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An NMR Study of the Stoichiometry and Stability of Lithium Ion Complexes with 12-Crown-4, 15-Crown-5 and 18-Crown-6 in Binary Acetonitrile–Nitrobenzene Mixtures

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Abstract. Proton NMR spectroscopy was used to study the complexation reaction between lithium ion and 12-crown-4, 15-crown-5 and 18-crown-6 in a number of binary acetonitrile–nitrobenzene mixtures. In all cases the exchange between free and complexed crowns was fast on the NMR time scale and only a single population average ^{1}H signal was observed. Formation constants of the resulting 1 : 1 complexes in different solvent mixtures were determined by computer fitting of the chemical shift–mole ratio data. There is an inverse relationship between the complex stability and the amount of acetonitrile in the mixed solvent. It was found that, in all solvent mixtures used, 15-crown-5 forms the most stable complex with Li^+ ion in the series.

Key words. Crown ethers, Li^+ ion, mixed-solvent, complex stability, NMR.

1. Introduction

Since the first synthesis of crown ether compounds by Pedersen [1] and his observation of their selective ion binding properties, a great deal of research work has been done on crown complexes with inorganic and organic cations [2, 3] and with neutral molecules [4]. The stoichiometry and stability of crown ether complexes depend largely on the nature of the guest, the nature of the host and, especially, the solvent system used. There is currently an increasing interest in the study of physicochemical phenomena, including complexation processes, in binary mixed solvent systems and their interpretation in terms of the solutes' preferential solvation by one of the solvent's components [5–13].

Among a wide variety of physicochemical techniques used for such studies [2, 3], nuclear magnetic resonance of ^{7}Li, ^{23}Na, ^{39}K, ^{133}Cs and ^{205}Tl nuclei have been used rather extensively to study the thermodynamics [14–18] and kinetics [19–23] of complexation of the above cations with crown ethers in different solvents.

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In recent years, proton NMR has been employed in our laboratories [11, 14] and elsewhere [25–28] to study the stoichiometry, stability and exchange kinetics of different crown ether complexes in nonaqueous and mixed solvents. In this communication we report a proton NMR study of Li^+ ion complexes with 12-crown-4, 15-crown-5 and 18-crown-6 in different binary acetonitrile–nitrobenzene mixtures at 25 °C. It should be noted that, although the complexation of Li^+ ion by crown ethers has been reported in different nonaqueous solvents [2, 3], to the best of our knowledge, there is only one published paper on the formation of Li^+-dibenzo-24-crown-8 complex in DMF–acetonitrile mixtures in the literature [13].

2. Experimental

The macrocyclic polyether 18-crown-6 (18C6, Aldrich) was precipitated as its acetonitrile complex [29]. The resulting crystals were isolated and kept under vacuum at room temperature for several days to drive off the acetonitrile. Crown ethers 15-crown-5 (15C5) and 12-crown-4 (12C4) were of the highest purity available (both from Merck) and were used as received. Lithium perchlorate (Merck) was purified and dried as described before [15]. Reagent grade deuterated acetonitrile (CD_3CN, Aldrich) and extra pure nitrobenzene (Merck) were used to prepare the solvent mixtures by weight.

All proton NMR spectra were recorded on a Jeol JNM-EX90 FTNMR spectrometer operating at a field of 21.15 kG (a frequency of 90 MHz) at 27.0 ± 0.1 °C. In all experiments, TMS was used as an internal standard.

3. Results and Discussion

For a series of samples in a given acetonitrile–nitrobenzene solvent mixture in which the concentration of crown ether was 0.02 M and the $LiClO_4$ concentration varied from 0.00 up to approximately 0.06 M the chemical shift of the single NMR signal due to the —CH_2— groups of the ligand was determined at 27 °C. Typical spectra are shown in Figure 1 and the resulting chemical shift–mole ratio plots in pure acetonitrile and in three different solvent mixtures are shown in Figure 2. As it is evident from Figure 2, the mole ratio plots in general, can be divided into two groups: (i) plots with a pronounced change in curvature at a mole ratio of 1 : 1; and (ii) plots which are formed by two straight lines intersecting at a mole ratio of 1 : 1. Beyond this mole ratio the chemical shifts remain essentially constant. Qualitatively, the data indicate (i) significant 1 : 1 complexation, and (ii) formation of a stable 1 : 1 complex with $K_f > 10^5$, respectively.

