Kinetics of Complexation of Macrocyclic Polyethers with Alkali Metal Ions. I. ^{23}Na Nuclear Magnetic Resonance of Sodium Dibenzo-18-crown-6 in *N,N*-Dimethylformamide

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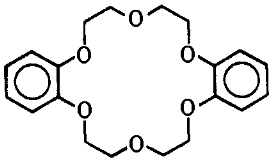
Abstract: A kinetic study of the complexation reaction of sodium ions with dibenzo-18-crown-6 (DBC) in DMF, using ^{23}Na nmr spectroscopy, is reported. The chemical shifts of ^{23}Na in the solvated sodium and in the DBC complex are very nearly the same, but due to the lack of cubic symmetry around sodium in the complex, fast quadrupole relaxation causes the line width in this species to be much broader (about 25 times) than in solvated sodium. In solutions containing both species, there is sodium exchange between the two. In the temperature range between -30 and 0°, the rate of this exchange is of the order of the relaxation rate of the ^{23}Na nuclei, thus affecting the nmr line shape. A quantitative analysis of the line shape yields values for the mean lifetimes of sodium in the two species. Measurements were performed in solutions containing 0.3–1.9 *M* NaSCN and 0.1–0.2 *M* DBC in the temperature range -60 to $+80$°. The ionic strength was adjusted by using LiSCN. In some runs BPh_4^- was used as a counteranion instead of SCN^-. Analysis of the concentration dependence of the results indicates that the dominant exchange mechanism involves the complexation equilibrium $Na^+ + DBC \rightleftarrows Na^+, DBC$. The pseudo-first-order rate constant for the decomplexation reaction at 25°, extrapolated to zero ionic strength, and the activation energy are found to be $\sim 10^5$ sec^{-1} and 12.6 ± 0.6 kcal/mol, respectively. The equilibrium constant for the complexation reaction was determined conductometrically between 0 and 40°. It is found to be $\sim$600 M^{-1} at 25° with $\Delta H = -6$ kcal/mol and $\Delta S = -7$ eu. From these results, the rate constant of the complexation reaction at 25° is estimated to be 6×10^7 M^{-1} sec^{-1}, with an activation energy of 6.5 kcal/mol.

Macrocyclic polyethers synthesized by Pedersen[1–3] have drawn considerable interest because of their activity, in promoting selective transport of alkali metal ions[4–8] and as catalysts in reactions involving ionic intermediates.[9] It has been suggested[2] that the formation of a complex between an alkali metal cation and a macrocyclic polyether is due to ion–dipole interactions and is, therefore, similar in nature to ordinary solvation, although more favorable because of the appropriate configuration and the polydentate character of the ligand. The specificity of the complexation is due to the required fit between the ionic radius and the size of the macrocyclic ring; nevertheless, it may be affected by the medium,[10] as the macrocyclic polyether must compete with the surrounding solvent for the cation.

The thermodynamics of formation of these ionic complexes in various solvents has recently been investigated by several authors.[11,12] Kinetic data are, however, scarce, despite their fundamental importance for the understanding of the mechanisms of transport and catalytic phenomena involving macrocyclic complexes. The rates involved in these reactions are often very fast and fall in the range accessible only by the relaxation methods or by the nmr line-broadening technique. The use of pmr of ligand nuclei is however limited by the small chemical shifts between the complexed and uncomplexed forms.[13,14] An interesting special case is that of the complexation of dimethyldibenzo-18-crown-6 with fluorenylsodium ion pair. In this case, the fluorenyl ring currents cause large chemical shifts of the ligand protons, thus allowing kinetic measurements to be made.[10]

Nmr spectroscopy of the cations seems to offer a more general approach to the investigation of the kinetics of complexation. However, while nmr studies of sodium and other alkali metal ions in various solvents have been carried out,[15–21] and in a recent study the effect of complexation with ionophores on the ^{23}Na line width was discussed,[22] no quantitative kinetic measurements based on the analysis of ^{23}Na nmr lines have yet been reported. In this paper we report results of kinetic measurements of the complexation of sodium ions with dibenzo-18-crown-6 (DBC) in



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N,*N*-dimethylformamide (DMF) using ^{23}Na nmr. The kinetic study is based on the fact that, although there is no appreciable chemical shift between solvated sodium and sodium complexed with DBC, there is a very large difference in the nuclear relaxation rates of ^{23}Na in the two species. In the complexed form, deviations from cubic symmetry around the sodium ion result in fast quadrupole relaxation and thus in a very broad nmr line, while a relatively narrow line is obtained for ^{23}Na in the more symmetric solvated form. In solutions containing both species, in the absence of exchange, the ^{23}Na signal is a superposition of the two lines, but when the rate of exchange between the two species is comparable to their line width (in sec^{-1}), the nmr signal is modified and may be used to derive kinetic parameters for the exchange reaction.

