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Nuclear Magnetic Relaxation Studies for Investigating the Hydration of 15-Crown-5 and 18-Crown-6 Ethers in Aqueous and Aqueous Salt Solutions

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Abstract

The results of experimental studies of ^1H and ^2H nuclear magnetic relaxation rates in the solutions of 15-crown-5 and 18-crown-6 ethers in D_2O and $CDCl_3$ (concentration range 0 to 5 m) at 298 K are reported. It is observed that the extreme narrowing condition is not fulfilled for ^1H relaxation data above 1 m concentration in case of 18-crown-6 in D_2O solutions. Some measurements for ^1H and ^2H spin-lattice relaxation rates for a fixed concentration of ethers in the presence of varying amounts of alkali bromides (LiBr, NaBr and KBr) were also carried out. It has been noted that the relaxation behaviour of crown ethers is not influenced appreciably by the presence of ions in solution except in the case of LiBr in the dilute concentration region. However, the solvent (D_2O) behaviour is found to be strongly and in a specific way influenced by the nature of the electrolytes. The ^2H relaxation data in the case of 1 m solutions of 18-C-6 in D_2O with variable concentrations of KBr indicate the formation of 1:1 and 1:2 host-guest type complexes. Attempts are being made to analyse the results in terms of hydrophobic interactions of the crown molecules in D_2O, the occupation of cavities by bridging water molecules (D_{3d} conformation of the crown), the replacement of these bridging water molecules by K^+ ions, corresponding ion-pair formation and structural interactions. It is concluded that preorganisation of the appropriate conformation of crown molecules and hydrogen bonding interaction play an important role in the formation of host-guest type complexes of crown ethers with alkali bromides.

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1. INTRODUCTION

The importance of the solvent in complexation processes involving crown ethers has been discussed by a number of authors [1]. The stability constants of alkali metal ion complexes with crown ethers are highly dependent upon the choice of solvent, they are relatively small in aqueous solutions [2]. Recently it was established that metal ions and water molecules or neutral organic polar molecules can simultaneously form complexes with crown ether or crypt ligands.

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It has also been reported that 18-crown-6 can form hydrates of varying stoichiometry with water as evidenced from X-ray diffraction and Raman spectral studies [3-5]. In an interesting molecular dynamics study of 18-crown-6 in aqueous solutions Kowall and Geiger have reported that two water molecules are bridging oxygen atoms to form the D_{3d} conformation of 18-C-6 [6]. They have shown that structural as well as dynamic properties of the hydration shell of the crown allow a clear distinction between hydrophylic and hydrophobic regions. The interactions are partly governed by fast conformational dynamics of 18-C-6 and partly by the hydrogen bonding properties of crown with water molecules. These simulation studies have been strongly supported by NIR and IR spectral studies as well as viscosity studies [7-9] where the presence of 4 water molecules as a prerequisite for the stability of the D_{3d} conformation of 18-C-6 has been postulated. The presence of two bridging water molecules and two singly hydrogen bonded water molecules accounts for the calculated hydration number of 4 in aqueous solutions of 18-C-6 [7, 9]. Moreover, the calculation of the cavity radius in the presence of water molecules yields 5.3 Å for perfect slipping and 3.5 Å for perfect sticking using the self-diffusion coefficient value of 18-C-6 which agrees well with viscosity and neutron diffraction data [9, 10]. In their neutron scattering study of 18-C-6 in D_2O solutions Pelc et al. have observed fast conformational dynamics at high water concentrations in the form of a broadening of the quasielastic line. They attribute this behaviour to water which exerts two opposing effects on the ring flexibility of 18-C-6 [10]. On the one hand the complexation of water molecules slows down the conformational change but on the other hand free water (exterior, hydrophobically hydrated) in the environment of the crown ether molecules has a promoting effect on the conformational dynamics. Thus as suggested by Kowall and Geiger the hydration shell of 18-C-6 plays an important role in determining the ionophoric abilities of 18-C-6 [6].

