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The Structure and Thermodynamics of Hydrogen Bonding Interactions of OCN^- with Methanol, Formamide, and *N*-Methylformamide

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Abstract: The primary solvation sphere surrounding the cyanate anion in nonaqueous protic solvents contains intimate hydrogen bonds with this anion. These interactions perturb the electron density and vibrational modes in OCN^-, as revealed experimentally by NMR and infrared spectroscopies. In neat methanol solutions of 0.1 M tetrabutylammonium cyanate, the anion participates in three distinct complexes: $OCN^-\cdots HOMe$, $OCN^-\cdots(HOMe)_2$, and $MeOH\cdots OCN^-\cdots HOMe$. At the same concentration in formamide solutions, only one is observed, the $OCN^-\cdots(FA)_2$ species, whereas in *N*-methylformamide solutions two solvates are present: $OCN^-\cdots NMF$ and $OCN^-\cdots(NMF)_2$. The thermodynamics for the formation of these complexes have been studied in nitromethane solutions in order to understand the factors involved in anion solvation. The differences observed in the extent of solvation of the cyanate anion by these protic solvents have been related to the self-association of the neat solvents.

Introduction

Although electrolyte solutions play an important role in many biochemical and industrial processes, our knowledge of the structure of such solutions, especially in the case of nonaqueous and mixed solvents, is rather rudimentary.[1] Many types of interactions may occur in an electrolyte solution; their strength varies from weak van der Waals forces to strong electrostatic attractions. This wide range of attractive forces and the abundance of interaction sites results in a large number of solution equilibria that are difficult to sort out experimentally. In an electrolyte solution, the types of interactions can be broadly categorized as solvent−solvent, ion−solvent, and ion−ion. The relative importance of the resulting equilibria depends upon the nature of the electrolyte and of the solvent.

The cyanate anion has been used to probe ionic associations in alkali cyanate solutions because its vibrational modes are accessible and sensitive to electrostatic interactions.[2] OCN^- has three fundamental vibrations, all of which are infrared active.[3] The highest frequency mode (ν_3), which occurs at $\sim$2140 cm^{-1}, is commonly labeled the ν_{CN} stretch.[4,5] The lowest frequency mode (ν_2), which occurs at $\sim$625 cm^{-1}, is the doubly degenerate bending vibration, labeled δ_{OCN}.[4,5] The ν_{CO} mode (ν_1), which should be observed at $\sim$1250 cm^{-1}, is in Fermi resonance with the first overtone of the bending mode ($2\delta_{OCN}$).[2−6] The Fermi resonance couples and splits the ν_{CO} and $2\delta_{OCN}$ absorptions, resulting in two bands of similar intensity in DMSO solutions that are centered at 1240 cm^{-1} and displaced by 44 cm^{-1} on each side.[2] Hereafter, absorption in this region will be termed ν_{CO} & $2\delta_{OCN}$. It should be noted that the labels ν_{CN} and ν_{CO} are convenient but somewhat misleading, since these vibrations are not localized at either the C−N or C−O bonds.[3,7] Rather, the ν_{CN} mode resembles the antisymmetric stretching vibration in CO_2 or N_3^-; likewise, the ν_{CO} mode is similar to the symmetric stretch in CO_2 or N_3^-.[7]

Thermodynamic parameters for the formation of the alkali metal cyanate ion pairs in DMSO solutions have also been determined by Chabanel and co-workers.[2,6] Despite the strong Coulombic attraction between the cation and anion, the important role of the solvent in ion pair formation equilibria makes the process, in general, entropy driven.[8] This is illustrated for the alkali cyanates in eq 1. The reduction in entropy resulting from the formation of the ion pair is more than balanced by the increase in entropy due to the release of solvent molecules from the separated solvated ions. Likewise, the negative enthalpy contribution from the Coulombic attraction of the cation and anion is balanced by the energy needed to break ion−solvent bonds in the solvated ions.

$$M^+(S_x) + OCN^-(S_y) \rightleftharpoons M^+NCO^-(S_n) + (x + y + n)S \quad (1)$$

Thus, the solvent in an electrolyte solution can play an important role in the formation of ion pairs. Several solvent properties have been identified as indicators of the extent of ion pairing in an electrolyte solution: the dielectric constant, the dipole moment, and the solvating ability of the solvent. The solvating ability is described by two empirical scales, the donor and the acceptor numbers.[9] Despite the importance of the nature of ionic solvation on ion pairing, the factors involved in ion−solvent interactions, especially anion solvation, have not been thoroughly studied.

From the perspective of the anion, the solvent in an electrolyte solution can be divided into three regions: the primary solvation shell surrounding the ion, the secondary solvation shell, and

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[1] Barthel, J.; Gores, H.; Schmeer, G.; Wachter, R. *Topics Curr. Chem.* **1983**, *111*, 33.

[2] Rannou, J.; Massé G.; Chabanel, M. *C. R. Acad. Sc. Paris, Série C* **1978**, 93.

[3] Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press, Inc.: Boston, 1990; p 239.

[4] Devore, T. C. *J. Mol. Struct.* **1987**, *162*, 273.

[5] Brooker, M. H.; Wen, N. *Can. J. Chem.* **1993**, *71*, 1764.

[6] Rannou, J.; Chabanel, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1980**, *77*, 201.

[7] Schultz, P. W.; Leroi, G. E.; Harrison, J. F. Submitted to *Mol. Phys.*

[8] Mamantov, G.; Popov, A. I. *Chemistry of Nonaqueous Solutions: Current Progress*; VCH: New York, 1994.

[9] Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum: New York, 1980.

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the bulk liquid.[10] Solvent molecules that are closest to and in intimate contact with an ion belong to the primary solvation shell. The ion's charge provides an electrostatic attraction that brings the solvent closer than the sum of the respective van der Waals radii.[10] In the secondary solvation shell the solvent molecules are attracted to the ionic charge, while not in intimate contact with the ion. The bulk liquid is free of any significant electrostatic effects from the ion.

