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^{1}H-NMR relaxation studies on complexation of diaza 18-Crown-6 ethers derivatives

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ABSTRACT

The effect of the Na^+ ion on proton longitudinal relaxation times (T_1) of 18-crown-6 ethers derivatives has been investigated by ^{1}H-NMR spectroscopy operating at 400 MHz. It was found that T_1 values for all derivatives were decreased upon addition of Na^+. The decrement was attributed to complexation of the 18-crown-6 ethers derivatives with Na^+.

KEYWORDS

^{1}H NMR;
Longitudinal relaxation time;
Supramolecular chemistry;
Crown ethers.

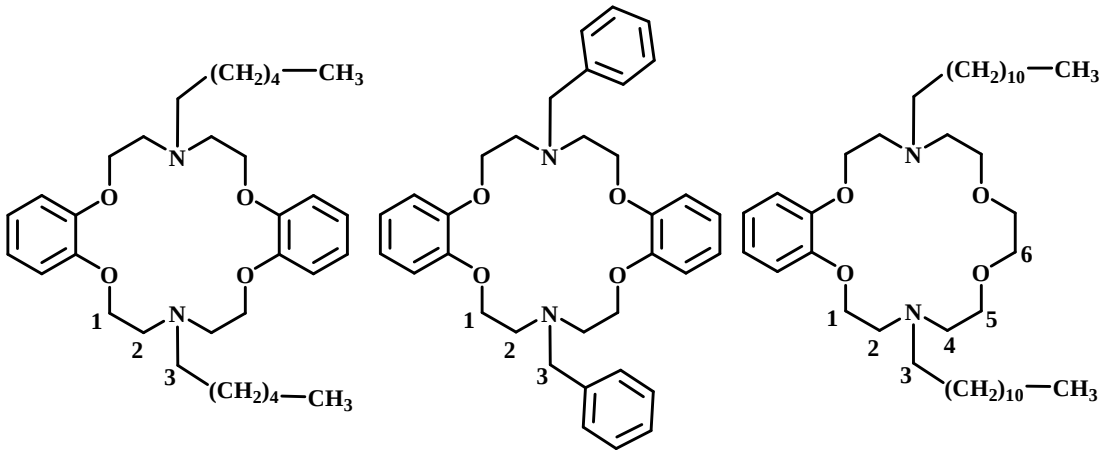
INTRODUCTION

For more than three decades, macrocyclic polyethers (crown ethers) have been synthesized and utilized in alkali and alkali earth metal cation determinations due to their superior binding ability to these metal ions[1-12].

Macrocycles design, synthesis and application for molecular recognition are of great interest in a variety of fields[13-16]. Remarkable recognition behaviour between hosts and guests occurs are widely used in many chemical interactions involving enzymes, antibodies, antigens and stereoselective catalysts.

Longitudinal relaxation time (T_1) is a sensitive probe for investigating dynamic properties of organic molecules[17]. Relaxation time, T_1, studies can provide useful information about rapid molecular motions on a time scale that is far shorter than that available with conventional NMR techniques[18]. The T_1 value for any given liquid molecule reflects molecular mobility (tumbling) and specific internal motions determined by the internal degree of freedom of the molecule[19,20]. Also, a comparison of T_1 values for a given proton in a free and complex crown ether gives information on complexation[1-8,12,17,21-23]. And it is also possible to compare T_1 values for specific sites within a molecule to understand changes in internal mobility that occurs selectively at particular location, thus giving information about molecular binding in the complex[1-3,17,21-23].

Here we report the ^{1}H-NMR studies on complexation of diaza 18-crown-6 ethers 1-3 for the numbered protons (SCHEME 1). We have previously reported the complexation behaviour of these diaza 18-crown-6 ethers with Na^+ ions by ^{1}H NMR and UV-VIS titration method[11]. In the present work, the complexation of the diaza 18-crown-6 ethers with Na^+ ions was studied by comparing the ^{1}H-NMR longitudinal relaxation times T_1 of the diaza 18-crown-6 ethers in presence and absence of Na^+ ions.



