^{23}Na NMR Studies of Stoichiometry and Stability of Sodium Ion Complexes with Several Crown Ethers in Binary Acetonitrile–Dimethylformamide Mixtures

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Abstract

^{23}Na NMR measurements were employed to monitor the stability of Na$^+$ ion complexes with 18-crown-6 (18C6), dicycloxyl-18-crown-6 (DC18C6), dibenzo-18-crown-6 (DB18C6), 15-crown-5 (15C5) and benzo-15-crown-5 (B15C5) in binary acetonitrile–dimethylformamide mixtures of varying composition. In all cases, the variation of [23]Na chemical shift with [crown]/[Na$^+$] mole ratios indicated the formation of 1:1 complexes. The formation constants of the resulting complexes were evaluated from computer fitting of the mole ratio data to an equation which relates the observed chemical shifts to the formation constants. It was found that, in pure acetonitrile, the stabilities of the resulting 1:1 complexes vary in the order 15C5 > DC18C6 > B15C5 > 18C6 > DB18C6, while in pure dimethylformamide the stability order is DC18C6 > 18C6 > 15C5 > B15C5 > DB18C6. The observed changes in the stability order could be related to the specific interactions between some crown ethers and acetonitrile. It was found that, in the case of all complexes, an increase in the percentage of dimethylformamide in the solvent mixtures would significantly decrease the stability of the complexes.

Introduction

Among several factors influencing the formation of macrocyclic complexes, the ability of solvent molecules to solvate metal ions and, thus, to compete with the donating groups of the ligands for the coordination sites of the central cation plays a fundamental role [1]. Perhaps equally important, but often neglected, is the interaction of some solvents with macrocyclic ligands [2–4]. Since both the cation and the macrocycle must be at least partially desolvated before the complex can be formed, the two solvation processes are expected to markedly influence the overall stability of the resulting complex in solution.

There has recently been increasing interest in the study of complexation reactions in binary mixed solvent systems and their interpretation in terms of the solute's preferential solvation by one of the mixed solvent components [5–8]. Actually, there is a simple coordination model in mixed solvents which assumes that all the thermodynamic changes in the system result from the successive replacement of the molecules of one solvent by those of the second solvent in the coordination

sphere of the solute [7–9]. However, this model does not account for the changes in solvent–solvent interactions, the changes in interactions of the coordinated solvent molecules with the surrounding and the changes in the permissivity of the solvent system.

During the past two decades, it has been shown that multinuclear NMR is a very powerful (although not ideal) technique for studies of alkali complexes with macrocyclic ligands, particulary in non-aqueous solutions [1, 8, 10–12]. In this paper we report the use of ^{23}Na NMR for the study of the sodium ion complexes with five crown ethers, namely 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6), in binary acetonitrile(AN)-dimethylformamide (DMF) mixtures.

Experimental

Crown ethers B15C5, 18C6, DC18C6 and DB18C6 (all from Merck) were purified and dried as described before [13, 14]. 15C5 (from Merck) was used as received. Reagent grade sodium thiocyanate (Merck) was recrystallized from acetonitrile and vacuum dried. Spectroscopic grade acetonitrile and dimethylformamide (both from Fluka) were used as received.

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All NMR measurements were made on a Jeol, FX90 Q FT-NMR spectrometer with a field strength of 21.13 kG. At this field, ^{23}Na resonates at 23.65 MHz. A 3.0 M aqueous sodium chloride solution was used as an external reference and the reported ^{23}Na chemical shifts referred to this solution. The paramagnetic (downfield) shift from the reference is designated as positive [15].

Results and discussion

The ^{23}Na chemical shifts were determined as a function of [crown]/[Na$^+$] mole ratio at 25.0 ± 0.5 °C in various AN-DMF solvent mixtures for different crown ethers

used, and the results are shown in Figures 1–5. In all cases studied, only one population average resonance of the metal ion was observed, indicating that the exchange of the metal ion between the two sites (i.e., the solvated and the complexed cation) is fast. In general, ^{23}Na chemical shifts vary almost linearly with the crown/Na$^+$ mole ratio up to a mole ratio of about 1, and begin to level off at higher mole ratios. All mole ratio plots revealed a distinct inflection point at a crown/Na$^+$ mole ratio of about 1, indicating the formation of a 1:1 crown–Na$^+$ complex in all cases. The sharper the observed inflection point, the more stable the 1:1 complex.