Nmr of ^{23}Na in other macromolecular systems as well as nmr of other alkali metal ions may give similar effects. Exchange between bound and solvated ions may be particularly important for the interpretation of ^{23}Na nmr data in biological systems.[23]

Experimental Section

Dibenzo-18-crown-6 (DBC) was prepared according to the procedure described by Pedersen.[1] A purification procedure based on the specific complexation of DBC was applied in order to remove residual impurities: DBC was dissolved in a methanolic solution of KSCN, filtered, and precipitated with water. The precipitate was washed with water to a negative test for thiocyanate ions, dried, and recrystallized from benzene. The pmr spectrum of the purified compound gave a ratio of 2.00 ± 0.05 of the aliphatic to the aromatic hydrogens compared to 2.15 ± 0.05 in the unpurified material. Conductance measurements of solutions of the purified DBC in DMF indicated absence of residual salts.

N,*N*-Dimethylformamide (DMF) (Fluka A. G., Switzerland, puriss) was dried over Molecular Sieves 4A and distilled under reduced pressure.

Lithium thiocyanate was prepared from $Ba(SCN)_2$ and Li_2SO_4 (BDH reagent grade) by precipitation of $BaSO_4$ from aqueous solution. Sodium thiocyanate (Baker, reagent grade) and sodium tetraphenylboron (Fluka A. G., Switzerland, puriss-p.a.) were used. All salts were dried on a high-vacuum line at 90°. The solutions were checked for traces of water before and after experiments. An F and M gas chromatograph with a 1-ft column filled with "para pack" type Q was used for these determinations. The water content was less than 0.1% in all samples.

Viscosities of solutions were measured with an Ubbelohde viscosimeter. Their conductance was determined in a 0.635-cm conductivity cell with a CDM-2 conductivity meter (Radiometer, Denmark).

The ^{23}Na nmr measurements were done on a Varian DP-60 nmr spectrometer operating at 8.13 MHz (7.22 kG) and using 5-mm O.d. sample tubes. The transverse relaxation rates were derived from the absorption spectra using 1980-Hz field modulation or from their derivatives using low-frequency modulations. Measurements were made between −60 and +80°. The temperature was monitored using a thermocouple housed in a thin capillary and inserted in the solution. During measurements a constant temperature was maintained within ±1°. Line widths were determined with an estimated accuracy of ±10% as an average of three to five successive runs.

Equilibrium Constant of Complexation

The equilibrium constant of the complexation reaction in DMF was determined conductometrically.

$$\mathrm{Na^+ + DBC \overset{K}{\rightleftharpoons} Na^+, DBC} \qquad (1)$$

Measurements were made on solutions containing approximately 10^{-3} *M* NaSCN and various amounts of DBC, up to saturation, at 0, 15, 30, and 40°. In Table I are summarized results for the apparent equivalent conductance, normalized to constant viscosity, $\Lambda = (\lambda/[\mathrm{Na^+}]_0)(\eta_0/\eta)$, where λ is the conductance of the solution, $[\mathrm{Na^+}]_0$ the total sodium concentration, η the viscosity of the solution, and η_0 the viscosity of a NaSCN solution of the same concentration but containing no DBC. The equilibrium constants were calculated by consecutive approximations from the equation

