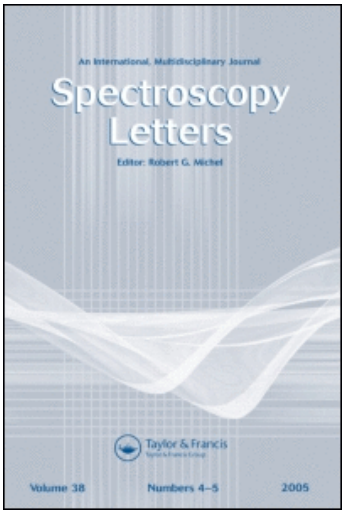

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THE DETERMINATION OF ASSOCIATION CONSTANTS OF Na^+,K^+,Mg^{2+} AND Ca^{2+} COMPLEXES WITH 1,4,7,10-TETRAOXACYCLODODECANE,(12.CROWN.4) IN DOH BY THE AID OF ^{13}C DIPOLE-DIPOLE RELAXATION TIME MEASUREMENTS§

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Abstract

The stabilities of some complexes of 1,4,7,10-tetraoxacyclo-dodecane were determined from the ^{13}C dipole-dipole relaxation time measurements of the free and complexed macrocyclic ligand in DOH. The association constants, K_a were obtained from the relationship of $P_c = (1/T_1^{obs} - 1/T_{10})/(1/T_1^o - 1/T_{10})$ in which T_1^o and T_{10} are of the relaxation times of complexed and the free ligands respectively and, P_c is the complexed ligand fraction.

K_a values found as described for the above cations were very much in agreement with the recently reported similar studies.

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Introduction

Since the discovery of the macrocyclic ethers by Pedersen, large number of binding constants have been reported(1-4). The studies given mostly deal with the cyclic polyethers determining the stability of the multidentate ligand in a solvent with the common analytical methods(5,10).

Most of the results depend on the polarity of the solvent particularly hydroxylic media strongly associates with the oxygen dipoles diminishing the role of template effect. Recently, we have developed a NMR method by detecting role of cation on the relaxation rate of macrocyclic cavity(11-14).

Due to the BPP theory the internal motion of the cyclic backbone, is closely bound to rotational correlation time of the related nuclei of a macromolecule, the complexing mostly governs the dipole-dipole relaxation times, particularly in the case of formation of specific conformations(10-16).

It has been recently discussed by Hertz et al, that the fast exchange model of the relaxing nuclei between different environments could be used for this type of exchanging ligand molecules,Equ.1(17).

In a solution due to the formation of "crown ether seperated ion pairs" in equilibrium with the free macrocyclic ether, the observed relaxation rate of macro molecules, $1/T_1^{obs}$ is the sum of relaxation rates of free molecules, $1/T_{1O}$ and the relaxation rate of the molecules,$1/T_1^O$ acting as a ligand shell,Eq.1.

$$1/T_1^{obs} = P_C\ (1/T_1^O - 1/T_{1O}) + 1/T_{1O} \qquad (1)$$

where the P_C is the mole fraction of bound-complexed-ligand molecules. The association constant K_a, is also given as follows,(Eq.2-5)(12,13).

$$K_a = [A^+C]/[A^+].[C] \qquad (2)$$

$$P_C = [A^+C]/[C_O] \quad \text{and} \quad P_A = [A^+C]/[A_O^+] \qquad (3)$$

$$A_O = [A^+]+[A^+C] \quad \text{and} \quad [C_O] = [C]+[A^+C] \qquad (4)$$

$$1/T_1^{obs} = P_A.[A_O^+]/[C_O](1/T_1^O - 1/T_{1O}) + 1/T_{1O} \qquad (5)$$

The association constants were determined by the use of Eqs.2-5.Namely, the observed relaxation rate,$1/T_1^{obs}$ values were ploted against the cation concentrations of $[A_O^+]$ while the ligand concentration $[C_O]$ is kept constant, (See Fig.1).

