

Anion Effects on the Kinetics of Na⁺-18-Crown-6 Complexation in Tetrahydrofuran Solutions

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Abstract: The influence of anions on the kinetics of complexation of the Na⁺ ion with the crown ether 18-crown-6 was studied in tetrahydrofuran solutions by sodium-23 NMR. With BPh₄⁻ the exchange of the Na⁺ ion between the free and complexed sites is slow at room temperature and two distinct ²³Na resonances are observed in solutions which contain an excess of the Na⁺ ion. The predominant exchange mechanism is the dissociative one. However, when SCN⁻ is the counterion, the exchange is fast at room temperature and the predominant exchange mechanism is the bimolecular process. Kinetic data have been obtained by a full sodium-23 NMR line shape analysis. For the dissociative step in the NaBPh₄·18C6 system in tetrahydrofuran solution at 25 °C, $E_a = 11.9$ (0.3) kcal·mol⁻¹, $\Delta H^\ddagger = 11.3$ (0.3) kcal·mol⁻¹, $\Delta S^\ddagger = -12.5$ (1.2) eu, $\Delta G^\ddagger = 15.1$ (0.1) kcal·mol⁻¹, and $k = 53$ (6) s⁻¹. When SCN⁻ is the counterion the kinetic parameters for the bimolecular exchange process at 25 °C are $E_a = 3.4$ (0.4) kcal·mol⁻¹, $\Delta H^\ddagger = 2.8$ (0.4) kcal·mol⁻¹, $\Delta S^\ddagger = -27.0$ (1.0) eu, $\Delta G^\ddagger = 10.68$ (0.01) kcal·mol⁻¹, and $k = 91600$ (1200) M⁻¹ s⁻¹. Stable contact ion pairs are formed when SCN⁻ is the counterion that offset the charge-charge repulsion of the sodium ions in the transition state of the bimolecular exchange process and allow this mechanism to predominate. The charge-charge repulsion is not offset when BPh₄⁻ is the counterion due to minimal amount of contact ion pairing.

Information concerning complexation kinetics of macrocyclic ligands such as crown ethers or cryptands with alkali metal ions is rather sparse despite the importance of such data for the elucidation of the mechanism of complexation reactions.

Petrucci and co-workers¹ have used ultrasonic techniques to investigate complexation kinetics of alkali metal ions with the macrocyclic crown ether 18-crown-6 (18C6). Their studies provide considerable insight into the rearrangement of the ligand conformation upon complexation of alkali metal ions.

Shchori et al.² used sodium-23 NMR to study the kinetics of complexation of sodium ion with dibenzo-18C6 and its derivatives in dimethylformamide, methanol, and dimethoxyethane solutions. The authors found similar values of the activation energies for the dissociative step and concluded that the major barrier to the decomplexation is the rearrangement of the complex conformation. Only the dissociative mechanism was found to occur in all systems investigated.

We recently reported³ the first known observation of the bimolecular exchange mechanism for the K⁺ ion exchange with 18C6. In the bimolecular exchange process one K⁺ ion leaves one side of the crown ether as another enters the opposite side.

Numerous previous NMR studies of macrocyclic complexes have shown that in the case of the crown ether complexes, the room temperature cationic exchange between the free and the complexed sites is fast on the NMR time scale. Only one population-averaged signal of the metal nucleus is observed in solutions which contain an excess of the metal ion. On the other hand, the exchange is slow (at room temperature) with the tridimensional cryptates, especially when the cation in question fits snugly into the macrocyclic cavity.⁴

It was rather surprising, therefore, when we found that in the NaBPh₄-18-crown-6-tetrahydrofuran system the exchange is slow at room temperature and two distinct ²³Na resonances are observed in solutions with a Na⁺:18C6 mole ratio of 2:1. The exchange is fast, however, when I⁻ or ClO₄⁻ are used as the counterions.⁵ We describe in the present paper some of the results we obtained

in trying to find an explanation for these unexpected results.

Experimental Section

Conductance Measurements. Resistance measurements were made at 1942 Hz or at 971 Hz with a conductance bridge and oscilloscope null detector.⁶ Details are given in a previous publication.⁷ All measurements were made at 25.00 ± 0.02 °C. Cell constants were determined by using aqueous potassium chloride solutions and applying the conductance equation of Barthel et al.⁸ All samples were prepared, and the conductance cells were filled and capped in a drybox under an inert atmosphere.

