

# Slow Solvation Dynamics of a Water–Nitrobenzene System

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## ABSTRACT

Very slow changes in solvation taking place in water-saturated nitrobenzene have been observed and studied by nuclear magnetic resonance (NMR), Fourier transform infrared, and inelastic neutron scattering spectroscopy. These changes are most likely caused by the rearrangement of the hydrogen-bonded water network. Lithium salts used as the “reporter” species in the  $^7\text{Li}$  NMR experiments accelerate this reorganization. Results of this work are important for electrochemical studies of the nitrobenzene–water interface.

## Introduction

Ion transfer at the liquid–liquid interface is a subject that impacts many fields of science. Understanding the kinetics of this process is critical for the study of biological membranes, separations science, and chemical sensors to name but a few fields. The kinetics of ion transfer at the liquid–liquid interface is usually investigated by dynamic electrochemical methods,<sup>1–6</sup> which perturb the system being studied. Other studies have focused on developing an understanding of the structure of the liquid–liquid interface, with models ranging from an essentially smooth water–organic interface to an interface with aqueous “fingers” reaching into the organic phase.<sup>7</sup> To our knowledge, the fate of an ion once it has traversed the water–organic phase, i.e., its solvation environment in the bulk organic phase, has been ignored. In essence, investigators in the field of liquid–liquid interfaces consider ions in the bulk phases as being rapidly solvated either by water or by organic solvent. Therefore, while much work in electrochemically probing the ion transfer has been undertaken, the identities of solvatomers and their dynamics in organic solvents are not fully understood. Outside the field of ion transfer, nuclear magnetic resonance (NMR) spectroscopy and vibrational spectroscopy have been standard techniques of study of solvation in homogeneous (bulk) phases.<sup>8</sup> Mass spectrometry studies<sup>9</sup> have proven

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that ions can exist in the organic phase shielded by clusters of water which have been cotransferred.

We had originally set out to conduct  $^7\text{Li}$  NMR studies of kinetics of  $\text{Li}^+$  ion transfer at the water–nitrobenzene interface. However, during initial experiments, very slow solvation dynamics were seen to take place in the bulk nitrobenzene. These observations, along with surging interest in solvation studies in bulk solvent, led us away from the purely interfacial studies to investigation of the state of water in nitrobenzene and its slow reorganization following some perturbation. Although  $^7\text{Li}^+$  has been used as the primary “reporter” species, in this account we outline the results of the study of the state of water in water-saturated nitrobenzene by various spectroscopic techniques.

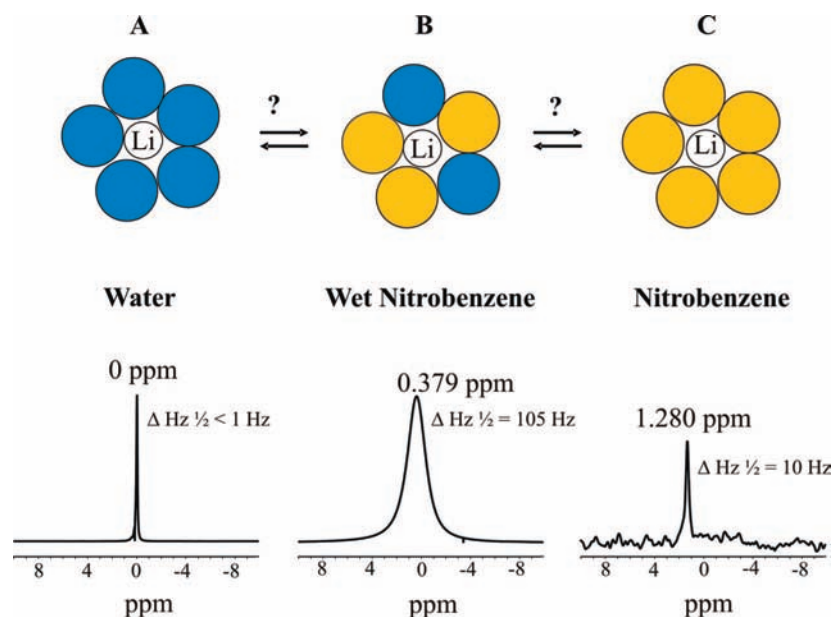
## $^7\text{Li}$ NMR Studies

The spectra of  $^7\text{LiBr}$  in dry NB and in water (Figure 1A,C)<sup>10</sup> show that it is possible to distinguish between the two different bulk solvation environments of  $\text{Li}^+$ , with a chemical shift separation of  $\sim 1.3$  ppm. Narrow resonant peaks were obtained for  $^7\text{Li}^+$  in pure water ( $\Delta\text{Hz}_{1/2} < 1$  Hz) and in dry nitrobenzene ( $\Delta\text{Hz}_{1/2} = 10$  Hz) in contrast to the  $^7\text{Li}^+$  peak in “wet” nitrobenzene ( $\Delta\text{Hz}_{1/2} = 105$  Hz), indicating the presence of multiple solvatomers (Figure 1B).

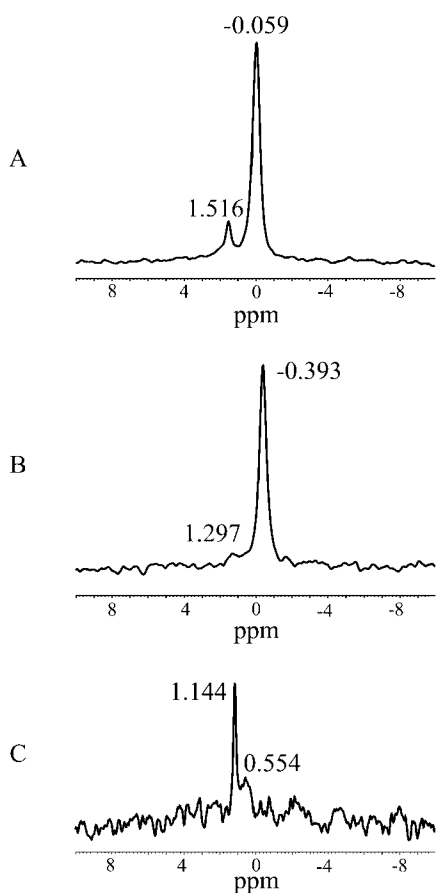
It was not recognized in the initial experiments (Figure 1B) that the dynamics of this mixed solvation is slow, spanning tens of hours. It was first noticed when the NMR spectrum of a 1-week-old sample was compared to the spectrum of the sample taken within 3 h of its preparation. The spectrum taken at 0 h shows two well-resolved peaks at  $\sim 0$  and  $\sim 1.52$  ppm (Figure 2A). After 90 h, the peak at  $\sim 1.52$  ppm disappears (Figure 2B). A 5 min immersion of the NMR sample in an ultrasonic bath caused the re-appearance of a similar peak at 1.14 ppm (Figure 2C). This experiment has been repeated many times, always yielding the reproducible pattern of behavior, although the peak separation varies slightly. The observed changes indicate that a reorganization of the solvated lithium ion is taking place on a very slow time scale. Surprisingly, the solvent reorganization could be reversed by sonication, while no noticeable changes in the  $^1\text{H}$  NMR spectra recorded simultaneously have been observed.

