phase transition. The only reasonable way for this to happen is for there to be intercalated islands of pure water and islands of liquid crystalline electrolyte hydrate in the aqueous solution. This is the essence of the new model for the structure of aqueous solutions of electrolytes.[10] The models of aqueous solutions that call for the existence of isolated ions with hydration spheres of nearby water molecules cannot be compatible with the existence of a phase transition that extrapolates smoothly back to the pure liquid. At all concentrations higher than infinite dilution, one would expect the presence of the isolated ions in the liquid to substantially perturb the local and globally averaged chemical structure of the liquid and, thus, nonlinearly impact the locus of the transition.

4. Summary and Conclusions

Plots of NMR chemical shifts for Li, K, F, and Cl nuclei as a function of electrolyte concentration in solutions of KF, KCl, and LiOH all exhibited straight line relationships between chemical shift and concentration both before and after the concentration at which the specific heat of the solution had a minimum at the temperature of the magnetic resonance experiment. These data permit the inference of a weak continuous phase transition occurring in aqueous solutions at the specific heat minimum of the solution. Extrapolation to low concentrations implies that a similar phase transition must occur in pure water at the minimum in the heat capacity at constant pressure (307.6 K,[11] 1 atm). These observations provide strong support for the new model[10] of aqueous solutions that is based on intercalated islands of pure water and islands of liquid crystalline electrolyte hydrate in the solution.

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