clusters with interstitial atoms should be treated with caution, as where we know that open faces may sometimes be present even when there is a closo electron count, e.g. $Rh_{13}(CO)_{24}H_3^{2-}$.

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Investigation of Lithium-Water Interactions in Acetonitrile Solutions Using Proton Nuclear Magnetic Resonance, Raman, and Infrared Spectroscopies and Extended Hückel Molecular Orbital Calculations

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Exchange of acetonitrile into and out of the coordination sphere of lithium ion is shown to be fast on the NMR time scale and slow on the vibrational time scale. Addition of water to solutions of lithium perchlorate in acetonitrile indicates that lithium is preferentially solvated by water and reveals that the solvation number of lithium ion is 4. Results from NMR, IR, Raman, and extended Hückel molecular orbital calculations are used to discuss the $LiClO_4-H_2O-CH_3CN$ system.

Introduction

Lithium has been considered for many years as an anode material for nonaqueous batteries. Acetonitrile (AN) is well suited as a nonaqueous solvent system for electrochemical studies because of its physical properties[1] and because of its ability to dissolve substantial quantities of salts to yield conductive solutions. Its physical properties, including its large electrochemical window, make it most attractive. The reactivity of lithium metal with acetonitrile has compromised AN as a solvent system for batteries. Passivated[2] lithium anodes cause a voltage delay when power is initially drawn, and this lasts until local electrode heating dissipates the film. The recent work by Keisele[3] on the purification of acetonitrile was used as a background for this research. A thorough surface spectroscopic study of the reactivity of lithium metal[4] with gases[5] was recently reported. Information about the physical state of the lithium ion in solution has been obtained from conductance and transference studies[6] of lithium salts in solution. The large charge to volume ratio for lithium makes its chemistry a curiosity. An attempt to obtain knowledge of the interface charge-transfer process must include a study of the lithium ion environment in solution.

Previous studies of lithium ion in aqueous solution have yielded hydration numbers[7] ranging from 2 to 22. Some of the methods employed, notably transference numbers[8] and mobility[9] measurements, clearly measure numbers of solvent molecules beyond the first coordination sphere. NMR results, which usually detect the first solvation shell only, report[10] hydration numbers of 3.4-5.0. In addition, calculated NMR shifts agree with experimental results[11] when a tetrahedral $Li(H_2O)_4^+$ ion is used. A potential energy surface calculation also suggests a four-coordinate T_d geometry for aqueous lithium ion[12] is most stable.

Solvation numbers of lithium ion in acetonitrile range from 4 to 9. Again, conductivity experiments yield the higher[13] values. Spectral measurements based upon infrared peak areas yield a solvation number[14] of 4. Solubility measurements also suggest a solvation number of 4, and $LiClO_4 \cdot 4CH_3CN$ (s) has been isolated.[15]

In a mixed-solvent system containing water and acetonitrile, the lithium ion is preferentially solvated by water. This has been shown by ^7Li NMR[16] and IR[17] measurements. Some workers have suggested that acetonitrile is inert in the presence of water and have made the claim that it is completely displaced by water from the lithium coordination[18] sphere, as it has been shown to displace tetrahydrofuran. Coordination of acetonitrile generally results in a shift of the CN stretching frequency to higher[19] values. Coordination to Zn^{2+}, for example, results in an increase of the CN stretching band[20] of 40 cm^{-1}. Molecular orbital calculations have been used to explain the vibrational[19,21] frequency enhancement. Interaction of CH_3CN with water in the absence of lithium results in an additional IR peak[22] at 2262 cm^{-1}.

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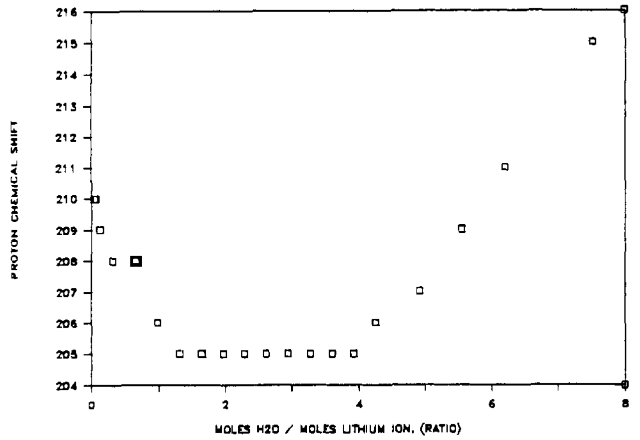

Figure 1. Chemical shift (Hz) at 60 MHz of water protons as a function of the water:lithium ion mole ratio in acetonitrile.

