

Influence of Solvent Properties on the Kinetics of Complexation of the Sodium Ion with 18-Crown-6

Bruce O. Strasser and Alexander I. Popov*

Contribution from the Department of Chemistry, Michigan State University, East Lansing, Michigan 48824. Received December 17, 1984

Abstract: The kinetics of complexation of the Na⁺ ion with the crown ether 18-crown-6 (18C6) were studied by sodium-23 NMR in neat methanol and propylene carbonate solutions as well as the tetrahydrofuran-methanol (60-40 mol %) and tetrahydrofuran-propylene carbonate (80-20 and 40-60 mol %) mixtures. Dissociative exchange mechanism was found in neat methanol, the THF-MeOH, and the 80-20 mol % THF-PC mixtures. On the other hand, in neat propylene carbonate and in 40-60 mol % THF-PC the bimolecular exchange mechanism predominates. Kinetics data, E_a , ΔG^\ddagger , ΔH^\ddagger , and ΔS^\ddagger were determined in the above systems by sodium-23 line shape analysis. A correlation has been found between the Gutmann donor number of the solvent and the free energy of activation, ΔG_{-2}^\ddagger , for the dissociative step in systems where the dissociative mechanism predominates.

Since Pedersen's first report on the synthesis and complexing properties of macrocyclic polyethers,¹ this field of research has become very popular, and well over 2100 macrocyclic ligands have been synthesized by 1981.² Complexing abilities of many of these ligands, primarily toward the alkali cations, have been studied rather intensely. The mechanisms of the reactions, however, have not attracted as much attention and, for the most part, the kinetics and the mechanisms of macrocyclic complexation reactions have been studied much less thoroughly. In particular, precise information on the influence of solvent properties on the rates of complexation reactions is quite sparse.

Shchori et al.³ studied Na⁺ ion complexation with dibenzo-18-crown-6 (DB18C6) and some derivatives of this ligand in dimethylformamide, methanol, and dimethoxyethane solutions by sodium-23 NMR. They observed the dissociative mechanism (see below) to be predominant in all of the investigated systems. Since in all cases the Arrhenius activation energies were similar, the authors concluded that the major barrier to the decomplexation is the rearrangement of the conformation of the complex prior to dissociation. However, all of the solvents in which the studies were carried out have similar solvation abilities as shown by the Gutmann donor numbers,⁴ and thus the solvent influence on the complexation kinetics was not fully examined.

Kinetic studies of Cox et al.⁵ on the complexation of alkali metal ions by cryptands showed a correlation between the Gutmann donor number of the solvent and the dissociation rate constant of the cryptates. Likewise Eyring, Petrucci, and co-workers⁶ observed influence of the solvent on the complexation kinetics of alkali metal ions with the crown ether 18C6. The number of observable steps in the complexation reaction was found to be dependent on the solvent.

We have previously reported⁷ on the bimolecular exchange process for the K⁺ ion complexation with 18C6 in several non-aqueous solutions. While the solvent was found to strongly influence the activation energies and entropies, the free energy of activation, ΔG_{-2}^\ddagger , was found to be essentially independent of the solvent. In more recent studies⁸ we looked at the influence of the counterion on Na⁺ ion complexation kinetics with 18C6 in tetrahydrofuran solutions. The predominant exchange mechanism for strongly ion paired salts, such as NaSCN, is the bimolecular process. For

less strongly associated salts, such as NaBPh₄, however, the predominant exchange mechanism is the dissociative process.

Thus, it was of interest to us to investigate more closely the solvent influence on the sodium ion complexation kinetics with 18C6 not only in neat solvents but also in binary solvent mixtures. We present here some results of such studies.

Experimental Section

Purification of salts, crowns, and tetrahydrofuran has been described previously.⁸ Methanol (MeOH, Fisher) was refluxed over granulated sodium methoxide for 2 days. Propylene carbonate (PC, Aldrich) was refluxed over barium oxide under reduced pressure for 2 days. The middle 60% fraction of the above solvents was collected and stored over activated molecular sieves in a drybox under nitrogen atmosphere. Water content was less than 100 ppm as determined by gas chromatography.

