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Self-diffusion of Alkali Ions in Aqueous Solutions of Crown Ether Complexes

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Sodium and lithium self-diffusion coefficients in aqueous solutions of crown ether complexes of 18-crown-6 and 15-crown-5 respectively, were measured using pulsed field gradient nuclear magnetic resonance. Small concentrations of 18-crown-6 in aqueous solution of sodium ions, while having negligible effect upon the macroscopic viscosity, cause, for some counterions, a quite significant suppression of sodium diffusion. For lithium complexes of 15-crown-5, no such effect was observed. This enhanced effect suggests that, for some counterions, each (Na^+;18-crown-6) complex may associate with a surprisingly large number of (Na^+) ions forming (Na^+)−(Na^+;18-crown-6) stable aggregates. Spin−lattice relaxation measurements of crown ether protons confirm this conclusion.

1. Introduction

Crown ethers[1] and cryptands[2] have been studied exhaustively, partly because of their ability to transport alkali ions such as sodium and potassium in aqueous solutions across lipophilic membranes. In crown ethers, as well as in the more recently synthesized, somewhat related calixarenes,[3] cavity size and metal−oxygen interaction energy appear to be the parameters most relevant to determine complexation properties.[4,5] Ions such as sodium interact more strongly and form relatively stable complexes with 18-crown-6, whereas 15-crown-5 is capable of complexing lithium ions.[6]

Nuclear magnetic resonance (NMR) has been employed extensively to study crown ethers[7] but the vast majority of this effort has been concentrated in nonaqueous solvents. On the other hand, the complexation of 18-crown-6 with alkali ions in aqueous solution has been studied in great detail by other methods,[4,8−12] especially calorimetry and X-ray diffraction. Particularly important to our present work is the verification, by solution X-ray diffraction techniques,[11,12] of the solvation of 18-crown-6 complexes with alkali metal ions in aqueous solution.

In this work, we employ NMR to study alkali metal diffusion and crown ether complexation. Our results confirm an earlier conclusion, obtained with more limited data,[13] indicating that selected counterions in aqueous solution can cause a considerable suppression of sodium diffusion in the presence of a small concentration of 18-crown-6. Here, we present convincing new evidence that expands the scope of the underlying suppression mechanism. We demonstrate that the solvation of (Na^+;18-crown-6) complexes favors, for those electrolytes where the diffusion reduction is more pronounced, the formation of stable aggregates containing possibly six or more sodium ions dynamically associated with a complexed sodium ion.

2. Experimental Details

Diffusion measurements were performed at 25 C in a magnetic field of 7.04 T using a spectrometer based upon a Tecmag system and a home-built, actively shielded probe. A modified Hahn[14] spin−echo sequence with pulsed magnetic field gradients[15−18] was employed. Magnetic field gradient strengths of up to 0.4 T/m were produced by a Maxwell pair of coils 6 cm in diameter separated by distance of 4.7 cm. The cylindrical samples employed were 10 mm in diameter and 10 mm in height and occupied a region of relatively uniform gradient.

Given that ^{23}Na, spin−lattice (T_1) as well as spin−spin (T_2) relaxation times in our samples are quite short, typically in the range of 30 ms, a time interval $\tau = 26$ ms between the $\pi/2$ pulse and the π pulse was adopted. The time duration of the gradient pulse was $\delta = 10$ ms and the interval between the beginning of the first gradient pulse and the second gradient pulse was $\Delta = 26$ ms. To avoid any possibility of heating of the conductive samples by the RF pulses, long recycle delays of 5 s with typically 100 scans were employed in the ^{23}Na diffusion measurements. With the exception of a longer recycle delay of 50 s, corresponding to 5T_1 for typical ^{7}Li T_1 values, the acquisition parameter for ^{7}Li diffusion measurements were preserved in order to permit a more accurate comparison with ^{23}Na. ^{1}H diffusion and spin−lattice relaxation measurements were also performed at 7.04 T, using for the latter a $\pi - \tau - \pi/2$ inversion recovery pulse sequence.

As a reference for the ^{23}Na diffusion measurements, a 0.5 M solution of NaCl was employed adopting $D = 1.24 \times 10^{-9}$ m^2/sec as the value of the self-diffusion coefficient at 25 °C.[19] Temperature was maintained at 25 ± 0.4 °C by a flow of thermostated water through a jacket in the probe The measured diffusion coefficients are estimated to be accurate to within approximately 4%.

