Investigation of alkali metal–water interactions in acetonitrile*

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Abstract

The exchange of acetonitrile into and out of the coordination sphere of alkali metal ions is fast on the NMR time scale and slow on the vibrational time scale. This results in separate infrared and Raman spectra for coordinated and non-coordinated solvents in solutions of alkali metal salts in acetonitrile. The ^1H NMR spectra, on the other hand, are averages of coordinated and non-coordinated environoments. Addition of water to solutions of alkali metal salts in acetonitrile indicates that the cation is again preferentially solvated by water. The water completely replaces acetonitrile in the lithium coordination sphere until four waters have been added. Water also displaces the first acetonitrile from the coordination sphere of sodium and potassium ions. However, when additional water is added there is an equilibrium mixture of various species. Spectroscopic study of these solutions allows one to gain insights about the energetics and geometry of the cation. Experimental results from NMR, Raman and IR measurements along with extended Hückel molecular orbital calculations are used to discuss the alkali metal cation–water–acetonitrile system.

Introduction

Complexation reactions and the solvation of alkali metal cation are of interest due to the low polarizability of their electron clouds. It is generally assumed that alkali metal cations are only weakly solvated which explains the low solubility of alkali metal salts in organic solvents [1]. Of compounds formed by the alkali metals, lithium compounds are generally the most covalent with larger members of the series forming mainly ionic compounds. As a result the chemistry of the lithium ion is often anomalous compared to the other alkali metal ions [2].

A number of methods have been used to study the solvation and hydration of ions, including NMR [3, 4], Raman spectroscopy [5], infrared spectroscopy [6], conductance [7] and transference methods [8]. Alkali metal ions dissolve in water to form hydrates of indeterminate stoichiometry. Previous studies of lithium ion in aqueous solu-

tion have yielded hydration numbers [9] ranging from 2 to 22. Some of the methods employed, notably transference numbers and mobility [10] measurements, clearly measure numbers of solvent molecules beyond the first coordination sphere. 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.

Reported values of the hydration numbers for sodium and potassium ions range from 2 to 13 for Na^+, and from 1 to 7 for K^+ [9]. Again the larger numbers generally consider hydration beyond the primary coordination sphere of the metal cation. In addition there are minor discrepancies about the primary coordination sphere of these cations. In both Na^+ and K^+, the primary shell contains four water molecules [13]. In our previous work, we have shown a primary hydration sphere for lithium of four waters in acetonitrile solution [14]. In this work, we compare the hydration sphere of lithium ion with sodium and potassium ions in acetonitrile through the use of vibrational spectroscopy, proton NMR spectroscopy and extended Hückel molecular orbital calculations.

Experimental

Materials

The materials used in this study are hygroscopic. In order to minimize contamination by water, solutions were prepared under an atmosphere of argon within a glove box. The acetonitrile (AN) used in this study was HPLC grade, purchased from Burdick and Jackson. The AN as received, was analyzed by passage through a capillary column chromatograph (HP 5890) containing a (HP-101) non-polar methyl silicone fluid capillary column and a flame ionization detector. The only detectable impurity (besides water) found was propionitrile [15]. The acetonitrile was dried by distillation from P_2O_5 followed by passage through and storage over activated alumina in a glove box. Analysis of the dried solvents for water using gas chromatography with a thermal conductivity detector indicated that the solutions contained less than 1 ppm water. After solutions of alkali metal salt in anhydrous acetonitrile were prepared, measured quantities of water were added to a known volume of solution.

Lithium perchlorate was purchased from Alfa Inorganics as the tri-hydrate salt, and was fused under vacuum in an all glass container immediately prior to solution preparation. Sodium hexafluoroarsenate and potassium hexafluoroarsenate were purchased from Alfa Inorganics and used without further treatment. These salts were checked for the presence of residual water by gas chromatography [16] and NMR before use.

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 glove box.