Experimental Section

Materials. The materials used in this study are hygroscopic. In order to minimize contamination by water, solutions were prepared in an atmosphere of argon within a glovebox. The acetonitrile (AN) used in this study was of HPLC grade, purchased from Burdick and Jackson. The as-received AN was analyzed by passage through a capillary-column chromatograph (HP 5890) containing a (HP-101) nonpolar methyl silicone fluid capillary column and a flame ionization detector. The only detectable impurity (besides water) found was propionitrile.[23] The acetonitrile was dried by passage and storage over activated alumina in a glovebox. After solutions of lithium perchlorate in ahydrous acetonitrile were prepared, measured quantities of water were added to a known mass of solution through the septum in the cap of an NMR tube.

Lithium perchlorate was purchased from Alfa Inorganics as the trihydrate salt and was fused under vacuum in an all-glass container immediately prior to solution preparation. The lithium perchlorate concentration of the solution was determined gravimetrically, by distilling the acetonitrile under vacuum from an aliquot of solution, followed by gently heating to 100 °C and then weighing the residue. An alternate procedure was to measure the lithium concentration by atomic absorption. A sample was diluted with water and the absorbance measured by using a Perkin-Elmer Model 363 atomic absorption spectrophotometer. The average lithium concentration of the six solutions was measured to be 1.60 ± 0.01 M.

Caution! Perchlorates, and particularly perchlorates in contact with organic solvents, are potentially explosive. All solutions used in this study were prepared on as small a scale as possible in a glovebox.

Instrumental Methods. Proton NMR measurements were made on a Varian EM360L NMR spectrometer. Anhydrous solutions of lithium perchlorate in acetonitrile were placed in NMR tubes with screw-on caps and Teflon septa. Water was added to these solutions by using a microliter syringe. Samples showed no indication of water uptake even after storage for several months.

Raman spectra were obtained on a Spex Model 1688 Raman system. Raman data were collected from solutions following their NMR spectral studies. The Raman system is based on a computer-controlled 0.25-μm double-focusing spectrometer with photon-counting detection. The light source for the Raman spectra was a Spectra Physics Model 2020 argon ion laser operating at 514 nm and having a power level at the sample of 100 mW. The spectrometer entrance and exit slits were set to 100 μm.

Infrared spectra were obtained on a Mattson Cygnus 100 FT-IR spectrometer (0.125-cm^{-1} resolution) equipped with a water-cooled source and an MCT detector. Internal reflectance spectra were obtained by using a 45° single-reflection ZnSe prism mounted in a Harrick PLC-11M Prism Liquid Cell. Solution samples were loaded into the liquid cell inside the glovebox, and the cell was sealed and inserted into the spectrometer. The spectrometer was thoroughly purged with dry nitrogen prior to data collection. The identical procedure was followed to collect the background interferogram.

Molecular Orbital Calculations. All calculations employed the extended Hückel method.[24,25] The weighted H_{ij} formula was used. Standard parameters, previously used in calculations on acetonitrile, were used.[26]

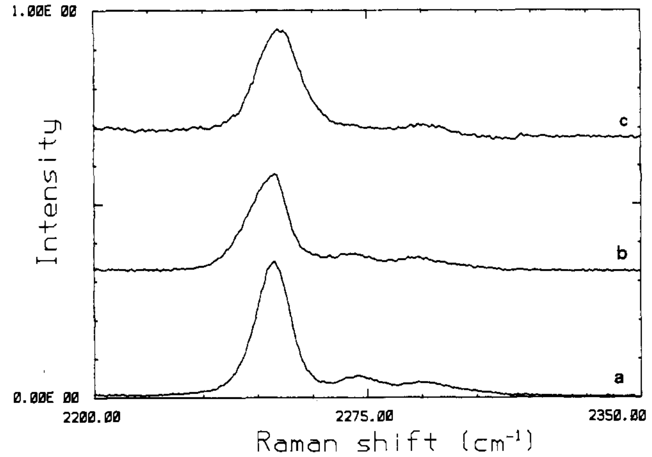

Figure 2. Raman specta of lithium perchlorate (1.6 M) in acetonitrile: (a) no added water; (b) water:Li$^+$ molar ratio = 1.5:1; (c) water:Li$^+$ molar ratio = 4:1.