Initially, experiments with wet nitrobenzene were performed in standard glass NMR tubes. After the samples had been stored for 4 weeks in such tubes, the  $^7\text{Li}^+$  peaks broadened and could no longer be restored into the original two-peak pattern by sonication. The spectra of the solutions stored in Teflon maintained their “free” solution appearance. On the basis of these experiments, we could conclude that the wall of the glass NMR tube sorbs and “immobilizes” the lithium ion. This was corroborated when the concentration of  $\text{Li}^+$  in solution kept in glass dropped below the detection limit of the atomic

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**FIGURE 1.**  $^7\text{Li}$  NMR spectra of (A) LiBr in D.I water (saturated), (B) LiBr in wet nitrobenzene, prepared by stirring equal parts nitrobenzene and saturated aqueous lithium salt, and (C) LiBr in dry nitrobenzene, prepared by shaking an excess of lithium salt with dry NB for 5 min and allowing the mixture to equilibrate for 3 h prior to measurement.

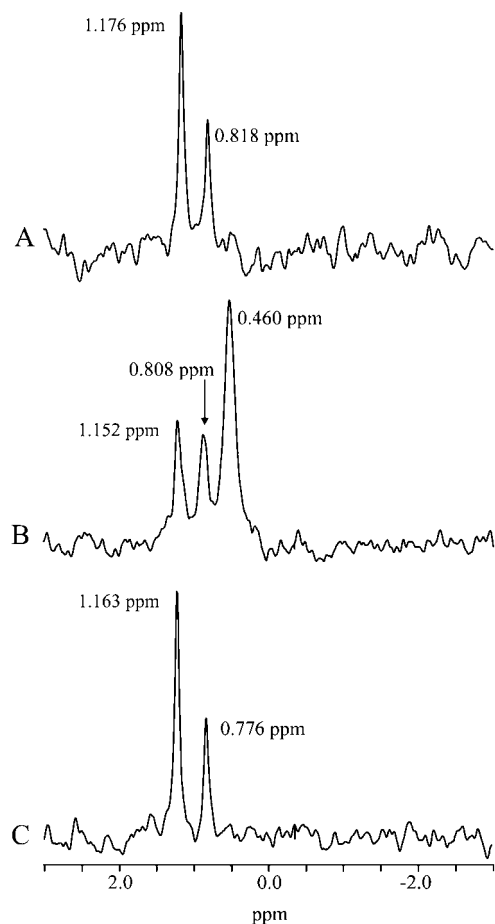


**FIGURE 2.** Dynamics of the self-organization in a  $\text{Li}^+$ –nitrobenzene (water) system.  $^7\text{Li}$  NMR spectrum of LiBr in wet nitrobenzene recorded (A) at 0 h (20 000 scans), (B) at 90 h (5500 scans), (C) as in panel B, but after sonication for 5 min (12 100 scans).

absorption spectroscopy instrument ( $10^{-6}$  M), while the  $\text{Li}^+$  concentration of the freshly prepared saturated solution of LiBr in “wet” NB could be determined to be 1.43

$\times 10^{-5}$  M. Glass so treated, analyzed by laser-induced breakdown spectroscopy, confirmed the irreversible incorporation of Li into the hydrated glass surface from wet NB. This observation is significant not only as a potential source of experimental error for normal glassware but also as an inexpensive way of doping lithium ions into oxide surfaces.<sup>11</sup>

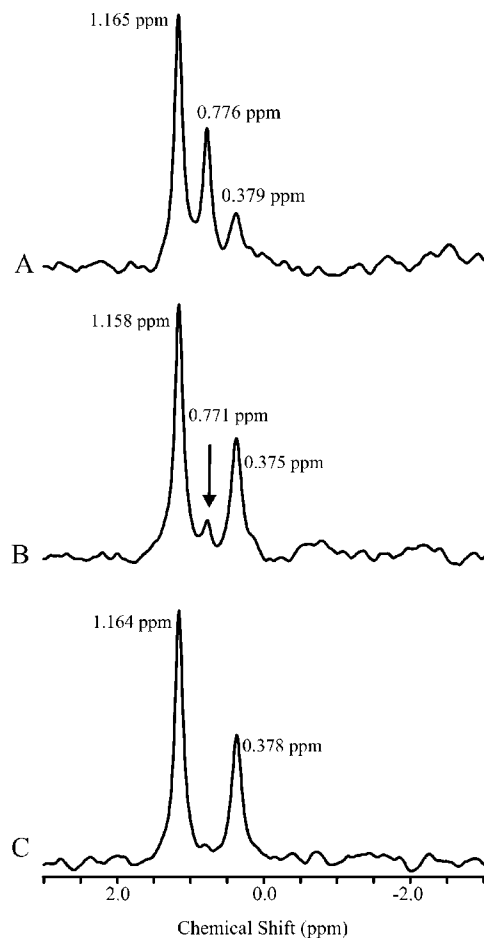
Numerous studies have suggested that ions move across the water–nitrobenzene interface as hydrated species<sup>12–15</sup> and exist in the organic phase as ion pairs. It is understandable that the anion identity strongly influences the water environment in the organic phase. The average hydration numbers of  $\text{Li}^+$ ,  $\text{Br}^-$ , and  $\text{ClO}_4^-$  in nitrobenzene have been determined experimentally to be 6.0, 2.1, and 0.2, respectively.<sup>16</sup> As such, the slow (up to 1 week) ordering of water in nitrobenzene by  $\text{Li}^+$  as reported earlier may be reliant on the presence of a hydrophilic anion such as  $\text{Br}^-$ . To study the effect of the anion, experiments analogous to those detailed above for LiBr were conducted with more soluble  $\text{LiClO}_4$ .<sup>17</sup> The first point of interest is that the concentration of lithium species, as determined by atomic absorption, is  $9.52 \times 10^{-4}$  M for lithium perchlorate and  $1.43 \times 10^{-5}$  M for LiBr. The higher solubility of  $\text{LiClO}_4$  yields a higher signal-to-noise ratio for  $^7\text{Li}$  NMR spectra.  $^7\text{Li}$  resonances were observable with as few as 64 scans. The high concentration made it possible to obtain kinetic information about solvation rearrangement. Since addition of  $\text{LiClO}_4$  to wet nitrobenzene did not result in the appearance of multiple  $^7\text{Li}$  resonances, it was an ideal opportunity to assess whether these ordered water species could be induced by alternative methods. We found three ways to produce metastable solvatomers in wet NB solution: by ultrasonication, by a temperature drop of  $\sim 10^\circ\text{C}$  over 5 min, and by addition of a small amount of water. The  $^7\text{Li}^+$  spectrum recorded within 5 min of such a perturbation exhibited a second