Other NMR measurements were performed at 7.04 T on samples 5 mm in diameter using a Varian UNITY plus-300 spectrometer. For the viscosity measurements at 25 °C a Ostwald viscosimeter was employed with a thermostated water bath maintained within ±0.4 °C of the specified temperature. All

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chemicals employed were of reagent grade and deuterium oxide used in spin−lattice relaxation measurements, was 99.8% D_2O.

3. Results and Discussion

The reaction kinetics of sodium 18-crown-6 complexation in aqueous solution can be represented by

$$\mathrm{Na}^+ + \mathrm{C} \overset{k_1}{\underset{k_{-1}}{\leftrightarrow}} (\mathrm{Na}^+;\mathrm{C}) \qquad (1)$$

If $[\mathrm{Na}]_F$ and $[\mathrm{C}]_F$ denote the concentrations of "free sodium" and "free crown", respectively, and $[\mathrm{Na}]_B = [\mathrm{Na}^+;\mathrm{C}] = [\mathrm{C}]_B$ represent the concentration of "bound sodium", the equilibrium condition for the first-order reaction yields

$$\frac{[\mathrm{Na}^+,\mathrm{C}]}{[\mathrm{Na}^+]_F[\mathrm{C}]_F} = \frac{k_1}{k_{-1}} = K_1 \qquad (2)$$

where K_1 represents the formation constant of the complex. For sodium-18-crown-6 complexes in aqueous solutions a value $\log_{10}(K_1/\mathrm{dm}^3\ \mathrm{mol}^{-1}) = 0.57$, has been determined by calorimetric titration[12] at 25 °C and shown to be consistent with ^{23}Na chemical shift and spin−spin relaxation measurements.[13] The dissociative reaction rate, represented by k_{-1} in eq 2, is expected to be very large, in aqueous solutions, compared to typical NMR rates. This can be inferred from the field-independent ^{23}Na resonance widths and the lack of structure of the line shapes.[13]

From eq 2 and the condition of mass balance, an expression for the fractions P_F and $P_B = 1 - P_F$, of free and bound sodium respectively, can be obtained[13]

$$P_F = -\frac{1}{2}\left[\frac{1}{K_1[\mathrm{Na}]_T} + \rho - 1\right] + \left[\frac{1}{4}\left\{\frac{1}{K_1[\mathrm{Na}]_T} + \rho - 1\right\}^2 + \frac{1}{K_1[\mathrm{Na}]_T}\right]^{1/2} \qquad (3)$$

In eq 3 $\rho = [\mathrm{C}]_T/[\mathrm{Na}]_T$ represents the molar ratio of crown ether to sodium, with $[\mathrm{Na}]_T = [\mathrm{Na}]_F + [\mathrm{Na}]_B$ and $[\mathrm{C}]_T = [\mathrm{C}]_F + [\mathrm{C}]_B$ denoting respectively, total molar concentrations of sodium and 18-crown-6 in each experiment.

Given the fast reaction kinetics on the NMR time scale, the variation with ρ of quantities such as the measured ^{23}Na chemical shift δ_m, can be reasonably well described[13] by a population weighted averages of form

$$\delta_m = P_F\delta_F + P_B\delta_B \qquad (4)$$

with δ_F and δ_B denoting respectively chemical shifts of "free" and "bound" sodium ions. A similar expression can be employed, within certain limits, for the measured spin−spin relaxation rate.$(1/T_2)_m$.[13]

The arguments leading to eq 4 are also expected to be applicable to the variation with ρ of the measured self-diffusion coefficient D_m, provided the time constant for chemical exchange is short compared to typical times employed in the diffusion measurement.[20] Because diffusion times for our measurements are in the same range as T_2 values, the fast exchange regime [21] should also prevail for the diffusion constant. However, unlike the chemical shift, a subdivision of alkali metal ions into "free" and "bound" species, with diffusion coefficients D_F and D_B, respectively, is not generally warranted Alkali ions which, according to eq 3, are considered as nominally free, may have different diffusion coefficients depending upon their environment. In particular, if they are associated in pairs with neighboring bound cations, these nominally free alkali ions may have a substantially reduced diffusion coefficient.

