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^{17}O, ^{13}C and ^{1}H Nuclear Magnetic Resonance Investigations on Ion–Solvent Interactions in N,N-dimethylformamide

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N,N-dimethylformamide (DMF) containing electrolytes were investigated using ^{17}O, ^{13}C and ^{1}H nuclear magnetic resonance. All chemical shifts are affected by the cations. According to the results of ab initio *calculations on 1:1 DMF–cation complexes it can be concluded that the changes of ^{17}O and ^{13}C chemical shifts are due mainly to changes in the p-electron populations induced by the cations. The change of the magnetic anisotropy of the carbonyl group affects significantly the proton chemical shifts. The effect of zinc ion on the ^{17}O, ^{13}C and ^{1}H chemical shifts is different from that of alkaline and alkaline earth metal ions. Line broadening of ^{17}O signals by electrolytes due to viscosity changes is also observed.*

Introduction

Although cations or anions in non-aqueous solution have been subject to extensive NMR investigations, almost no solvation studies on the non-aqueous solvent itself employing ^{17}O as nuclear probe have been reported so far. The existence of the ^{17}O quadrupole moment (I = 5/2) and the low natural abundance (0.037%) might be reasons for this. Oxygen atoms usually interact, however, directly with the cations. Thus ^{17}O NMR could be expected to supply direct informations on the solvation process.

N,N-dimethylformamide (DMF) is frequently used as a polar non-aqueous solvent for electrolytes, and numerous investigations on DMF have been reported. The molecule also contains the biologically important peptide linkage group (NCO), so that further understanding of the interaction of DMF with cations could be useful for peptide and protein chemistry. Since the oxygen of DMF gives a sharp signal (line width = 76 Hz), it is also a suitable substance for ^{17}O NMR investigations.

Ab initio calculations on 1:1 cation–ligand complexes are strictly valid for the gas phase only. It has been shown, however, that such calculations are very useful for the discussion of experimental data in a series of similar systems [1–3].

We have investigated the interaction of DMF with Li^+, Na^+, Mg^{2+}, K^+, Ca^{2+} and Zn^{2+} using ^{17}O, ^{13}C and ^{1}H NMR and *ab initio* calculations with minimal GLO basis set.

Experimental

Measurement

All ^{17}O and ^{13}C NMR spectra were recorded on a Bruker WP 80 DS spectrometer operating in the Fourier transform (FT) mode with an external D_2O lock. Chemical shifts of ^{17}O NMR are reported in ppm downfield from the external standard H_2O. The accuracy of the chemical shift measurement is better than 2 ppm. Since the deviation of the chemical shifts due to the differences of the bulk diamagnetic susceptibility among the solution were smaller than 0.1 ppm, no correction was performed. Typical ^{17}O spectral parameters were as following: spectrometer frequency = 10.9 MHz, sweep width = 10 kHz, pulse delay = 0 and pulse width = 30 μs. Normally accumulation of 30,000 scans proved to be adequate for obtaining a well-resolved spectrum.

Chemical shifts of ^{13}C NMR are given in ppm downfield from the internal standard TMS. The accuracy of the chemical shift measurement is better than 0.1 ppm. Typical ^{13}C spectral parameters are as following: spectrometer frequency = 20.1 MHz, sweep width = 10 kHz, pulse delay = 2s and pulse width = 10 μs. Accumulation of 100 scans was sufficient for adequate resolution. All spectra were recorded at 303 K.

^{1}H NMR spectra were recorded by a Varian EM-360 spectrometer at 60 MHz. The chemical shifts are given in ppm downfield from the internal standard TMS.

Viscosities were measured at (302.7 ± 0.2) K inside a constant temperature water bath using an Ostwald type viscometer calibrated with distilled water. The average value of at least three flow times was used to calculate the viscosities.

