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Complexation Study of UO_2^{2+} Ion with 18-Crown-6, Dicyclohexyl-18-crown-6 and Dibenzo-18-crown-6 in Binary Nitromethane-Acetonitrile Mixtures by a Competitive NMR Technique Using ^{7}Li Nucleus as a Probe

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Lithium-7 NMR measurements were used to determine the stability of 1:1 Li^+ complexes with 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in various binary nitromethane-acetonitrile mixtures. A competitive ^{7}Li NMR technique was also employed to probe the complexation of UO_2^{2+} ion with these crown ethers in the mixed solvents used. In all solvent mixtures, the stability of the resulting 1:1 complexes was found to decrease in the order DC18C6 > 18C6 > DB18C6. There is an inverse relationship between the complex stability and the amount of acetonitrile in the mixed solvents.

Key words: competitive ^{7}Li NMR, UO_2^{2+} ion, crown ethers, complexation, stability, binary mixed solvents

Due to their pronounced selectivity and extraction efficiency [1–4], crown ether derivatives have been extensively used as suitable neutral ion carriers for selective transport through liquid membranes [5,6] and for constructing polymeric membrane sensors for different metal ions [7,8]. Information about the selectivity and stability of metal ion complexes with macrocyclic ligands are of critical importance in development of new methods for the removal, concentration, purification and determination from their mixtures.

Among different methods employed for the study of thermodynamics and kinetics of metal ion complexation with macrocyclic ligands in solution [1–4], nuclear magnetic resonance as a powerful technique has received a widespread attention [9,10]. In recent years, we have used the proton an alkali metal NMR techniques to study the stoichiometry and thermodynamics [11–15] and exchange kinetics [16–19] of a variety of metal ion-macrocycle complexes in nonaqueous and mixed solvents.

Uranyl ion is among such cations for which search for selective complexing agents continues owing to its importance in various physiological, medicinal and industrial processes. Uranium is extensively used in nuclear industry and is highly ra-

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dioactive. Among a wide variety of organic complexing agents investigated, crown ether derivatives have been frequently used in liquid-liquid extraction experiments [20,21] and in the preparation of potentiometric membrane sensors for UO_2^{2+} ion [22–23]. Thus, studies dealing with the complexation of uranyl ion with crown ethers are of critical importance for such practical applications.

In this study, we were interested in investigating the complexation of UO_2^{2+} ion with 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) in nonaqueous solvents. However, this cation possesses unsuitable NMR properties such as low receptivity, high quadrupole moment, insensitive chemical shifts, *etc.* [10,26]. Thus, we employed ^{7}Li NMR as a very sensitive probe [12–14,17,18] to study the cation-macrocycle complex of interest in different binary nitromethane-acetonitrile mixtures.

EXPERIMENTAL

Macrocyclic crown ethers 18C6, DC18C6 and DB18C6 and lithium perchlorate (all from Merck) were purified and dried as described elsewhere [11–19]. Uranyl nitrate was of the highest purity available from Fluka and used without any further purification except for vacuum drying over P_2O_5. Spectroscopic grade nitromethane (NM, Riedel) and acetonitrile (AN, Merck) were used as received.

All nuclear magnetic resonance measurements were made using a JEOL FX90Q FT-NMR spectrometer with a field strength of 21.13 kG. At this field, ^{7}Li resonates at 33.74 MHz. A 4.0 M aqueous LiCl solution was used as an external reference and the reported ^{7}Li chemical shifts refer to this solution. The concentration of cation solutions used was 5.0×10^{-3} M. All chemical shift measurements were carried out at a probe temperature of 25.0± 0.1°C.

RESULTS AND DISCUSSION

In contrast to ^{7}Li and other NMR active alkali metals [1,10], uranyl ion cannot be accurately used in an NMR study of their macrocyclic complexes. This is mainly because of its high quadrupole moment and low receptivity [26]. Thus, in this work, we decided to employ ^{7}Li NMR as a very sensitive probe [12–14,17,18] to investigate the complex formation of UO_2^{2+} with 18C6, DC18C6 and DB18C6 in different NM-AN mixtures.

Lithium-7 chemical shifts were monitored as a function of the crown ether to Li^+ ion mole ratio in the absence (A) and presence (B) of equimolar amount of UO_2^{2+} ion in different solvent mixtures with NM-to-AN wt. percents of 100/0, 75/25, 50/50, 25/75 and 0/100. In all cases, only one population-averaged resonance was observed, indicating that the exchange rate of the cation between the bulk solution and the complexed site is quite fast on the NMR time scale (Fig. 1). The resulting chemical shift-mole ratio data for all systems studied are shown in Figs. 2–4.