Instrumental methods

Proton NMR measurements were made using 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 using a microliter syringe. Samples showed no indication of water uptake even after storage for several months.

Raman spectra were obtained using a Spex model 1688 Raman system. The Raman data were collected from the same solution following NMR spectral study. The Raman system is based on a computer controlled 0.25 M double 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 50 mW. The spectrometer entrance and exit slits were set to 100 μM.

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

Molecular orbital calculations

All calculations employed the extended Hückel method [17, 18]. The weigthed H_{ij} formula was used. Standard parameters, previously used in calculations on acetonitrile were used [19].

Results

Vibrational spectroscopy

Solutions of lithium perchlorate, sodium hexafluoroarsenate and potassium hexafluoroarsenate were examined using IR and Raman spectroscopy. The vibrational spectra of these solutions have the same general features, however the position of the C–N stretching vibration is found to be very sensitive to coordination of the acetonitrile. Previous work by Purcell and Drago attributes the change in frequency to an increase in the C–N force constant [20]. The increased energy of the C–N vibration in the IR and Raman spectra indicates that the C–N bond is weakest in the uncoordinated acetonitrile and strongest in the $Li(CH_3CN)_4{}^+$ complex cation. The data in Table 1 shows that the strength of the CN bond for acetonitrile coordinated to sodium and potassium is intermediate between free acetonitrile and acetonitrile coordinated to lithium. The IR spectra of lithium, sodium and potassium hexafluoroarsenates dissolved in acetonitrile are shown in Fig. 1.

TABLE 1. CN stretching frequency of the CN vibration of acetonitrile in various environments

Species	$1/\lambda$ (cm^{-1})
CH_3CN	2253
$K(CH_3CN)_n{}^+$	2258
$Na(CH_3CN)_n{}^+$	2264
$Li(CH_3CN)_n{}^+$ [a]	2275

[a]The data in this paper and in ref. 14 suggest that the lithium ion has a solvation number of 4 in acetonitrile. In addition we have isolated a solid which analyzes as $Li(CH_3CN)_4ClO_4$. The preparation of this compound and its characterization will be published elsewhere.
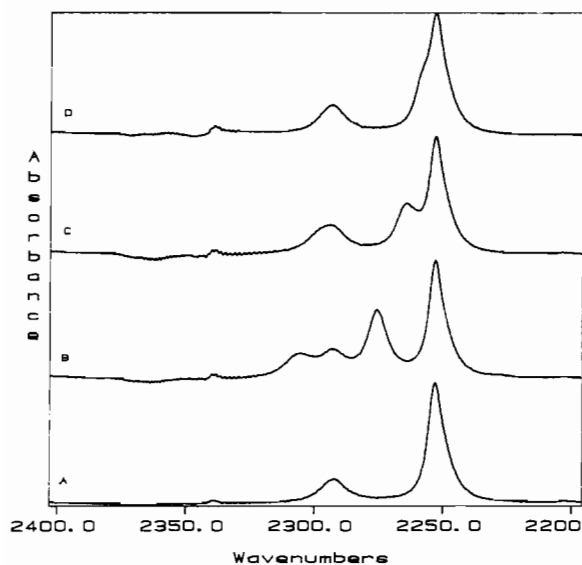
Fig. 1. The CN stretching region of the IR spectrum of pure acetonitrile (A); 1 M LiAsF$_6$ in acetonitrile (B); 1 M NaAsF$_6$ in acetonitrile (C); 1 M KAsF$_6$ in acetonitrile (D).

TABLE 2. Nitrile stretching frequency for various solvated species for LiClO$_4$ and NaAsF$_6$ in acetonitrile

[H$_2$O]/[Li$^+$]	$1/\lambda$ (cm^{-1})	[H$_2$O]/[Na$^+$]	$1/\lambda$ (cm^{-1})
0	2275.09	0	2264.01
1	2274.75	1	2263.55
2	2274.40	2	2262.69
3	2273.98		
4	2273.68		
5	2273.22		

The IR spectra of acetonitrile solutions of alkali metal salts are very sensitive to added water. As water is added, the intensity of the vibrational mode due to the alkali metal bound acetonitrile decreases. The energy of this vibrational mode also measurably decreases as the water is added. The position of the C–N vibrational feature as a function of water added is shown in Table 2.