$$(\Lambda_A - \Lambda)/[\mathrm{DBC}]_e = K(\Lambda - \Lambda_B) \qquad (2)$$

where $[\mathrm{DBC}]_e = [\mathrm{DBC}]_0 - [\mathrm{Na}]^+{}_0(\Lambda_A - \Lambda)/(\Lambda_A - \Lambda_B)$ is the equilibrium concentration of DBC, Λ_A is the equivalent conductance of NaSCN, and Λ_B is the normalized equivalent conductance of the complex (*cf.* Table I). A typical plot of $(\Lambda_A - \Lambda)/[\mathrm{DBC}]_e$ *vs.* Λ is shown in Figure 1 and the plot of log *K* *vs.* $1/T$ is shown in Figure 2. From the latter, the following thermodynamics parameters for reaction 1 were estimated: $\Delta H = -6$ kcal/mol and $\Delta S = -7$ eu. It is interesting to note that, in spite of the fact that the complexation involves replacement of several molecules of DMF by a single molecule of DBC, the overall entropy of the process is negative. Apparently, sodium ions act in DMF solutions as "structure breakers," and the formation of a planar Na$^+$,DBC complex results in an overall increase of organization in the solution. For aqueous and methanolic solutions, negative entropies of complexation of dicyclohexyl-18-crown-6 with alkali metal ions have recently been reported by Izatt, *et al.*[11] The difference in the mobility between solvated and complexed species (*cf.* Table I) indicates that the cross section of the complex is about 20% larger than that of solvated sodium.

Table I. Equivalent Conductance of ~10^{-3} *M* Solutions of NaSCN in DMF in the Presence of DBC[a]

10^3 $[\mathrm{DBC}]_0$, *M*	Λ (0°)	Λ (15°)	Λ (30°)	Λ (40°)
0	60.1[b]	73.85[b]	90.55[b]	101.55[b]
0.5	58.75	72.25		
1	57.75	71.15	88.1	
2	56.25	69.65	86.9	97.6
4	55.2	68.2	85.35	95.7
6			84.25	
8	54.75	67.35	83.7	94.0
10			83.4	
14		67.1		
20	54.4		82.9	92.8
35		66.6		
50			82.3	92.65
∞	54.2[c]	66.45[c]	82.0[c]	91.5[c]

[a] Values of Λ are in ohm^{-1} equiv^{-1} cm^2 corrected for viscosity changes due to addition of DBC. [b] Value of Λ_A. [c] Extrapolated value corresponding to Λ_B.

As expected, from results reported in the literature for other solvents,[1,2] complexation of LiSCN with DBC in DMF is negligible. Addition of DBC to solutions of LiSCN in DMF does not lead to any significant change in the normalized conductance. Lack of complexation of Li$^+$ by DBC has also been checked by solubility measurements. At room temperature, no detectable increase of the solubility of DBC in DMF could be obtained in the presence of 0.2–1 *M* LiSCN. It may therefore be concluded that $K_{\mathrm{Li}}{}^{25°} < 1$, hence $K_{\mathrm{Na}}/K_{\mathrm{Li}} \gg 100$.

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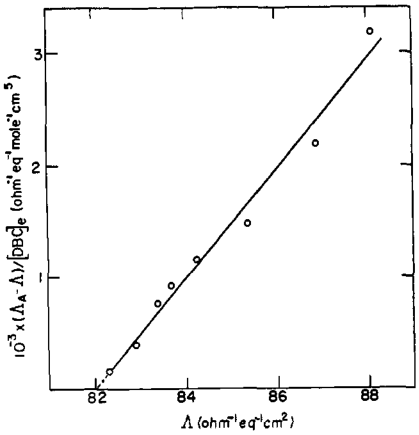

Figure 1. Plot of $(\Lambda_A - \Lambda)/[DBC]_e$ *vs.* Λ, temperature 30°.

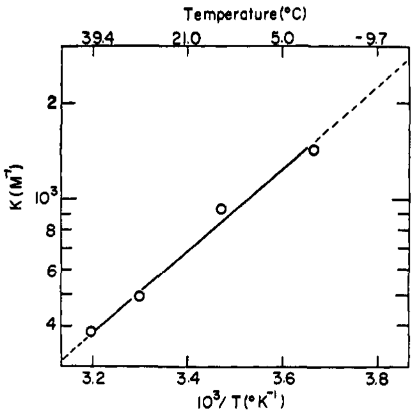

Figure 2. Semilog plot of the complexation constant, *K*, *vs.* reciprocal absolute temperature.

^{23}Na Nmr of Solvated and Complexed Sodium in the Absence of Chemical Exchange

In order to understand the results of the kinetic measurements discussed in the next section, the ^{23}Na nmr lines of solvated and complexed sodium in the absence of exchange are described. As indicated in the introduction, the dominant mechanism of the ^{23}Na relaxation in diamagnetic solutions is the modulation of the quadrupole interaction *via* molecular tumbling. For ^{23}Na ($I = {}^3/_2$), the nuclear relaxation rates (in the extreme narrowing limit) are given by[24]