**FIGURE 3.**  $^7\text{Li}$  NMR spectra of (A)  $\text{LiClO}_4$  in wet NB with  $5\ \mu\text{L}$  of D.I. water added, (B)  $\text{LiClO}_4$  in wet NB with  $5\ \mu\text{L}$  of aqueous  $\text{LiClO}_4$  (1 mM) added, and (C)  $\text{LiClO}_4$  in wet NB cooled to 290 K. The temperature of the NMR probe was controlled to an accuracy of  $\pm 1$  K.

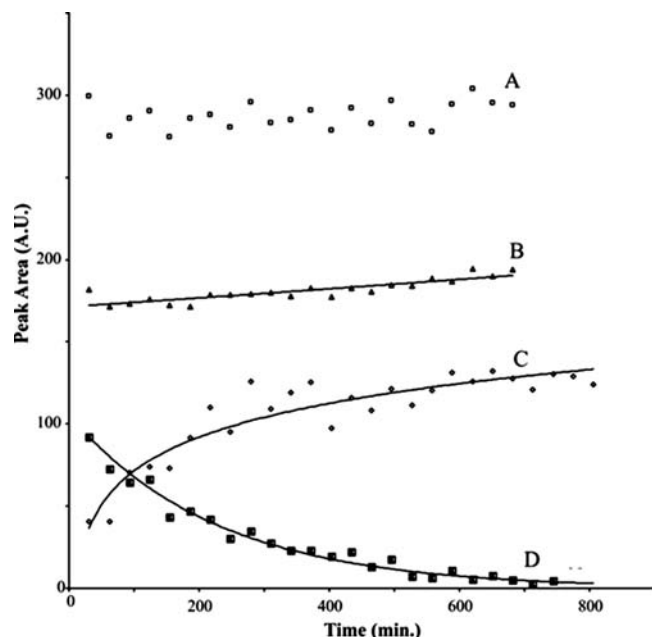
resonance at 0.818 ppm (Figure 3A), which is reminiscent of the  $\text{Li}_{(\text{NB}/\text{W})}$  water solvatomer from the LiBr experiments. When a small amount of aqueous  $\text{LiClO}_4$  was added to the initial sample, a third solvatomer of lithium appeared at 0.460 ppm (Figure 3B), which can be viewed as lithium ion solvated mostly by water,  $\text{Li}_{(\text{W})}$ . Figure 3C shows the effect when the sample initially equilibrated at 298 K was cooled to 290 K in the NMR probe. In this case, the most downfield (1.163 ppm) and intermediate (0.776 ppm) peaks are present. No samples scattered laser light (632.8 nm) after addition of the aqueous phase or after cooling, indicating that solutions were homogeneous on the  $< 1\ \mu\text{m}$  scale.

To follow the kinetics of solvatomer transformations,  $^7\text{Li}$  peaks were observed over a period of 15 h after  $\text{LiClO}_4$  in wet NB was perturbed by cooling. Successive NMR spectra were recorded as described above. It is clear from Figure 4 (spectrum A) that three primary solvatomers exist. The downfield peak at 1.165 ppm is nearly identical in chemical shift to that of  $\text{LiClO}_4$  dissolved in dry nitrobenzene. Therefore, this solvatomer must consist of lithium solvated mostly by nitrobenzene,  $\text{Li}_{(\text{NB})}$ . The small peak at 0.379 ppm has a chemical shift similar to that of 20 mM  $\text{LiClO}_4$  in  $\text{H}_2\text{O}$ . This solvatomer likely represents

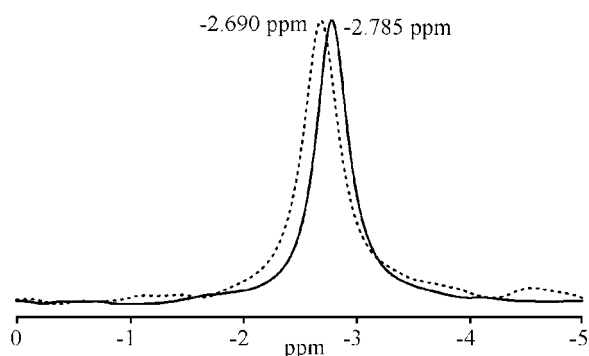


**FIGURE 4.**  $^7\text{Li}$  NMR spectra of  $\text{LiClO}_4$  in wet NB cooled in the NMR probe to 290 K: (A) 0, (B) 310, and (C) 806 min.