The observed downfield shift in Figures 1 and 2 represent, of course, the difference in the environment of the —CH_2— groups in the free and complexed crown ethers. The magnitude of the shift is not related to the stability of the resulting 1 : 1 complex, but reflects rather the tightness of the crown–lithium ion juxtaposition;

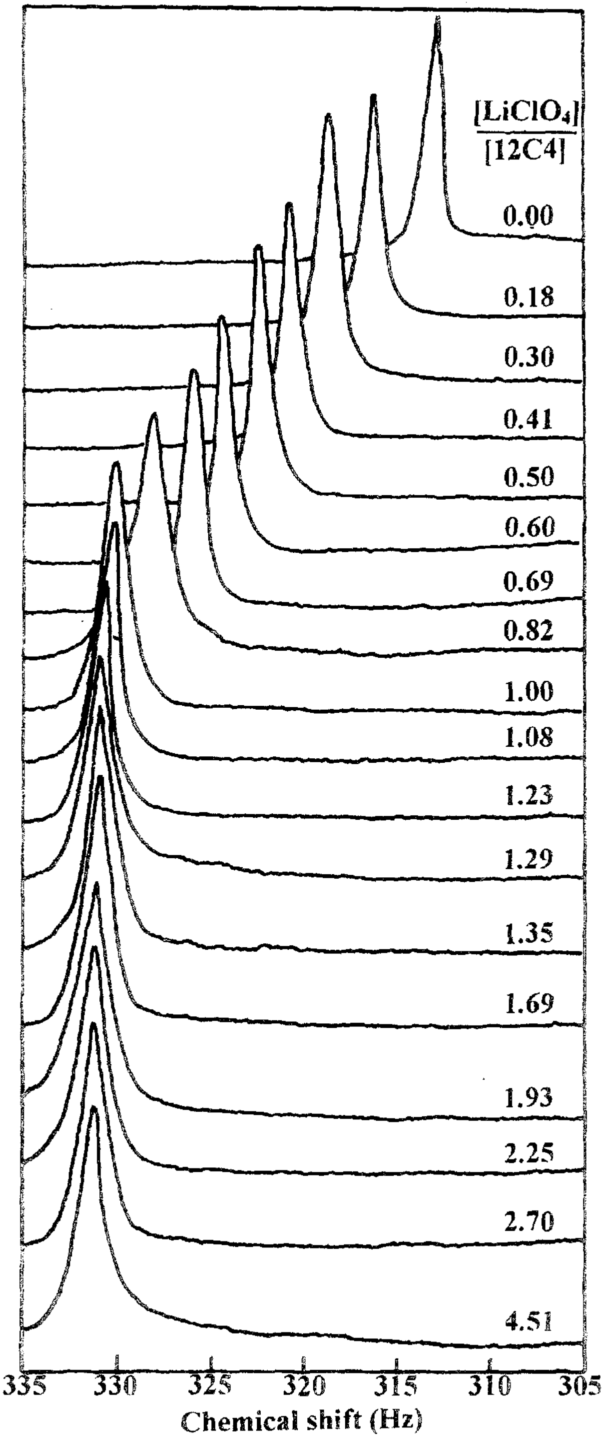

Figure 1. Proton NMR spectra of 12C4 at various Li^+/12C4 mole ratios in 60% nitrobenzene solution at 27 °C (at a frequency of 90 MHz).