$$1/T_2 = 1/T_1 = (1/10)(eqQ/\hbar)^2\tau \propto (\eta/T) \qquad (3)$$

where τ is the correlation time for the molecular tumbling and $(eqQ/\hbar)$ the quadrupole interaction. The ^{23}Na transverse relaxation rate of solvated sodium $(1/T_{2A})$ was studied in DMF solution of NaSCN ranging in concentration from 0.3 to 1.9 *M*, while that of ^{23}Na in the complexed form $(1/T_{2B})$ was obtained from 1:1 solutions of NaSCN and DBC containing 0.05–1 *M* of each. The concentration dependence (Table II) and temperature dependence (Figure 3) of $1/T_{2A}$ and $1/T_{2B}$ are both consistent with eq 3. As may be seen from Table II, the large increase in the line width with increasing concentration can be satisfactorily accounted for in terms of increasing viscosities of the solutions: when normalized to the viscosity of the neat solvent (η_0), the line widths are very nearly independent of concentration. The normalized line width in the DBC complex is about 25 times larger than in the solvated form.

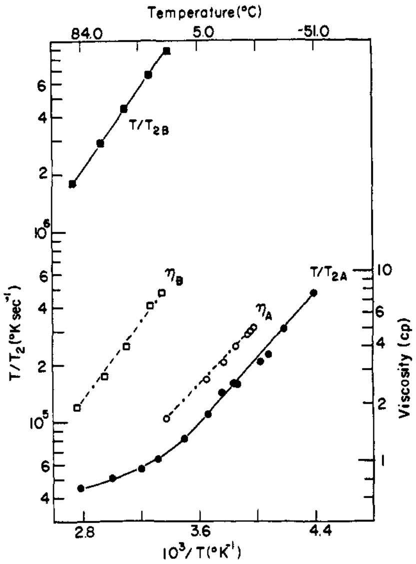

Figure 3. Semilog plots of T/T_2 (for ^{23}Na) and viscosity, η, *vs.* reciprocal absolute temperature in DMF: (○, ●) 1 *M* solution of NaSCN, (□, ■) 1 *M* solutions of the complex.

Table II. Viscosities and Transverse Relaxation Rates

Concn, *M*	η, cP	$1/T_2$, sec^{-1}	$\eta_0/T_2\eta$, sec^{-1}
(a) NaSCN in DMF at 27.5°			
0.0	0.767		
0.3	0.96	145	119
0.5	1.10	151	109
0.6	1.19	160	107
1.0	1.56	210	107
1.5	2.19	305	110
2.0	3.66	380	83
(b) Ionic Complex (NaSCN-DBC) in DMF at 21.5°			
0.0	0.830		
0.05	0.900	2760	2550
0.1	0.975	3150	2680
0.2	1.152	3450	2490
0.3	1.375	3950	2380
0.4	1.69	5100	2500
0.5	2.10	6900	2720
0.6	2.65	7900	2480
0.8	4.21	14400	2840
1.0	9.10	28000	2560

Plots of log T/T_{2B} and log T/T_{2A} *vs.* $1/T$ (Figure 3) give straight lines with slopes nearly identical with those obtained from plots of log η *vs.* $1/T$, as expected from eq 3. The only significant deviations occur for $1/T_{2A}$ at high temperatures, possibly due to some ion pairing which might take place in such fairly concentrated solutions.

An attempt was made to measure the chemical shift of ^{23}Na in the complex relative to that in the solvated form. This was done by recording alternately the ^{23}Na signal in the two solutions. Although the uncertainty of these measurements is quite large, because of broadness of the signal due to the complex, it appears that the shift is negligibly small compared to the line width. An average of ten measurements

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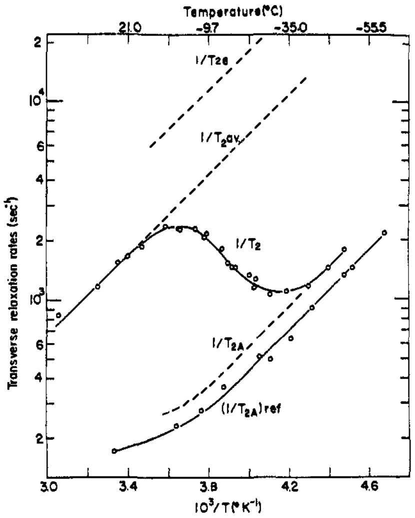