It has been observed that the partial molar volume of 18-C-6 goes through a minimum at concentrations about 2 m to 2.5 m in H_2O as well as in D_2O [11, 12]. The limiting excess partial molar volume is largely negative (approx. -13 cm^3 mol^{-1}) which indicates hydrophobic hydration with volume loss [11]. Recent ab initio calculations carried out by Gadre and Pingle have indicated that co-operative electrostatic interactions govern the crown ether hydration pattern in aqueous solutions [13]. Therefore it is certain that electrostatic, hydrophobic and hydrogen bonding interactions must be playing a major role in stabilizing a particular type of conformation (D_{3d}) in liquid phase. The understanding of these interactions will certainly shed light on the mechanisms of ionic transport and molecular recognition involved in more complicated enzymatic and biological processes. It has been postulated that the bridging water molecules may be functionally replaced by K^+ ions. However, the information available on such exchange reactions is rather limited.

In order to gain more insight into the complexation process, the role of water molecules inside the cavities of 18-C-6, hydrophobic hydration effects and the ion-pairing electrostatic interaction, we have studied the ^1H and ^2H spin relaxation times in solutions of 18-C-6 in D_2O and $CDCl_3$ in the concentration range of 0 to 5 m at 298 K. For the sake of comparison, these measurements were extended to solutions of 15-C-5 in the same solvents. Additional measurements of proton and deuterium relaxation rates were made for solutions containing a fixed 18-C-6 concentration (1 m in D_2O) but having variable concentrations of alkali bromide salts (LiBr, NaBr, KBr). In case of 15-C-5 only one salt, KBr, was studied in the ternary system. The results of our investigations are presented and discussed below.

2. MATERIALS AND EXPERIMENTAL

Commercial 18-crown-6 (99%) and 15-crown-5 (98%) were purchased from Aldrich and Merck-Schuchardt, Düsseldorf, Germany, and used without any further purification. The solvents D_2O (99.8%) and $CDCl_3$ (99.9%) from Sigma were also used directly. The salts LiBr, KBr and NaBr (Merck, Suprapur) were dried at 120°C under vacuum. All binary solutions were prepared on molality basis. The salt solutions were prepared on aquamolality basis (moles of salt per kg of D_2O). The samples were freed from oxygen by the freeze-pump-thaw technique.

The ^1H spin-lattice relaxation rates were measured at 80 MHz using a Bruker WP-80 FT-NMR spectrometer. Some measurements were also made at 300 MHz using a Bruker CXP-300 pulsed NMR spectrometer. The ^2H (D) spin-lattice relaxation times of D_2O or $CDCl_3$ were measured at 13.8 MHz or 46.07 MHz with Bruker SXP or CXP-300 pulsed NMR-spectrometers. The relaxation rate values were obtained by the 90°–τ–90° pulse sequence or the inversion recovery method. The temperature was $T = (298 \pm 0.2)$ K, it was controlled with a Bruker BVT 1000 unit. The experimental error was estimated to be of the order of 2 to 3 % for the relaxation time measurements.

3. RESULTS

In Fig. 1 the total ^1H relaxation rates $(1/T_1)_{^1H}$ for 15-C-5 in $CDCl_3$ and D_2O are shown as a function of crown ether concentration. It is observed that the rates and the corresponding increase with concentration of crown are higher in D_2O solutions than in $CDCl_3$ solutions. The extrapolation to infinitely dilute solution yields the rate values of (0.51 ± 0.02) s^{-1} and (0.91 ± 0.04) s^{-1} for 15-C-5 in $CDCl_3$ and D_2O respectively. These values represent the intramolecular relaxation rates for 15-C-5 since at infinite dilution the contribution due to intermolecular relaxation vanishes.
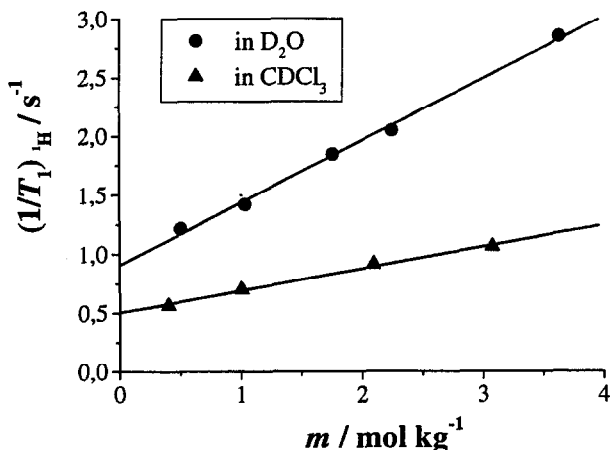

Figure 1. Proton relaxation rates of 15-C-5 in D_2O and in $CDCl_3$ at 80 MHz and 298 K.