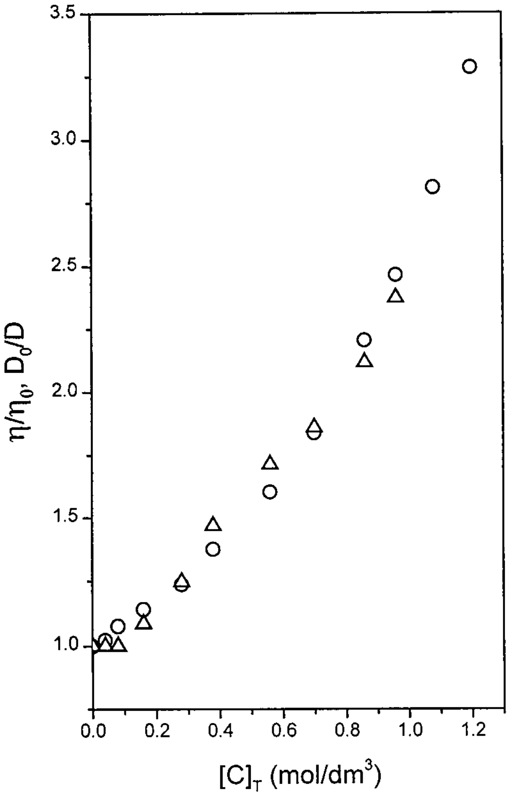

Figure 1. (△) ^{1}H relative inverse self-diffusion coefficient D_0/D and (○) relative viscosity η/η_0 at 25 °C in a 0.2 M aqueous solution of NaN_3 as a function of $[\mathrm{C}]_T$, the molar concentration of 18-crown-6.

Before discussing alkali metal diffusion data, it should be pointed out that, as the concentration $[\mathrm{C}]_T$ of 18-crown-6 in aqueous solution is increased, the macroscopic viscosity, as well as the inverse of the self-diffusion coefficient of water protons, also increase. This process, which is unrelated to ionic association and pair formation, could mask the effects of the latter and must be considered first. The data of Figure 1 show the relative variations of the inverse diffusion coefficient of protons and of the viscosity as a function of the total molar concentration of total 18-crown-6 $[\mathrm{C}]_T$ in a 0.2 molar aqueous solution of NaN_3. The inverse ^1H self-diffusion coefficient can be seen from Figure 1 to scale reasonably well with the macroscopic viscosity[13] over a considerable range of 18-crown-6 concentrations. The region of very low crown ether concentrations, $[\mathrm{C}]_T < 0.09$ mol/dm^3, is particularly interesting to interpret our alkali metal diffusion data. For $[\mathrm{C}]_T < 0.04$ mol/dm^3, the variations of proton self-diffusion coefficient and macroscopic viscosity are quite small and amounts to less than 4%. For larger values of $[\mathrm{C}]_T$ the variations rapidly become significant.

We next discuss our ^{23}Na self-diffusion measurements for 18-crown-6 complexes in aqueous solutions presented in Figure 2 and Figure 3. If an equation similar to eq 4 is assumed to be valid, the self-diffusion coefficient could be written as

$$D_m = P_F D_F + (1 - P_F)D_B \qquad (5)$$

where P_F is given by eq 3. The variation with ρ predicted by eq 5 would be most pronounced if the condition $D_B < < D_F$ were satisfied leading to $D_m \approx P_F D_F$. However, even with this rather drastic assumption, the ρ dependence would still be barely detectable within the experimental error for $\rho \leq 0.05$. Figure 2