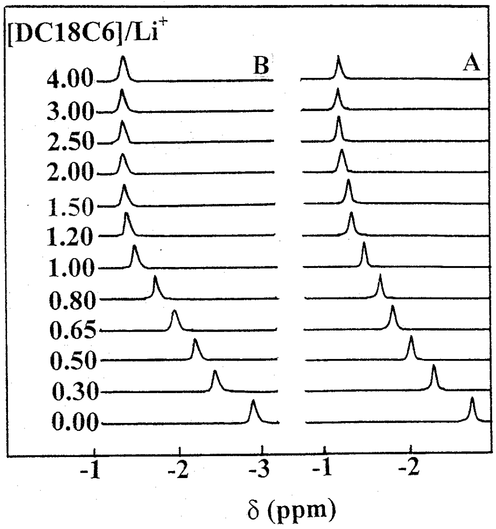

Figure 1. Lithium-7 NMR spectra for Li^+-DC18C6 (A) and Li^+-DC18C6-UO_2^{2+} (B) systems in 50% NM-50% AN mixture.

As is seen from Figs. 2–4, in the absence of UO_2^{2+} ion (A plots), addition of crown ethers to lithium ion solutions causes a gradual paramagnetic (downfield, in pure AN and its mixtures with NM) or diamagnetic (upfield, in pure NM) shift revealing an inflection point at a ligand to metal mole ratio of 1. This is an obvious indication for the formation of a 1:1 Li^+-crown complex in solution. However, Figs. 2A–4A show that the sharpness of the inflection point at a mole ratio of 1 depends strongly on the nature of crown ether as well as the composition of the binary mixed solvents used. The sharper the inflection point of a mole ratio plot, the higher the stability of the corresponding complex. It is interesting to note that, for each macrocycle, the sharpness of the inflection point decreases with increasing amount of AN in the NM-AN mixtures; while, in each binary mixture used, it decreases in the order DC18C6 > 18C6 > DB18C6.

Formation constants of the 1:1 complexes between Li^+ ion and the macrocycles used were evaluated from the variation of the ^7Li chemical shift with crown/Li^+ mole ratio. It has been shown previously [27] that the observed chemical shift is given by:

$$\delta_{obs} = \{[(K_{Li}C_{Li}C_{crown} - 1) + (K^2_{Li}C^2_{crown} + K^2_{Li}C^2_{Li} - 2K^2_{Li}C_{crown}C_{Li} + 2K_{Li}C_{crown} + 2K_{Li} + 2K_{Li}C_{Li} + 1)^{1/2}]/(\delta_{Li} - \delta_{Li\text{-crown}})/2K_{Li}C_{Li}\} + \delta_{Li\text{-crown}} \qquad (1)$$

where K_{Li} is the formation constant for the 1:1 complex, C_{Li} and C_{crown} are the analytical concentrations of Li^+ and crown ether, respectively, and δ_{Li} and $\delta_{Li\text{-crown}}$ are the respective chemical shifts of the free and complexed lithium ion.

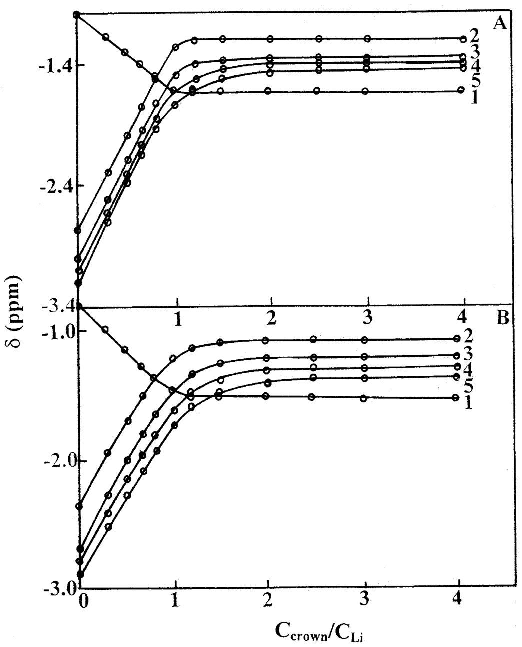

Figure 2. Lithium-7 chemical shift as a function of [18C6]/[Li^+] mole ratio in the absence (A) and presence (B) of UO_2^{2+} ion in different NM-AN mixtures. The weight percent of NM in the solvent mixture is: (1) 100, (2) 75, (3) 50, (4) 20, (5) 0.