Similar data of proton relaxation rates $(1/T_1)^1_H$ for 18-C-6 in $CDCl_3$ and D_2O are depicted in Fig. 2. The 18-C-6 relaxation was studied at two spectrometer frequencies i.e. 80 MHz and 300 MHz. Again it is found that at 80 MHz the rates and their variation with concentration are higher in D_2O solutions than in $CDCl_3$ solutions. The extrapolated values for 18-C-6 to infinite dilution yield the intramolecular relaxation rates which are (0.62 ± 0.03) s^{-1} and (1.25 ± 0.04) s^{-1} in $CDCl_3$ and D_2O solutions respectively. The pure liquid 18-C-6 can be supercooled and the total relaxation rate of 2.65 s^{-1} at 298 K has been reported [15]. The proton relaxation rates for solutions of 18-C-6 in D_2O at higher concentrations (> 1 m) differ from each other at the two frequencies studied.
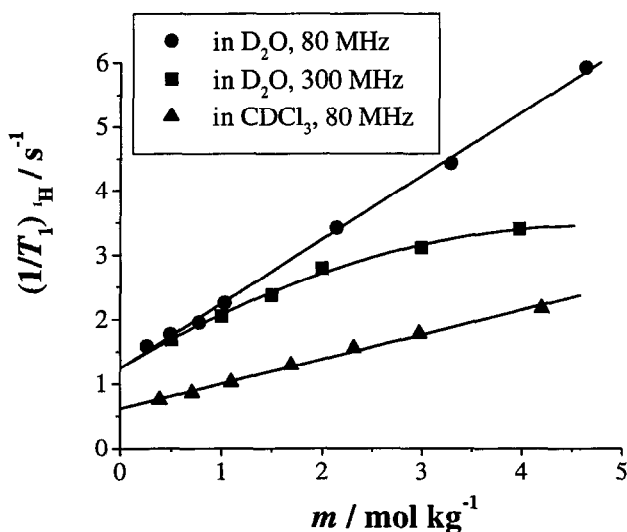

Figure 2. Proton relaxation rates of 18-C-6 in D_2O and in $CDCl_3$ at 298 K.

The solvent deuterium relaxation rates of the solutions of 15-C-5 in $CDCl_3$ and D_2O as a function of crown ether concentration are shown in Fig. 3. It is observed that solvent relaxation rates increase with increase in concentration of the crown ether. The nature of the curves indicates that solute-solvent interactions are of different type in the two solvent systems. Similar data for 18-C-6 in D_2O and $CDCl_3$ as a function of 18-C-6 concentration are shown in Fig. 4. The system 18-C-6 + D_2O was studied at 13.8 and 46 MHz frequencies and we did not find any dependence on the frequency for the solvent deuterium relaxation rate.
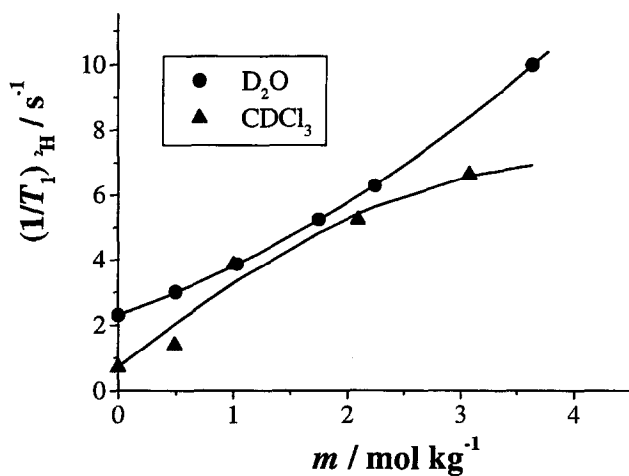
Figure 3. Deuterium relaxation rates of D_2O and $CDCl_3$ for different concentrations of 15-C-5 at 13.8 MHz and 298 K.
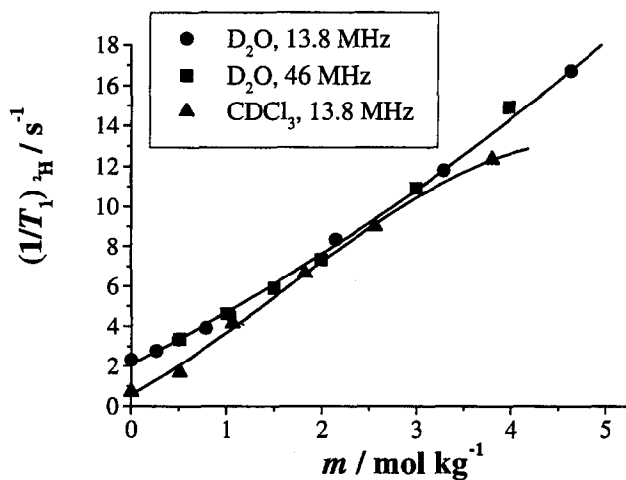