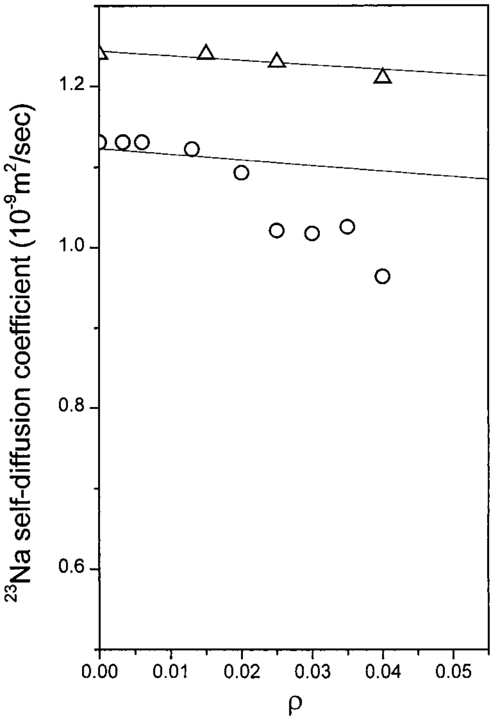

Figure 2. ^{23}Na self-diffusion coefficient at 25 C in aqueous NaCl solutions as a function of the molar ratio ρ of 18-crown-6 to sodium. (△) for $[Na]_T = 0.5$ mol/dm^3 and (○) for $[Na]_T = 2$ mol/dm^3. The solid lines represent the expected variations in the absence of pairing.

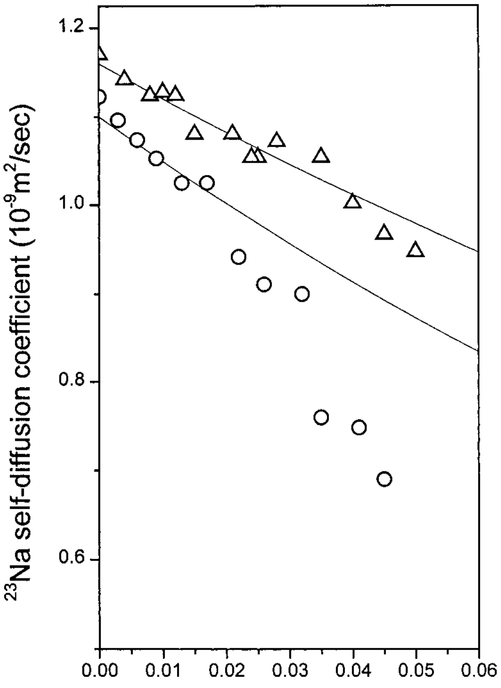

Figure 3. ^{23}Na self-diffusion coefficient at 25 C in aqueous solutions of NaN_3 as a function of the molar ratio ρ of 18-crown-6 to sodium. (△) for $[Na]_T = 0.5$ mol/dm^3 and (○) $[Na]_T = 2$ mol/dm^3. The solid lines represent expected variations caused by the formation of associated aggregates.

shows calculated values of D_m as a function of ρ for $[Na]_T = 0.5$ mol/dm^3 and $[Na]_T = 2$ mol/dm^3, using the above-mentioned assumption, which confirm this result. Although it did not affect significantly the ρ dependence, an approximate scaling with the square root of the masses[22] was employed for the calculated D_m. This leads to a value $D_B \approx (1/3.5)D_F$ which should be more realistic than completely neglecting D_B. Scaling with the inverse cubic root of the masses, as implied by Stoke's[17] formula, yielded essentially the same values of D_m.

Figure 2 also shows measured ^{23}Na self-diffusion coefficients as a function of ρ for $[Na]_T = 0.5$ mol/dm^3 and $[Na]_T = 2$ mol/dm^3 in aqueous NaCl solutions containing 18-crown-6. For $[Na]_T = 0.5$ mol/dm^3, in the range $\rho \leq 0.04$ the total concentration of 18-crown-6 is $[C]_T \leq 0.02$ mol/dm^3. From the data of Figure 1, the effects caused by a possible increase in macroscopic viscosity are expected to be quite small and the decay of D_m with increasing ρ, for $[Na]_T = 0.5$ mol/dm^3, can be seen to be negligible in this range. This result agrees with a simple model of "free" and "bound" ions with fast exchange, implicit in eq 5.

For $[Na]_T = 2$ mol/dm^3, the increase in macroscopic viscosity with ρ is expected to become significant within the range $\rho \leq 0.04$, corresponding to $[C]_T \leq 0.08$ mol/dm^3. From the data of Figure 1, the onset of the bulk viscosity effect should take place approximately for $\rho \geq 0.02$, corresponding to $[C]_T \geq 0.04$ mol/dm^3 The data of Figure 2, corresponding to $[Na]_T = 2$ mol/dm^3, can be seen to follow the theoretical prediction up to $\rho \approx 0.02$ where the bulk viscosity effect takes over.