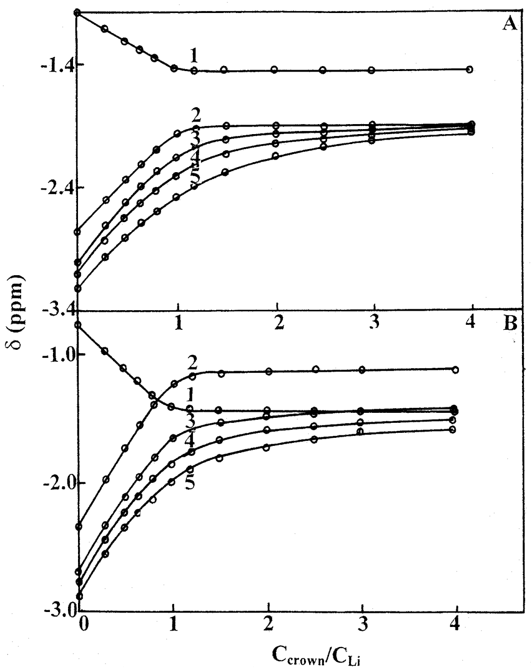

Figure 3. Lithium-7 chemical shift as a function of [DC18C6]/[Li^+] mole ratio in the absence (A) and presence (B) of UO_2^{2+} ion in different NM-AN mixtures. The weight percent of NM in the solvent mixture is: (1) 100, (2) 75, (3) 50, (4) 20, (5) 0.

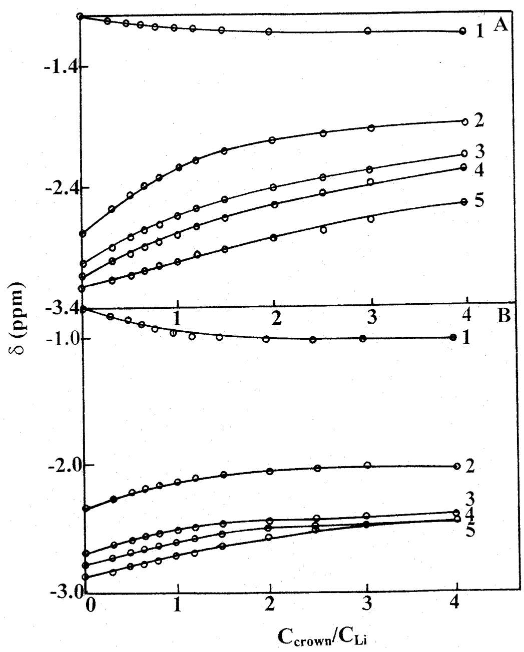

Figure 4. Lithium-7 chemical shift as a function of [DB18C6]/[Li^+] mole ratio in the absence (A) and presence (B) of UO_2^{2+} ion in different NM-AN mixtures. The weight percent of NM in the solvent mixture is: (1) 100, (2) 75, (3) 50, (4) 20, (5) 0.

A non-linear least-squares curve-fitting program KINFIT [28] was used to evaluate K_{Li} and $\delta_{Li\text{-}crown}$ values for the 1:1 complexes by fitting the δ_{obs} *versus* C_{crown} data (at constant $C_{Li} = 5.0 \times 10^{-3}$ M) to equation (1). A sample computer fit of the ^{7}Li chemical shift-mole ratio is shown in Fig. 5A, and the calculated K_{Li} values are given in Table 1. A fair agreement between the observed and calculated chemical shifts shown in Fig. 5A further supports the formation of complexes with 1:1 stoichiometry between Li^+ and macrocycles 18C6, DC18C6 and DB18C6.

Table 1. Formation constants of different 18-crown complexes with Li^+ and UO_2^{2+} ions in various NM-AN mixtures.