Infrared Measurements. A Digilab FTS-15 FT-IR operating at 2-cm⁻¹ resolution was used for all infrared measurements. Either KBr or CaF₂ salt plates were used; cell path lengths were approximately 0.05–0.1 mm. The CaF₂ plates were used whenever sodium ion-18C6 solutions were measured since in most solvents the potassium ion complex with 18C6 has a higher stability than the sodium complex. No noticeable fogging or deterioration of the salt plates was observed after the spectra were taken. The solvent spectra were taken and then subtracted from those of the samples to eliminate interferences from the solvent bands.

NMR Measurements. Sodium-23 NMR measurements were carried out either on a Bruker WH-180 spectrometer at a field of 42.27 kG and a frequency of 47.61 MHz or on a modified⁹ Varian DA-60 spectrometer at a field of 14.09 kG and a frequency of 15.87 MHz. Sodium-23 chemical shifts are corrected for bulk magnetic susceptibility and are referenced to infinitely dilute aqueous sodium chloride solution.

Line widths were measured by fitting a Lorentzian function to the spectra or by measuring the width at half height. Two procedures were used to correct line widths for daily variations in field homogeneity depending on the instrument. When the Varian DA-60 spectrometer was used (NaBPh₄ system) the method of Ceraso et al.,¹⁰ which makes use of a line-width reference, was employed for homogeneity corrections which were always less than 3 Hz. With this technique it is possible to reference all 1/T₂ values to a known value. When the WH-180 spectrometer was employed, homogeneity was checked by comparing the line width of the uncomplexed sodium salt solution in a given solvent with previously obtained values. In general, these were always the same within experimental error (estimated total error ±10% on all line width measurements).

Temperature was measured with a calibrated Doric digital thermocouple to within ±1 °C.

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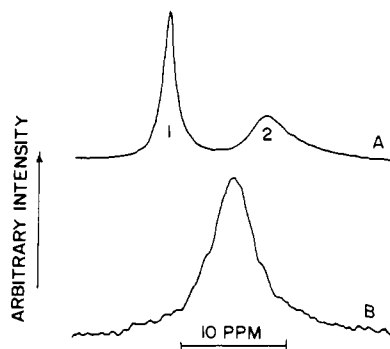


Figure 1. Room temperature sodium-23 NMR spectra of the tetrahydrofuran solutions containing [salt]/[18C6] in a mole ratio of ~ 2 : (A) NaBPh₄, (1) solvated NaBPh₄, (2) Na⁺·18C6, BPh₄⁻; (B) NaSCN salt.

Table I. Equivalent Conductances of Free and Complexed Sodium Salts in THF Solutions at 25 °C

solution	Λ (ohm ⁻¹ ·cm ² ·equiv ⁻¹)
0.1000 M NaBPh ₄	26.64
0.1004 M NaSCN	0.1414
0.0998 M NaClO ₄	0.4436
0.1001 M NaI	0.2151
0.1001 M NaBPh ₄ + 0.1108 M 18C6	14.83
0.0999 M NaSCN + 0.1123 M 18C6	2.017

Reagents and Solvents. Macrocyclic polyether 18-crown-6 (18C6, Aldrich) was precipitated as the acetonitrile complex;¹¹ the crystals were filtered and acetonitrile was removed by placing the complex under vacuum at room temperature for at least 24 h; mp 37–38 °C (lit. mp 36.5–38,¹² 39–40 °C¹³).

Sodium tetraphenylborate (NaBPh₄, Aldrich, Gold Label) was dried under vacuum at 25 °C for 24 h. Sodium thiocyanate (NaSCN, Mallinckrodt, reagent grade) was recrystallized from acetonitrile and dried under vacuum at 60 °C for 2 days.

Tetrahydrofuran (THF) was distilled from a mixture of metallic potassium and benzophenone. Water content of the solvent was always <50 ppm as determined by gas chromatography.