Figure 4. Deuterium relaxation rates of D_2O and $CDCl_3$ for different concentrations of 18-C-6 at 298 K.

The total proton relaxation rates of 15-C-5 and of 18-C-6 at 1 m concentration in the ternary systems 15-C-5 (1 m) + D_2O + KBr and 18-C-6 (1 m) + D_2O + KBr are shown in Fig. 5. For the sake of comparison the data of similar 18-C-6 solutions involving LiBr and NaBr instead of KBr are also included in the same figure. The data for the system 18-C-6 + D_2O + KBr are obtained at a frequency of 300 MHz while all other data correspond to a frequency of 80 MHz.
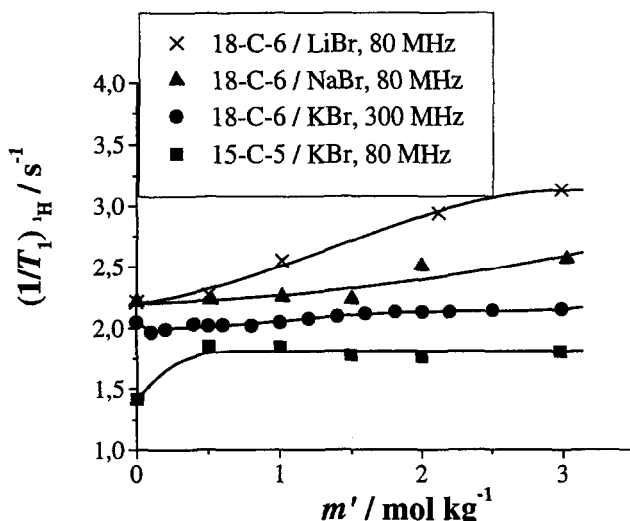

Figure 5. Variation of proton relaxation rates of 15-C-5 and 18-C-6 with the concentration (m') of added salt at 298 K for 1 m ethers in D_2O.

In Fig. 6 the variation of the solvent deuterium relaxation rate for a fixed 1m concentration of 15-C-5 and 18-C-6 as a function of the salt aquamolality is shown. The data for the system 18-C-6 + D_2O + KBr have been recorded at a frequency of 46 MHz while the rest of the data was obtained at 13.8 MHz. In all studied systems the variation of $(1/T_1)_{2H}$ with salt concentration is found to be strongly dependent on the nature of the salt cation. The solvent relaxation rate decreases with addition of KBr for both crown systems but the variation is characteristic of the individual crowns. The data for LiBr and NaBr solutions show distinct differences, as for Lithium ions the rate initially decreases slightly and then rises monotonously with increase in concentration, however, in case of NaBr up to 1 m salt concentration the rate decreases and thereafter remains more or less constant at higher concentrations. These observations are the highlights of the present work and resemble the curves obtained in electrochemical studies involving acid-base or oxidative-reductive titration equilibria. The trends in Fig. 6 probably suggest that 15-C-5 forms host-guest type complexes with KBr having a stoichiometry of 1:1 while 18-C-6 can form 1:1 and 1:2 complexes. Such complex formation equilibria are not evident in the case of the system 18-C-6 + D_2O + LiBr but there are indications that NaBr can form a 1:1 complex with 18-C-6 in solution. Thus the