Vibrational and magnetic resonance spectroscopies can be sensitive probes of ionic solvation. Chabanel and co-workers have shown that the ν_{CN} mode in OCN^- shifts to higher frequencies and the bandwidth dramatically broadens when a protic solvent is added to a solution of NBu_4OCN in CCl_4.[11] They were able to correlate the frequency shifts of the ν_{CN} mode in OCN^- to the acidity of the hydrogen bond donor, $\sim$12 cm^{-1} for alcohols and $\sim$18 cm^{-1} for various phenols.[11] Recently, Hochstrasser and co-workers have studied the vibrational relaxation of OCN^- in D_2O and MeOH.[12,13] Their results are consistent with the solvent hydrogen bonding to the nitrogen end of the anion. A number of authors have used NMR spectroscopy to determine the solvation numbers of alkali metal cations with a variety of nonaqueous solvents.[14−17]

Like interionic interactions, hydrogen bonding perturbs the vibrational modes of a hydrogen bond acceptor. Previous studies of alkali cyanates in DMSO solutions have shown that the stretching modes in each solution species, whether an ion pair, a dimer, or a triple ion, are characterized by a unique frequency shift relative to the uncomplexed cyanate anion. In order the assess the effect of hydrogen bonding on the vibrational modes of OCN^-, *ab initio* calculations of cyanate-water and cyanate-hydrogen fluoride complexes were performed. A detailed discussion of the results and similar computations for interionic aggregates will be presented in a separate publication.[7]

In this paper, we address the structure of the primary solvation shell surrounding the cyanate anion in nonaqueous protic solvents. The protic solvents used in this investigation are methanol (MeOH), formamide (FA), and *N*-methylformamide (NMF); this series allows a variety of hydrogen bonding interactions to be studied. NMR and infrared spectroscopies are employed to probe the interactions in these solutions and to provide data from which the thermodynamics of the equilibria which exist in them can be calculated. Spectroscopic measurements are reported for the cyanate anion both in neat solutions of the appropriate salt and protic solvents and in an "inert" solvent where the concentration of the hydrogen bonding solvent and salt can be varied independently.

Experimental Methods

Methanol [MeOH] (absolute, EM Science, 500 mL) was dehydrated by refluxing over CaH_2 (5 g, Baker) for 2 h. The dried solvent was distilled under a dry N_2 atmosphere onto freshly activated 4Å molecular sieves (Linde). The first 50 mL of the distillate was discarded and the next 300 mL was collected. *N,N*-Dimethylformamide [DMF] (99%, EM Science), *N*-methylformamide [NMF] (99%, Aldrich), and formamide [FA] (99%, EM Science) were dried by adding 5 g of BaO (Baker) to 500 mL of each solvent. Each mixture was allowed to sit for 12 h and then distilled over fresh BaO under reduced pressure onto 4 Å molecular sieves. Nitromethane [NM] (96%, Aldrich) was dried by the addition of 5 g of CaH_2 to 500 mL and allowed to sit for 24 h. The dried solvent was distilled under reduced pressure onto fresh CaH_2. All solvents were stored in dark glass bottles in a drybox under a nitrogen atmosphere.

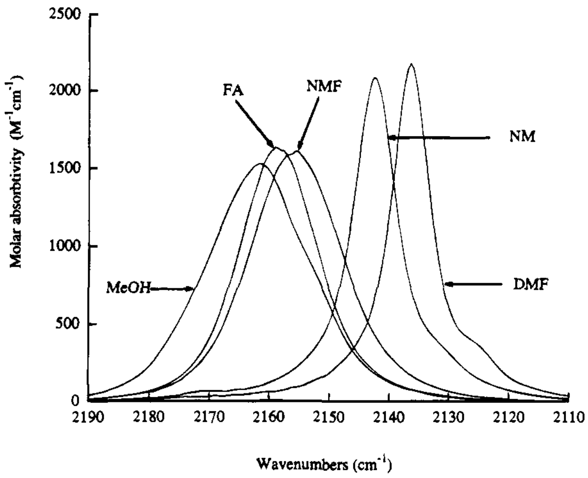

Figure 1. ν_{CN} stretch of $\sim$0.1 M NBu_4OCN in DMF, NM, NMF, FA, and MeOH.

Tetrabutylammonium cyanate [NBu_4OCN] (>96%, Fluka) was dissolved into ethyl acetate and filtered to remove insoluble material. The solvent was removed and the purified cyanate salt was dried under vacuum over P_2O_5 at 45 °C for 24 h.

Solutions with known concentrations were prepared by weighing the solute on an analytical balance in a 5 or 25 mL volumetric flask and diluting with the appropriate solvent. All solution preparation was done in a drybox under a nitrogen atmosphere. Ternary solutions of the tetrabutylammonium salt and hydrogen bonding solvent in nitromethane were prepared from stock nitromethane solutions of the salt or the hydrogen bonding solvent. Aliquots (1, 2, 3, and 4 mL) of the salt or hydrogen bonding solvent solution were pipetted into 5 mL volumetric flasks so that the concentration of the salt and of the hydrogen bonding solvent could be varied independently.

Infrared spectra were recorded on a Nicolet 520P (Nicolet, Inc.) FTIR spectrometer. The 4800−900 nm^{-1} region was obtained at 1 cm^{-1} resolution using CaF_2 windows. The number of scans was varied from 200 to 10 000 depending on the signal intensity of the band studied. Teflon spacers were used to vary the pathlength of the cell, the pathlength value being determined by the fringe method.[18] Between each sample, the cell was flushed with 1−2 mL of the new sample to be studied; and the spectrometer was purged with N_2 for 5 min prior to the collection of a new spectrum.

Multinuclear NMR spectra (^{14}N and ^{17}O) were obtained on a VXR-500 FT-NMR spectrometer (Varian, Inc.). Each sample was placed in a 5 mm NMR tube with a coaxial insert containing an external reference and lock solvent. ^{14}N spectra were externally referenced to 1 M NBu_4NO_3 in $(CD_3)_2CO$ with respect to nitromethane (0.00 ppm). ^{17}O spectra were externally referenced to D_2O. In addition, the ^{17}O spectra were 64k zero filled in order to increase the resolution. The temperature probe in the spectrometer was calibrated by the known temperature dependence of the proton chemical shifts in methanol.[19]

Results and Discussion

The ν_{CN} stretching vibration of the OCN^- anion is sensitive to interactions in solution. Hydrogen bonding broadens the absorption and shifts the peak frequency of the ν_{CN} band with respect to this mode in solutions of OCN^- in aprotic solvents, as shown in Figure 1 and summarized in Table 1. The

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(10) Ohtaki, H.; Yamatera, H. *Structure and Dynamics of Solutions*; Elsevier: Amsterdam, 1992; p 15.

(11) Goralski, P.; Berthelot, M.; Rannou, J.; Legoff, D.; Chabanel, M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2337.

(12) Owrutsky, J.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Chem.* **1994**, *45*, 519.

(13) Owrutsky, M.; Sarisky, M.; Culver, J.; Yodh, A.; Hochstrasser, R. M. *J. Chem. Phys.* **1993**, *98*, 5499.

(14) Wuepper, J. L.; Popov, A. I. *J. Am. Chem. Soc.* **1969**, *91*, 4352.

(15) Delpuech, J. *Analyst* **1992**, *117*, 267.

(16) Wong, M. K.; McKinney, J. W.; Popov, A. I. *J. Phys. Chem.* **1971**, *75*, 56.

(17) Lassigne, C.; Muller, K.; Hertz, H. *Z. Phys. Chem. N. F.* **1984**, 64.

(18) Robinson, J. W. *Practical Handbook of Spectroscopy*; CRC Press: Boca Raton, FL, 1991; p 508.

(19) Mason, J. *Multinuclear NMR*; Plenum: New York, 1985.