Results

The anion influence on the rate of exchange between the free and complexed sodium sites in tetrahydrofuran solutions is seen in Figure 1. At room temperature the exchange is slow when NaBPh₄ is the salt that is used, but fast exchange is observed when SCN⁻, ClO₄⁻, or I⁻ are the counterions. It is reasonable to assume that ion association must play a role in this phenomenon, especially since THF has a low dielectric constant ($D = 7.6$). It has been shown¹⁴ that in THF solution NaBPh₄ exists primarily in the form of solvent-separated ion pairs. Chabanel and co-workers have recently reported¹⁵ that in this solvent NaSCN forms contact ion pairs as well as higher ionic aggregates. We used conductance, infrared, and NMR techniques in order to obtain some qualitative information concerning the degree of ionic association of these salts and of their 18C6 complexes in tetrahydrofuran solutions.

Conductance. Table I lists the equivalent conductances of ~ 0.1 M solutions of sodium salts and of their complexes with 18C6. The conductance of the NaBPh₄ solution is two orders of magnitude higher than that of the other salt solutions. Presumably, this is due to the differences in ionic association found by other workers as described above.

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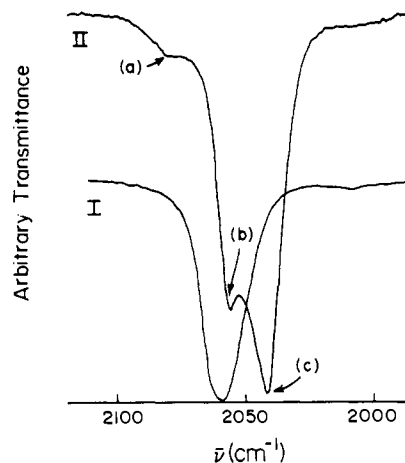


Figure 2. Room temperature infrared spectra of tetrahydrofuran solutions containing NaSCN: (I) 0.126 M NaSCN + 0.140 M 18C6, spectrum of Na⁺·18C6·NCS⁻; (II) 0.074 M NaSCN, (a) Na⁺·NCS⁻·Na⁺, (b) Na⁺NCS⁻, (c) (Na⁺NCS⁻)₂. Assignments from ref 15.

Upon complexation the NaBPh₄·18C6 solution has a slightly lower conductance than the pure salt solution. Such behavior is to be expected in the absence of contact ion pairing, since the mobility of the sodium ion would be reduced upon complexation. Thus the complexed NaBPh₄ probably exists as a crown-separated ion pair.

When NaSCN is complexed by 18C6 the conductance actually increases as compared to the pure salt solution. Presumably, this is due to the increased dissociation of contact ion pairs and of higher ionic aggregates.¹⁵ The conductance of the complexed NaSCN solution is still an order of magnitude lower than that of the complexed NaBPh₄ solution. Mobility considerations would argue in favor of the complexed NaBPh₄ solution having a lower conductivity if ion pairing is negligible since BPh₄⁻ is the larger counterion. Thus, the complexed NaSCN must be contact ion paired to some extent.

Infrared. Room temperature infrared spectra of the C–N stretching region of the SCN⁻ ion for ~ 0.1 M NaSCN solution and of its complex with 18C6 are shown in Figure 2. The spectrum of the uncomplexed salt solution agrees with that found by Chabanel et al.,¹⁵ and their band assignments are shown. It is important to note the absence of a band at 2052 cm⁻¹ which would correspond to a “free” SCN⁻ ion.^{15,16}

Upon complexation of the sodium ion by 18C6 only one band at 2058 cm⁻¹ was observed in this region. This band has been assigned to the contact ion paired SCN⁻ ion. No free SCN⁻ band is observed for this solution. As expected, the complexation of the sodium ion breaks up the higher ionic aggregates found in the pure salt solution. Thus, the conductance and infrared measurements complement each other.

Sodium-23. NMR Measurements in the Absence of Exchange. The sodium-23 nucleus has a spin $I = 3/2$ and thus a quadrupole moment. The dominant relaxation mechanism is through quadrupolar interaction modulated either by rotational diffusion of the complex or by diffusional motions of solvent molecules in and out of the solution sphere around the Na⁺ and thereby changing the electrical field gradient at the nucleus. In the case of quadrupolar relaxation in the motionally narrowed limit¹⁷ ($\omega\tau_c \ll 1$)

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

where T_1 and T_2 are the relaxation times, I is the spin of the

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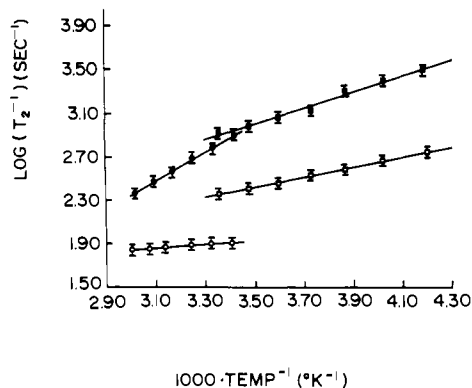