observed trends of the variation of solvent relaxation rates with salt concentration can be regarded as the effect of formation of different types of host-guest complexes with crown ether molecules and they are in harmony with the results of apparent molar volume studies of salts in such mixtures [12]. The characteristic differences in trends can be attributed to the cavity size and ionic radius differences for the Li^+, Na^+ and K^+ ions.
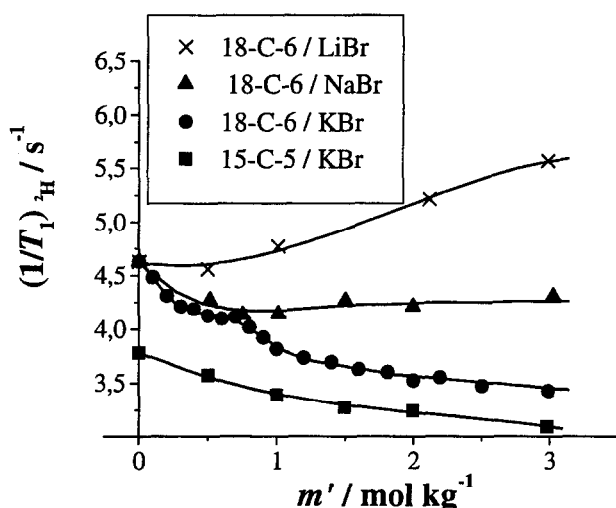

Figure 6. Variation of deuterium relaxation rates of D_2O in 1 m solutions of 15-C-5 and 18-C-6 with the concentration (m') of added salt at 298 K.

4. DISCUSSION

Observations of Figs. 1 and 2 point out that the total proton relaxation rates of 15-C-5 and 18-C-6 in D_2O as well as in $CDCl_3$ rise with increase in concentration of the ether molecules. The higher values of $(1/T_1)^1H$ in D_2O compared to those in $CDCl_3$ can be accounted for satisfactorily on the basis of viscosity and polar nature of the two solvent systems. A similar behaviour was also noted for the self-diffusion coefficient (D) of the crown ether in D_2O and $CDCl_3$ solutions, D being smaller in D_2O than in $CDCl_3$ [12]. It has been indicated that pure crown ether molecules in liquid phase have intra- as well as intermolecular relaxation rate contributions to the total proton relaxation rate [15]. This implies that in pure liquid state there is some association between crown ether molecules. The increase in $(1/T_1)^1H$ with concentration in case of $CDCl_3$ can be viewed in terms of stronger crown-crown molecule interactions (coiling or stacking type). However, the concentration dependence of $(1/T_1)^1H$ is still of higher magnitude in case of D_2O solutions, suggesting further that in addition to

solute-solute association, solute-solvent interactions or solute-induced solvent-solvent interactions are also prominent in D_2O solutions.

Partial molar volume, viscosity B coefficient and neutron scattering studies of solutions of 18-C-6 in D_2O [9-11] as well as computer simulation studies of Kowall and Geiger all point out that the crown hydration shell, water structural effects and the conformation equilibria of the 18-C-6 molecule play an important role in exhibiting the structural and dynamic properties in liquid solutions. One can observe from Fig. 2 that in case of 18-C-6 solutions the proton relaxation rate above 1 m crown concentration varies at the two studied frequencies. Recently, Moll using the isotopic dilution method has shown that the intermolecular relaxation rate for the 18-C-6 is almost zero up to 1 m 18-C-6 concentration, it increases thereafter with increase in crown concentration and goes through a maximum at 0.50 mole-fraction of the crown [16]. It is expected that effects due to intermolecular interactions as well as viscosity effects would be more sensitive to frequency changes and hence in concentrated solutions, as their contribution increases, more dispersion in $(1/T_1)^1{}_H$ values may occur and this is found to be the case indeed. Moreover, for aqueous 18-C-6 solutions (below 1 m concentration of 18-C-6) a relaxation process with a concentration independent ultrasonic absorption maximum at 101 MHz has been observed and attributed to a conformational rearrangement of two conformers: $CR_1 \leftrightarrows CR_2$ with a characteristic relaxation time $\tau = 1.6$ ns [17]. We interpret this as a conversion of conformers in C_i form to the more symmetrical D_{3d} form which is facilitated by the availability of polar water molecules interacting through hydrogen bonding to the ether oxygen atoms. The presence of two bridging water molecules thus imparts the stability to the ring structure of the D_{3d} type.