Results and Discussion

Proton Magnetic Resonance. The proton NMR spectrum of anhydrous acetonitrile shows a singlet at 120 Hz downfield from TMS. The proton NMR spectrum of a saturated solution of fused lithium perchlorate in acetonitrile has one peak 119 Hz downfield from TMS. Thus, we find that the lithium ion can cause only a very small change in the chemical shift. The presence of only a single peak indicates that the system is in the fast-exchange region.

If hydrated lithium perchlorate is dissolved into acetonitrile, there appears, in addition to the peak at 119 Hz, a small peak at 205 Hz due to the water. Subsequent addition of water to the system results in an increase in the intensity of the peak at 205 ppm and a shift in its position. The chemical shift of a series of such solutions is shown in Figure 1. The chemical shift decreases slightly until the water to lithium ratio is approximately 1:1. It then remains constant until a water to lithium ratio of 4:1 is reached, at which time the chemical shift increases (see Figure 1).

These data suggest that the water is incorporated into the lithium ion coordination sphere. Above water to lithium molar ratios of 4:1, we interpret the observed peak as being due to the average of the chemical shifts for coordinated and free water. The initial decrease of the chemical shift (below 1:1 molar ratio) is interesting and may be due to complex equilibria involving interaction of the water with the lithium ion, the AN, or both. Water exchange into and out of the Li ion coordination sphere is also fast on the NMR time scale. As water is added to the system, the water peak shifts toward the free-water position. Plots like Figure 1 have been used to determine lithium ion solvation numbers of 4.5 in 1-methyl-2-pyrrolidone,[27] 4.3 in acetone,[28] and 3.8 in dimethylformamide.[29] This method applied to our data establishes that the solvation number of the lithium ion is 4.

Raman Spectroscopy. The Raman spectra of solutions of lithium perchlorate in acetonitrile show two distinct carbon-nitrogen stretching vibrations. One is at 2249 cm^{-1}. The other is at 2270 cm^{-1}. The 2249-cm^{-1} band is at the normal position for free acetonitrile. The band at 2270 cm^{-1} is due to acetonitrile coordinated to the lithium ion. Other vibrational bands in the acetonitrile spectrum change very little with the addition of lithium perchlorate, consistent with previous observations.[22] The existence of two separate CN stretching bands demonstrates that the exchange of acetonitrile into and out of the lithium ion coordination

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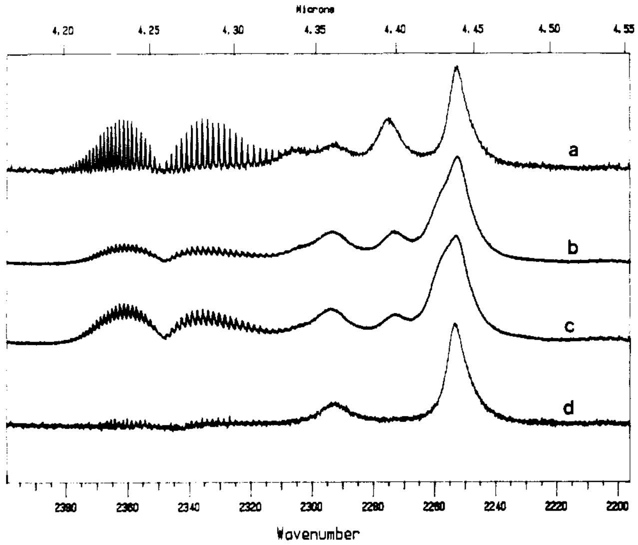

Figure 3. Infrared spectra of lithium perchlorate (1.6 M) in acetonitrile containing various amounts of water: (a) no added water; (b) 5.0 M water; (c) 7.0 M water; (d) no added water, no $LiClO_4$, neat acetonitrile.

sphere is slow on the Raman time scale. If it were fast, only one averaged peak would occur, as is found in the NMR results. Thus, we have a chemical reaction that is fast on the NMR time scale and slow on the Raman time scale. This places the residence time of an acetonitrile molecule in the lithium coordination sphere between 10^{-9} and 10^{-13} s.[30]