Table 1. Infrared Parameters for the ν_{CN} Mode of ~0.1 M NBu_4OCN in Several Solvents

solvent system	ν_{CN} (cm^{-1}) ± 0.5 cm^{-1}	FWHH (cm^{-1}) ± 0.5 cm^{-1}
DMF	2136.5	8
NM	2142.0	9
NMF	2155.5	18
FA	2159.0	16
MeOH	2161.5	21

Table 2. Peak Position, Bandwidth, and Molar Absorptivity Parameters of Component Bands of the ν_{CN} Spectral Envelope of ~0.1M OCN^- in DMF, NM, NMF, FA, and MeOH

solvent system	peak position (cm^{-1})	$\nu_{1/2}$ (FWHH) (cm^{-1})	absorptivity (cm^{-1})
DMF	2136.5 ± 0.1	7.9 ± 0.1	249 ± 6
	2124.3 ± 0.1	6.5 ± 0.1	14 ± 1
NM	2142.5 ± 0.1	8.8 ± 0.1	246 ± 5
	2130.4 ± 0.2	8.1 ± 0.2	11 ± 1
NMF	2151.7 ± 0.5	18.4 ± 0.1	147 ± 10
	2157.3 ± 0.2	16.3 ± 0.1	78 ± 10
FA	2158.5 ± 0.1	15.6 ± 0.1	230 ± 1
MeOH	2151.8 ± 0.1	13.2 ± 0.1	35 ± 4
	2160.6 ± 0.2	12.1 ± 0.7	63 ± 29
	2166.4 ± 1.0	18.4 ± 0.8	69 ± 14

bandshape of the spectral envelope is complex and results from several overlapping component bands that can be resolved by techniques such as Fourier self-deconvolution. Quantitative information about the component bands was obtained by fitting the observed spectral envelopes with Gaussian–Lorenztian bandshapes. The resulting peak positions, bandwidths, and absorbances are collected in Table 2. In the aprotic solvents DMF and NM, the ν_{CN} mode consists of two component bands. The more intense is assigned as the "free" ν_{CN} vibration, whereas the weaker component (4–5% of the main band) is attributed to a hot band transition emanating from the first bending vibrational excited state ($\nu_3 + \nu_2 - \nu_2$), located below the fundamental.[6] Dramatic changes are observed in the 2200–2100 cm^{-1} spectral envelopes for ~0.1 M NBu_4OCN in the hydrogen bonding solvents: NMF, FA, and MeOH, with respect to the ν_{CN} mode in DMF and NM. In NMF, the ν_{CN} spectral envelope is comprised of two bands, each about a factor of two broader than the absorption in aprotic solvents. Only the higher frequency component is observed in FA solutions. Interestingly, the ν_{CN} mode of OCN^- in MeOH consists of three constituent bands, two of which are similar to those seen in the amide solvents, plus a new band at a higher frequency. Unfortunately, the ν_{CO} & $2\delta_{OCN}$ and δ_{OCN} vibrations are obscured by the hydrogen bonding solvents, so no information could be obtained about these modes from the neat solution spectra.

A clearer picture of the formation of anion–solvent adducts can be obtained by adding either the protic solvent or the cyanate anion to a dilute solution of the other in a weakly solvating (inert) solvent, such as nitromethane (NM), for which the donor number is low.[9] Infrared studies of the C-H stretching modes for NM show that this solvent only weakly solvates anions.[20] Thus, the solvation of the cyanate anion by methanol can be followed by measuring the 2200–2100 cm^{-1} spectral envelope of NBu_4OCN in NM as a function of added MeOH. When no methanol is present, the ν_{CN} stretch of OCN^- is a sharp absorption at 2142 cm^{-1}. As MeOH is added, the intensity of the 2142 cm^{-1} band falls, with the spectral envelope broadening and shifting to higher frequencies as shown in Figure 2. In order to address the underlying composition of the spectral envelopes, the lineshapes were Fourier self-deconvolved (Figure 3). The deconvolution procedure reveals that the absorbances of the ν_3 fundamental and the ($\nu_3 + \nu_2 - \nu_2$) mode of the OCN^- anion dramatically decrease as the concentration of MeOH increases. Concurrently, a new band at 2154 cm^{-1} grows. Toward the highest MeOH concentrations employed in this titration study (>2 M), the intensity of the 2154 cm^{-1} band decreases and a new band at 2163 cm^{-1} grows with increasing MeOH concentration. Similar results are seen in the titration studies with NMF and FA.

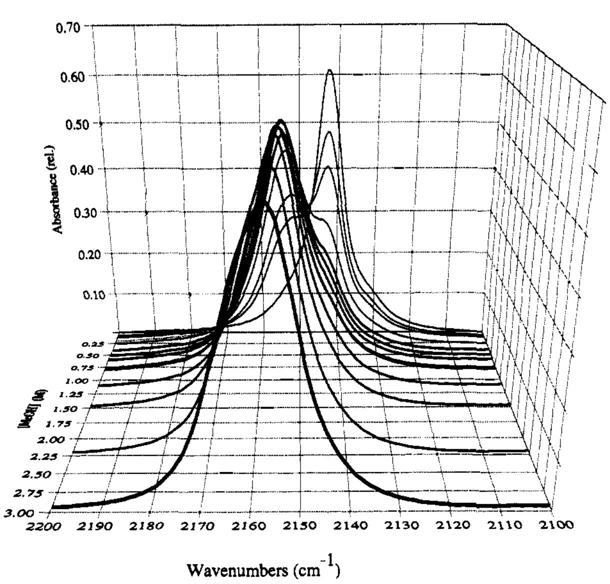

Figure 2. ν_{CN} stretch of ~0.1 M NBu_4OCN in NM as a function of MeOH added.

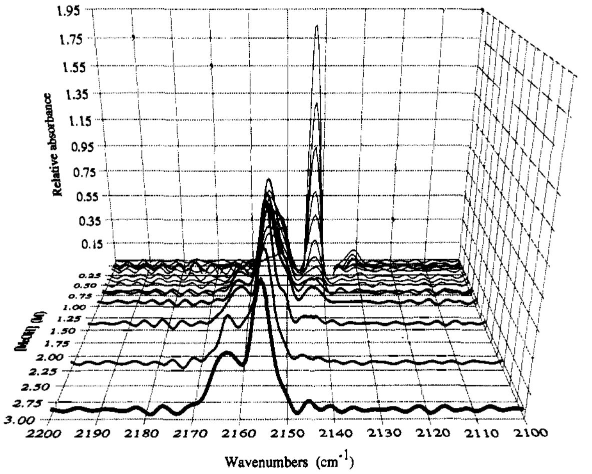

Figure 3. Fourier self-deconvolution of the ν_{CN} stretch for ~0.1 M NBu_4OCN in NM as a function of MeOH added.