Figure 4. Semilog plots of $1/T_2$ for ^{23}Na *vs.* reciprocal absolute temperature in a DMF solution containing 0.57 *M* NaSCN and 0.2 *M* DBC, and of $(1/T_{2A})_{ref}$ for a 0.57 *M* solution of NaSCN: (---) extrapolated as described in the text, (—) calculated from eq 6c.

gave -50 ± 100 Hz (at 8.13 MHz). Shifts of similar order of magnitude have been reported for $^{23}Na^+$ nmr between DMF and ethereal solvents,[16,17] as well as for sodium complexes with ionophores.[22]

Kinetic Measurements

Kinetic data for the exchange of sodium between the DBC complex and the solvated form were obtained from the temperature dependence of the ^{23}Na nmr solutions containing both species. The solutions contained at least a threefold excess of NaSCN over DBC; thus, the concentration of the complexed form is practically identical with $[DBC]_0$, the initial concentration of DBC. In all solutions only a single resonance, assumed to be Lorentzian, was observed under normal experimental conditions. A typical semilog plot of $1/T_2$, the observed ^{23}Na nmr line width, *vs.* reciprocal absolute temperature, $1/T$, for a solution containing 0.2 *M* DBC and 0.57 *M* NaSCN is shown in Figure 4. It may be seen that with increasing temperature $1/T_2$ first decreases, then passes through a minimum at $\sim -30°$, a maximum at $\sim 0°$, and again decreases monotonically at higher temperatures. This behavior is indicative of chemical exchange, which in the present case must involve sodium exchange between the complexed and solvated forms and can be understood in the following way. Below $-40°$ the exchange rate is too slow to affect the nmr spectrum; there are two resonances, of which only the narrow one, due to the solvated species, is observed—the intensity of the broad line due to the complexed sodium being negligible under the experimental conditions. In this temperature range the values of $1/T_2$ are similar to those of $(1/T_{2A})_{ref}$ of a reference NaSCN solution of the same concentration but without DBC added. The small difference between $1/T_2$ and $(1/T_{2A})_{ref}$ is due to differences in viscosities of the two solutions. At the other extreme above $+10°$ the exchange rate is very fast and the nmr spectrum consists of a single line with a width equal to the weighted average width in the two magnetic environments.

In the intermediate region between -40 and $+10°$, the rate of exchange is of the order of the nuclear relaxation rate. In this range the kinetic parameters for the exchange reaction can be derived by a quantitative analysis of the nmr line using the Bloch–McConnell equations. In our case the chemical shift between the two magnetic environments is negligible compared to the relaxation rates, and the Bloch–McConnell equations for the steady-state transverse magnetizations, M_+, in the absence of saturation become particularly simple

$$\left(i\omega + \frac{1}{T_{2A}} + \frac{1}{\tau_A}\right)M_+^{A} - \frac{1}{\tau_B}M_+^{B} = iCP_A \quad (4a)$$

$$\left(i\omega + \frac{1}{T_{2B}} + \frac{1}{\tau_B}\right)M_+^{B} - \frac{1}{\tau_A}M_+^{A} = iCP_B \quad (4b)$$

where C is a constant proportional to the rf field intensity, ω is the frequency relative to the line center, P_A and P_B are the fractional populations of Na^+ in the solvated and complexed environments, and τ_A and τ_B are the mean lifetimes of the corresponding species. The solution of these equations for the nmr line-shape function $I(\omega) \propto \mathrm{Im}(M_+^{A} + M_+^{B})$ is

$$I(\omega) \propto \frac{P_A'T_{2A}'}{1 - \omega^2 T_{2B}'^2} + \frac{P_B'T_{2B}'}{1 - \omega^2 T_{2B}'^2} \quad (5)$$

which corresponds to a superposition of two Lorentzians with apparent intensities and widths given by

$$P_A' = 1 - P_B' \quad (6a)$$

$$P_B' = (^1/_2 - (^1/_2)[(1/\tau_B - 1/\tau_A)(1/T_{2A} - 1/T_{2B}) + 1/\tau_A + 1/\tau_B]/[(1/T_{2A} - 1/T_{2B} + 1/\tau_A - 1/\tau_B)^2 + 4/\tau_A\tau_B]^{1/2} \quad (6b)$$

$$1/T_{2A}' = (^1/_2)\{1/T_{2A} + 1/T_{2B} + 1/\tau_A + 1/\tau_B - [(1/T_{2A} - 1/T_{2B} + 1/\tau_A - 1/\tau_B)^2 + 4/\tau_A\tau_B]^{1/2}\} \quad (6c)$$

$$1/T_{2B}' = (^1/_2)\{1/T_{2A} + 1/T_{2B} + 1/\tau_A + 1/\tau_B + [(1/T_{2A} - 1/T_{2B} + 1/\tau_A - 1/\tau_B)^2 + 4/\tau_A\tau_B]^{1/2}\} \quad (6d)$$