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Reagents

LiCl, LiBr, KSCN, KCl and $Ca(NO_3)_2 \cdot 4H_2O$ were purchased from Merck. LiI, $LiNO_3$, NaSCN and $MgCl_2$ (98%) were purchased from PCR, Mallinckrodt Chemical Works, Fluka and Alfa Ventron products respectively. DMF (Fluka) was dried over 4 Å activated molecular sieves for at least 24 hours. Except for $MgCl_2$, all of the chemicals were of analytical grade and used without further purification. The concentration of magnesium ion was determined by titration with EDTA. $Ca(NO_3)_2$ was obtained by drying $Ca(NO_3)_2 \cdot 4H_2O$ at 440 K to constant weight. Except for LiI, all of the salts were dried by heating above 400 K overnight before use. The DMF solution of LiSCN was obtained as following: Equivalent amounts of LiCl and KSCN were dissolved in DMF. After mixing of the two solutions, the precipitated KCl was removed by centrifugation.

Quantum Chemical Calculations

The *ab initio* calculations with minimal GLO basis sets for DMF and cation complexes were performed at the CDC Cyber 170 computer of the Interuniversity Computer Centre in Vienna [4]. The experimental geometry of DMF was kept constant throughout the calculations [5]. The cation positions (except Zn^{2+}) were optimized with respect to total energy [1, 3, 6]. Experimental data of the distance between zinc ion and water molecule in aqueous solution [7–9] was used to determine the position of zinc ion.

Results and Discussion

^{17}O chemical shifts of DMF solutions of LiCl as a function of the salt concentration are shown in Fig. 1. Linear correlation is obtained within the methodical accuracy limits. This observation holds also for the other cations under investigation.

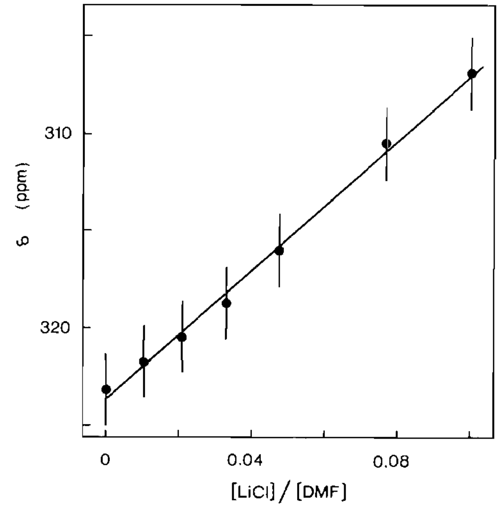

Fig. 1. Plots of ^{17}O chemical shifts *versus* the molar ratio between LiCl and DMF. The correlation coefficient is 0.998.

Table I presents the ^{17}O and ^{13}C chemical shifts of lithium salt solutions at the same concentration. The chemical shifts were not influenced by varying anions within experimental error.

The chemical shifts of ^{17}O, ^{13}C and ^1H of all electrolyte solutions and pure DMF are listed in Table II and III. The molar ratio (DMF/salt) was 26.0 ± 0.3 for ^{17}O and 10.0 ± 0.1 for ^{13}C and ^1H except the case of $MgCl_2$. Since the deviation of the molar ratio of $MgCl_2$ is considerable (27.1 for ^{17}O and 10.5 for ^{13}C and ^1H), the chemical shifts were corrected to the molar ratio 26.0 and 10.0 according to the linear shift/concentration relation. When the molar ratio exceeds 26, the measurement of ^{17}O chemical shifts becomes difficult because of line broadening.

Since the influence of anions on the chemical shifts seemed to be negligible, and since the chemical shift differences in the carbonyl group (which is located closer to the cation than the methyl groups [1]) are apparently larger than that of the methyl groups, the chemical shift differences should be dominated by the effect of the cations. Table II and III present the Mulliken populations at the nuclei of the 1:1 DMF–cation complexes and the correlation coefficients between chemical shifts and electron populations. Eliminating the zinc complex, a considerably better correlation is established, indicating a different interaction of this ion compared to the main group metal ions.

^{17}O and ^{13}C Chemical Shifts

The total shielding constant, σ, for a particular nucleus has been approximated by a sum of three terms [10]

$$\sigma = \sigma_d + \sigma_p + \sigma' \qquad (1)$$

where σ_d is the diamagnetic contribution, σ_p the paramagnetic contribution and σ' the contribution from neighboring groups.

TABLE I. ^{17}O and ^{13}C Chemical Shifts of DMF Relative to External H_2O (^{17}O) and Internal TMS (^{13}C) in the Presence of Lithium Salts. $[DMF]/[Li^+] = 26.0 \pm 0.5$.