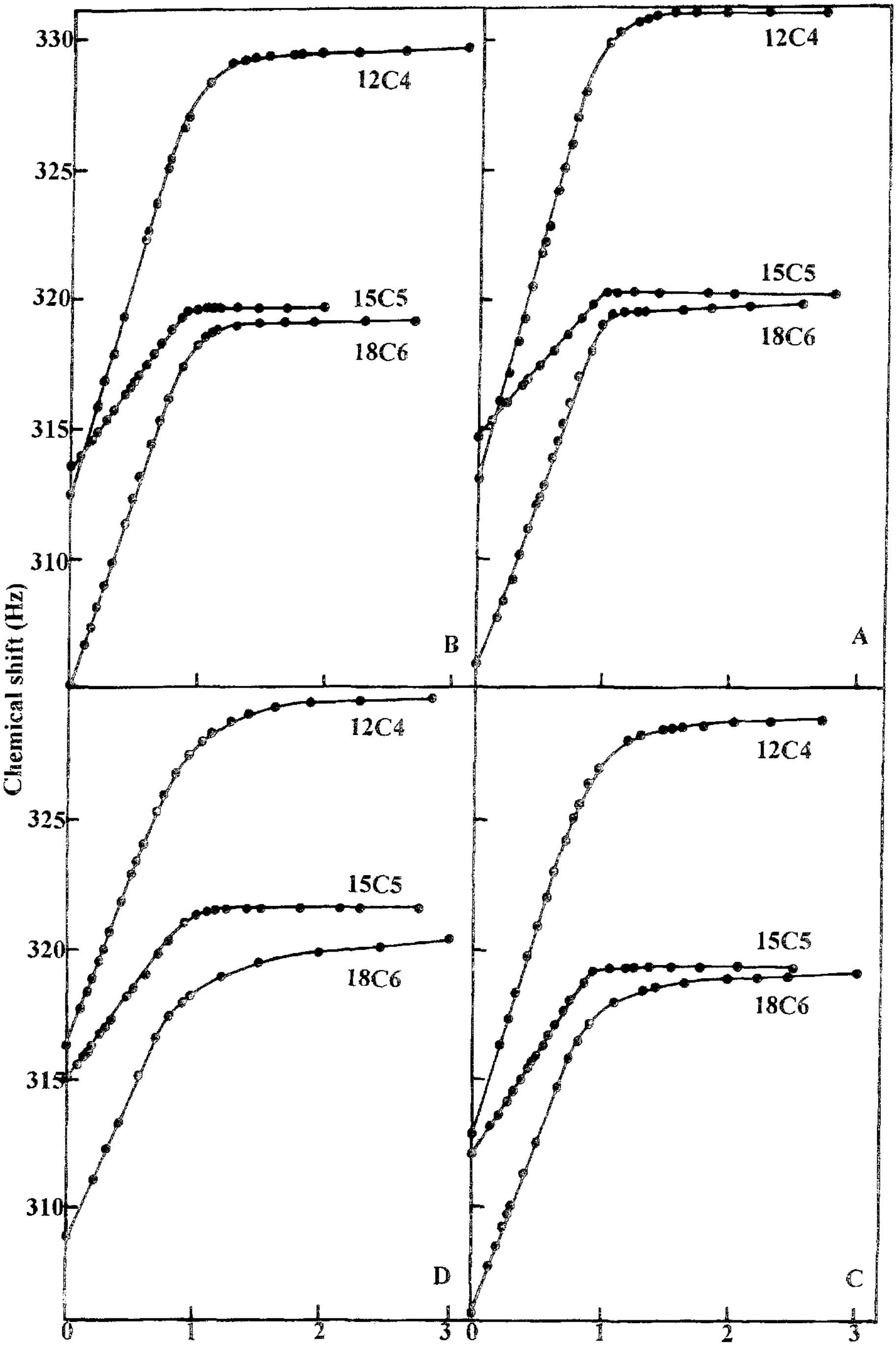

Figure 2. Variation of the ^1H chemical shift as a function of Li^+/crown ether mole ratio in various acetonitrile-nitrobenzene mixtures at 27 °C (at a frequency of 90 MHz). Mole percent of nitrobenzene in the acetonitrile-nitrobenzene solvent mixtures is: A (60), B (40), C (20), D (0).