lithium solvated in majority by water,  $\text{Li}_{(\text{W})}$ . The peak at 0.776 ppm is a solvatomer comprising lithium solvated by both nitrobenzene and water. This solvatomer will be termed  $\text{Li}_{(\text{NB}/\text{W})}$ . The changes in the relative intensities of the intermediate and of the upfield peaks suggest that lithium in the mixed solvation state seems to exchange its mixed solvation sphere for one dominated by water. The results of the 15 h kinetic experiment are summarized in Figure 5. Plot A is the plot of the sum of all three peak areas seen in Figure 4. The sum is constant, indicating that the total level of lithium species in the NMR active region of the sample tube does not decrease over the 15 h period. This is an important observation corroborating the incorporation of  $\text{Li}^+$  into glass. The increase in the  $\log(\text{area})$  of the most downfield peak [1.165 ppm (Figure 4B)] corresponding to the solvatomer  $\text{Li}_{(\text{NB})}$  is linear, indicating first-order kinetics with a rate constant  $k$  of  $3 \times 10^{-6}\ \text{s}^{-1}$ . The increase in the area of the most upfield peak [0.379 ppm (Figure 4)] corresponding to  $\text{Li}_{(\text{W})}$  is shown in plot C. The  $\log(\text{area})$  plot of the intermediate peak [0.776 ppm (Figure 4A)] corresponding to a decrease in the level of  $\text{Li}_{(\text{NB}/\text{W})}$  is also linear. This indicates first-order kinetics with a rate constant  $k$  of  $7 \times 10^{-5}\ \text{s}^{-1}$ . If we take the end point of the kinetic experiment to be 651 min, the peak areas corresponding to  $\text{Li}_{(\text{NB})}$ ,  $\text{Li}_{(\text{NB}/\text{W})}$ , and



**FIGURE 5.** Plot of peak area vs time for the solvatomers produced when a  $\text{LiClO}_4$ -wet NB system is cooled to 290 K and followed by  $^7\text{Li}$  NMR over 15 h. (A) Sum of peak areas of  $\text{Li}_{(\text{NB})}$ ,  $\text{Li}_{(\text{NB/W})}$ , and  $\text{Li}_{(\text{W})}$  solvatomers. (B) Growth in concentration of the  $\text{Li}_{(\text{NB})}$  solvatomer. (C) Increase in concentration of the  $\text{Li}_{(\text{W})}$  solvatomer. (D) Decrease in concentration of the  $\text{Li}_{(\text{NB}/\text{H}_2\text{O})}$  solvatomer.



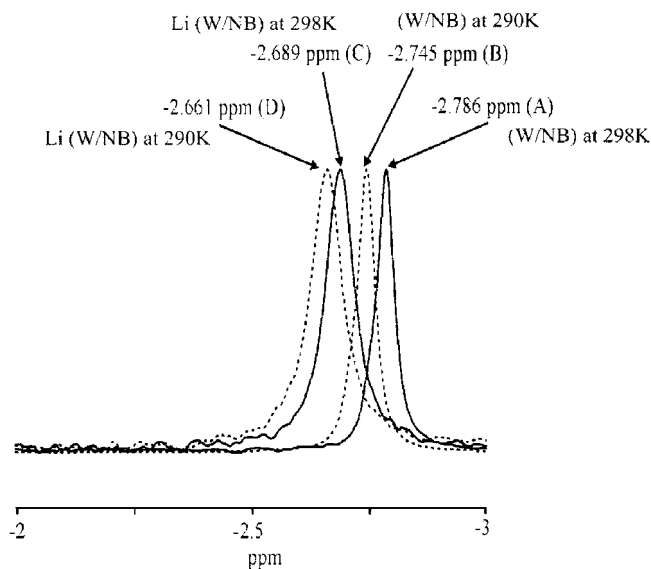
**FIGURE 6.**  $^2\text{H}$  NMR spectrum of nitrobenzene saturated with  $\text{D}_2\text{O}$  (—) and nitrobenzene saturated with  $\text{LiClO}_4$  in  $\text{D}_2\text{O}$  (6 M) (---).

$\text{Li}_{(\text{W})}$  solvatomers at the end of the 15 h period were 57.6, 2.3, and 40.2%, respectively.

## Deuterium NMR Studies<sup>18</sup>

The drawback of using  $^7\text{Li}$  as the NMR reporting nucleus is its effect on the restructuring of the water environment by itself. Using deuterium as the NMR-active nucleus allows comparison of the water environment in nitrobenzene by itself. This applies also to FTIR and neutron scattering studies (vide infra).

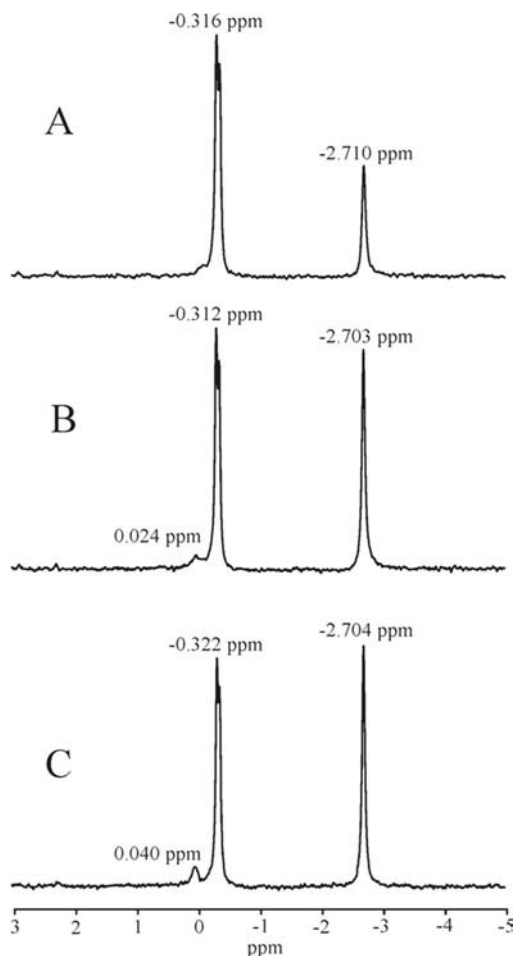
The effect of  $\text{LiClO}_4$  on the ordering of water in nitrobenzene was studied via a one-dimensional  $^2\text{H}$  NMR experiment (Figure 6). Pure  $\text{D}_2\text{O}$  was calibrated to 0 ppm, and then two spectra were recorded in succession. Spectrum 1 (solid line) is the  $^2\text{H}$  NMR spectrum for nitrobenzene saturated with  $\text{D}_2\text{O}$ . Spectrum 2 (dashed line) is the  $^2\text{H}$  NMR spectrum for nitrobenzene equilibrated with 6 M  $\text{LiClO}_4$  in  $\text{D}_2\text{O}$ . This shift of the  $^2\text{H}$



**FIGURE 7.**  $^2\text{H}$  NMR spectrum of nitrobenzene saturated with  $\text{D}_2\text{O}$  at (A) 298 K (—) and (B) 290 K (---) and nitrobenzene saturated with  $\text{LiClO}_4$  in  $\text{D}_2\text{O}$  at (C) 298 K (—) and (D) 290 K (---).

resonance toward 0 ppm suggests an increase in the extent of water ordering leading to a  $^2\text{H}$  resonance that resembles that of bulk  $\text{D}_2\text{O}$ .