Proton nuclear magnetic resonance

The proton NMR spectra of the acetonitrile solutions of alkali metal salts show the actonitrile resonance shifting only slightly (1–2 Hz) from the value from pure acetonitrile. The addition of even very small (0.1 µl) amounts of water results in the observation of a second peak due to water. A plot of the chemical shift of the water peak as a function of the amount of water added to pure acetonitrile and solutions of alkali metal salts is shown in Fig. 2. A comparison of the chemical shift of the water resonance indicates differences between samples of pure acetonitrile and samples where alkali metal salts are present. Solutions of

sodium and potassium hexafluoroarsenate are similar to one another and are different from pure acetonitrile and also different from solutions containing lithium ion. Solutions containing lithium ion show the displacement of acetonitrile from the coordination sphere of the lithium until a stoichiometry of 4:1 is reached as evidenced by the flat region of the curve. Plots like Fig. 2 have been used to determine lithium ion solvation numbers of 4.5 in 1-methyl-2-pyrrolidone [21], 4.3 in acetone [22] and 3.8 in dimethyl formamide [23]. Such plots of chemical shift versus ratio of coordinating solvent to amount of metal ion have shown that the solvation number of Na$^+$ is 4 in THF [24] and 1-methylpyrrolidone [25]; and 6 in DMSO [24].

Solutions of sodium and potassium salts in acetonitrile show that the water displaces acetonitrile completely until a stoichiometry of approximately 1:1 is reached as indicated by the drop in chemical shift for the water protons similar to the changes observed for the lithium ion. The chemical shift of the water protons then increases as additional water is added paralleling the addition of water to pure acetonitrile. This behavior is indicative of a rapid equilibrium involving a mixture of species involving partial replacement of acetonitrile in the coordination sphere of the metal ion. The parallel nature of the curves for sodium and potassium ions with water added to acetonitrile indicates that the water is in a rapid equilibrium between coordinated and uncoordinated water [26]. The NMR chemical shift for the water protons indicates an average environment between complexed and uncomplexed water molecules.

While the data for lithium salts in acetonitrile indicated a preferred coordination number of four, the NMR data for sodium and potassium ion in acetonitrile–water mixtures do not indicate a preferred hydration number. All of the data indicates that exchange of both water and acetonitrile between the bulk solvent and alkali metal ion coordination sphere is rapid on the NMR time frame, similar to observations for some transition metal ions [27, 28].