Although for 18-crown-6 complexes in aqueous NaCl solutions, variations of D_m, not attributed to changes in bulk viscosity, can be seen from Figure 2 to be quite small, for other electrolytes the situation is different. ^{23}Na self-diffusion coefficients measured in aqueous NaN_3 solutions with $[Na]_T = 0.5$ mol/dm^3 and $[Na]_T = 2$ mol/dm^3 are shown in Figure 3. Here D_m, can be seen to decay significantly for $[Na]_T = 0.5$ mol/dm^3, even though no appreciable change in the macroscopic viscosity is expected in this range. For $[Na]_T = 2$ mol/dm^3, one can observe an initial decay with a slope only slightly larger than for $[Na]_T = 0.5$ mol/dm^3 followed, for $\rho \geq 0.02$, by a faster decay. The latter can be attributed to bulk viscosity effects, as suggested by the data of Figure 1.

^{23}Na self-diffusion measurements in 18-crown-6 complexes were also performed for other counterions and the same range of ρ values as in Figures 2 and 3. For NaF aqueous solutions with $[Na]_T = 0.5$ mol/dm^3, the suppression of sodium diffusion was found to be negligible as in the case of NaCl. However, for SCN^- , a counterion isoelectronic with N_3^- , a measurable reduction was also observed.

^{7}Li self-diffusion measurements in aqueous solutions of 15-crown-5 complexes were measured as a function of the molar ratio ρ of total 15-crown-6 to total lithium. for $[Li]_T = 0.5$ mol/dm^3. Given the smaller quadrupolar coupling constant of ^{7}Li relative to ^{23}Na and the consequently longer spin−spin relaxation time T_{2B}, measurements could be performed for larger values of ρ. From the data of Figure 4 it appears that the variation of D_m with ρ is very small for both LiCl and LiN_3.

The considerable reduction of sodium diffusion with a rather small increase of ρ at constant $[Na]_T = 0.5$ mol/dm^3, shown in Figure 3 for NaN_3, can be explained if one postulates the formation of $(Na)^+ - (Na^+;$18-crown-6) pairs.[13] These associated structures, which can expected to be slower diffusers than nonassociated cations, appear to be stable, for some electrolytes, on a time scale of many milliseconds.

In simple aqueous solutions of electrolytes such as NaCl, $(Na)^+ - (Na)^+$, associated pairs are formed when a cation shares at least one of the water molecules of its hydration shell with another cation. According to Bjerrum's[23] model for the water molecule, the two negative charges that simulate the effect of unshared electrons on the oxygen atom located at the center

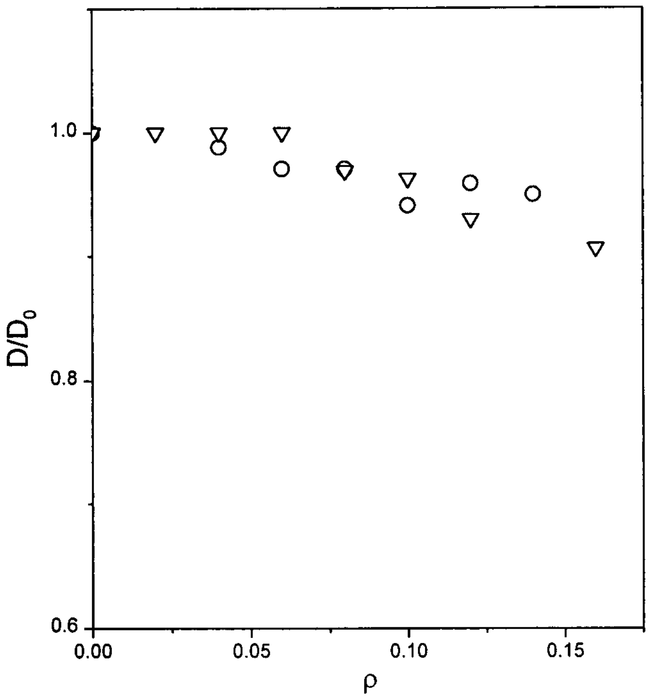

Figure 4. ^{7}Li relative self-diffusion coefficient D/D_0 at 25 °C as a function of the molar ratio ρ of 15-crown-5 to total lithium in aqueous solutions. (▽) for 0.5 M LiN_3 and (○) 0.5 M LiCl.

of the tetrahedron, can balance the electrostatic repulsion between two monovalent cations and form a stable pair. Recent Monte Carlo calculations indicate that, for a 1 M NaCl aqueous solution, approximately 20% of all cations are associated in pairs with other cations.[24] Although this type of pairing should also be present in our systems it is not likely to responsible for the effects observed as a function of ρ.