An equivalent solution to eq 5 was previously given by Woessner[25] for the decay of the magnetization in pulse experiments and was applied by Woessner and Zimmerman[26] to the study of motional phenomena of molecules adsorbed on silica gel. Equations 6 are in the same form as those derived by Woessner and Zimmerman. In our system the concentrations were chosen so that $P_A/P_B \geqslant 2$; since $T_{2A} \gg T_{2B}$ it follows from eq 6 that $P_A'T_{2A}' \gg P_B'T_{2B}'$ over the whole range of τ's. Hence $I(\omega)$ is given approximately by a single Lorentizian with a half-width $1/T_2 = 1/T_{2A}'$. The experimental results, such as those illustrated in Figure 4, are consistent with this equation and can be used in the intermediate region to determine the exchange rate. Rearrangement of eq 6c based on the equilibrium condition $P_A/\tau_A = P_B/\tau_B$ yields the following expression for $1/\tau_A$

$$\frac{1}{\tau_A} = \frac{(1/T_{2B} - 1/T_2)(1/T_2 - 1/T_{2A})P_B}{(1/T_{2av} - 1/T_2)} \quad (7)$$

where

$$1/T_{2av} = P_A/T_{2A} + P_B/T_{2B} \quad (8)$$

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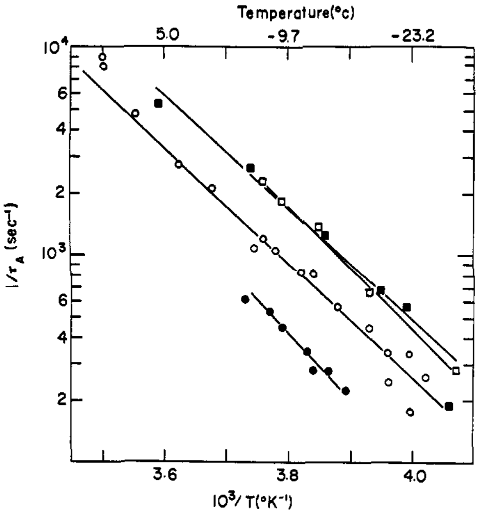

Figure 5. Arrhenius plots of $1/\tau_A$ in DMF solutions of constant ionic strength (1 *M*): (■) $[NaSCN]_0 = 0.29$ *M*, $[LiSCN]_0 = 0.7$ *M*, $[DBC]_0 = 0.1$ *M*; (□) $[NaSCN]_0 = 0.57$ *M*, $[LiSCN]_0 = 0.4$ *M*, $[DBC]_0 = 0.2$ *M*; (○) $[NaSCN]_0 = 0.96$ *M*, $[DBC]_0 = 0.2$ *M*; (●) $[NaSCN]_0 = 0.98$ *M*, $[DBC]_0 = 0.1$ *M*.

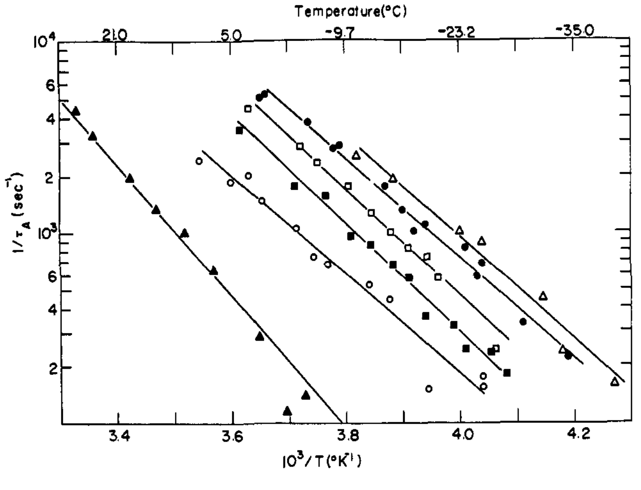

Figure 6. Arrhenius plots of $1/\tau_A$ in DMF solutions with ionic strength varying from 0.3 to 1.9 *M*: (△) $[NaSCN]_0 = 0.29$ *M*, $[DBC]_0 = 0.1$ *M*; (●) $[NaSCN]_0 = 0.57$ *M*, $[DBC]_0 = 0.2$ *M*; (□) $[NaBPh_4]_0 = 0.57$ *M*, $[DBC]_0 = 0.2$ *M*; (■) $[NaSCN]_0 = 0.59$ *M*, $[DBC]_0 = 0.1$ *M*; (○) $[NaBPh_4]_0 = 0.58$ *M*, $[DBC]_0 = 0.1$ *M*; (▲) $[NaSCN]_0 = 1.89$ *M*, $[DBC]_0 = 0.2$ *M*.