Figure 3. Semilog plots of $1/T_2$ vs. reciprocal temperatures for tetrahydrofuran solutions containing solvated and 18C6 complexed Na⁺ ion: (○) 0.2 M NaBPh₄; (●) 0.2 M Na⁺·18C6, BPh₄⁻; (□) 0.05 M NaSCN; (■) 0.05 M Na⁺·18C6, NCS⁻.

Table II. Sodium-23 NMR Parameters for Solvated and Complexed Na⁺ Ion Sites in Tetrahydrofuran Solutions at 25 °C

solution	ppm	$1/T_2$ (s ⁻¹)	E_r (kcal·mol ⁻¹)
0.2 M NaBPh ₄	-7.5	80.1	0.82
0.4 M NaBPh ₄	-7.4	96.9	0.86
0.5 M NaSCN	-2.9	225	2.1
0.2 M NaBPh ₄ ·18C6	-15.9	660	6.2
0.05 M NaSCN·18C6	-12.1	805	3.3

nucleus, η is the asymmetry parameter, Q is the quadrupole moment, $\partial^2 V/\partial Z^2$ is the Z -th component of the electric field gradient at the nucleus produced by solvent fluctuations, and τ_c is the correlation time which characterizes these fluctuations. For a simple process τ_c may be expressed by

$$\tau_c = A' \exp(E_r/RT)$$

where E_r is an activation energy for solvent reorientation.¹⁸ The relaxation process varies exponentially with temperature provided that the quadrupolar coupling constant is independent of temperature. Figure 3 shows such plots for the free and complexed NaBPh₄ and NaSCN in tetrahydrofuran solutions. In all such cases a linear plot was observed. Table II lists chemical shifts, inverse relaxation times, and activation energies for solvent reorientation for these systems at room temperature along with those of Ceraso¹⁹ for 0.4 M NaBPh₄ in THF for comparison. As discussed above the larger relaxation rates for the free NaSCN, as compared to free NaBPh₄, and for complexed NaSCN as compared to complexed NaBPh₄, as well as differences in chemical shifts and in activation energies, reflect the differences in the ion pairing of these salts and their complexes with 18C6. A faster relaxation rate is consistent with a less symmetrical environment around the nucleus which would occur if the salt was ion paired or complexed by a planar macrocycle such as 18C6. Ion pairing would also influence the chemical shifts of the nucleus. While the activation energies for solvent reorientation, E_r , are more difficult to interpret, the influence of the counterion on these values must be recognized. The slightly larger relaxation rate for NaBPh₄ in tetrahydrofuran solutions found by Ceraso¹⁹ may be simply due to the increased viscosity of the more concentrated solution.

Kinetic Studies. A full NMR line shape analysis technique was used to obtain the kinetic parameters for exchange between the free and complexed sodium sites. The equations used were of similar format as those used by Ceraso et al.¹⁰ except that some modifications were made in order to include exponential line broadening and delay time effects on the spectra.²⁰ A nonlinear least-squares program KINFIT²¹ was used to fit 70–100 points of the spectra to the NMR exchange equations in order to extract the mean lifetime, τ , at several temperatures for each system.

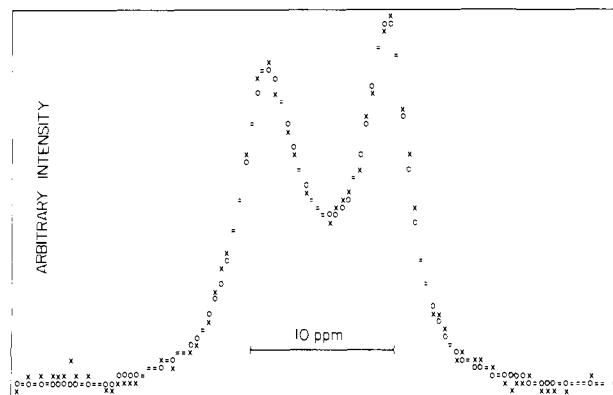


Figure 4. Example of computer fit of the NMR spectrum of a system undergoing two-site chemical exchange: (X) experimental point; (O) calculated point; (=) no difference between calculated and experimental values within experimental error.