Pairs of type $(Na)^+ - (Na^+;$18-crown-6) could explain our data because an increasingly large number of cations would become slower diffusers with increasing ρ at constant $[Na]_T$. Moreover, the reaction kinetics of complexation and the type of counterion appear to have an effect upon the structure of these pairs. Our results suggest that the associated structures relevant to the present problem should involve not two but several cations. Furthermore, any cation in the aggregate must exchange very rapidly with the complexed cation during the diffusion time. Thus, a dynamic association, involving several rapidly exchanging cations around a central crown molecule, needs to be invoked. This slowly diffusing structure, with a lifetime which is longer than typical diffusion times, could "immobilize" an unusually large number of cations causing the effects shown in Figure 3.

The above model of pairing permits a simplified estimate of the ρ dependence of the measured diffusion coefficient D_m in the $\rho < < 1$ range. If each bound cation is thought to be dynamically associated with, for example, $n - 1$ free cations and these structures are assumed to diffuse very slowly, D_m would be dominated by those free cations which are nonassociated. These can be considered to be a subgroup of free cations whose $n - 1$ neighboring cations are all free also. The fraction of nonassociated cations would then be of order $(P_F)^n$ and the expected variation of the measured diffusion coefficient with ρ would be governed by: $D_m = P_F{}^nD_F + (1 - P_F{}^n)D_B$. This last expression can be written, for the ρ values of Figure 3, in a simpler and more transparent form. Because $P_B = 1 - P_F \leq 0.03$ in this range, keeping only first-order terms in P_B, one has, to a quite good approximation, $D_m \approx (1 - nP_B)D_F + (nP_B)D_B$. Thus, as ρ and consequently P_B increase, the fraction of "immobilized" cations increases as nP_B suggesting that each bound cation associates with $n - 1$ cations forming an aggregate.

Although the data of Figure 3 appear to indicate that n must be significantly larger than one, a more precise determination requires the knowledge of the ratio D_B/D_F. It has been suggested by Hertz,[22] that the diffusion coefficient of an ion in an electrolyte may scale with the inverse square root of the mass rather than with the inverse cubic root. The latter is expected in the hydrodynamic limit for relatively large particles. Figure 3 shows plots of calculated values of D_m for $n = 7$ as a function of ρ for $[Na]_T = 0.5$ mol/dm^3 and $[Na]_T = 2$ mol/dm^3. D_F denotes measured diffusion coefficients for NaN_3 solutions ($\rho = 0$) and a value $D_B = (1/4.30)D_F$, which results from a direct scaling with the square root of the masses of the atoms involved. The good agreement with the experimental data of Figure 3, using the accepted value of K_1 (eqs 2−3) would suggest the formation of a slow diffusing aggregate of $n - 1 = 6$ cations, dynamically associated with a bound central cation. In reality, this conclusion is not immune to criticism because not only the form of the scaling is not well established but also the masses of the solvation shells are not known. This could introduce some uncertainty and yield a value of $n - 1$ somewhat different from six. However, this does not seriously affect our conclusions. If one adopts the hydrodynamic scaling with the inverse cubic root of the masses, the solid lines of Figure 3 also represent quite accurately the expected variation of D_m for this case, but with a value $n - 1 = 8$ and $D_B = (1/2.73)D_F$. An even larger value of $n - 1$ would be necessary if a larger ratio D_B/D_F is assumed. On the other hand, if the extreme condition $D_B < < D_F$ is assumed to prevail, one would conclude, from a fit to the data of Figure 3, that $n - 1 \approx 5$.