Computation of $1/\tau_A$ from eq 7 is very convenient because all its parameters can be read directly off plots of the type shown in Figure 4. The following procedure is used. (i) It is assumed that $1/T_{2A}$ in the solution has the same temperature dependence as $(1/T_{2A})_{ref}$. $1/T_{2A}$ in the intermediate range is then obtained by extrapolation of the low-temperature values of $1/T_2$ (lower dashed curve in Figure 4). (ii) Since at high temperatures $1/T_2 = 1/T_{2av}$, the latter is obtained by extrapolation of the high-temperature values of $1/T_2$ in parallel to the $1/T_{2A}$ line (middle dashed curve in Figure 4). (iii) Values of $1/T_{2B}$ are obtained from $1/T_{2A}$, $1/T_{2av}$, and the known fractional concentrations P_A and P_B using eq 8 (upper dashed curve).

Semilog plots of $1/\tau_A$ *vs.* $1/T$ for the solutions studied are shown in Figures 5 and 6. A linear relationship is expected, since in our system P_B is virtually independent of the temperature. The evident linearity of the plots in the figures is gratifying. From the slopes of these curves (except for the 1.9 *M* solution) an average activation energy of 12.6 ± 0.6 kcal/mol is calculated. In Table III are summarized the results for $1/\tau_A$ at −13° for all the solutions studied. In these experiments the NaSCN concentration is in the range 0.3–1.9 *M* and the DBC concentrations are 0.1 and 0.2 *M*. Also given are results of experimental runs in which the total ionic strength was held constant at 1 *M* by adding LiSCN and results of experiments in which sodium tetraphenylboron was used instead of NaSCN. The kinetic results for −13° are considered to be the most reliable, since at this temperature the nmr line width in all experiments was sensitive to the exchange rate. These results are used in the next section to discuss the possible mechanism of the exchange reaction.

Table III. Apparent Activation Energies of Decomplexation and Reciprocal Mean Lifetimes of Sodium Ions in DMF at −13°

Expt	$[Na^+]_0$,[a] *M*	$[DBC]_0$, *M*	$\frac{1}{\tau_A}$ (−13°), sec^{-1}	E_{app}, kcal/mol
1	0.96	0.2	660	12.7
2	0.98	0.1	295	
3	0.57[b]	0.2	1230	13.5
4	0.29[b]	0.1	1250	12.5
5	0.29	0.1	2350	12.3
6	0.57	0.2	1800	12.0
7	0.57	0.2	1220	12.8
8	0.59	0.1	800	13.3
9	0.58	0.1	445	12.0
10	1.89	0.2	62[c]	16.3

[a] SCN^- was used as a counteranion except in experiments 7 and 9, in which BPh_4^- was used. [b] Solution maintained at constant ionic strength of 1 *M* by addition of LiSCN. [c] Extrapolated value.

Mechanism of Exchange

Two possible routes for the exchange of sodium between the solvated and the complex forms may be visualized

$$^*Na^+,n(DMF) + Na^+,DBC \overset{k_1}{\rightleftharpoons} {}^*Na^+,DBC + Na^+,n(DMF) \qquad (I)$$

$$Na^+,n(DMF) + DBC \underset{k_{-2}'}{\overset{k_2}{\rightleftharpoons}} Na^+,DBC + n(DMF) \qquad (II)$$

The specific rate of sodium exchange in the solvated species is accordingly given by

$$1/\tau_A = k_1[B] + k_{-2}'[DMF]^n[B]/[A] \qquad (9)$$

where [B] and [A] are concentrations of complexed and solvated sodium ions, respectively.