Electrolyte	Chemical Shift (ppm)			
	^{17}O	^{13}C		
		C=O	CH3	
LiCl	315.9	163.1	31.0	36.3
$LiNO_3$	315.9	163.0	31.0	36.1
LiSCN	316.9	162.9	30.9	36.2
LiBr	315.5	163.0	30.9	36.2
LiI	314.1	163.1	31.2	36.4

TABLE II. Chemical Shifts, δ {ppm Relative to External H_2O (^{17}O) and Internal TMS (^{13}C and ^1H)}, of the Nuclei of the Carbonyl Group of DMF, Mulliken Populations at the Nuclei of the 1:1 Complexes of DMF + Cation, q, and Linear Correlation Coefficients. The Used Electrolytes were KSCN, NaSCN, LiCl, $Ca(NO_3)_2$, $MgCl_2$ and $ZnCl_2$.

Cation	^{17}O		^{13}C		^1H	
	δ	q	δ	q	δ	q
–	321,3	8.280	162.5	5.468	8.03	0.949
K^+	319.4	8.406	163.1	5.389	8.02	0.905
Na^+	317.7	8.490	163.2	5.383	8.07	0.904
Li^+	315.9	8.556	163.4	5.360	8.17	0.896
Ca^{2+}	313.2	8.607	163.5	5.323	8.04	0.856
Mg^{2+}	308.7	8.798	164.2	5.282	8.30	0.840
Zn^{2+}	315.9	8.603	163.5	5.300	8.07	0.835
		Correlation Coefficient				
With Zn^{2+}		0.972		0.942		0.461
Without Zn^{2+}		0.996		0.969		0.630

TABLE III. Chemical Shifts, δ {ppm Relative to External H_2O (^{17}O) and Internal TMS (^{13}C and ^1H) }, of the Methyl Groups of DMF, Mulliken Populations at the Nuclei of the 1:1 Complexes of DMF + Cation, q, and Linear Correlation Coefficients. Electrolytes as in Table II.

Cation	^{13}C				^1H			
	cis		*trans*		*cis*		*trans*	
	δ	q	δ	q	δ	q	δ	q
–	30.9	6.1616	35.9	6.1581	2.77	0.8252	2.93	0.8340
K^+	31.0	6.1586	36.2	6.1606	2.77	0.8182	2.96	0.8132
Na^+	31.0	6.1569	36.2	6.1614	2.80	0.8183	2.99	0.8115
Li^+	31.1	6.1570	36.4	6.1623	2.80	0.8157	2.97	0.8083
Ca^{2+}	31.1	6.1555	36.3	6.1675	2.80	0.8104	2.97	0.7891
Mg^{2+}	31.5	6.1545	36.5	6.1707	2.84	0.8061	3.10	0.7821
Zn^{2+}	31.3	6.1589	36.6	6.1689	2.81	0.8031	3.00	0.7816
			Correlation Coefficients					
With Zn^{2+}		0.618		0.846		0.795		0.734
Without Zn^{2+}		0.858		0.730		0.769		0.780

TABLE IV. Distances between Carbonyl Oxygen and Cations.

Cation	Distance (A)
K^+	2.5
Na^+	2.1
Li^+	1.8
Ca^{2+}	2.2
Mg^{2+}	1.8
Zn^{2+}	2.1[a]

[a] Experimental value (Ref. 7, 8, 9).

The paramagnetic term, σ_p, has been shown to dominate in the case of ^{17}O and ^{13}C chemical shifts (>90%) [11–13]. In the isotropic case, the paramagnetic term can be given as following [11]:

$$\sigma_p = -\frac{2}{3}\left(\frac{eh}{mc}\right)^2 \frac{\langle r^{-3}\rangle_{2p}}{\Delta E} \sum_B Q_{NB} \tag{2}$$

where ΔE is an average excitation energy for electronic transition, $\langle r^{-3}\rangle_{2p}$ is the average value of the inverse cube of the '2p orbital radius' and Q_{NB} is the bond-order charge density term, where the summation runs over all other nuclei B in the molecule, N being the nucleus under consideration.