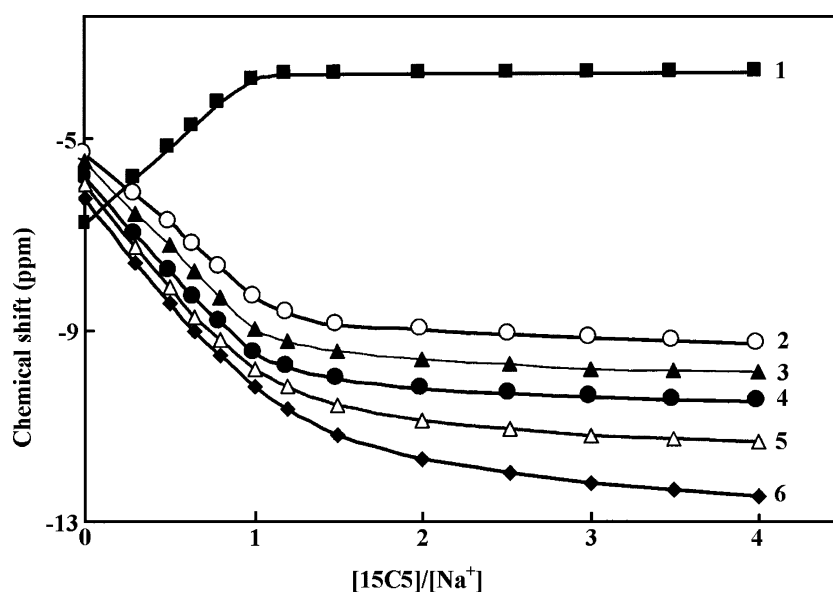The formation constants of corresponding 1:1 complexes were calculated from the variation of the

Figure 1. ^{23}Na chemical shifts as a function of [15C5]/[Na$^+$] mole ratio in various AN-DMF mixtures at 25 °C. % AN in the binary mixtures are: 1, 100; 2, 80; 3, 60; 4, 40; 5, 20; 6, 0.
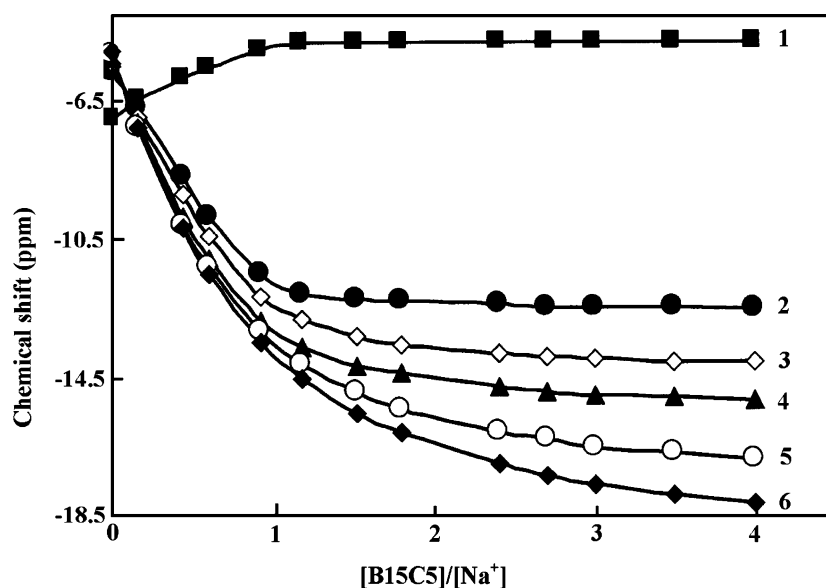