i.e. the overlap of the lone pair orbitals of the oxygen atoms of the macrocyclic ring and the outer p-orbital of Li$^+$ ion, which in turn induces a rather large change in the electronic environment of the —CH$_2$— groups. Thus, although 15C5 forms a much more stable complex with Li$^+$ ion than 12C4 and 18C6, the chemical shift of the complexed crown in the latter cases is much more than that in the case of 15C5. Since the size of 12C4 (1.2–1.5 Å) [30] is smaller than that of Li$^+$ ion (1.56 Å) [31], the constraints on the Li$^+$–12C4 geometry suggest that the overlap will be particularly strong for this complex [32].

Assuming that only a 1 : 1 Li$^+$–crown ether complex is formed (Figure 2) and that the fast exchange conditions prevail (only one resonance of the —CH$_2$— groups was observed in all cases, Figure 1), it can be readily shown [33] that in solutions containing fixed concentration of crown ether and varying amount of Li$^+$ ion, the observed chemical shift of the crown ether is given by the equation:

$$\delta_{\mathrm{obs}} = [(K_{\mathrm{f}}C_{\mathrm{crown}} - K_{\mathrm{f}}C_{\mathrm{Li}} - 1) + (K_{\mathrm{f}}^2C_{\mathrm{crown}}^2 + K_{\mathrm{f}}^2C_{\mathrm{Li}}^2 - 2K_{\mathrm{f}}^2C_{\mathrm{crown}} \times$$

$$\times\, C_{\mathrm{Li}} + 2K_{\mathrm{f}}C_{\mathrm{crown}} + 2K_{\mathrm{f}}C_{Li} + 1)^{1/2}][\delta_{\mathrm{f}} - \delta_{\mathrm{c}})/2K_{\mathrm{f}}C_{\mathrm{crown}}] + \delta_{\mathrm{c}}, (1)$$

where K_{f} is the concentration formation constant, C_{crown} and C_{Li} are the total concentrations of the crown ether and cation, respectively, δ_{f} is the chemical shift of the uncomplexed crown, and δ_{c} is the chemical shift of the complexed crown. For most complexes the accurate value of δ_{c} cannot be obtained directly. Thus, the procedure for the evaluation of K_{f} and δ_{c} values was to introduce the values of the experimental parameters δ_{obs}, δ_{f}, C_{crown} and C_{Li} and to vary K_{f} and δ_{c} values until the calculated shifts correspond, within the experimental errors, to the experimental values, δ_{obs}. A nonlinear least-squares program KINFIT [34] was used in the calculations. However, in general, this technique is not applicable if the complexation constants are greater than 10^5. A sample computer fit of the chemical shift–mole ratio data is shown in Figure 3 and all the resulting K_{f} values are summarized in Table I. A fair agreement between the observed and calculated chemical shifts shown in Figure 3 further supports the formation of a complex with 1 : 1 stoichiometry between Li$^+$ and the crown ether used. As is obvious, the method used for the calculation of formation constants does not take account of the possible ion association in LiClO$_4$ solutions. The literature indicates that ionic association of the salt is quite small is acetonitrile [35]. It is reasonable to expect that similar conditions will prevail in nitrobenzene, which has about the same dielectric constant as acetonitrile. Thus, in the dilute solutions used, it seems unlikely that the complex formation had a significant competition from ion pair formation.

The stability constants of Li$^+$–crown ether complexes in solution could be interpreted as representing the overall equilibrium constants of a series of reactions [36] including: (i) partial or complete desolvation of Li$^+$ ion; (ii) partial or complete desolvation of the macrocycle; (iii) conformational change of the macrocycle; (iv) formation of the Li$^+$–crown complex; and (v) solvation of the resulting complex.