Quantitative information can be obtained by fitting the absorption envelopes to Gaussian–Lorenztian sum components, which yields the absorbance, bandwidth, and peak position of each constituent band. The absorption curves in the methanol series can be well simulated with four components: at 2130 cm^{-1} for the hot band, at 2143 cm^{-1} for the free anion, at 2154 cm^{-1} for the first solvated complex, and at 2163 cm^{-1} for the second solvated complex. The intensities of the fundamental constituents, plotted in Figure 4, are qualitatively similar to those obtained by the Fourier self-deconvolution of the observed spectral envelopes. Similar titration experiments were performed by adding NMF and FA to 0.1 M NBu_4OCN in NM. Curve fitting and Fourier self-deconvolution of the 2200–2100 cm^{-1} spectral envelopes also show that the line shape in each case is a convolution of four component bands: the hot band ($\nu_3 + \nu_2 - \nu_2$), the free ν_{CN} band, a 1:1 hydrogen bonded

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(20) Ramana, K.; Surjit, S. *J. Mol. Struct.* **1989**, *194*, 73.

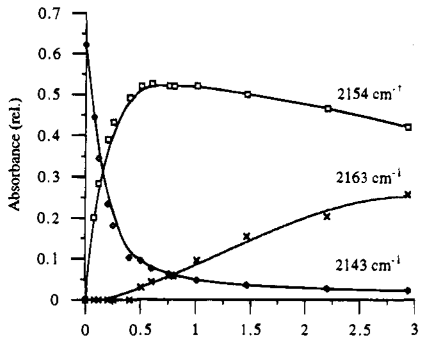


Figure 4. Intensity of the component bands in the 2200–2100 cm^{-1} region for ~0.1 M NBu_4OCN/NM solutions as a function of MeOH concentration.

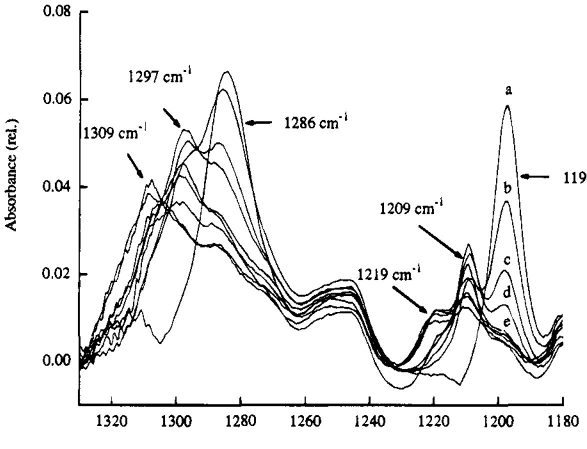


Figure 5. ν_{CO} and $2\delta_{OCN}$ mode in ~0.1 M NBu_4OCN in NM as a function of MeOH added (a. 0 M, b. 0.04 M, c. 0.08M, 0.12M, and e. 0.16 M MeOH).

complex, and a 1:2 hydrogen bonded complex (from lowest to highest frequency).

The 1350–1180 cm^{-1} spectral region contains the ν_{CO} & $2\delta_{OCN}$ bands. In a 0.1 M NBu_4OCN solution in NM, these bands are centered at 1286 cm^{-1} and 1198 cm^{-1}. Addition of MeOH broadens the absorptions and shifts the maxima of the spectral envelopes to higher frequencies. Moreover, new bands grow in with the increasing methanol concentration, as illustrated in Figure 5. Resolution enhancement techniques are not necessary to determine the positions of these new bands: at 1309 and 1297 cm^{-1} for the higher frequency component of the ν_{CO} and $2\delta_{OCN}$ absorption and at 1219 cm^{-1} and 1209 cm^{-1} for the lower frequency component. The concentration dependence of the 1286 and 1198 cm^{-1} peaks is qualitatively similar to that of the 2142 cm^{-1} free ν_{CN} stretch.

The spectral envelopes of the ν_{CO} and $2\delta_{OCN}$ bands also can be modeled by Gaussian–Lorenztian sums. The lower frequency band (1230–1180 cm^{-1}) is more amenable to curve fitting, since this spectral region has fewer interferences from the protic solvents. The concentration dependence of the three bands in the 1230–1180 cm^{-1} region is similar to that of the component bands in the ν_{CN} stretch, in that the absorbance of the band attributable to free OCN^- plunges with increasing MeOH concentration, with the concomitant growth of new bands. Qualitatively similar results are obtained in this spectral region from the NMF and FA titrations. The results in both stretching spectral regions for the three protic solvents are summarized in Table 3.

Assignments. The structure of the primary solvation sphere surrounding the cyanate anion in neat solutions of NBu_4OCN in MeOH, FA, and NMF can be understood by identifying the component bands of the ν_{CN} stretch. The concentration behavior of the infrared absorbances of the component bands in the titration studies of the cyanate anion with protic solvents shows clearly that the OCN^- anion is involved in two equilibria. Moreover, the increase in the absorbance of the 2163 cm^{-1} component in the MeOH titration comes at the expense of the 2154 cm^{-1} absorption (Figure 4), suggesting that the 2154 cm^{-1} band can be attributed to a 1:1 methanol:OCN^- adduct and the 2163 cm^{-1} band arises from a 2:1 MeOH:OCN^- complex. Since the negative charge is distributed between the oxygen and nitrogen ends of the anion, the methanol in these 1:1 complexes might be hydrogen bonded to either the nitrogen or oxygen atom.

The $OCN^-\cdots$HOMe and $NCO^-\cdots$HOMe complexes can be easily distinguished from one another by their infrared spectra. *Ab initio* calculations of these complexes show that the frequency of the ν_{CN} mode will increase relative to free OCN^- in either case. However, these calculations predict that the frequency of the ν_{CO} stretch will increase in a $OCN^-\cdots$HOMe complex and decrease for a $NCO^-\cdots$HOMe adduct.[7] With respect to free cyanate, it is also predicted that the absorptivity of the ν_{CN} mode in $OCN^-\cdots$HOMe will increase and that of the ν_{CO} mode will decrease.[7] The opposite trend is predicted for the molar absorptivities of the stretching modes in a $NCO^-\cdots$HOMe complex. From the observed spectroscopic behavior, the 1:1 complex can be assigned with confidence as $OCN^-\cdots$HOMe. This assignment is supported by experimental studies of alkali cyanates, where positive frequency shifts in the ν_{CN} and ν_{CO} and $2\delta_{OCN}$ modes of OCN^- with respect to OCN^- have been assigned to an alkali metal ion pairing to the nitrogen end of the cyanate anion.[2,6] Likewise, the infrared spectra of OCN^- in the NMF and FA titration series are also consistent with the amide solvents hydrogen bonding to the nitrogen end of the cyanate anion.