Crown ether	Cation	log K_f				
		100% AN	75% AN	50% AN	25% AN	0% AN
18C6	Li^+	2.29±0.01	2.70±0.04	3.20±0.08	4.11±0.06	4.91±0.20
	UO_2^{2+}	0.94±0.29	1.09±0.22	1.33±0.17	1.56±0.22	1.77±0.28
DC18C6	Li^+	3.42±0.03	3.65±0.03	4.09±0.10	4.83±0.06	5.59±0.45
	UO_2^{2+}	2.50±0.04	2.57±0.04	2.72±0.02	2.85±0.20	3.02±0.15
DB18C6	Li^+	0.97±0.05	1.45±0.04	1.81±0.03	2.33±0.03	2.70±0.02
	UO_2^{2+}	< 0.5	< 1	1.11±0.13	1.32±0.10	1.49±0.26

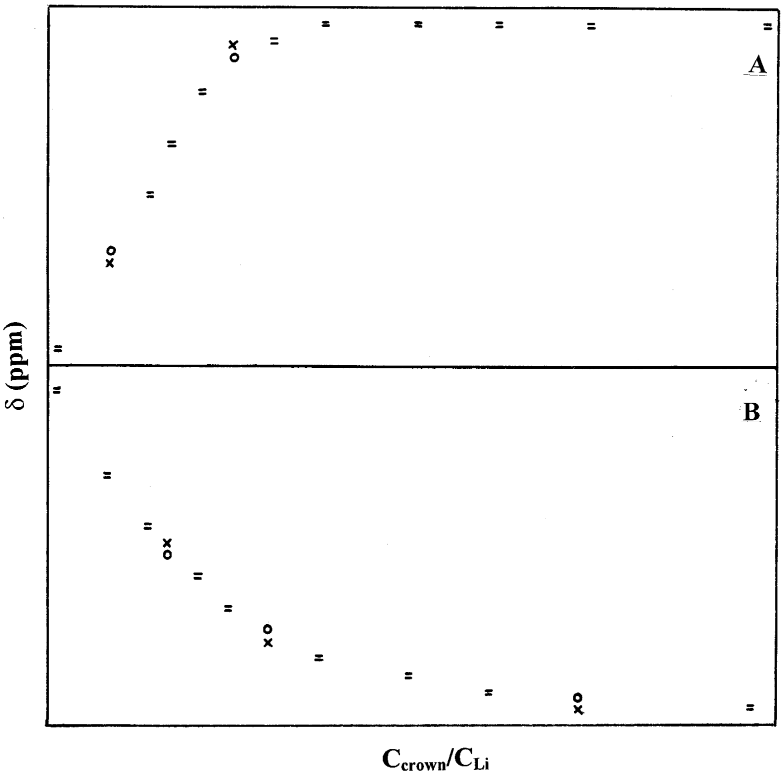

Figure 5. Computer fit of ^{7}Li chemical shift vs. crown/Li$^+$ mole ratio for Li$^+$-DC18C6 system in 75% NM-25% AN (A) and for Li$^+$-18C6-UO$_2^{2+}$ system in NM (B): (×) experimental point, (o) calculated point, (=) experimental and calculated points are the same within the resolution of the plots.

In order to evaluate the stability of UO$_2^{2+}$-crown ether complexes, the variation of lithium-7 chemical shift in the presence of an equimolar concentration of uranyl ion (5.0×10^{-3} M) as a function of crown/Li$^+$ mole ratio in different solvent systems, shown in Figs. 2B–4B, was considered. A comparison between the mole ratio plots in the absence and presence of UO$_2^{2+}$ ion for macrocycles 18C6 and DC18C6, given in Figs. 2 and 3 clearly revealed some distinct difference. For example, in pure NM and in 80% NM-AN mixture, unlike the cases involved in the formation of 1:1 Li$^+$-crown complexes (A labeled plots) in which the change in chemical shift with the crown/Li$^+$ mole ratio is quite linear at mole ratios between 0 and 1, the ^{7}Li chemical shift in the presence of UO$_2^{2+}$ ion (corresponding B labeled plots) shows a kind of curved relationship in this mole ratio region. Moreover, in the presence of uranyl ion, the sharp inflection points, observed at a mole ratio of one for the Li$^+$-crown systems, are obviously shifted to mole ratios >1, while its sharpness is diminished. These observations are obviously indicative of a competition between Li$^+$ and UO$_2^{2+}$ ions for the macrocyclic ligands during their titration with the ligands. However, in the case of DB18C6 (Fig. 4) such a distinct change in the corresponding mole ratio plots in the absence and presence of uranyl ion cannot be realized, due to the weak interaction between the cations and the macrocycle [3,4].