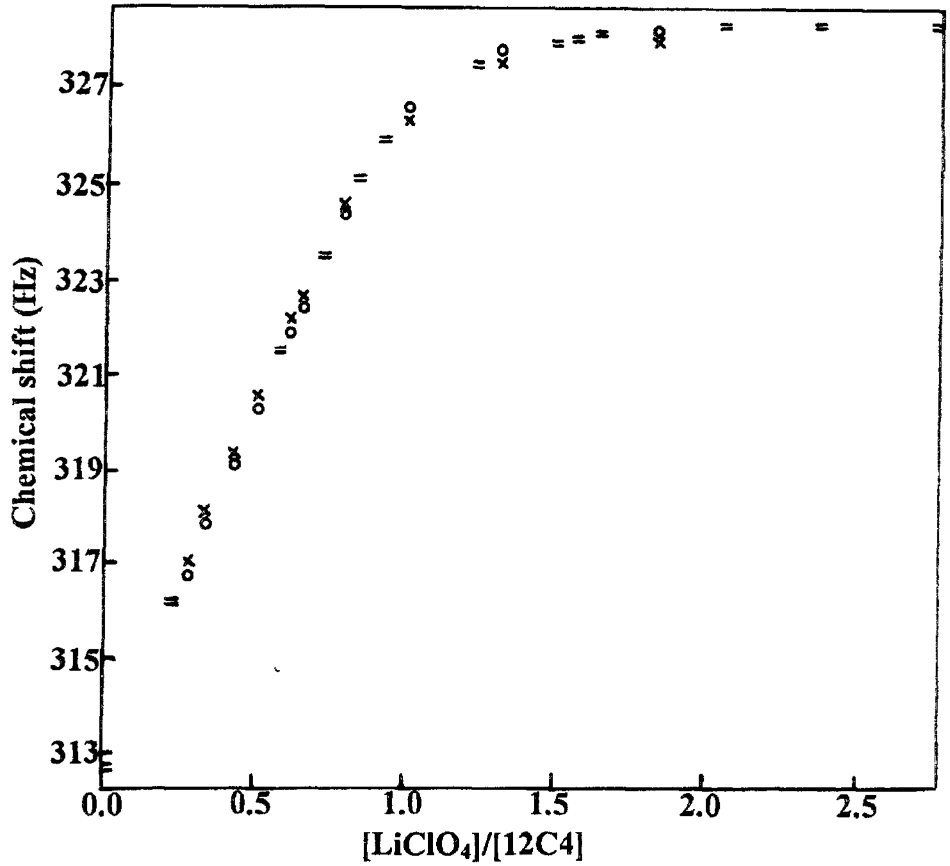

Figure 3. Computer fit of the variation of the ^{1}H chemical shift of 12C4 as a function of Li$^+$/12C4 mole ratio in 80% acetonitrile solution: (x) experimental; (o) calculated; (=) experimental and calculated points are the same within the resolution of the plot.

Table I. Formation constants of Li$^+$ ion complexes, K_f, with different crown ethers in various acetonitrile-nitrobenzene mixtures.

mol.-% nitrobenzene in solvent mixture	log K_f [a] 12C4	15C5	18C6
0	3.25 ± 0.06	4.73 ± 0.42	3.07 ± 0.09
20	3.51 ± 0.05	> 5	3.48 ± 0.09
40	3.63 ± 0.03	> 5	3.99 ± 0.11
60	4.00 ± 0.11	> 5	4.18 ± 0.19

[a] The uncertainties associated with the formation constants are reported as ± standard deviations.

As is evident, the solvent molecules are directly involved in three of the five possible equilibria. Thus it is expected that solvent properties such as dielectric constant, donicity and potentiality for hydrogen bonding will affect the process of complexation considerably.