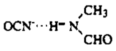
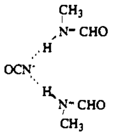
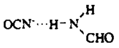
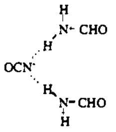
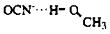
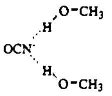
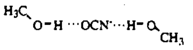
There are three possible ways that two MeOH molecules can interact with OCN^-: $OCN^-\cdots(HOMe)_2$, $NCO^-\cdots(HOMe)_2$,

Table 3. Summary of Peak Positions and Bandwidths of the Curve-Fitted Component Bands of the ν_{CN} Stretch of 0.1M NBu_4OCN/NM Solutions with NMF, FA, or MeOH Added

solvent system	ν_{CN} peak position (cm^{-1})	$\nu_{1/2}$ FWHH (cm^{-1})	ϵ_{CN} (km/mol)	ν_{CO} & $2\delta_{OCN}$[a] peak position (cm^{-1})	$\nu_{1/2}$ FWHH (cm^{-1})	ϵ_{CO} (km/mol)
NMF	2141.8 ± 0.8	10.4 ± 0.8	309 ± 7	1198.2 ± 0.5	11.2 ± 1	5.4 ± 0.6
	2150.8 ± 0.8	13.5 ± 0.2	358 ± 7	1207.2 ± 0.2	5.0 ± 1	1.8 ± 0.4
	2159.2 ± 0.2	13.9 ± 0.8	320 ± 20	*b*	*b*	*b*
FA	2142.0 ± 0.5	10.6 ± 1.2	322 ± 7	1199.1 ± 1.0	10.0 ± 1	4.8 ± 0.6
	2150.6 ± 0.9	12.9 ± 0.6	371 ± 7	1207.1 ± 0.5	6.6 ± 1	2.4 ± 0.6
	2158.9 ± 0.4	12.8 ± 1.0	330 ± 20	1215.4 ± 0.4	6.2 ± 1	0.8 ± 0.2
MeOH	2142.8 ± 0.7	10.5 ± 1.6	311 ± 4	1198.3 ± 0.5	9.8 ± 0.4	5.0 ± 0.4
	2154.0 ± 0.9	12.3 ± 1.2	399 ± 4	1209.0 ± 0.5	8.2 ± 1	3.6 ± 0.6
	2163.3 ± 0.4	14.0 ± 0.3	450 ± 20	1219.4 ± 0.4	8.2 ± 1	2.2 ± 0.4

[a] Only values for the lower frequency component are reported. [b] Obscured by an NMF vibration.

Table 4. Assignments for the ν_{CN} & ν_{CO} and $2\delta OCN$ Modes for ~0.1M OCN^- in Neat Solutions with MeOH, FA, or NMF and in Titration Studies with these Solvents

solvent system	assignment	ν_{CN} component bands in neat solutions (cm^{-1})	ν_{CN} component bands in titration studies (cm^{-1})	ν_{CO} & $2\delta_{OCN}$ component bands in titration studies (cm^{-1})
NMF		2152	2151	1207
		2157	2159	a
FA		b	2151	1207
		2159	2159	1215
MeOH		2152	2154	1209
		2161	2163	1219
		2166	b	b

[a] Obscured by solvent. [b] Not observed at the studied concentrations.

and MeOH···OCN^-···HOMe. Of these possibilities, the NCO^-···$(HOMe)_2$ complex, where two methanol molecules form a hydrogen bond to the oxygen end, can be easily dismissed since no NCO^-···HOMe adducts were observed. Moreover, the accompanying red shifts in the frequencies of the ν_{CO} and $2\delta_{OCN}$ modes relative to those in OCN^- are not observed experimentally. *Ab initio* calculations for 1:2 complexes of cyanate with water or hydrogen fluoride indicate that it is difficult to distinguish the three structures based on the frequency shifts in the ν_{CN} mode alone.[7] Again, the frequency of the ν_{CO} mode and the molar absorptivities of the ν_{CN} and ν_{CO} modes provide the best way to discriminate between the MeOH···OCN^-···HOMe and the OCN^-···$(HOMe)_2$ complexes. The experimental frequency shift values and absorptivities in the MeOH, FA, and NMF titration series suggest that both hydrogen bonding interactions are with the nitrogen end of the cyanate anion in all three 2:1 solvates.

The vibrational assignments from the titration studies provide a firm foundation for assigning the vibrational components of the ν_{CN} mode of 0.1 M OCN^- in neat solutions of the anion in MeOH, FA, and NMF. They are collected in Table 4. The 2152 and 2157 cm^{-1} components observed in neat NMF are similar to those seen in the titration experiment. In neat FA solutions the 2151 cm^{-1} band is absent; only the 2159 cm^{-1} component is observed. In neat MeOH solutions the component bands of the ν_{CN} mode are shifted by ~2 cm^{-1} from the values determined in the titration studies. The 2152 cm^{-1} component can be attributed to the OCN^-···HOMe complex and the 2161 cm^{-1} component to the OCN^-···$(HOMe)_2$. An additional component at 2166 cm^{-1} is observed in neat MeOH solutions which can be assigned to the MeOH···OCN^-···HOMe complex. The assignment is based on *ab initio* calculations, which predict the frequency of the ν_{CN} mode will be higher than those of the OCN^-···HOMe and the OCN^-···$(HOMe)_2$ species.[7] Additional support is provided by the experimental studies of alkali cyanates, where of the ν_{CN} frequency for the $LiOCNLi^+$ triple ion is the highest of all of lithium cyanate complexes studied to date.[2,6]

Table 5. ^{14}N and ^{17}O NMR Chemical Shifts of ~0.1M NBu_4OCN in DMF, NM, NMF, FA, and MeOH

solvent system	^{14}N chemical shift (±0.02) (ppm)	^{17}O chemical shift (±0.1) (ppm)
DMF	−290.76	39.0
NM	−293.28	38.4
NMF	−301.25	42.9
FA	−295.61	46.9
MeOH	−310.65	41.1

NMR Measurements. Chemical shifts from the ^{14}N and ^{17}O NMR spectra of the cyanate anion in the five solvents employed in this investigation are summarized in Table 5. The information provided by NMR spectroscopy is less specific because the observed chemical shifts are a population average over all species involved in the solution equilibria. Nonetheless, these NMR results are consistent with the vibrational assignments. In NMF, the cyanate anion is present in two hydrogen bonding environments. Relative to their values in aprotic solvents, the decrease in the ^{14}N chemical shift (more negative) and the increase in the ^{17}O chemical shift (more positive) suggest that the electron density of the anion is shifted from the oxygen end toward the nitrogen end. *Ab initio* calculations predict that a single or double hydrogen bonding interaction to the nitrogen end will shift the distribution of the negative charge in this direction.[7] In FA, the further increase in the extent of the solvation of the cyanate anion suggested by the infrared results is reflected by the increased positive shift of the ^{17}O NMR chemical shift. On the other hand, the ^{14}N chemical shift becomes more positive with respect to the value in NMF solutions, which is not predicted by the model *ab initio* calculations. This discrepancy shows that care must be employed in correlating chemical shifts with atomic charges.