The competitive complexation equilibria for the case of 1:1 complexation between Li^+ and UO_2^{2+} ions and the crown ethers used can be written as:

$$Li^+ + \text{crown} = Li^+\text{-crown} \qquad K_{Li} = [Li^+\text{-crown}]/[Li^+][\text{crown}] \tag{2}$$

$$UO_2^{2+} + \text{crown} = UO_2^{2+}\text{-crown} \qquad K_U = [UO_2^{2+}\text{-crown}]/[UO_2^{2+}][\text{crown}] \tag{3}$$

The free crown concentration, [crown], is then obtained from equation (4) [29]:

$$K_{Li}K_U[\text{crown}]^3 - \{K_{Li}K_U(C_{crown} - C_{Li} - C_U) - K_{Li} - K_U\}[\text{crown}]^2 - \{K_{Li}(C_{crown} - C_{Li}) + K_U(C_{crown} - C_{Li}) - 1\}[\text{crown}] - C_{crown} = 0 \tag{4}$$

where C_{crown}, C_{Li} and C_M are the analytical concentrations of crown ether, Li^+ and UO_2^{2+} ions, respectively. In this case, the observed ^7Li chemical shift is obtained from equation (5) [27]:

$$\delta_{obs} = X_{Li}\delta_{Li} + X_{Li\text{-crown}}\,\delta_{Li\text{-crown}} \tag{5}$$

where X_{Li} and $X_{Li\text{-crown}}$ are the mole fractions of the free and complexed lithium ion, respectively. By substitution from equation (2) and the mass balance equation $C_{Li} = [Li^+] + [Li^+\text{-crown}]$, equation (5) can be written as:

$$\delta_{obs} = \{\delta_{Li} + \delta_{Li\text{-crown}}[\text{crown}]K_{Li}\}/\{1 + K_{Li}[\text{crown}]\} \tag{6}$$

The K_U values were evaluated by obtaining the free [crown] from equation (4) and fitting the chemical shift-mole ratio data to equation (6) using the KINFIT program.

A sample computer fit of the mole ratio data for a ternary Li^+-18C6-UO_2^{2+} system is shown in Fig. 5B and the resulting log K_f values for all UO_2^{2+}-crown complexes are also included in Table 1. Our assumption of the 1:1 stoichiometry for both Li^+-crown and UO_2^{2+}-crown complexes seems reasonable in the light of a fair agreement between the observed and calculated chemical shifts [3,4].

From Table 1 it is obvious that, in all cases, the stabilities of Li^+ complexes are higher than that of the UO_2^{2+} complexes. It is well known that, in the process of crown ether complexation with metal ions, the consonance between the size of the macrocycle's cavity and the ionic size of the cation is a very important factor in determining the stability of the resulting complexes [1–4]. Lithium ion with an ionic size of 1.7 Å [30] can be easily fitted inside the cavity of 18-membered crown ethers with a size of 2.6–3.2 Å [31] to form a relatively stable complex [3,4,11–14]. While, the UO_2^{2+} ion has an elliptic form with the axes of 4.7 Å and 2.8 Å [32], so that it does not seem likely that uranyl ion can be located completely inside the cavity of 18-crowns to form a stable inclusive complex.

Comparison of the data given in Table 1 reveals that the stability of crown ether complexes with both Li^+ and UO_2^{2+} ions varies in the order DC18C6 > 18C6 > DB18C6. The results indicate that, among three different 18-membered crown ether derivatives used, where the ring frame remains the same, the stability of the resulting complexes depends significantly on the nature of substituents on the ring, which control both the electron-pair donicity and the flexibility of the ligand molecules. The presence of two cyclohexyl groups in DC18C6 molecule can pump electrons into the ligand ring so that the basicity of the oxygen atoms of the ring increases, while the flexibility of the ligand remains more or less the same as 18C6. Thus, the stability of DC18C6 complexes is higher than that of 18C6 complexes. The diminished stability of Li^+ and UO_2^{2+} complexes because of the aromatic substituents on 18C6 ring (*i.e.*, DB18C6) may be attributed to some combination of the decreased ligand flexibility and the electron-withdrawing effect of benzo groups, which weakens the electron-donor ability of oxygen atoms, resulting in weaker metal ion interaction [3].

The data given in Table 1 illustrate clearly the fundamental influence of the solvent properties on the complexation reactions of crown ethers with Li^+ and UO_2^{2+} ions. In all cases, the stability of the resulting 1:1 complexes increases rapidly by increasing weight percent of nitromethane in the mixed solvent. It has been shown that the solvating ability of the solvent, as expressed by the Gutmann donor number [33], plays an important role in different complexation reactions [1–4,9,11–14]. AN is a solvent of relatively higher solvating ability (DN = 14.1), which can have stronger competition with crown ethers for the cations than NM as a solvent of low solvating ability (DN = 2.7) [33]. Thus, it can be expected that addition of NM to AN will increase the extent of interaction between the macrocycles' donor atoms and Li^+ and UO_2^{2+} ions.

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