Unlike  $^7\text{Li}$  NMR studies, the formation of multiple solvatomers by cooling cannot be detected by  $^2\text{H}$  NMR due to the strong resonance of the excess  $\text{D}_2\text{O}$ . Figure 7 shows the effect of cooling on the  $^2\text{H}$  chemical shift for nitrobenzene stirred with a saturated solution of  $\text{LiClO}_4$  in  $\text{D}_2\text{O}$ . Spectra A and B are for  $\text{D}_2\text{O}$  in wet nitrobenzene at 298 and 290 K, respectively. Spectra C and D are for  $\text{LiClO}_4$  in wet nitrobenzene at 298 and 290 K, respectively. The cooling of both solutions results in the subtle shift (0.03 ppm) toward 0 ppm, indicating that the water species take on increasingly bulk water character. This suggests that in both solutions there is an aggregation of water upon cooling. The chemical shift difference upon addition of lithium ion [0.95 ppm (Figure 7)] is large in comparison to that caused by cooling. However, cooling does not result in the occurrence of multiple  $^2\text{H}$  resonances as seen in the  $^7\text{Li}$  NMR spectra. It is important to remember that this is the same experiment only using a different “reporter species”. The apparent discrepancy in this result can be explained by considering their relative abundances. When cooled and followed by  $^7\text{Li}$  NMR, the solution evidently becomes supersaturated with water and becomes microheterogeneous; i.e., the temperature decrease causes clusters of water to form. This indicates that lithium partitions into this phase, resulting in two “solvatomers”, one consisting of lithium solvated in majority by nitrobenzene and one resulting from cooling, resembling lithium solvated by a mixed solvation shell,  $\text{Li}_{(\text{NB}/\text{w})}$ . The water clusters that form after a modest temperature drop of 8 K are a small fraction of the overall water content of nitrobenzene. It is for this reason that in the case of the  $^2\text{H}$  spectrum (Figure 7B) the second solvatomer is unobservable. Conversely, when  $^7\text{Li}$  NMR is used, lithium species preferentially solvate with the newly

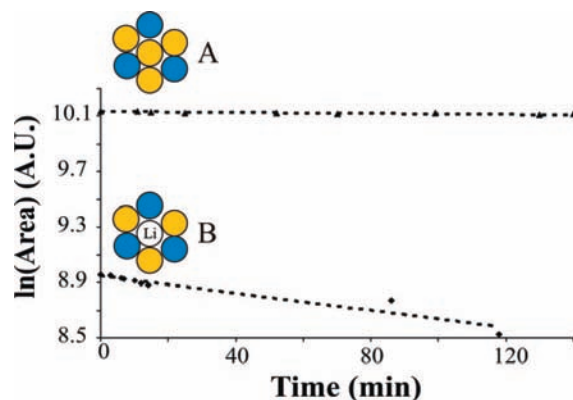


**FIGURE 8.**  $^2\text{H}$  NMR spectra of  $\text{LiClO}_4$  (wet NB) with  $5\ \mu\text{L}$  of  $\text{D}_2\text{O}$  added and shaken: (A) 0, (B) 90, and (C) 180 min.

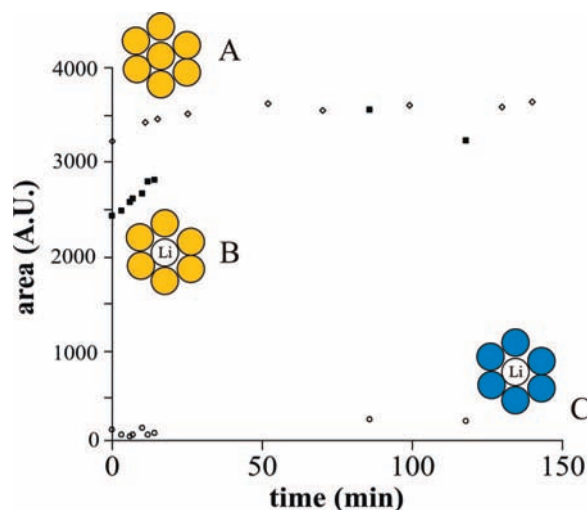
formed species, therefore “illuminating” the water-rich solvatomer  $\text{Li}_{(\text{W}/\text{NB})}$ .

The same effect as cooling can be induced by addition of a small amount of water as an adherent film on the surface of a glass capillary. This introduces into the initial  $\text{LiClO}_4$ –wet nitrobenzene system an additional  $5\ \mu\text{L}$  of  $\text{D}_2\text{O}$ . Spectra A–C of Figure 8 show the solvatomer transformation at time zero (insertion of a wet glass capillary), 90 min, and 180 min, respectively. It is clear that three primary solvatomers exist. Pure  $\text{D}_2\text{O}$  is assigned to 0 ppm. Nitrobenzene containing a  $\text{LiClO}_4/\text{D}_2\text{O}$  mixture gives a single resonance at ca.  $-2.7$  ppm. Therefore, the downfield peak at  $-0.316$  ppm is a mixed solvation shell with nitrobenzene and water, and the peak at  $-2.710$  ppm represents a species almost entirely solvated by nitrobenzene. The shoulder which grows at  $0.040$  ppm is consistent with  $^7\text{Li}$  NMR results and represents a water layer formed at the glass capillary surface. The changes in the relative intensities of the three peaks suggest that the solvatomer formed immediately upon addition of  $5\ \mu\text{L}$  of  $\text{D}_2\text{O}$  is metastable and exchanges its mixed solvation sphere for one dominated by water ( $0.040$  ppm) and one dominated by nitrobenzene ( $-2.704$  ppm). This is in direct agreement with the results of the analogous  $^7\text{Li}$  experiments.