Figure 2. ^{23}Na chemical shifts as a function of [B15C5]/[Na$^+$] mole ratio in various AN-DMF mixtures at 25 °C. % AN in the binary mixtures are: 1, 100; 2, 80; 3, 60; 4, 40; 5, 20; 6, 0.
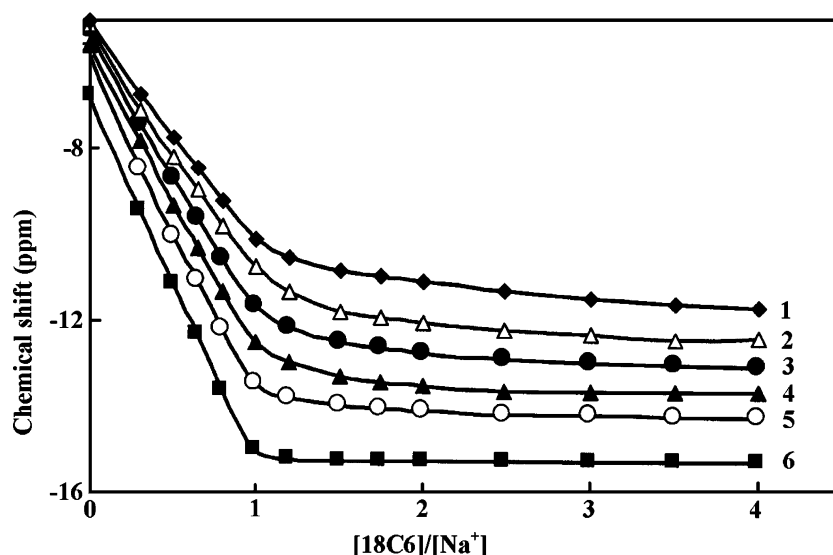
Figure 3. ^{23}Na chemical shifts as a function of [18C6]/[Na$^+$] mole ratio in various AN-DMF mixtures at 25 °C. % AN in the binary mixtures are: 1, 0; 2, 20; 3, 40; 4, 60; 5, 80; 6, 100.

^{23}Na chemical shift with the crown/Na$^+$ mole ratio. It has been shown previously that the observed chemical shift is given by [16]:

$$\delta_{obs} = \{[K_f C_M - K_f C_L - 1) + (K_f^2 C_L^2 + K_f^2 C_M^2 \\ - 2K_f^2 C_L C_M + 2K_f C_L + 2K_f C_M + 1)^{1/2} \\ \times (\delta_M - \delta_{ML})/2K_f C_M]\} + \delta_{ML} \quad (1)$$

where K_f is the concentration formation constant for the 1:1 complex, C_L and C_M are the analytical concentrations of the crown ether and Na$^+$ ion, respectively, and δ_M and δ_{ML} are respective chemical shifts of the free and complexed sodium ion. A non-linear least-squares curve fitting program KINFIT [17] was used to evaluate K_f and δ_{ML} values for the 1:1 complexes.

The formation constants of all 1:1 complexes, evaluated by computer fitting of the chemical shift–mole ratio data to Equation (1), are given in Table 1. A sample computer fit of the ^{23}Na chemical shift–mole ratio data is shown in Figure 6. A fair agreement between the observed and calculated chemical shift's shown in Figure 6 further supports the formation of a complex with 1:1 stoichiometry between Na$^+$ and DC18C6.

From the data given in Table 1 is immediately obvious that, for a given crown ether, the stability of the resulting sodium complex varies strongly depend on the composition of the binary solvent mixture. In all cases, the complex stability decreases with increasing mole fraction of DMF in the solvent mixture. It is well known that the solvating ability of the solvent, as expressed by the Gutmann donor number [18], plays a fundamental role in different complexation reactions [8, 10, 19–21]. DMF is a solvent of high solvating ability (DN = 26.6) which can strongly compete with the crown ethers for
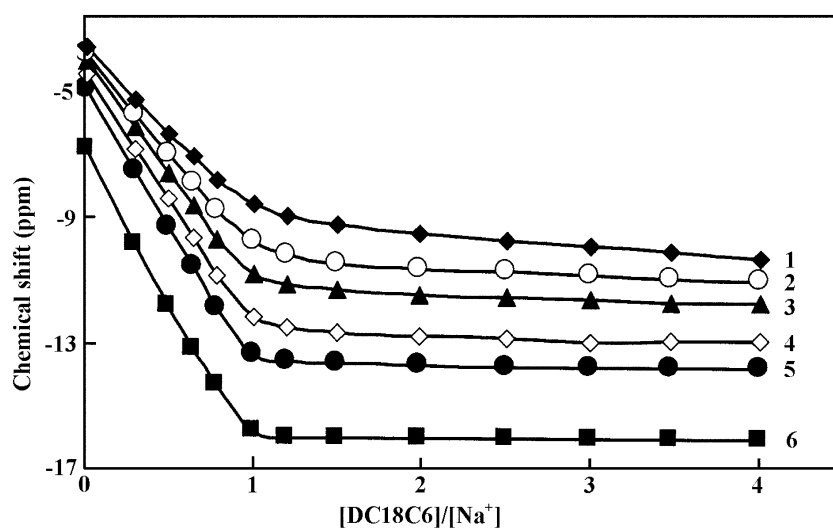