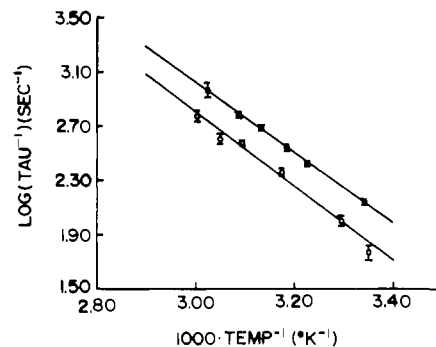


Figure 5. Semilog plot of $1/\tau$ vs. $1/T$ at various [NaBPh₄]/[18C6] mole ratios in tetrahydrofuran solutions: (○) [NaBPh₄]/[18C6] = 0.735; (●) [NaBPh₄]/[18C6] = 0.412.

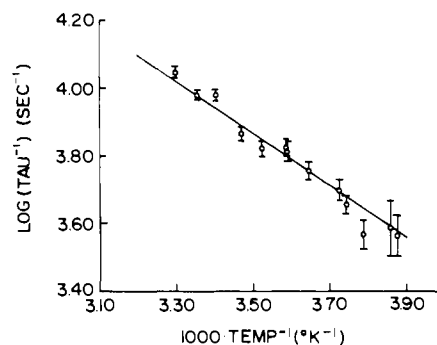
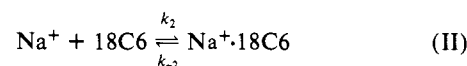
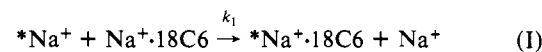


Figure 6. Semilog plot of $1/\tau$ vs. $1/T$ for [NaSCN]/[18C6] in a mole ratio of 0.475 in tetrahydrofuran solutions.

Figure 4 shows an example of such a fit.

The exchange of the sodium ion between the solvated and complexed sites may proceed via two mechanisms as proposed by Shchori et al.,² the bimolecular exchange process (I) and the dissociative mechanism (II).



The general expression for the mean lifetime in terms of these mechanisms is

$$\frac{1}{\tau} = 2k_1[Na^+]_{tot} + k_{-2} \frac{[Na^+]_{tot}}{[Na^+]_f}$$

where $[Na^+]_{tot}$ is the total concentration of the sodium salt while $[Na^+]_f$ is the concentration of the uncomplexed sodium ion. The contributions of the two mechanisms may be determined at a given

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Table III. Kinetic Parameters for Sodium Ion Complexation by 18C6 in Tetrahydrofuran Solutions at 25 °C

salt	k_d	E_a (kcal/mol)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (eu)	ΔG^\ddagger (kcal/mol)	mechanisms ^a
NaBPh ₄	53 ^b (6) ^c	11.9 (0.3)	11.3 (0.3)	-12.5 (1.2)	15.1 (0.1)	II
NaSCN	91600 ^d (1200)	3.4 (0.4)	2.8 (0.4)	-27.0 (1.0)	10.68 (0.01)	I

^aSee text for exchange mechanisms. ^bs⁻¹. ^cAll errors are standard deviation estimates. ^dM⁻¹ s⁻¹.

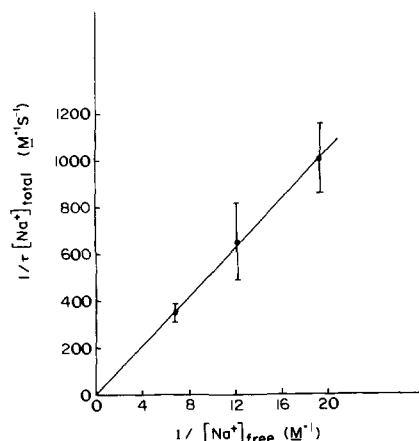


Figure 7. Plot of $1/\tau[\text{Na}^+]_{\text{total}}$ vs. the inverse of the free sodium ion concentration for NaBPh₄·18C6 in tetrahydrofuran solutions at 25 °C.

temperature by plotting $1/(\tau[\text{Na}^+]_{\text{tot}})$ vs. $1/[\text{Na}^+]_{\text{f}}$.