The results of these experiments are summarized in Figures 9 and 10. Figure 9 represents the decay of the

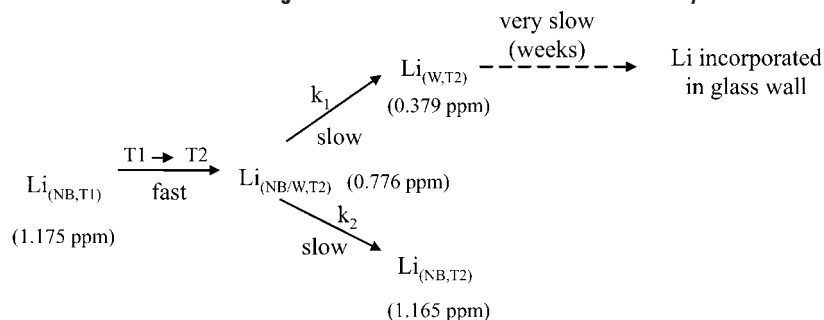


**FIGURE 9.** Decrease in the concentration of the  $\text{Li}_{(\text{NB}/\text{W})}$  solvatomer without (A) and with (B)  $\text{LiClO}_4$  (6 M) in  $\text{D}_2\text{O}$  during preparation of wet nitrobenzene.



**FIGURE 10.** Increase in the concentration of the  $\text{Li}_{(\text{NB})}$  solvatomer without (A) and with (B)  $\text{LiClO}_4$  (6 M) in  $\text{D}_2\text{O}$  during preparation of wet nitrobenzene. Increase in the concentration of the  $\text{Li}_{(\text{W})}$  solvatomer (C).

peak at ca.  $-0.3$  ppm (Figure 8) corresponding to  $\text{Li}_{(\text{NB}/\text{W})}$ . The two curves represent the decay of this metastable species without (A) and with (B)  $\text{LiClO}_4$  in  $\text{D}_2\text{O}$ . In both cases, the logarithm of (peak area) versus time is linear, indicating first-order kinetics. The rate of decrease of the peak area is much greater in the presence of lithium ion than without it, suggesting that  $\text{Li}^+$  increases the rate of decomposition for this species. The increase in the area of the most upfield peak [ca.  $-2.7$  ppm (Figure 8)] corresponding to  $\text{Li}_{(\text{NB})}$  is shown in Figure 10. Plots A and B represent the experiment performed without and with  $\text{LiClO}_4$  in  $\text{D}_2\text{O}$ . The increase in the area of the most downfield peak [ $0.040$  ppm (Figure 8)] corresponding to  $\text{Li}_{(\text{W})}$  is shown in plot C. There is no observable growth in this peak without lithium. The increases in peak areas shown in plots A–C do not follow first-order kinetics. On decay of the metastable  $\text{Li}_{(\text{NB}/\text{W})}$  species, there is clearly a subsequent transport of water from the capillary wall followed by incorporation of this water into the  $\text{Li}_{(\text{W})}$  and  $\text{Li}_{(\text{NB})}$  species. The two superimposed processes make kinetics difficult to interpret; nonetheless, the kinetics of the process is comparable to that induced by cooling

Scheme 1. Slow Reorganization of the  $\text{Li}^+$ –Nitrobenzene–Water System <sup>a</sup>

<sup>a</sup>T1 indicates room temperature and T2 a cooled solution.

(Figures 4 and 5). It can be represented schematically (Scheme 1).

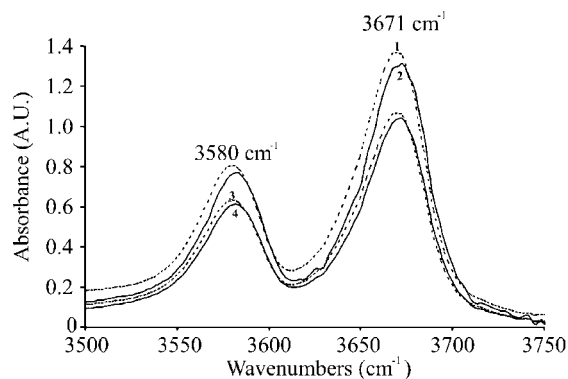
The diffusion constants of individual species were determined using diffusion-ordered NMR spectroscopy (DOSY). Values were measured for the  $^2\text{H}$  resonance corresponding to  $\text{Li}_{(\text{NB})}$ . The resulting hydrodynamic radii,  $r_h$ , were calculated from the Stokes–Einstein equation.<sup>19</sup> Somewhat surprising is the finding that the ordering effect of lithium on water in nitrobenzene does not result in a measurable increase in the hydrodynamic radii for the solvatoomer  $\text{Li}_{(\text{NB})}$ .<sup>20</sup> Addition of lithium to the wet nitrobenzene [observed in the  $^2\text{H}$  experiments (Figure 8)] may result in an increased level of hydrogen bonding of the water dissolved in nitrobenzene.  $^7\text{Li}$  NMR results for LiBr in wet nitrobenzene suggest that lithium can order water to the point that a second clear solvatoomer,  $\text{Li}_{(\text{NB}/\text{W})}$ , is observed. However, this does not mean that the  $\text{Li}_{(\text{NB})}$  solvatoomer [ $^2\text{H}$ ,  $-2.7$  ppm (Figure 8)] should experience an increase in size. The apparent failure of lithium to increase the hydrodynamic radii of the solvatoomer at ca.  $-2.7$  ppm in the  $^2\text{H}$  spectra does not contradict the results of the earlier  $^7\text{Li}$  experiments. It is possible that the addition of lithium ion does not lead to formation of “pockets” of isolated hydrated species in the organic phase, but rather formation of a network of H-bonded water. This hypothesis agrees with the fact that hydrodynamic radii obtained from DOSY are similar to those obtained in water. A simple calculation of Loschmidt’s number for lithium (ions per cubic centimeter) shows an interatomic separation for the lithium ions of  $\sim 100$  Å, making it reasonable for  $\text{Li}^+$  to order water through H-bonding of its multiple solvation shells. Further evidence that  $\text{Li}^+$  contributes to an increase in the extent of water H-bonding was obtained by observing the free OH stretch of wet nitrobenzene by FTIR.<sup>17</sup>

One explanation for the apparent small change in the hydrodynamic radii upon addition of  $\text{Li}^+$  is the misinterpretation of DOSY results. DOSY assesses the diffusion of the NMR active nucleus (i.e., proton) irrespective of whether it truly represents the movement of the entire species (i.e., water). In our experiment, it is possible that the diffusion of  $^2\text{H}$  (instead of  $\text{D}_2\text{O}$ ) is being measured (hence the large value of  $D$ ) as the deuterium “hops” from one water molecule to another.