Sodium-23 NMR measurements were carried out on a Bruker WH-180 spectrometer at a field of 42.27 kG and a frequency of 47.61 MHz. Sodium-23 chemical shifts are corrected for bulk magnetic susceptibility and are referenced to infinitely dilute aqueous sodium chloride solution. Details concerning line width measurements and data analysis have been previously reported.^{8,9}

Results

We have used a complete sodium-23 NMR line shape analysis to measure the kinetics of complexation of the Na⁺ ion with 18C6 in methanol, propylene carbonate and in mixtures of those solvents with tetrahydrofuran. The choice of methanol allows a further comparison of crown influence on Na⁺ complexation kinetics as done by Shchori et al.³ for DB18C6 and for DC18C6 (isomer B) in this solvent. Propylene carbonate has a much lower donor number than does methanol ($DN_{PC} = 15.0$,⁴ $DN_{MeOH} = 25.7$ ¹⁰), while the high dielectric constants of both solvents should reduce the ion pairing effects ($D_{PC} = 65.0$, $D_{MeOH} = 32.7$). Therefore, in combination with our earlier results for NaBPh₄·18C6 in tetrahydrofuran ($DN_{THF} = 20.0$, $D_{THF} = 7.6$) solutions, the solvent influence on sodium ion complexation kinetics should become clearer. The study of solvent mixtures should provide additional information concerning solvent effects on complexation kinetics.

Characterization of the Solvated and the Complexed Sites in the Absence of Chemical Exchange. The dominant relaxation mechanism of the sodium-23 nucleus ($I = 3/2$) is through quadrupolar interaction through molecular tumbling. In the absence of chemical exchange and in the motionally narrowed limit ($\tau_c \ll 1$) the quadrupolar relaxation rate is given by the equation,¹¹

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

(9) Ceraso, J. M.; Smith, P. B.; Landers, J. S.; Dye, J. L. *J. Phys. Chem.* 1977, 81, 760.

(10) Greenberg, M. S.; Bodner, R. L.; Popov, A. I. *J. Phys. Chem.* 1973, 77, 2449.

(11) Abragam, A. "The Principles of Nuclear Magnetism"; Oxford University Press: London, 1961.

(1) Pedersen, C. J. *J. Am. Chem. Soc.* 1967, 89, 2495, 7017.

(2) Gokel, G. W.; Korzeniowski, S. H. "Macrocyclic Polyether Syntheses"; Springer-Verlag: Berlin and New York, 1982.

(3) (a) Shchori, E.; Jagur-Grodzinski, J.; Luz, Z.; Shporer, M. *J. Am. Chem. Soc.* 1971, 93, 7133. (b) Shchori, E.; Jagur-Grodzinski, J.; Shporer, M. *Ibid.* 1973, 95, 3842.

(4) Gutmann, V.; Wychera, E. *Inorg. Nucl. Chem. Lett.* 1966, 2, 257.

(5) Cox, B. G.; Garcia-Rosas, J.; Schneider, H. *J. Am. Chem. Soc.* 1981, 103, 1054.

(6) (a) Maynard, K. J.; Irish, D. E.; Eyring, E. M.; Petrucci, S. *J. Phys. Chem.* 1984, 88, 729. (b) Chen, C.; Wallace, W.; Eyring, E. M.; Petrucci, S. *Ibid.* 1984, 88, 2541.

(7) Schmidt, E.; Popov, A. I. *J. Am. Chem. Soc.* 1983, 105, 1873.

(8) Strasser, B. O.; Hallenga, K.; Popov, A. I. *J. Am. Chem. Soc.*, in press.