Molecular orbital calculations

Extended Hückel molecular orbital calculations were done on CH$_3$CN and all possible solvated species, M(CH$_3$CN)$_x$(H$_2$O)$_y$. The change in C–N bond strength, seen in the vibrational spectra, is also shown by these calculations (Table 3). The values of the reduced overlap population matrix (ROPM), a measure of the interaction between the two atoms, shows a consistent decrease as water is added stepwise to the complex. The same trend is seen in the IR spectrum. A plot
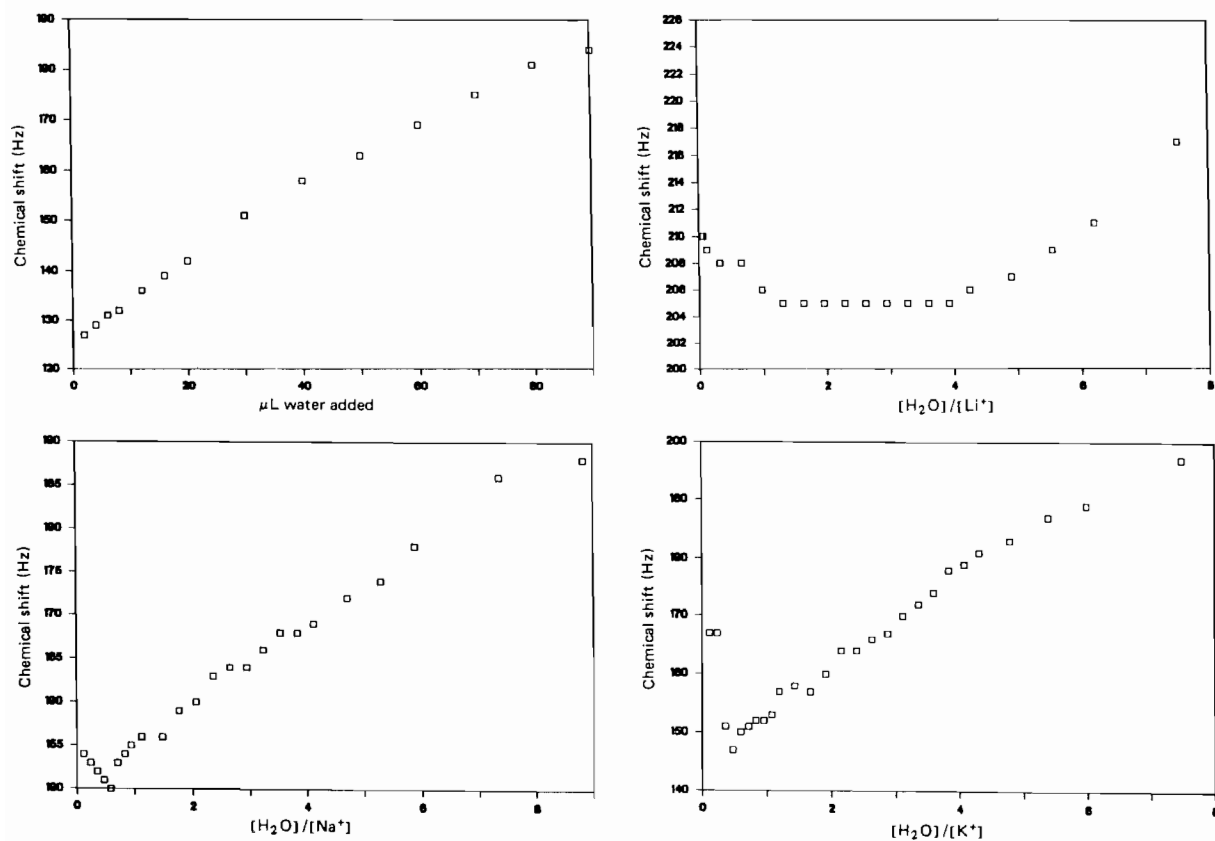
Fig. 2. Effect of added water on the chemical shift of the water protons in (a) pure acetonitrile; (b) 1 M $LiAsF_6$ in acetonitrile; (c) 1 M $NaAsF_6$ in acetonitrile, (d) 1 M $KAsF_6$ in acetonitrile.

TABLE 3. Nitrile vibration frequency and reduced overlap population matrix values for various species in the lithium, acetonitrile, water system

Species	σ ROPM	π ROPM	Total ROPM	$1/\lambda(cm^{-1})$[a]	q_m
CH_3CN	0.870	0.810	1.680	2254.0	
$Li(CH_3CN)(H_2O)_3^+$	0.951	0.815	1.7664	2273.98	0.92
$Li(CH_3CN)_2(H_2O)_2^+$	0.951	0.817	1.7670	2274.40	0.88
$Li(CH_3CN)_3(H_2O)^+$	0.951	0.819	1.7695	2274.75	0.84
$Li(CH_3CN)_4^+$	0.951	0.821	1.7713	2275.09	0.80

[a]Experimental value from IR spectroscopy.

of the IR vibrational frequency versus ROPM is linear with a correlation coefficient of 0.9999.