The solvent relaxation rates for the systems 15-C-5 and 18-C-6 in D_2O and $CDCl_3$ rise with increase in concentration of ether molecules. As noted previously, there is no frequency effect as far as this rate is concerned in case of 18-C-6 solutions (Figs. 3 and 4). The deuterium having $I = 1$ relaxes due to quadrupole interaction which is due to statistical fluctuations of the electric field gradient at the nuclear site caused by molecular motions [18]. The spectral intensity of the interaction energy at the magnetic resonance frequency determines the rate of relaxation. Under conditions of extreme narrowing the intramolecular relaxation rate is given by equation 1:

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40} \frac{2I+3}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{eQ}{\hbar} \frac{\partial^2 V}{\partial z'^2}\right)^2 \tau_c \qquad (1)$$

where Q is the electric quadrupole moment of the nucleus, η is the asymmetry parameter, $\partial^2 V / \partial z'^2$ is the z' component of the field gradient and τ_c is the time constant characterizing the correlation function. Thus similar to other polar organic cosolutes (having methyl or methylene groups) crown ether molecules also exert the effect of lengthening the correlation time if we assume that the field gradient is constant [19]. It has been observed from neutron scattering studies that rotational motion of organic crown molecules in aqueous solutions is fast, or one can say that rapid, large internal motion must take place in CH_2- chains [10]. The lengthening of the reorientation times is considered to be a consequence of the increase of structure in the aqueous solvent [20]. The hydration shell as well as the bridging water

molecules are important in governing the structural entities in crown-solutions. These effects appear to be stronger in 18-C-6 than in 15-C-5 indicating the importance of additional hydrophobic CH_2- groups in 18-C-6. Similar effects with respect to $CDCl_3$ relaxation rate and its concentration dependence can be viewed as manifestation of association between ether molecules meaning in turn further solute-solute interaction influence on the ^2H nucleus of $CDCl_3$ molecules via increased solvent-solvent interaction.

The salt effect on the proton relaxation rates of 15-C-5 and 18-C-6 is summarized in Fig. 5. If the concept of occupancy of the cavities of 18-C-6 by bridging water molecules is accepted, one can further imagine the replacement of these water molecules by cations of appropriate size. This should be feasible since cations can exert a stronger electrostatic effect on the ring oxygen atoms of the crown molecules. Such complexes are well studied in the solid state. We observe that the proton relaxation rate is hardly affected in the case of addition of KBr up to 1 m concentration. Therefore, it is logical to think that replacement of one water molecule from the cavity by K^+ ions does not alter the correlation times of the crown protons. However, at higher concentration a small increase can be noted. The situation in case of Li^+ ions is different and the relaxation rate is found to be increased. The Li^+ ion is known to be an electrostrictive structure making ion in aqueous solutions [21]. The interactions of Li^+ ions with water as well as with crown oxygen may not facilitate the stability of the cyclic D_{3d} structures of crown ether molecules. The case of NaBr is an intermediate one. The Na^+ ion is a slightly structure making ion with a smaller ionic size than the K^+ ion. The ability of the former to form 1:1 complexes with 18-C-6 is evident since $(1/T_1)^1_H$ does not vary at lower concentrations. At higher concentrations probably other types of ion-solvent or ion-ion interactions predominate. Thus effectively the Na^+ ion can also replace the bridging water molecules without altering the motional characteristics of 18-C-6 molecules in the D_{3d} conformation in the dilute concentration region. The case of 15-C-5 is altogether different and not much information about its conformational properties is available. In this case the proton relaxation rate initially increases with addition of KBr and thereafter remains more or less constant. It seems that the size of the cation radii and the conformational characteristics of crown ether molecules dictate the replacement of water molecules from the crown cavities.

The most dramatic effect of the ionic radii or a charge density of the cations on the deuterium relaxation rates can be seen at fixed concentration of crown ether in D_2O solutions. In Fig. 6 we observe that the ^2H relaxation rate decreases characteristically by addition of KBr. The curve involves steps indicating stepwise removal of water molecules from the crown cavities and replacing by K^+ ions having stoichiometry 1:1 and 1:2. The computer simulation studies of Kowall and Geiger indicate oscillations of K^+ ions above the crown cavities and also reveal a solvent bridged pair 18-C-6-H_2O-K^+ having an independent minimum of the free energy profile. The presence of a free energy barrier between the contact pair and the solvent bridged pair probably quenches the electric field gradient on the solvent molecules which in turn depends upon the concentration of K^+ ions and the corresponding stability constant of the complexes in solution phase. It is difficult to obtain the stability constant for the complexes in the solution from the present data. However, the data indicate the subtle effect induced by the conformation of the crown ether molecule.