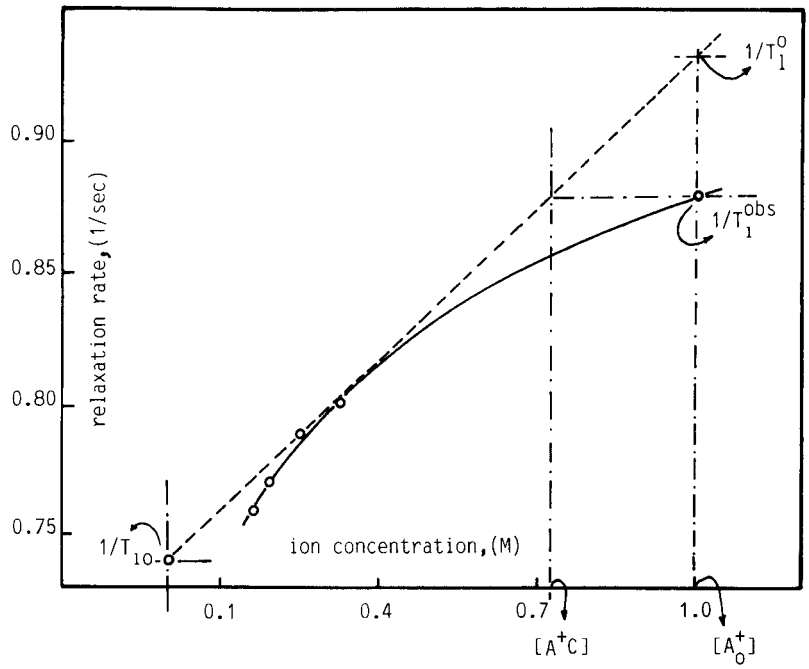

Fig.1.The dependence of relaxation rate of 12.Crown.4 (1,00 M) versus the KI concentration in DHO solutions at 30°C.

In such a case in the absence of cation in solution where $[A_o^+]=0,0$ the observed relaxation rate, $1/T_1^{obs}$ is of course the relaxation rate of the pure ligand, $1/T_{1o}$ in solution. In the other hand the relaxation rate of fully complexed ligand, $1/T_1^o$ for a stoichiometric ratio is obtained by the extrapolation of the straight line of the plot for low cation concentrations at constant ligand concentration. It means that, if the cation concentration is too low with respect to ligand concentration the cation could be easily assumed that it is completely complexed, which means if $[A_o^+]/[C_o] \ll 1$ and then $[A_o^+]=[A^+C]$. So that $P_A=1$ could be assumed for low cation concentrations up to 0,3 M which of course depends on the association degree of the ligand (cation binding power of the macrocyclic ether). Therefore, the line of $1/T_1^{obs}$ versus $[A_o^+]$ ploting from 0,0 to 0,2 or 0,3 M cation concentration is extrapolated up to 1,0 M value in the presence of 1,0 M ligand concentration. The extrapolated value of T_1^{obs} can be taken as

Table-1. The association constants of 1,4,7,10-tetraoxacyclododecane complexes of K^+,Na^+,Ca^{2+} and Mg^{2+} ions in DHO.

TEMP.°C	SALT	$[C_o]$	$K_a^{\neq}$	$LnK_a^{\neq}$	ΔG^+	K_a^+	LnK_a^+	ΔG^+
30	KI	1,0	8,9147	2,1877	-1,326			
40	KI	1,0	4,0078	1,3882	-0,851			
50	KI	1,0	1,6929	0,5264	-0,328			
40	NaI	1,0	3,9484	1,9733	-0,842	10,5307	2,3543	-1,443
40	NaI	2,0				1,7213	0,5431	-0,333
40	KI	2,0				2,4812	0,9087	-0,557
30	(a)$CaCl_2$	1,0				8,6455	2,1570	-1,307
30	(b)$MgCl_2$	1,0				19,4827	2,9878	-1,802

(≠). The complexing constant of 1:1 ratio,l/mole,calculated from the equation of $K_a=[A^+C] / [C_o-A^+C].[A_o^+-A^+C]$

(+). The complexing constant of 1:2 ratio according to above formula.