Upon coordination of the acetonitrile to the lithium ion, that part of the ROPM due to the σ type interaction increases from 0.870 to 0.951, a 10% change. There is also a change in the CN π orbitals. The change in the π orbital overlap population is smaller than the change in the σ orbital overlap population. The π ROPM (2_{px} and 2_{py}) for the CN bond is 0.810 in free acetonitrile and 0.821 in $Li(CH_3CN)_4^+$. This smaller change (1%) in the π orbital overlap population clearly contributes to the change in bond strength, but less so than the change in the σ orbital overlap population.

While the difference between free and bound acetonitrile is mainly due to the σ interaction, it is the π electrons which cause the differences in the vibrational frequencies for coordinated acetonitrile in the series $Li(CH_3CN)_4^+$ through $Li(CH_3CN)(H_2O)_3^+$. As acetonitrile is replaced in the coordination sphere by water, the σ ROPM remains constant at 0.951. The π ROPM, however, changes from 0.821 in $Li(CH_3CN)_4^+$ to 0.815 in $Li(CH_3CN)(H_2O)_3^+$. A plot of $1/\lambda$ versus ROPM is linear with a correlation coefficient of 0.9999. Since the coordination shell in Na^+ and K^+ is less well defined, a similar plot was not made for those ions.

A similar phenomenon is observed with the C–C stretch at around 920 cm^{-1}. Upon coordination of acetonitrile to the lithium ion, a new peak appears at about 935 cm^{-1}. EHMO calculations reveal that coordination of the acetonitrile to the metal also results in a strengthening of the C–C bond of the acetonitrile. The ROPM of this bond increases from 0.859 in CH$_3$CN to 0.869 in Li(CH$_3$CN)$_4^+$ to 0.871 in Li(H$_2$O)$_3$(CH$_3$CN)$^+$. This increase (1.4%) is less than that observed for the CN bond (5.5%), but larger than the increase in the C–C strength caused by the presence of Na$^+$ (1.1%).

Discussion

A comparison of the spectroscopic results for the various alkali metal cations indicates a strong preference of the lithium ion for the coordination of four waters. The other alkali metal cations have much less definite preference for water over acetonitrile. NMR evidence suggests that the displacement of acetonitrile by water in the coordination sphere of the other alkali metal cations forms complexes of less definite composition. The NMR results indicate that the water added to the solution up to a stoichiometric ratio of one, is strongly held by all three alkali metal ions. Subsequent added water is strongly held by lithium up to a coordination number of four, but much less strongly held by sodium and potassium ions. Sodium and potassium do not appear to have a simple and well defined coordination sphere on the NMR time scale in the acetonitrile–water solvent system. This result is expected due to the larger size of the sodium and potassium ions.

Extended Hückel molecular orbital calculations, in addition to demonstrating that the coordination to the lithium and sodium ions causes a strengthening of the CN bond, provide insight into the mechanism whereby the bond strength increases. This is due to the donation of the lone pair from the nitrogen towards the alkali metal atom. The antibonding character of these electrons has been well established. Thus, their removal results in a strengthening of the CN bond. This σ orbital effect is the principal reason for the shift to higher frequency in the IR and Raman spectra.

As water enters the coordination sphere of the alkali metal ion, the decrease in the π ROPM is as expected. This is due to the larger electronegativity of the oxygen atom as compared to the nitrogen atom. The metal accepts less electron density from the oxygen and therefore can donate less into the empty π^* orbital of CH$_3$CN. Electron density from the π orbitals of acetonitrile interacts more strongly with the alkali metal ion as acetonitrile molecules are added. As the water molecules enter the coordination sphere of the alkali metal ion more electron density is removed from the remaining coordinated acetonitrile molecules decreasing the π orbital population.

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