The present results yield more credence to the hypothesis of the presence of two bridging water molecules in the interior of 18-C-6 molecules which get replaced by the K^+ ions, less effectively by Na^+ ions. Interactions become altogether different if ions of high charge densities like Li^+ are being used.

The decrease in relaxation rate of D_2O in the system 18-C-6 + D_2O + KBr can be examined in another way. We calculated the change in D_2O relaxation rate $\Delta(1/T_1)^2_H$ for the transfer from aqueous KBr solutions to solutions having the same concentration of KBr in 1 m 18-C-6 solution. The parameter :

$$\Delta\left(\frac{1}{T_1}\right)_{2_H} = \left(\frac{1}{T_1}\right)_{2_H}^{1m18-C-6+KBr} - \left(\frac{1}{T_1}\right)_{2_H}^{KBr}$$

is plotted in Fig. 7 as a function of KBr concentration. The relaxation rates of D_2O in KBr solutions were obtained from Müller's studies [22]. We can see that the trend of the curve clearly supports the interpretation of stepwise replacement of bridging water molecules by K^+ ions. If we assume a constant correlation time for the D_2O molecules, the corresponding decrease in $(1/T_1)^2_H$ suggests on an average a decrease in quadrupole coupling constant or a change in field gradient of the D_2O molecules. Thus in 18-C-6 + D_2O solutions the picture of bridging molecules − hydrogen bonding with crown oxygens − and the hydrophobic hydration of crown molecules lead on an average to an increase of the quadrupole coupling constant of the water molecules which decreases in the presence of K^+ ions. Calculations of the quadrupole coupling constant of D_2O in the presence of 18-C-6 by Merkling and Zeidler [23] support the interpretation above.
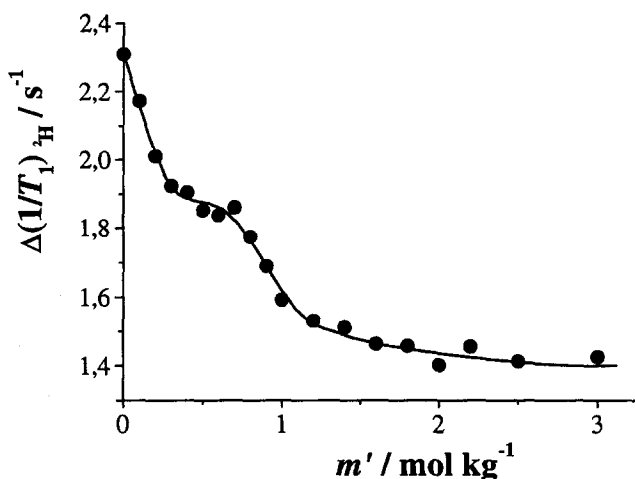

Figure 7. The change in deuterium relaxation rate of D_2O on transfer from KBr solutions to 1 m 18-C-6 + KBr solutions as a function of KBr concentration at 298 K.

Water hydration of macromolecules in aqueous media is very complex and many types of hydration spheres have been evoked [24]. Mayzel and Cohen, on the basis of NMR diffusion and chemical shift data, reached to the conclusion that water hydration of 18-C-6 and its KI complex in deuterated chloroform exhibit different modes of solute-water interaction in the two cases. According to these authors 18-C-6 acts as an effective hydration shell for the potassium ions, effectively reducing the number of water molecules which are associated with the potassium salt from 1.3 to 0.3 [26]. In the present work, we observed that D_2O relaxation rates of solvent D_2O vary characteristically in 18-C-6 and 15-C-5 solutions as well as in salt solutions and indicate the presence of bridging water molecules which can be replaced by K^+ ions inducing changes in the field gradients in a subtle way. Comparatively, the proton relaxation rates of crown molecules are affected little by such replacement interactions.

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