According to Slater's rule, $\langle r^{-3}\rangle_{2p}$ is given by eqn. (3).

$$\langle r^{-3}\rangle_{2p} = \frac{1}{24}\left(\frac{Z^*}{a_0}\right)^3 \tag{3}$$

where a_0 is the Bohr radius and Z^* is the effective charge given by eqn. (4) in the case of oxygen and carbon.

$$\begin{aligned} Z_O^* &= 4.55 - 0.35\,(p_z - 1) \quad \text{for oxygen} \\ Z_C^* &= 3.25 - 0.35\,(p_z - 1) \quad \text{for carbon} \end{aligned} \tag{4}$$

p_z being the electron population of the p_z orbital at the nucleus.

Since $\langle r^{-3}\rangle_{2p}$ and ΔE are the dominant contributions to σ_p [14–19], σ might be written as following:

$$\sigma = \sigma_p = -k\,\frac{(Z^*)^3}{\Delta E} \qquad (5)$$

where k is a constant. According to the plots of the chemical shifts of ^{17}O and ^{13}C *versus* $(Z^*)^3$ calculated by eqn. (4) (Fig. 2 and 3), one can assume that the cations alter mainly the p-electron population, which could be interpreted formally as an 'increase' of the 'orbital radius' in the model according to eqn. (3). These observations can be compared also to former studies on cation/amide systems by metal NMR [20], which have shown a correlation to exist between the p-electron population of the metal ions and the metal NMR shifts.

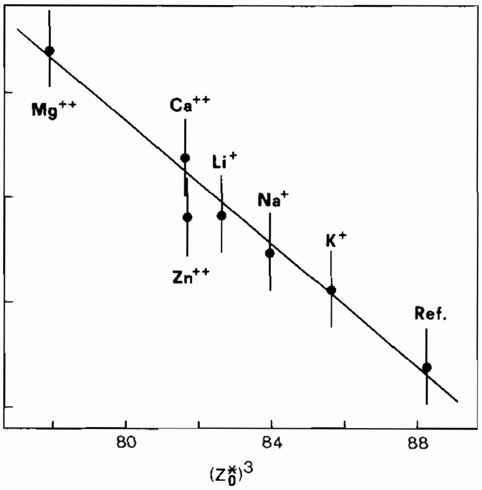

Fig. 2. ^{17}O chemical shifts of the electrolyte solutions *versus* the cube of the effective nuclear charge at the oxygen nucleus of the 1:1 complexes. The correlation coefficient omitting zinc is 0.996.

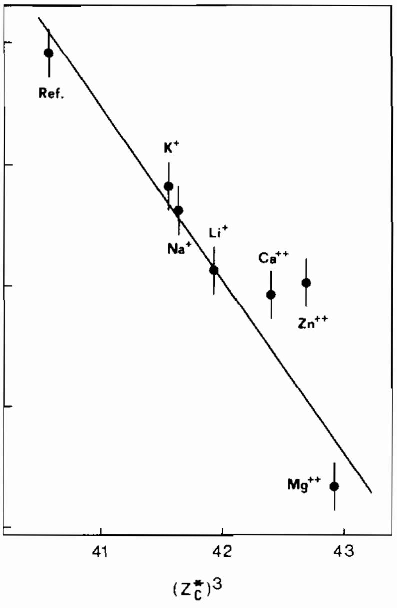

Fig. 3. ^{13}C chemical shifts of the electrolyte solutions *versus* the cube of the effective nuclear charge at the carbon nucleus of the 1:1 complexes. The correlation coefficient omitting zinc is 0.970.

^1H Chemical Shift

In the case of ^1H chemical shift, the paramagnetic contribution σ_p is far less important [21]. The total shielding constant σ might be given by eqn. (6).

$$\sigma = \sigma_d + \sigma' \qquad (6)$$

σ_d and σ' are approximately presented by eqns. (7) and (8) [21–23].

$$\sigma_d = 17.8\,\lambda \qquad (7)$$

$$\sigma' = \sigma_E + \sigma_a \qquad (8)$$

where λ is the electron density at the proton, σ_E is the electric field effect and σ_a is the magnetic anisotropy effect.

Since there exists a fairly linear correlation between the methyl proton shifts and the total electron density, the diamagnetic contribution, σ_d, should be the dominant factor in the chemical shift differences induced by cation (eqn. 7). In the case of the carbonyl proton, however, the magnetic anisotropy effect is considerably higher. This anisotropy effect should lead to a deviation from the linear correlation, since the changes in the electron population at the carbon and oxygen atom of C=O will have a significant influence on the anisotropy (Fig. 4).