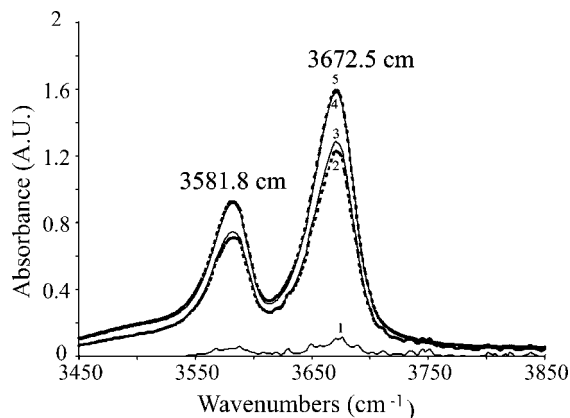
## Vibrational Spectroscopy

The IR bands corresponding to the antisymmetric ( $\nu_3$ ) and symmetric ( $\nu_1$ ) stretching modes are normally seen at  $3000\text{--}3800$   $\text{cm}^{-1}$ . The antisymmetric ( $\nu_3$ ) and symmetric ( $\nu_1$ ) stretching modes have different positions and intensities depending on the water environment and the association of water molecules through H-bonding absorbing at  $3756$  and  $3657$   $\text{cm}^{-1}$ , respectively.<sup>20</sup> The difference in the maximum positions of these bands is ca.  $100$   $\text{cm}^{-1}$ , for the example of water bound in symmetric complexes, with both protons hydrogen bonded. For water dissolved in a hydrophobic solvent, especially when the  $\text{H}_2\text{O}$  concentration is  $< 1 \times 10^{-3}$  M, the  $\nu_3$  and  $\nu_1$  bands are two separate absorptions.<sup>19</sup> As the water content increases in less hydrophobic solvents, the bands appear to merge, and for pure water, a broad band with a maximum at approximately  $3300$   $\text{cm}^{-1}$  is observed.<sup>19</sup> In reality, this broad absorption, which is the familiar “OH peak”, is comprised of the  $\nu_3$  and  $\nu_1$  bands that broaden considerably due to hydrogen bonding and can be deconvoluted for elucidation of states of water in organic solvents.<sup>22–25</sup>

Spectra of wet NB without (1 and 2) and with (3 and 4)  $\text{LiClO}_4$  at room temperature and  $288$  K are shown in Figure 11. The data suggest a minor decrease in free water content upon cooling (1 to 2). While this effect is not unambiguously detectable, the decrease in the level of free water due to the addition of  $\text{LiClO}_4$  (1 to 3) is obvious. This result shows that  $\text{LiClO}_4$  is capable of bonding significant amounts of free water in its solvation sphere.



**FIGURE 11.** FTIR spectra of (1) wet NB at room temperature, (2) wet NB at  $10$   $^{\circ}\text{C}$ , (3) a  $\text{LiClO}_4$ /wet NB mixture at room temperature, and (4) a  $\text{LiClO}_4$ /wet NB mixture at  $100$   $^{\circ}\text{C}$ . Each experiment was recorded vs a background spectrum of dry NB.



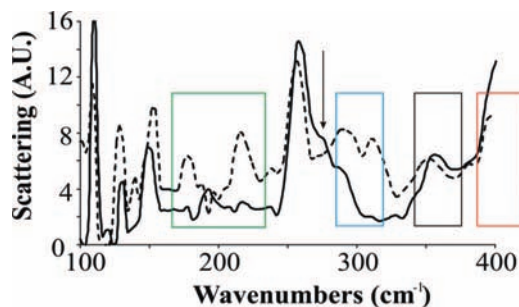
**FIGURE 12.** FTIR spectra of (1) a LiBr/wet NB mixture, (2) that mixture diluted 50% with wet NB, (3) a LiClO<sub>4</sub>/wet NB mixture, (4) that mixture diluted 50% with wet NB, and (5) wet NB.

The spectrum of LiBr in wet NB (Figure 12, spectrum 1) shows weak absorbance in the free water region. On dilution to 50% with wet nitrobenzene, spectrum 2 is observed. The free water content increases by a factor of 10, indicating that the water ordering effect of the LiBr is disturbed by dilution. On the other hand, when a solution of LiClO<sub>4</sub> in wet nitrobenzene (3) is diluted to 50% with wet nitrobenzene (4), the resulting absorbance in the free water region is indistinguishable from that of wet nitrobenzene (5). It is clear from the significant differences between the LiClO<sub>4</sub> and LiBr spectra that the anion plays a major role in organization of water in the nitrobenzene phase. Furthermore, addition of the hydrophobic salt LiHCB<sub>11</sub>Me<sub>11</sub> (kindly donated by J. Michl) did not alter the spectrum versus a background of wet nitrobenzene, leading to the conclusion that the efficacy of “LiX” on ordering of water increases with the hydrophobicity of the anion in the following order: HCB<sub>11</sub>Me<sub>11</sub><sup>−</sup> < ClO<sub>4</sub><sup>−</sup> < Br<sup>−</sup>.

## Inelastic Neutron Scattering

The bonded OH species cannot be observed by FTIR due to the large absorbance of the nitrobenzene between 3000 and 3500 cm<sup>−1</sup>. In this respect, inelastic neutron scattering (INS) can be used. The large inelastic scattering cross section of H<sub>2</sub>O versus D<sub>2</sub>O yields scattering patterns arising from the various states of water that are not obscured by H atoms on the nitrobenzene as is the case of FTIR. However, the INS measurements have to be taken at cryogenic temperatures. Therefore, the samples are rapidly cooled to 12 K. The system remains amorphous at this temperature which is confirmed by low-temperature X-ray diffraction studies. Figure 13 shows the neutron vibrational spectra for deuterated nitrobenzene saturated with H<sub>2</sub>O (dashed line) and LiBr<sub>(aq, saturated)</sub> (solid line).