Additional evidence for the formation of sodium associated aggregates was obtained by comparing, for various counterions, spin−lattice relaxation times of 18-crown-6 protons with and without Na present. To that end, 0.5 molar solutions of various sodium salts in D_2O containing the same molar fraction $\rho = 0.04$ of 18-crown-6, were compared with a $[C]_T = 0.02$ mol/dm^3 solution of 18-crown-6 in D_2O containing no alkali ions. The recovery of the longitudinal magnetization of the single line of the methylene protons was measured by a $\pi - \tau - \pi/2$, inversion recovery pulse sequence and is shown in Figure 5. Figure 5a compares a $[Na]_T = 0.5$ mol/dm^3 solution of NaCl containing a crown ether molar fraction $\rho = 0.04$ with a $[C]_T = 0.02$ mol/dm^3 18-crown-6 solution containing no alkali ions. Figure 5b shows the same comparison as Figure 5 but with NaN_3 substituting for NaCl.

From Figure 5a we obtain T_1(crown) = 0.71 ± 0.01 s for the methylene protons in 18-crown-6 and a slightly lower value T_1(NaCl) = 0.70 ±0.01 s for the methylene protons in a NaCl solution. In contrast, from Figure 5b, we obtain an appreciably lower value $T_1(NaN_3)$ = 0.60 ±0.01 s with a ratio T_1(crown)/$T_1(NaN_3)$ = 1.18 ±0.03. Proton spin−lattice relaxation measurement were also performed for NaSCN, where, as in the case of NaN_3, a significant reduction of ^{23}Na diffusion compared to NaCl was found to be present. As expected, the value T_1(NaSCN) = 0.63 ±0.01 s for this counterion was also shorter than for Cl^-.

To infer from the difference observed in Figure 5a and 5b that a slower 18-crown-6 molecular tumbling prevails in the case of NaN_3, a possible effect caused by the presence of a very small amount of paramagnetic impurities in NaN_3 should be ruled out. To that end, we dissolved a small amount of H_2O in D_2O, maintaining the same proton concentration as in Figure