The ^{14}N chemical shift of the OCN^- anion has the most negative value in MeOH solutions, where the ^{17}O chemical shift has the smallest positive value among the protic solvents. This pattern also fits well with the infrared results. The predicted atomic charges on the anion in the MeOH···OCN^-···HOMe species are similar to those of the free anion. The increase in the negative charge on the oxygen end is reflected by a decrease in the ^{17}O chemical shift with respect to the values for the OCN^-

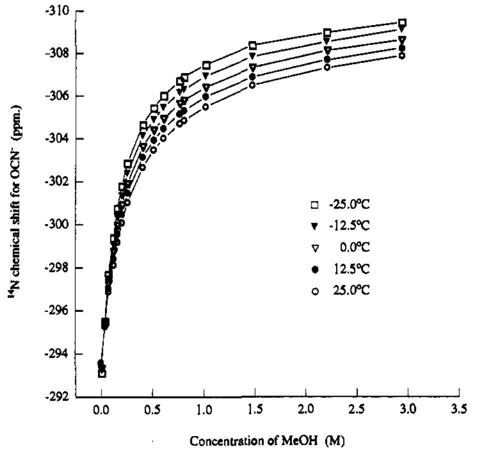


Figure 6. ^{14}N NMR chemical shift of ~0.1 M NBu_4OCN in NM as a function of MeOH added.

anion in the amide solvents. The large negative ^{14}N chemical shift of OCN^- in MeOH solutions can also be explained through the three hydrogen bonded species described earlier. The MeOH hydrogen bond is stronger than those of NMF and FA, which results in a greater ^{14}N chemical shift in $OCN^-\cdots HOMe$ and $OCN^-\cdots(HOMe)_2$ relative to the analogous NMF and FA species. Although the ^{14}N chemical shift in $MeOH\cdots OCN^-\cdots HOMe$ should be more positive than that in $OCN^-\cdots HOMe$ and $OCN^-\cdots(HOMe)_2$, the observed chemical shift is dominated by contributions from the $OCN^-\cdots HOMe$ and $OCN^-\cdots(HOMe)_2$ complexes.

Thermodynamic Parameters. The ^{14}N and ^{17}O chemical shifts of the cyanate anion were measured by NMR spectroscopy for the MeOH, NMF, and FA titration series in NM in order to complement the infrared studies. The temperature dependence of the ^{14}N chemical shifts was also determined. The concentration dependence of the ^{14}N chemical shift for OCN^- upon addition of MeOH, representative also of the NMF and FA systems, is shown in Figure 6. The concentration dependence displays a classic saturation curve for associating complexes. The temperature dependence of the NBu_4OCN/MeOH/NM dilution series shows that the solvated complexes are more stable at lower temperatures.

In order to extract thermodynamic parameters from the concentration dependence of the ^{14}N and ^{17}O chemical shifts or the intensity of the component infrared bands of the ν_{CN} or ν_{CO} & δ_{OCN} absorption, an appropriate model must be applied to the NMR and infrared results. The concentration dependence of the intensities of the 2154 and 2163 cm^{-1} bands in the methanol dilution series implies that methanol initially forms a 1:1 complex with the cyanate anion. At higher MeOH concentrations the 1:1 cyanate–methanol complex associates with an additional methanol molecule, forming a 1:2 cyanate–methanol complex. Thus the components of the ν_{CN} absorption provide an important clue to the equilibria responsible for the concentration dependence of the NMR and infrared measurements.

In addition to multiple associations of the cyanate anion with the hydrogen bonding solvents, both the self-association of the hydrogen bonding solvent and ion pairing of the NBu_4OCN salt must be considered and possibly incorporated into the model. Previous investigations of tetraalklyammonium salts in nitromethane have shown that ion pairing is negligible at 0.1 M.[21] Therefore, the NMR and infrared investigations have been modeled by three equilibria: (a) the self-association of the hydrogen bonding solvent (limited to the dimerization of the solvent), (b) formation of a 1:1 cyanate–hydrogen bonding solvent adduct, and (c) formation of a 1:2 cyanate–hydrogen bonding solvent complex, as illustrated in eqs 2–4. Although these equilibrium expressions are written with the hydrogen bonding interaction at the nitrogen end of OCN^-, the determination of the equilibrium constants is independent of the site of the hydrogen bonding interaction. At the low concentrations of the cyanate anion employed in this work, the equilibrium constants can be written in terms of the concentrations of the species in the equilibria; the activity coefficients can be neglected. Thus the equilibria can be expressed by eqs 5–7.

$$\mathrm{OCN^- + MeOH \overset{K_1}{\rightleftharpoons} OCN^-\cdots HOMe} \tag{2}$$

$$\mathrm{OCN^-\cdots HOMe + MeOH \overset{K_2}{\rightleftharpoons} OCN^-\cdots(HOMe)_2} \tag{3}$$

$$\mathrm{2MeOH \overset{K_D}{\rightleftharpoons} (MeOH)_2} \tag{4}$$

where

$$K_1 = \frac{[\mathrm{OCN^-\cdots HOMe}]}{[\mathrm{OCN^-}]_f[\mathrm{MeOH}]_f} \tag{5}$$

$$K_2 = \frac{[\mathrm{OCN^-\cdots(HOMe)_2}]}{[\mathrm{OCN^-\cdots HOMe}][\mathrm{MeOH}]_f} \tag{6}$$

$$K_D = \frac{[\mathrm{(MeOH)_2}]}{[\mathrm{MeOH}]_f^2} \tag{7}$$

Equation 8 gives the total concentration of OCN^- in terms of the concentration of the free OCN^- anion, $[OCN^-]_f$, the concentration of the 1:1 complex, $[OCN^-\cdots HOMe]$, and the concentration of the 1:2 complex, $[OCN^-\cdots(HOMe)_2]$. Likewise, the total concentration of MeOH, $[MeOH]_T$, can be written in terms of the concentrations of free MeOH, $[MeOH]_f$, the 1:1 complex, the 1:2 complex, and the methanol dimer, $[(MeOH)_2]$, eq 9.

$$[\mathrm{OCN^-}]_T = [\mathrm{OCN^-}]_f + [\mathrm{OCN^-\cdots HOMe}] + [\mathrm{OCN^-\cdots(HOMe)_2}] \tag{8}$$

$$[\mathrm{MeOH}]_T = [\mathrm{MeOH}]_f + [\mathrm{OCN^-\cdots HOMe}] + 2[\mathrm{OCN^-\cdots(HOMe)_2}] + 2[\mathrm{(MeOH)_2}] \tag{9}$$

Substitution of eqs 5–7 into eqs 8 and 9 and solution of the resulting eqs simultaneously for $[OCN^-]_f$ yields a quartic expression in $[MeOH]_f$ eq 10.

$$(2K_1K_2K_D)[\mathrm{MeOH}]_f^4 + (K_1K_2 + 2K_1K_D)[\mathrm{MeOH}]_f^3 + (K_1K_2(2[\mathrm{OCN^-}]_T - [\mathrm{MeOH}]_T) + K_1 + 2K_D)[\mathrm{MeOH}]_f^2 + (K_1([\mathrm{OCN^-}]_T - [\mathrm{MeOH}]_T) + 1)[\mathrm{MeOH}]_f - [\mathrm{MeOH}]_T = 0 \tag{10}$$

The roots of eq 10 can be determined analytically, from which an expression for the concentration of free methanol can be derived in terms of the association constants (K_1, K_2, and K_D), $[MeOH]_T$, and $[OCN^-]_T$. An expression for $[OCN^-]_f$ can then be written in terms of the association constants and the total

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[21] Hojo, M.; Miyauchi, Y.; Imai, Y. *Bull. Chem. Soc. Jpn.* 1990, *63*, 3288.