The band that extends from 400 to 420 cm<sup>−1</sup> (“400 cm<sup>−1</sup> band”) contains one or more librational modes of water. For a water molecule in a general force field, there are three librations, one for each axis of rotation, seen only if there is a restoring force present for each libration. There is the “rock”, which is motion in the plane of the water



**FIGURE 13.** Neutron vibrational spectra of nitrobenzene-*d*<sub>5</sub> saturated with H<sub>2</sub>O (thin line) and H<sub>2</sub>O and LiBr (thick line). The regions of the spectrum highlighted by boxes and assigned vibrations are discussed in the text. A blank (pure nitrobenzene-*d*<sub>5</sub>) was measured as well as a spectrum for nitrobenzene-*d*<sub>5</sub> saturated with H<sub>2</sub>O and another nitrobenzene-*d*<sub>5</sub> sample stirred for 18 h with H<sub>2</sub>O saturated with LiBr.

molecule; the “twist”, which is rotation about the C<sub>2</sub> diad; and the “wag”, which is rotation about the H–H axis with increasing frequency.<sup>26</sup> In free water, the librational modes are weak and appear as extremely broad, ill-defined bands in Raman and IR spectra. In systems where water is a ligand to a metal cation, these librational modes become much more pronounced.<sup>27</sup> Unlike FTIR spectroscopy, the librational modes are usually the strongest contribution to the INS vibrational spectrum of water. Just as interesting is the disappearance of intensity in the vibrational spectrum at 175 and 220 cm<sup>−1</sup>. These modes are attributed to hindered translations in ice and other forms of associated water molecules (clusters). According to Bertie and Whalley,<sup>28</sup> these modes are assigned to maxima in the density of vibrational states of water clusters because of longitudinal acoustic and transverse optic vibrations, respectively. Their disappearance from the vibrational spectrum upon addition of LiBr is likely indicative of a drastic rearrangement of water molecules in the system. Upon addition of LiBr to the system, some intensity appears as a shoulder on the high-frequency side of the 260 cm<sup>−1</sup> peak (arrow in Figure 13) and is most likely associated with a Li–O stretching mode,<sup>29</sup> further proof of the association of water with Li<sup>+</sup>. The peaks at 260 and 350 cm<sup>−1</sup> are largely unaffected by the presence of LiBr in the system. However, they are not present in the blank (pure nitrobenzene-*d*<sub>5</sub>) and are undoubtedly associated with water in the system. The 260 cm<sup>−1</sup> mode may be associated with H<sub>2</sub>O molecules binding to nitrobenzene (N–O···H–O–H stretch). The region between 280 and 320 cm<sup>−1</sup> (here called the 300 cm<sup>−1</sup> band) is characterized by a decrease in intensity upon addition of LiBr, possibly another librational mode of water. If this is the case, we may associate the modes at 300, 350, and 400 cm<sup>−1</sup> with water librations. All three librational modes are present in the nitrobenzene-*d*<sub>5</sub>–H<sub>2</sub>O system. One mode is suppressed (rock) and one mode enhanced (wag) when LiBr is added. The water twist at 350 cm<sup>−1</sup> seems unaffected. Its assignment as a librational mode is supported by its width, which is significantly larger than the sharp 260 cm<sup>−1</sup> mode.

In summary, the inelastic neutron scattering adds evidence to FTIR results which suggest that addition of lithium salt to wet nitrobenzene increases the extent of hydrogen bonding between water molecules. The INS technique has also confirmed the association of water around  $\text{Li}^+$ , as suggested by the earlier  $^7\text{Li}$  and  $^2\text{H}$  NMR experiments.

## Conclusions

Contrary to current thinking in the field of ion transfer at the liquid–liquid interface, the organic phase is not static and homogenous. There are (at least) three solvatoomer configurations in wet nitrobenzene undergoing slow reorganization upon perturbation.  $^2\text{H}$  NMR allowed us to study the wet nitrobenzene phase, and we concluded that these solvatomers exist whether lithium salts are present. On the other hand,  $^7\text{Li}$  NMR experiments suggest that the first solvatoomer contains a majority of nitrobenzene, the second is a mixed solvation shell consisting of nitrobenzene and water, and the third solvatoomer is a large water aggregate of immobilized water on a hydrophilic surface. The mixed solvation state is relatively short lived ( $t_{1/2}$  of approximately hours) and can be induced by addition of water or by supersaturating the system upon cooling. This is a metastable state and decays back into the homogenous bulk NB solvatoomer or to the hydrophilic surface if present. In the  $^7\text{Li}$  NMR experiments, the hydrophobicity of the salt, determined by the anion, affects the relative intensity of the three  $^7\text{Li}$  resonances.

Addition of lithium ion serves to promote hydrogen bonding in water and accelerates the decay of the metastable solvatoomer. There is no experimental evidence that it has a measurable effect on the size of the mixed solvatoomer or on the water aggregate immobilized on the glass surface. The system can be summarized as follows.

Below a critical water concentration ( $\sim 200$  mM) water is bound but homogeneously distributed in nitrobenzene. Addition of lithium salt to this system, be it by mixing or by interfacial ion transfer during an electrochemical experiment, has two main effects. First, the lithium promotes H-bonding between the dissolved water molecules, as confirmed by FTIR and neutron scattering. Second, the H-bonded water may aggregate causing microheterogeneity of the system, and a second resonance is observed in both the  $^2\text{H}$  and  $^7\text{Li}$  NMR spectra of solvated lithium ion [ $\text{Li}_{(\text{NB}/\text{W})}$ ]. In the presence of glass, a third solvation state can form at the glass surface, having character even closer to that of bulk water [ $\text{Li}_{(\text{W})}$ ]. These two supplementary solvation states can be induced by adding aliquots of water or by cooling. Although lithium is not essential for the formation of multiple water structures in nitrobenzene, it accelerates decomposition of the mixed solvation state  $\text{Li}_{(\text{NB}/\text{W})}$  as confirmed by comparative  $^2\text{H}$  kinetic studies with and without lithium species. Perhaps the most significant finding of our study is that very slow changes in water structure in wet nitrobenzene take place with or without ionic species

present. Therefore, it is possible to speculate that it is a general phenomenon that would affect solvation of many species and not be limited to electrochemical experiments involving interfacial ion transfer.

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