With either one or the other mechanism being predominant, a plot of $\log 1/\tau$ vs. $1/T$ will essentially be an Arrhenius plot (since $1/\tau \propto k_d$) with a slope proportional to the Arrhenius activation energy. Such a plot is shown in Figure 5 for two relative free populations of NaBPh₄ with 18C6 and in Figure 6 for one relative free population of NaSCN with 18C6. Actually two experiments with different relative free populations of NaSCN were carried out in THF solutions, but the plots of $\log 1/\tau$ vs. $1/T$ were the same within experimental error. One immediately notices the differences in magnitudes of the $1/\tau$ values depending on the counterion present. The difference in Arrhenius activation energies for these two systems is equally striking, as can be seen in Table III.

In order to determine which mechanism is the predominant one, plots of $1/(\tau[\text{Na}^+]_{\text{tot}})$ vs. $1/[\text{Na}^+]_{\text{free}}$ were constructed and are shown in Figures 7 and 8. As can be seen, when BPh₄⁻ is the counterion the exchange proceeds via the dissociative mechanism (the intercept is zero). This mechanism has been found to occur for Na⁺ exchange with analogues of 18C6 by Shchori et al.² in dimethylformamide, methanol, and dimethoxyethane solutions. In all cases the authors found an activation energy of approximately 12.5 kcal·mol⁻¹ and therefore concluded that the major barrier to decomplexation is the rearrangement of the complex into a conformation which allows the release of the sodium ion. However, all three solvents have similar donor numbers ($\text{DN}_{\text{DMF}} = 26.6$,²² $\text{DN}_{\text{MeOH}} = 25.7$,²³ $\text{DN}_{\text{DME}} = 24$)²⁴ and, therefore, the solvent influence on the activation energy for this process is not fully understood. For the system NaBPh₄·18C6 in THF the activation energy also falls in the range found by Shchori and co-workers. In this solvent

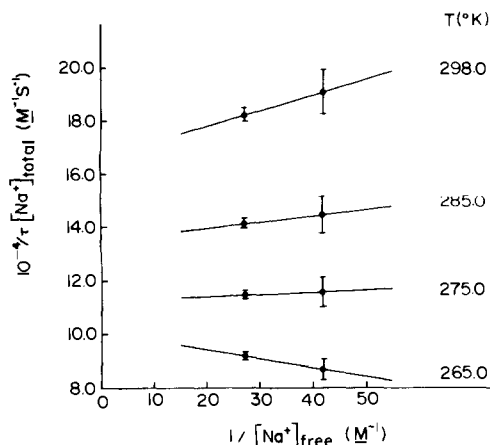


Figure 8. Plots of $1/\tau[\text{Na}^+]_{\text{total}}$ vs. the inverse of the free sodium ion concentration for NaSCN·18C6 in tetrahydrofuran solutions at several temperatures.

the donor number is lower than those used by Shchori et al. ($\text{DN}_{\text{THF}} = 20.0$). It seems that more work is needed in order to elucidate the influences of the solvent properties on the exchange kinetics.

The slope of the plot shown in Figure 8 is zero within experimental error. Thus the bimolecular exchange mechanism is the predominant one when SCN⁻ is the counterion. This is the first known observation of this mechanism for sodium ion exchange with 18C6, although we have recently observed the bimolecular process for K⁺ exchange with 18C6.³

Once the mechanisms were known, the rate parameters listed in Table III for the two systems were calculated from the Eyring theory. The anion or, more precisely, the degree of ion pairing determines which mechanism is predominant. In the transition state of the bimolecular exchange mechanism two sodium ions must approach each other. Because NaSCN and its complex with 18C6 are strongly ion paired, the charge-charge repulsion which must exist in the transition state is reduced. When BPh₄⁻ is the counterion the charge-charge repulsion is not offset, and thus the dissociative mechanism is preferred.

Conclusions

Ion pairing influences which exchange mechanism predominates for sodium ion exchange with 18C6 in tetrahydrofuran. When strong ion pairing occurs the bimolecular exchange process is preferred. Otherwise, the dissociative mechanism will predominate.

We are continuing our investigations concerning anion and solvent influences on alkali metal ion-18C6 complexation kinetics.

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Registry No. Na, 7440-23-5; NCS⁻, 302-04-5; BPh₄⁻, 4358-26-3; 18-crown-6, 17455-13-9.

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