Table 6. Association Constants, K_1, K_2 and K_D, for the Formation of $OCN^-\cdots HB$, $OCN\cdots(HB)_2$, and $BH\cdots BH$ Where HB can be NMF, FA, or MeOH, Determined by ^{14}N and ^{17}O NMR Spectroscopy

solvent	temp (±0.2 °C)	K_1 (M^{-1})	K_2 (M^{-1})	K_D (M^{-1})
NMF				
	^{14}N NMR			
	25.0° C	4.8 ± 0.1	0.26 ± 0.04	0.06 ± 0.01
	12.5° C	5.7 ± 0.2	0.28 ± 0.09	0.07 ± 0.02
	0.0	6.8 ± 0.2	0.28 ± 0.02	0.07 ± 0.02
	−12.5	8.3 ± 0.2	0.31 ± 0.12	0.09 ± 0.02
	−25.0	10.0 ± 0.1	0.34 ± 0.06	0.09 ± 0.02
	^{17}O NMR			
	25.0	2.7 ± 1	0.33 ± 0.20	0.04 ± 0.02
FA				
	^{14}N NMR			
	25.0	4.4 ± 0.1	*a*	0.06 ± 0.03
	12.5	5.2 ± 0.1	*a*	0.07 ± 0.03
	0.0	5.9 ± 0.1	*a*	0.11 ± 0.03
	−12.5	7.3 ± 0.1	*a*	0.10 ± 0.03
	−25.0	8.8 ± 0.1	*a*	0.09 ± 0.04
	^{17}O NMR			
	25.0	3.2 ± 1.0	0.53 ± 0.20	0.06 ± 0.03
MeOH				
	^{14}N NMR			
	25.0	8.8 ± 0.4	0.40 ± 0.15	0.10 ± 0.01
	12.5	10.9 ± 0.4	0.55 ± 0.40	0.10 ± 0.01
	0.0	13.5 ± 1.0	0.71 ± 0.17	0.16 ± 0.02
	−12.5	18.0 ± 1.0	0.98 ± 0.17	0.15 ± 0.02
	−25.0	21.4 ± 1.1	1.24 ± 0.13	0.17 ± 0.02
	^{17}O NMR			
	25.0	8.5 ± 3	0.47 ± 0.20	0.12 ± 0.1

[a] Not determinable.

Table 7. Association Constants, K_1, K_2, and K_D, for the Formation of $OCN^-\cdots HB$ and $OCN\cdots(HB)_2$, and $HB\cdots HB$, Where HB Can Be NMF, FA, or MeOH, Determined by Infrared Spectroscopy

solvent	temperature (24 ± 1 °C)	K_1 (M^{-1})	K_2 (M^{-1})	K_D (M^{-1})
NMF				
	A_{1198}	4.3 ± 0.8		
	A_{2142}	6.7 ± 0.6		
	A_{2151}	5.5 ± 0.4	0.20 ± 0.05	0.10 ± 0.01
FA				
	A_{1199}	5.8 ± 0.9		
	A_{2142}	5.6 ± 0.7		
	A_{2151}	5.0 ± 0.4	0.46 ± 0.07	0.13 ± 0.03
MeOH				
	A_{1198}	9.4 ± 0.7		
	A_{2142}	8.3 ± 1.0		
	A_{2154}	8.7 ± 0.7	0.37 ± 0.04	0.12 ± 0.02

Table 8. Thermodynamic Parameters for the Formation of 1:1 and 1:2 $OCN^-\cdots$Solvent Complexes in Nitromethane Solutions

solvent system	$\Delta H_1°$ (kJ/mol)	$\Delta S_1°$ (J $mol^{-1}K^{-1}$)	$\Delta H_2°$ (kJ/mol)	$\Delta S_2°$ (J $mol^{-1}K^{-1}$)
NMF	−9.0 ± 0.3	−17 ± 1	−4.7 ± 5.2	−27.8 ± 17
FA	−8.5 ± 0.3	−16 ± 2	*a*	*a*
MeOH	−12.1 ± 0.7	−22 ± 2	−12.1 ± 0.6	−47 ± 2

[a] Not determinable.

MeOH and OCN^- concentrations by substituting eq 5, eq 6, and the solution for eq 10 into eq 8.

The observed chemical shift of either the ^{14}N or the ^{17}O nucleus of the cyanate anion, δ_{obs}, is a population average of those for the free anion, the 1:1 complex, and the 1:2 complex as shown in eq 11, where χ_{free} is the mole fraction and δ_{free} is the chemical shift of the free anion, χ_1 is the mole fraction of the 1:1 complex and δ_1 is its chemical shift, and χ_2 is the mole fraction of the 1:2 complex, which has the chemical shift δ_2. With the appropriate substitutions, eq 11 can be rewritten (eq 12) such that the

$$\delta_{obs} = \chi_{free}\delta_{free} + \chi_1\delta_1 + \chi_2\delta_2 \tag{11}$$

$$\delta_{obs} = K_1[OCN^-]_f[MeOH]_f(\delta_1 - \delta_{free})/[OCN^-]_T + K_1K_2[OCN^-]_f[MeOH]_f^2(\delta_2 - \delta_{free})/[OCN^-]_T + \delta_{free} \tag{12}$$

observed chemical shift is a function of the association constants (K_1, K_2, and K_D), the free OCN^- concentration, the free MeOH concentration, and the limiting chemical shifts for OCN^-, $OCN^-\cdots HOMe$, and $OCN^-\cdots(HOMe)_2$. Following substitution of the expressions for $[OCN^-]$ and [MeOH], the values for the equilibrium constants, including K_D, can then be calculated by fitting eq 12 to the chemical shifts observed at different methanol concentrations. These values are summarized in Table 6.