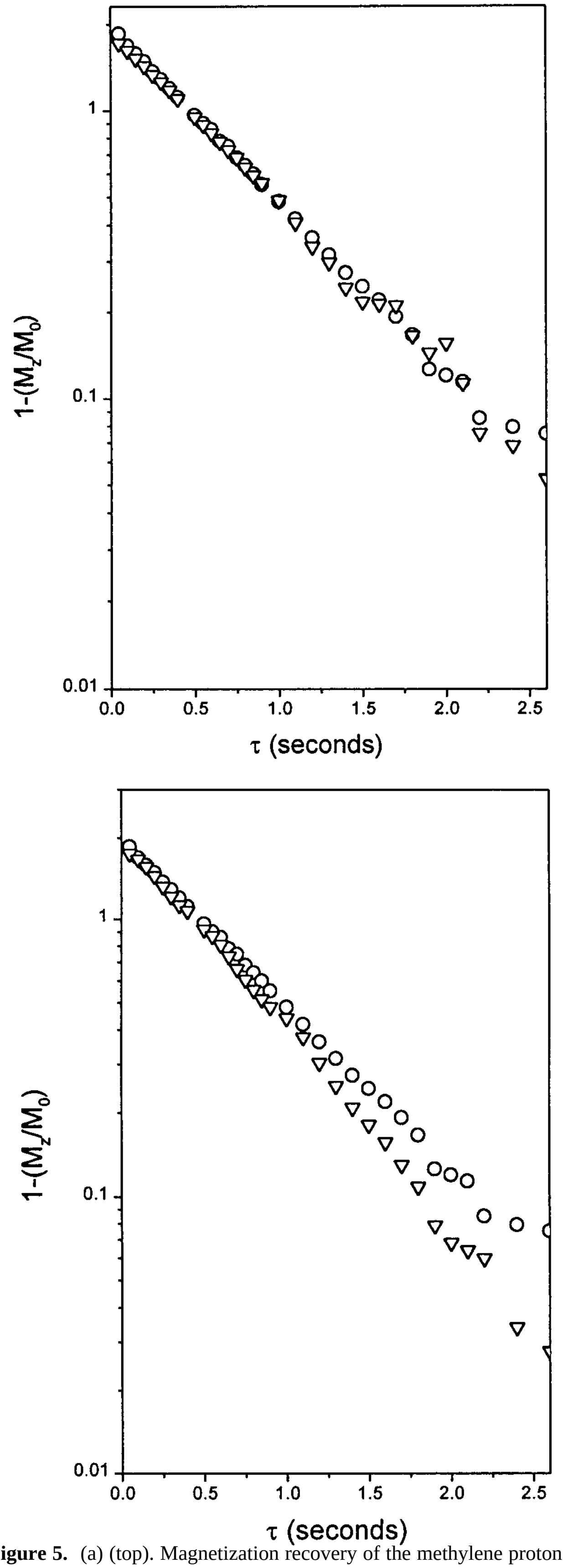

Figure 5. (a) (top). Magnetization recovery of the methylene protons from 18-crown-6 in *D_2O* solution. (○) for a 0.02 M solution of 18-crown-6 in D_2O. (▽) for a 0.5 M NaCl solution in D_2O with molar fraction $\rho = 0.04$ of 18-crown-6 to total sodium, corresponding to $[C]_T = 0.02$ mol/dm^3 **b** (bottom). (▽) magnetization recovery for a 0.5 M NaN_3 solution in D_2O containing a molar fraction $\rho = 0.04$ of 18-crown-6 corresponding to $[C]_T = 0.02$ mol/dm^3 (○) 0.02 M solution of 18-crown-6 in D_2O as in top figure.

5b. Because HDO is rapidly formed in such mixtures, the proton spin−lattice relaxation[25] becomes very long (~14 s). The difference ΔR between the relaxation rate of a 0.5 molar NaN_3 solution in H_2O-D_2O and the relaxation rate of the pure H_2O-D_2O mixture was found to be $\Delta R = 0.012$ s^{-1}**.** Thus, the upper limit of such an additional source of relaxation appears be completely negligible compared with the measured value $1/T_1(NaN_3) = 1.66$ s^{-1} obtained from Figure 5b.

The difference between Figure 5a and 5b can then be attributed to a slower molecular reorientation in the NaN_3 case compared to NaCl. Because in both cases, the correlation times for molecular reorientation are expected to be much shorter than the inverse Larmor frequency, the measured relaxation rate should be directly proportional to the correlation time.[26] Furthermore, if the translational diffusion were correlated with the molecular reorientation, the measured relaxation time would also be proportional to the diffusion coefficient[27] and the effect shown in Figure 5 could be estimated.

With these assumptions, the ratio of the measured relaxation times obtained from Figs.5b should be determined by the fraction $[C]_B/[C]_T$of complexed 18-crown-6 molecules and by the ratio of the diffusion coefficients. A simple calculation yields

$$\frac{T_1(\text{crown})}{T_1(\text{NaN}_3)} = \left[1 - \frac{P_B}{\rho}\right] + \left[\frac{P_B}{\rho}\right]\frac{D_B(\text{crown})}{D_B(\text{NaN}_3)} \tag{6}$$

where $P_B = 1 - P_F$ is given by eq 3. If one adopts $n - 1 = 6$ and a scaling of the diffusion constant inversely proportional to the square root of the masses, a value $T_1(\text{crown})/T_1(NaN_3) = 1.175$ is obtained from eq 6, in good agreement with the data of Figure 5b. On the other hand, the hydrodynamic scaling with the inverse cubic root of the masses yields, for $n - 1 = 8$, $T_1(\text{crown})/T_1(NaN_3) = 1.138$ The ratio $T_1(\text{crown})/T_1(\text{NaCl})$-can also be calculated from eq 6, assuming $n = 1$ for NaCl with both types of scaling. Both results, 1.028 and 1.018 for square root and cubic root scaling respectively, appear to also be consistent with the data of Figure 5a.

Conclusions

The above results reveal a new cooperative effect involving the reaction kinetics of sodium complexation by 18-crown-6 in aqueous solution and the formation of associated structures. Aggregates containing a surprisingly large number of cations dynamically associated with a central (Na$^+$;18-crown-6) complex, can explain our experimental results. Isoelectronic counterions such as N_3^- and SCN$^-$ are capable of stabilizing these large structures but not spherically symmetric anions such as Cl$^-$ or F$^-$. In contrast, for (Li$^+$;15-crown-5) complexes such effect could not be detected.

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