Rates of reactions involving ionic species may be strongly affected by the ionic strength of the solution. Assuming that at a constant ionic strength the activities of various species in the solution are independent of its composition, we may determine the relative importance of mechanisms I and II by plotting $1/\tau_A[B]$ *vs.* $1/[A]$. Such a plot yields indeed a straight line when a constant ionic strength is maintained by addition of appropriate amounts of LiSCN (see full line in Figure 7). The zero intercept of this line indicates that the contribution of mechanism I to $1/\tau_A$ is negligible. From Figure 7 an upper limit of 10^3 M^{-1} sec^{-1} can be estimated for k_1. The relative small contribution of route I is consistent with the fact that it requires a collision between identically charged species.

Comparison of experiments with identical sodium concentrations but with and without LiSCN shows that

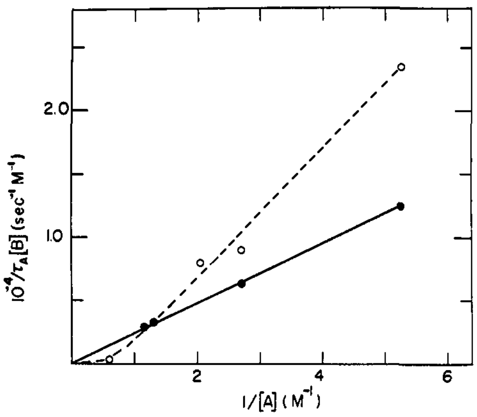

Figure 7. Plot of $1/\tau_A[B]$ *vs.* reciprocal concentration of uncomplexed sodium thiocyanate (temperature −13°): (●) solutions with constant ionic strength (1 *M*), (○) solutions with ionic strength varying between 0.3 and 1.9 *M*.

addition of the second salt slows down the rate of exchange (see Figure 7 and experiments 3–6 in Table III). Since it was shown above that lithium ions do not compete effectively with sodium ions for DBC ($K_{Li^+}/K_{Na^+} \ll 100$), this result must be ascribed to changes in activity and/or to ion pairing. Conductivity measurements indicate that even in 1 *M* solutions the fraction of ion pairs is not very large, and the constancy of the apparent activation energies E_{app} (Table III and Figures 5 and 6) seems to rule out any significant changes of ionic association due to decrease in temperature or concentration. It appears therefore that the effect of ionic strength on the rate constant is due to changes of activities rather than to ion pairing. In terms of the transition-state theory the observed rate constant k_{-2}' is given by $K^{\ddagger}(kT/h)(y^{n}_{DMF}y_{NaDBC}/y^{\ddagger})$, where $K^{\ddagger}$ is the equilibrium constant for the formation of the activated complex and the y's are molar activity coefficients. Assuming that the activity coefficients of the charged species are approximately the same, it follows that the change in solvent activity must be the most important factor responsible for the decrease of k_{-2}' with increasing electrolyte concentration. The results obtained with sodium tetraphenylboron solutions are instructive in this respect. Replacement of the relatively small SCN$^-$ anion ($a \simeq 2.4$ Å) by the very bulky tetraphenylboron anion ($a \simeq 5.0$ Å) leads to a considerable decrease in the rate of exchange (see Table III, experiments 6 and 8 *vs.* 7 and 9). For a 0.6 *M* solution of 1:1 electrolyte one calculates 11.2 Å for the average interionic distance. Hence, the very bulky tetraphenylboron anion may hinder the reorganization of solvent molecules in the vicinity of the sodium complex more effectively than the small SCN$^-$ ion, thus decreasing the activity of the solvent. The pseudo-first-order rate constant of the decomplexation reaction ($k_{-2} = k_{-2}'[\mathrm{DMF}]^n$) was obtained by a graphical extrapolation of the kinetic results to infinite dilution of the electrolyte, giving k_{-2}^0 (−13°) = 4.8×10^3 sec^{-1}. Extrapolation to room temperature based on the activation energy of decomplexation, 12.6 kcal/mol, yields k_{-2}^0 (25°) = 1.0×10^5 sec^{-1}. From the results for K (Figure 2), it follows that the activation energy of the complexation reaction (forward of mechanism II) is 6.5 kcal/mol and $k_2^0(25°) \simeq 6 \times 10^7$ M^{-1} sec^{-1}, which is of the same order as that reported recently by Eigen, *et al.*[27] (3×10^8 M^{-1} sec^{-1}), for the complexation of the biologically active macrocyclic ligand monactin with sodium in methanol. On the other hand, complexation reactions of sodium ions with the cage-like "cryptates" in aqueous solutions studied recently by Lehn, *et al.*,[28] appear to be several orders of magnitude slower.

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