The formation constants for the hydrogen bonded complexes can also be determined from the infrared band absorptivities. For example, the concentration of the 1:1 $OCN^-\cdots HOMe$ complex is proportional to the absorbance of the 2154 cm^{-1} component (A_{2154}) as shown in eq 13, where ϵ is the molar absorptivity and l is the pathlength of the infrared cell. Upon substitution for $[OCN^-]_f$ and $[MeOH]_f$, the absorbance of the 2154 cm^{-1} component becomes a function of the molar absorptivity, pathlength, equilibrium constants, and the total concentrations of OCN^- and MeOH.

$$A_{2154} = \epsilon_{2154}l\,[OCN^-\cdots HOMe] = K_1\epsilon_{2154}l\,[OCN^-]_f[MeOH]_f \tag{13}$$

The fitting of eq 13 to the absorbance of the component band resulting from the 1:1 complex also provides the formation constants of the solvated complexes and the self-association of the hydrogen bonding solvent (K_1, K_2, and K_D). Likewise, the K_1 association constant can be determined by relating the ν_{CN} and ν_{CO} and $2\delta_{OCN}$ infrared bands that are attributable to the free OCN^- anion to the total methanol and cyanate concentrations, as shown in eq 14. This neglects the self-association of the hydrogen bonding solvent, since this equilibrium is negligible when the protic solvent concentration is less than 0.5M, as shown by the small equilibrium constant, K_D, for this association. The results are listed in Table 7.

$$A_{2142} = \epsilon_{2142}l[OCN^-]_f/(1 + K_1[MeOH]_f) \tag{14}$$

The good agreement between the association constants obtained from the NMR and infrared measurements confirms that these spectroscopic measurements were modeled with the correct equilibria. The equilibrium constants for the 1:2 complexes in the amide solvents should be considered approximate, since the measurements that are important in their determination lie near the detection limit. It is interesting to note that the 1:1 $OCN^-\cdots HOMe$ adducts, which have the largest ν_{CN} frequency shifts relative to those observed for the corresponding FA and NMF bands, have the highest formation constant for these complexes. A similar result has been obtained for alkali cyanates and alkali thiocyanates, where ion pairings that result in the largest frequency shifts of the ν_{CN} mode, as in LiNCO ion pairs, also have the greatest ion pair formation constants.[2,6,8,22,23]

From the temperature dependence of the association constants derived from the ^{14}N NMR measurements, the enthalpy, $\Delta H°$,

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(22) Chabanel, M. *Pure Appl. Chem.* **1990**, *62*, 35.

(23) Chabanel, M.; Bencheikh, A.; Danuta, P. *J. Chem. Soc., Dalton Trans.* **1989**, 2193.

and the entropy, $\Delta S°$, for these complexation equilibria were determined; they are summarized in Table 8. The negative enthalpy term is a result of the ion-dipole attraction between the anion and the hydrogen bond donor. The thermodynamic parameters for the complexation equilibrium in NMF, FA, and MeOH show that the entropy change is an important consideration in the formation of the complexes. There is little difference among the enthalpies and entropies of formation for the 1:1 complexes of OCN^- with NMF, FA, and MeOH, although the MeOH complex has the highest $\Delta H_1°$. The dramatic reduction of K_2 from K_1 appears to result primarily from the decrease in the entropy of the system as demonstrated by the methanol complexes.

Conclusions

The infrared and NMR spectroscopic studies of ternary nitromethane solutions provide a consistent and coherent picture of the structure and thermodynamics of anion–solvent complexes in the primary solvation sphere surrounding the cyanate anion the hydrogen bonding solvents MeOH, FA, and NMF. Our investigations reveal that hydrogen bonding interactions in the amide solvents occur at the nitrogen end of the anion. In moderately dilute, neat formamide solutions, each OCN^- is hydrogen bonded to two FA molecules, whereas in MeOH, presumably a stronger hydrogen bonding solvent, the cyanate anion participates in both singly and doubly hydrogen bonded complexes. In neat methanol solutions, two distinct 1:2 cyanate: methanol adducts are observed.

An understanding of the difference between the hydrogen bonding interactions of the amide and methanol solvents is provided by *ab initio* calculations of the molecular electrostatic potential (MEP) of the cyanate anion in various electrostatic environments.[7] The MEP predicts the site of a potential electrostatic interaction.[24] For example, it predicts that a single ionic or hydrogen bonding interaction will occur at the nitrogen end of OCN^-, although population analysis suggests that the negative charge is almost equally distributed between the oxygen and nitrogen ends. In $FH\cdot\cdot\cdot NCO^-$, which models a strong hydrogen bond, the most negative MEP is found in a ring surrounding the oxygen end of the anion. The weaker hydrogen bond in an $OCN^-\cdot\cdot\cdot HOH$ complex only slightly perturbs the MEP in OCN^- such that the minimum lies in an arc that is slightly off the nitrogen end of the OCN^- anion. These calculations demonstrate that the MEP in OCN^- is very sensitive to the strength of an electrostatic interaction and that strength of the first hydrogen bonding interaction will determine the site of the second hydrogen bond.[7]

From the association constants, it is clear that the amide solvents form weaker hydrogen bonds with OCN^- than those by MeOH. Moreover, in the titration studies the perturbations of the ν_{CN} and ν_{CO} and $2\delta_{OCN}$ frequencies in the cyanate–methanol complexes are larger that those observed for similar amide complexes, which also reflects the relatively greater strength of the cyanate–methanol interaction. The weaker amide interactions with the cyanate anion result in hydrogen bonding only to the nitrogen end, owing to the smaller perturbation in the MEP for the OCN^- anion.

The thermodynamic parameters obtained in the titration studies provide insight into the factors that are involved in the solvation of anions. Interestingly, the enthalpy and entropy of formation for the hydrogen bonded complexes have similar values, which is probably a leveling effect due to the nitromethane solvent. The negative entropy values show that this term is dominated by the loss of freedom of the cyanate anion and the protic solvent upon formation of the complex, rather than by the release of nitromethane molecules that weakly solvate the complexation partners. In the MeOH titration, the entropy of formation for the second hydrogen bonded complex is more negative than that for the first complex. This is not surprising since in the 1:1 complex the nitrogen end of the anion will be less solvated by nitromethane than the free cyanate. Therefore, the entropy of formation for the second complex, $\Delta S_2°$, will be even more dependent on the loss of freedom of the complexation partners than on the nitromethane molecules liberated.

The extent of solvation of cyanate in neat solutions of MeOH, FA, and NMF can be understood by considering the role of entropy in the formation of intimate ion-molecule complexes. The overall entropy loss when these solvents form a hydrogen bond with the cyanate anion will be smaller than for the association of two free particles, since these solvents are highly self-associated. This can be clearly demonstrated by comparing the degree of solvation of OCN^- in NMF and FA solutions. Although the association constants for cyanate:amide complexes are comparable in NM, in neat solutions the cyanate anion is more solvated in FA than in NMF. Since FA is more self-associated than is NMF,[10,25,26] the entropy loss upon cyanate solvation will not be as great in FA as it is in NMF. Comparison of the solvation of OCN^- in FA with that of MeOH also supports this hypothesis. The perturbations in the ν_{CN} stretch show that the $OCN^-\cdot\cdot\cdot HOMe$ hydrogen bond is much stronger than that with FA. Yet, the cyanate anion is more highly solvated in neat FA solutions than in MeOH. This seemingly inconsistent can be rationalized by the greater self-association of FA relative to MeOH; the entropy loss upon hydrogen bonding with OCN^- will be smaller in FA solutions.

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[24] Lin, K.-J.; Cheng, M.-C.; Wang, Y. *J. Phys. Chem.* **1994**, *98*, 11685.

[25] Ohtaki, H.; Itoh, S.; Rode, B. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2117.

[26] Ohtaki, H.; Itoh, S.; Rode, B. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 271.