Deviation of Zinc Complex Data

Although the structure of the DMF–Zn^{2+} complex should not be too different from that with other

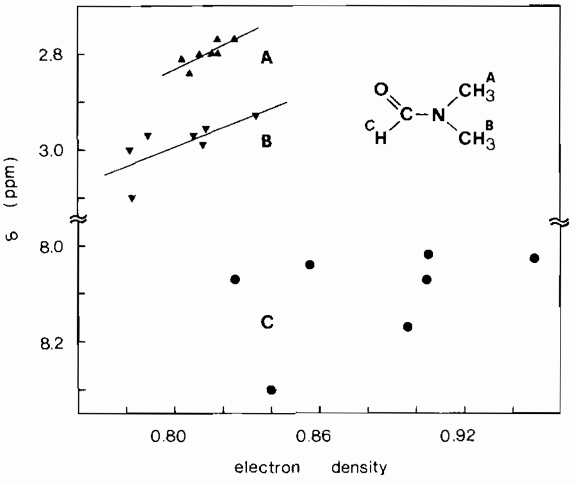

Fig. 4. ^1H chemical shifts of the electrolyte solution *versus* the electron densities at the protons of the 1:1 complexes.

metal ions, and although there exist no significant differences between hydrates of these cations [24], the correlation coefficients are considerably improved by omitting the zinc complex (Table II and III). This fact might be due to the large number of electrons and the existence of d-electrons in the case of Zn^{2+}, which leads to a rather similar oxygen-cation distance as for Na^+ despite the much larger atomic number. The electrons of the zinc ion might have influence on the electronic structure of DMF in a quite different and probably stronger way, and they might thus cause a deviation from the linear correlation observed for the other ions.

Line Width of ^{17}O

Under extreme motional narrowing conditions ^{17}O line width is presented as follows [25]:

$$\frac{1}{T_2} = \frac{1}{125}\left(1 + \frac{\eta^2}{3}\right)\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c \qquad (9)$$

where η is an assymmetry parameter of the electric field gradient, $e^2qQ/\hbar$ is the quadrupole coupling constant and τ_c is the correlation time for molecular reorientation. By Stocks' equation τ_c is given by:

$$\tau_c = \frac{4\pi a^3 \eta^*}{3kT} \qquad (10)$$

where a is the molecular radius, k Boltzmann's constant, T the absolute temperature and η^* the viscosity. On the other hand, the observed line width in the case of rapid exchange between bulk and cation-coordinated molecules is presented by as follows:

$$\frac{1}{T_2'} = \frac{p_B}{T_{2B}} + \frac{p_c}{T_{2C}} \qquad (11)$$

where p_B and p_C are mole fractions of the different species, and T_{2B} and T_{2C} are the line widths of the bulk and coordinated oxygen, respectively [21].

If the line width is not affected by the cation it should be proportional to the viscosity at the fixed temperature [26].

$$\frac{1}{T_2'} \sim \eta^* \qquad (12)$$

Table V presents the viscosity η^* of the solutions investigated and the value of $\Delta\nu^1/_2/\eta^*$. Since the error in the line width measurements can be estimated to be 10–20%, it can be concluded that their variations are substantially due to the difference of the solution's viscosities, except for the magnesium salt solution. It is not obvious why the value of $\Delta\nu^1/_2/\eta^*$ of magnesium salt solutions should be significantly different from the others. It might be possible that the small and doubly charged cation enlarges the asymmetric parameter of the electric field, shortening T_{2C} in eqn. (11) and leading to an increase in line width. It cannot be excluded, however, that impurities of the salt being used are responsible for the unusual line width.

TABLE V. Line Widths of ^{17}O NMR Signal and Viscosities of the Solutions.

Electrolyte	$\Delta\nu^1/2$ (Hz)	$\eta^* \times 10$ (N·S/m)	$\Delta\nu^1/_2/(\eta^* \times 10)$
–	76	0.716	106
KSCN	95	1.067	89
NaSCN	91	1.052	86
LiCl	110	1.096	100
$Ca(NO_3)_2$	151	1.407	107
$MgCl_2$	221	1.592	139
$ZnCl_2$	106	1.055	100

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