SCHEME 1: The structures of the diaza 18-crown-6 ether derivatives 1-3

TABLE 1: Relaxation times (T_1) and relaxation time drops (%) of protons (H_1-H_3 for 1-2 and H_1-H_6 for 3) of the macrocyclics upon complexation with $NaClO_4$ in a ratio of 1:1 in CD_3CN

	H_1		H_2		H_3		H_4		H_5		H_6	
	T_1(s)	T_1 drop(%)	T_1(s)	T_1 drop(%)	T_1(s)	T_1 drop(%)	T_1(s)	T_1 drop(%)	T_1(s)	T_1 drop(%)	T_1(s)	T_1 drop(%)
Free ligand 1	0.385	-	0.337		0.373		-		-		-	
Na/lig. (1:1)	0.291	24.4	0.283	16.0	0.283	22.5	-	-	-	-	-	-
Free ligand 2	1.087	-	0.387	-	0.403	-	-	-	-	-	-	-
Na/lig. (1:1)	0.978	10.0	0.351	9.3	0.359	10.9	-	-	-	-	-	-
Free ligand 3	0.452	-	0.485	-	0.487		0.357	-	0.391	-	0.399	-
Na/lig. (1:1)	0.350	22.6	0.392	19.2	0.393	19.3	0.327	8.4	0.345	11.8	0.364	8.8

EXPERIMENTAL

Diaza 18-crown-6 ether derivatives 1-3 were prepared as previously described[24]. The ^1H NMR spectra of the samples dissolved in CD_3CN were recorded on a Bruker 400 MHz spectrometer. The 5 mm tubes were used and the samples were degassed by at least three freze-pump-thaw cycles and then sealed under vacuum. T_1 was measured using conventional inversion recovery pulse sequence of 180°-τ-90°-FID, where τ is variable recovering delay time of ten different values at 298 K. The pre-pulse delay was 15 s to make sure the magnetization was fully equilibrated. T_1 values were calculated by the instrument automatically. Standard deviation of T_1 was less than 3%. The concentrations of crown ethers were kept constant (2.5×10^{-3}M) with an increasing concentration of the added $NaClO_4$ (6.0×10^{-5}-1.2×10^{-2}M).

The relaxation times for the different protons were measured for free 18-crown-6 ether solutions and 18-crown-6 ether solutions containing increasing amount of $NaClO_4$. However, only T_1 values of well-separated peaks, i.e., H_1-H_3 for 1 and 2 and H_1-H_6 for 3, were changed significantly by the addition of the Na^+ ions. The T_1 values of the free ligand and the Na^+/ligand (1:1) complexes were determined. Also the effects of the Na^+ ion on the relaxation times T_1 are expressed as the percentages by which the relaxation times T_1 of the free crown ethers dropped upon complexation (T_1 drops (%)).

RESULTS AND DISCUSSION

The effect of the Na^+ ion on the relaxation times of the protons H_1-H_6 of diaza 18-crown-6 ethers derivatives are shown in TABLE 1.

TABLE 1 nicely demonstrates that the relaxation times T_1 of the free ligands are shortened by the addition of Na^+ ions. However, significant drop in T_1 was observed for the H_1 in macrocycles 1, 2 and 3 with decrement of about 24%, 10% and 23%, respectively. The same trend was also observed for H_2 and H_3. The finding are consistent with previous studies on complexation of crown ethers[1,6,17]. The observed T_1

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changes which are the sum of molecular tumbling and specific internal motions between free crown ethers and 1:1 complexes, strongly support the formation of the complexation of crown ethers with the added Na^+ ions [1-3,17,21-23]. Furthermore, the TABLE 1 also shows that the change in the relaxation times of the macrocycles 1 and 3 upon complexation with Na^+ ions is much effective than in the case of 2, which can be attributed to the stronger complex formation of the macrocycles 1 and 3 with Na^+ ions. This finding implies that Na^+ ions probably fit much better to the cavity of the diaza 8-crown-6 ethers 1 and 3 than to that of 2. For this reason, the intramolecular flexibility of the complexes 1 and 3 are much more reduced through Na^+ ion binding [3,12,17,21-23]. In addition to this, the complexation of 1 with Na^+ ions is stronger than that with 3, which may be attributed to better fit of the Na^+ ions to the cavity of 1. In fact, the cavity size of crown ethers does not change, thus all three crown ethers should complex identical but do not. This may be attributed to the number of phenyl in the macrocyclic ring and the N-substituents determine the differences. Furthermore, formation of a complex results in an increase in overall molecular weight, therefore, the complex should tumble more slowly than the free state. Such a slowed motion can also cause a decrease in the T_1 values[21-23]. On the other hand, two interactions, which are modulated by the reduced motions, can be suggested for relaxation mechanism in crown ethers: (1) inter-proton dipole-dipole interaction[25] and (2) the interaction of proton dipole and randomly changing magnetic fields created at the position of the proton by molecular currents induced by variation of charge density in the crown ether upon the cation complexation[5].

CONCLUSION

The measured relaxation times support that Na^+ ions seem fit well in the diaza 8-crown-6 ethers (1 and 3) cavity than in the diaza 18-crown-6 ether 2. Upon complexation with Na^+, proton signals (H_1-H_6) of the crown ethers undergo chemical shift changes[11] and indicate the interaction of the Na^+ ions with both macroring and side arms. So the mobility of the complexes 1 and 3 are reduced more than 2 through Na^+ binding.

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