The data given in Table I clearly show the fundamental influence of solvent properties on the stability of the Li^+-crown complexes studied. In all cases, the stability of the complexes increases rapidly with increasing amount of nitrobenzene in the mixed solvent. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [37], plays an important role in different complexation reactions [15, 16, 20–22, 24, 32, 38, 39]. The two components of the solvent mixtures used in this study have about the same dielectric constants (i.e. 34.8 for nitrobenzene and 38.0 for acetonitrile), but quite different donor numbers (i.e. 4.4 for nitrobenzene and 14.1 for acetonitrile) [37]. Acetonitrile, as a solvent of intermediate solvating ability, can thus compete with the crown ethers for Li^+ ion more than nitrobenzene, which is a low donicity solvent. In addition, it has been shown that acetonitrile can solvate macrocyclic ligands very largely through hydrogen bonding between the —CH_3 group of the solvent and the ether oxygens of the crown ethers [40, 41], while nitrobenzene has no significant interaction with macrocyclic ligands [4]. Thus it is not surprising that addition of nitrobenzene to acetonitrile will increase the stability of the Li^+–crown ether complexes.

There is actually a linear relationship between log K_f of the Li^+–18C6 and Li^+–12C4 complexes and the mole fraction of nitrobenzene (X_{NB}) in the mixed solvent. The regression equations between log K_f and X_{NB} for the 18C6 and 12C4 complexes are $\log K_f = 3.10 + 1.92X_{NB}$ (regression coefficient $r = 0.99$) and $\log K_f = 3.24 + 1.18X_{NB}$ (regression coefficient $r = 0.98$), respectively. A similar trend has already been reported for several different metal complexes in various solvent mixtures [7, 8, 10–13]. Such monotonic behavior could be related to the preferential solvation of the reactants with acetonitrile molecules.

It is interesting to note that the variation of the stability of Li^+ complexes with X_{NB} in the mixed solvent for the Li^+–18C6 complex is more than that for Li^+–12C4 (i.e. the slopes of the corresponding log K_f vs. X_{NB} plots are 1.92 and 1.18, respectively). Since the effect of solvent–cation interaction on the complexation reaction is actually the same, such a difference must arise from unequal contributions of the solvent–crown and solvent–complex interactions on the complexation reactions. Previous studies have shown that there are rather strong interactions between macrocyclic ligands and solvent molecules in some solvents [40–43], in which the extent of interaction depends on the structure of the ligand, as well as the nature of the solvent molecules. It is evident that such interactions can modify the complexing abilities of the macrocyclic ligands in solution. The extent of Li^+-macrocycle solvation also depends on the degree of isolation of the central cation by the macrocycle's backbone from the reach of solvent molecules. A combination of the two interactions (i.e. solvent–macrocycle and solvent–complex interactions) results in a more pronounced effect of the mixed solvent composition on the Li^+–18C6 complex, in comparison with that on the Li^+–12C4 complex.

The data given in Table I indicate that, among the three crown ethers used, 15C5 forms the most stable complex with Li^+ ion in the series. This is obviously due to the comfortable fit of the cation with an ionic size of 1.56 Å [31] inside the crown's cavity with a size of 1.7–2.2 Å [30]. Consequently, the corresponding chemical shift–mole ratio plots (Figure 2) show very sharp breaks of 1 : 1 mole ratio in all solvent mixtures tried. However, 12C4 and 18C6 complexes form much less stable 1 : 1 complexes with Li^+ ion than 15C5, in different solvent mixtures. Evidently, the cavity of 12C4 is too small to comfortably accommodate the metal ion; in this case Li^+ ion can only partially penetrate inside the ligand cavity to cause some weak interactions with the four oxygen atoms of the ring. It is interesting to note that, despite the under size cavity of 12C4 for Li^+ ion, no evidence for the formation of a $Li^+(12C4)_2$ sandwich complex was observed in solution (see Figure 2). However, formation of such 2 : 1 complexes between Na^+ ion and 12C4 has already been reported in the literature [44–46].

On the other hand, in the case of 18C6, despite the increased number of donating oxygen atoms in the ring, the resulting Li^+ complex is much weaker than Li^+–15C5. Here, due to the over large cavity size of the macrocycle (i.e. 2.6–3.2 Å) [30], Li^+ ion can presumably interact with only few of the six available atoms of the ring; consequently, a weaker 1 : 1 complex will be formed in solution.

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