(+). The free enthalpy of complexing in kCal/mole.

(a). The salt of $CaCl_2.2H_2O$.

(b). The salt of $MgCl_2.6H_2O$.

the $1/T_1^o$ value of fully complexed ligand.One could accordingly obtain the actual $[A^+C]$ value for any cation concentration,$[A_o^+]$ from the differences of the assymptotic curve and the straight line for the $1/T_1^o$ value in Fig.1.This procedure is ,however,only tried for 1:1 ratio of complexing associations displaced in Table.1.

Experimental

1,4,7,10-tetraoxacyclododecane was available to us from the earlier studies(10-14).The twice distilled compound was dissolved in DHO as 1,0 or 2,0 M solutions then the 1,00 mL of this stock solutions were trasfered into the 10 mm pyrex capillary in which the appropriate amount of salts have already been placed.The complex solutions were then degassified under reduced pressure of $\approx 10^{-5}$ torr then sealed off.

The ^{13}C inversion recovery experiments for the T_1 measurements were conducted on a JEOL spectrometer,model FX-60Q operating at 15.0 MHz field.

180^{o} and 90^{o} pulses were applied in the range of $0,1T_1 < t_1 < 5T_1$ pulse interval time then it was applied to following equation of magnetization.

$$M_t = M_o [\, 1\text{-}2 \exp(-t/T_1) \,] \qquad (6)$$

The least squares fitting were applied to calculate the experimental T_1^{obs} values in a stacked program.However,NOE values were obtained according to the Equ.7.The enhancement factor was determined from the ratio of the integral values of ^{13}C signals obtained at complete decopled and pulse modulated decoupled conditions.

$$T_1^{DD} = T_1^{obs} \cdot 1,99/\eta_{CH} \qquad (7)$$

A typical experimental result of dipolar relaxation measurements at the various ion concentrations of 12.Crown.4 ligand was displayed on Fig.1 and resulting K_a values were shown at Table.1.

Results and Discussions

Besides of the sensitivity and the utility of the method described here we could discuss the features of the binding of 12.Crown.4 to K^+,Na^+,Mg^{2+} and Ca^{2+} ions although the polarity of mother solvent caused lower power of ion-dipole interaction of the ether with cations.The Na^+ ion of smaller diameter was found to be more strongly bound to macrocyclic ether as compare to K^+ ion of larger radius.As it was reported,similar results were obtained for 15.Crown.5 and 18.Crown.6 (12-14).Most interesting is the experimental k_a values are increased by lowering temperature of complex solutions and are explained in terms of ion pairs theory (16,19).

The association of an ion surrounded by a tight solvation shell with its counterion proceeds till the solvent shell comes into contact with the partner.Then either of the pairs retain its structures of an ion pair seperated by solvent molecules (9,18,19).In such a structure the relaxation time of the ligand is decreased due to the increased correlation time of internal motion in extreme narrowing conditions.

$$\text{ION} + \text{C.E} \rightleftharpoons \text{C.COMPL.ION PAIRS} \rightleftharpoons \text{C.SEP.IONS} \rightleftharpoons \text{FREE IONS} \qquad (8)$$

The formation of a shell is opposed by the loss of translational entropy of those solvent molecules which become immobilized around the ion. The solvents like THF or dioxane could only form loose ion pairs or its aggregates by the lost of their translational energy while DMSO or cyclic polyethers are able to generate the solvent seperated ion pairs by the lost of rotational energy (9).The driving force for the formation of the seperated ion pairs is essentially the coordination of solvent molecules.However,the

formation of loose ion pairs is usually exdthermic but the charge delocalization facilitates the ion pair seperation.It was particularly explained by Szwarc that the fluctuating environment of the solvating macromolecules affect the vibrational motion of the ions in the ions pairs.Namely,exchange of the cation is involved in the vicinity of complexed macrocyclic cavity (18,19).

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