The addition of water to saturated solutions of lithium perchlorate in acetonitrile brings about a decrease in the vibrational band at 2270 cm^{-1} (Figure 2). The decrease in intensity is believed due to the displacement of acetonitrile from the coordination sphere of the lithium ion by the added water. Other changes that are observed in the Raman spectra as water is added include a broadening of the band at 2249 cm^{-1}, due to proton interaction with the nitrogen lone pair and the appearance of bands around 3500 and 1800 cm^{-1}. As the ratio of moles of water to moles of lithium ion approaches 4:1, the frequency of the vibrational band around 2270 cm^{-1} decreases slightly as the intensity decreases. When the ratio of water to lithium ion is 4 or above, the band at 2270 cm^{-1} is absent.

The observations in the Raman spectra support the NMR data by also showing that water is preferentially coordinated and that the hydration number of the lithium ion is 4.

Infrared Spectroscopy. The infrared spectra of lithium perchlorate in acetonitrile have many of the same features as the Raman spectra (Figure 3). The major differences are in the intensities of the peaks. The absorption band at 2270 cm^{-1} is much more intense in the infrared spectrum than is found in the Raman spectrum.

Again we find two separate CN peaks, which indicates that acetonitrile exchange is slow on the IR time scale ($>10^{-13}$ s).[30] This is in agreement with previous results that show a lifetime for water molecules within the lithium ion first shell to equal approximately 3×10^{-9} s.[31]

Table I. Molecular Orbital Results for CH_3CN and $Li(CH_3CN)_4^+$

	CN ROPM			charges	
species	σ	π	total	Li	N
CH_3CN	0.87	0.81	1.68	(1.0)	−0.98
$Li(CH_3CN)_4^+$	0.95	0.82	1.77	0.80	−0.80

The addition of water to these solutions decreases the intensity of the absorption at 2270 cm^{-1} and brings about a very noticeable broadening of the 2249-cm^{-1} band. The 2270-cm^{-1} band does not completely disappear from the IR spectrum, as it does from the Raman. The broadening of the infrared band is due to the appearance of a new band at 2262 cm^{-1}, which has been attributed to hydrogen bonding between water and acetonitrile.[22]

Molecular Orbital Calculations. Extended Hückel molecular orbital calculations have been attempted on acetonitrile and upon the lithium acetonitrile complex. The results of these calculations are shown in Table I. The coordination of acetonitrile to the lithium ion results in a strengthening the CN bond, as can be seen in the increase in the reduced overlap population value (ROPM), which is a measure of the magnitude of the interaction between the two atoms. The value of the ROPM for the nitrile C and N atoms is 1.68 for acetonitrile and increases to 1.77 in the $Li(CH_3CN)_4^+$ complex. Essentially all of the increase in the ROPM is due to the bonding interaction. These data suggest that the nitrogen lone pair in acetonitrile must be slightly antibonding. This result is similar to what is found in the case of complexes of carbon monoxide but opposite to the behavior of N_2, where the donor orbital is slightly bonding.[32]

In addition to the increase in the ROPM, a decrease in the negative charge on the nitrile nitrogen from −0.98 to −0.82 is observed. This also results in a decrease in the charge on the lithium ion from +1.0 to +0.80 in $Li(CH_3CN)_4^+$. In an intermediate complex, $Li(CH_3CN)_2(H_2O)_2^+$, the charge on the lithium is calculated to be +0.88. These calculations are consistent with the spectral observations that a 20-cm^{-1} shift in the CN stretching frequency is a result of the 5% increase in the CN interaction.

Conclusions

Exchange of acetonitrile molecules into and out of the first coordination sphere of lithium ion is fast on the NMR time scale and slow on the IR–Raman time scale. This places the residence time of the acetonitrile molecules within the first coordination sphere between 10^{-9} and 10^{-13} s. The exchange of water is also fast on the NMR time scale. The hydration number of Li^+ in acetonitrile–water mixtures is determined by NMR and Raman spectroscopies to be 4. Coordination of acetonitrile to the lithium ion through bonding involving the nitrogen lone pair strengthens the nitrile CN bond. This results in the shift of the nitrile stretch to higher energies.

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