Figure 4. ^{23}Na chemical shifts as a function of [DC18C6]/[Na$^+$] mole ratio in various AN-DMF mixtures at 25 °C. % AN in the binary mixtures are: 1, 0; 2, 20; 3, 40; 4, 60; 5, 80; 6, 100.

Figure 5. ^{23}Na chemical shifts as a function of [DB18C6]/[Na$^+$] mole ratio in various AN-DMF mixtures at 25 °C. % AN in the binary mixtures are: 1, 0; 2, 20; 3, 40; 4, 60; 5, 80; 6, 100.
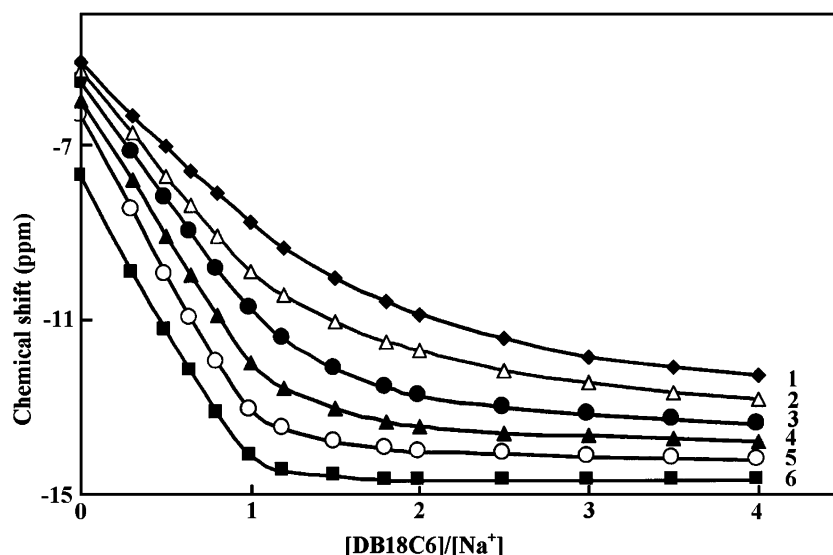
sodium ion. Thus, it is not unexpected that addition of AN, as a relatively low donicity solvent (DN = 14.1), to DMF will increase the stability of the complexes.

In AN solution, the stabilities of 1:1 complexes of Na$^+$ with different crown ethers decrease in the order 15C5 > DC18C6 > B15C5 > 18C6 > DB18C6. Obviously, the consonance between the ionic size of Na$^+$ (2.04 Å)^2 and the size of the macrocyclic ring is an important factor in determining the stability of the resulting complexes. The ring sizes of crown ethers are not known precisely, but on the basis of molecular models the ring size of 18C6 and 15C5 are 2.6–3.2 Å and 1.7–2.2 Å, respectively [22]. Thus, it seems reasonable to assume a better fitting condition of Na$^+$ inside the cavity of 15C5 to result in a formation of the most stable complex in the series.

However, the stability sequence of the Na$^+$ complexes with different crown ethers used in DMF solution is somewhat different from that in acetonitrile, i.e. DC18C6 > 18C6 > 15C5 > B15C5 > DB18C6. Such a change in the order of stability with the nature of solvent could be most probably related to the variations in the specific solvation of the crown ethers used and the resouting charged crown–Na$^+$ complexes with solvent molecules [2–4, 23]. It is worth mentioning that the specific solvation of macrocyclic ligands usually proceeds through hydrogen bonding between the –CH$_3$

groups of the solvent molecules and the ether oxygens of crown ethers [3].

Comparison of the data given in Table 1 indicates that, among the 18-crowns used, where ring frame remains the same, the stabilities of the resulting 1:1 complexes vary in the order DC18C6 > 18C6 > DB18C6, in all solvent mixtures studied. The presence of two cyclohexyl groups in DC18C6 can inductively enhance the electron density of the ligand ring and thus increases the basicity of the oxygen atoms, while the flexibility of the macrocycle remains more or less the same as 18C6 [14, 18]. Thus, it is not surprising to observe the highest stability for the DC18C6 complex among the 18-crowns used. On the other hand, the addition of two benzo groups to 18C6 lowers the stability of the resulting sodium complex. This behavior may be attributed to some combination of the electron withdrawing effect of benzo groups, which weakens the electron donating ability of the oxygen atoms of the ring and the reduced flexibility of the ligand which prevents the macrocyclic molecules wrapping itself around the cation. The net result is a weaker cation–ligand interaction. The substitution of a benzo ring on the 15C5 may also have a similar effect on the stability of the corresponding Na$^+$ complexes.

The above results strongly emphasize the variability of factors which affect the stability and selectivity of the macrocyclic complexes. While the relative sizes of the

Table 1. Stability constants of different Na$^+$-crown ether complexes in various acetonitrile–dimethylformamide mixtures at 25 °C

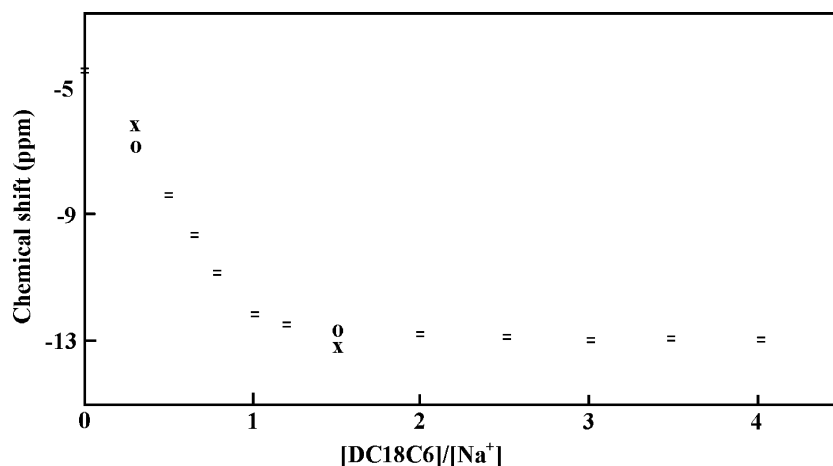| Solvent composition	Log K_f				
	15C5	B15C5	18C6	DC18C6	DB18C6
100%AN	5.02 ± 0.09	4.71 ± 0.05	4.50 ± 0.04	4.89 ± 0.03	3.53 ± 0.02
80%AN	3.98 ± 0.02	3.30 ± 0.04	3.24 ± 0.05	4.15 ± 0.06	2.94 ± 0.03
60%AN	3.51 ± 0.04	3.05 ± 0.02	3.00 ± 0.09	3.64 ± 0.03	2.86 ± 0.05
40%AN	3.02 ± 0.03	2.48 ± 0.03	2.71 ± 0.03	3.16 ± 0.05	1.96 ± 0.04
20%AN	2.72 ± 0.05	2.06 ± 0.06	2.60 ± 0.01	2.84 ± 0.02	1.59 ± 0.03
0%AN	2.23 ± 0.02	1.85 ± 0.02	2.34 ± 0.04	2.52 ± 0.06	1.40 ± 0.07

Figure 6. Computer fit ^{23}Na chemical shift vs. [DC18C6]/[Na$^+$] mole ratio in 40% AN-60% DMF: (*x*) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

cation and of the macrocyclic ring play an important role, they are certainly not the unique, and not always the most important, factors in determining the stabilities of the resulting complexes. The relative donor abilities of the ether oxygens of the macrocyclic ring as well as the degree of flexibility of the macrocyclic molecule are also of considerable importance.

Moreover, the importance of solvent properties is very evident. It seems obvious that, particularly in non-aqueous solutions, one should consider not only the solvent–cation, but also the solvent–ligand and solvent–complex interactions as important factors in the complexation reactions.

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