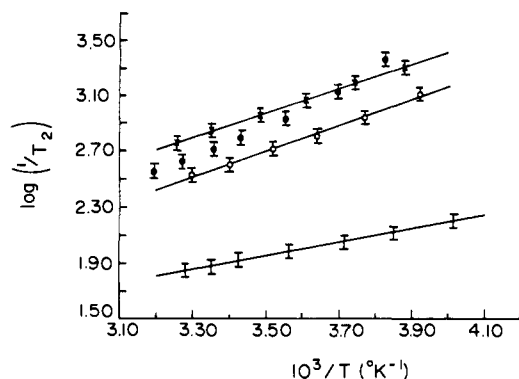


Figure 1. Plots of $\log 1/T_2$ vs. reciprocal temperature for solutions containing free (solvated) and complexed Na^+ in methanol and propylene carbonate solutions. (+) NaSCN uncomplexed in MeOH, (x) NaSCN·18C6 in MeOH, (O) NaBPh₄ uncomplexed in PC, (●) NaBPh₄·18C6 in PC.

Table I. Sodium-23 NMR Parameters for 0.1 M Solvated and Complexed Na^+ Ion Sites at 25 °C

solution	δ (ppm) ^a	$1/T_2$ (s ⁻¹)	E_r (kcal/mol)
0.1 M NaBPh ₄ in PC	-9.18	365.0	4.3
0.1 M NaBPh ₄ ·18C6 in PC	-15.8	517.0	4.9
0.1 M NaSCN in MeOH	-3.43	76.2	2.2
0.1 M NaSCN·18C6 in MeOH	-14.1	698.0	4.1

^a Referenced to infinitely dilute aqueous solution of a sodium salt.

where T_1 and T_2 are the relaxation times, I is the spin of the nucleus, η is the asymmetry parameter, $\partial^2 V/\partial Z^2$ is the Z 'th component of the electric field gradient at the nucleus produced by molecular tumbling, and τ_c is the correlation time which characterizes the tumbling. For a simple process

$$\tau_c = A' \exp(E_r/RT) \quad (2)$$

where E_r is an activation energy for solvent reorientation.¹² If the quadrupolar coupling constant $[(eQ/h)(\partial^2 V/\partial Z^2)^2]$ is assumed to be constant for a given temperature range, the relaxation rate will vary exponentially as a function of temperature. Semilog plots of $1/T_2$ vs. inverse temperature for solvated and complexed sodium salt in PC, MeOH, and mixtures of these solvents with THF are shown in Figure 1. Since in these solvents the stability constants of $\text{Na}^+\cdot 18\text{C}6$ are greater than 10^4 M^{-1} ,^{13,14} solutions in which the mole ratio $[18\text{C}6]/[\text{salt}] \geq 1$ essentially contain only the complexed sodium ion. As may be seen in Figure 1, a linear relationship does exist in all cases except for $\text{Na}^+\cdot 18\text{C}6$, BPh_4^- in PC solution. The origin of this deviation is unknown. However, viscosity effects are unlikely due to the linearity observed for the "free" salt solution. In addition, ion pairing influences do not seem likely being given the high dielectric constant of this solvent. Other workers¹⁵ have concluded that NaBPh₄ does not form contact ion pairs in propylene carbonate solutions.

Table I lists the room-temperature values obtained for chemical shifts, inverse relaxation times, and activation energies for molecular tumbling for these systems. The larger relaxation rates and activation energies of the solvated salt in PC, as compared to MeOH, likely reflect the higher viscosity of PC solutions ($\eta_{\text{PC}} = 2.53 \text{ cP}$, $\eta_{\text{MeOH}} = 0.597 \text{ cP}$). The chemical shift difference of the solvated salt solutions is due to the higher solvating ability of MeOH as compared to PC. Upon complexation with 18C6 the sodium ion is partially shielded from the solvents, and the similarity in NMR parameters for the complexed salt solutions reflects this shielding.

It is interesting to note that the values for E_r obtained in the solvent mixtures for the uncomplexed sodium ion fall between those

Table II. Observed and Predicted Activation Energies in Mixed Solvents for Uncomplexed Sodium Ion at 298 °C.

mixed solvent	E_r (kcal/mol ⁻¹)	
	observed	predicted ^a
80–20 mol% THF–PC	1.54	1.50
40–60 mol% THF–PC	2.58	2.88
60–40 mol% THF–MeOH	1.37	1.37

^a Calculated as described in text.

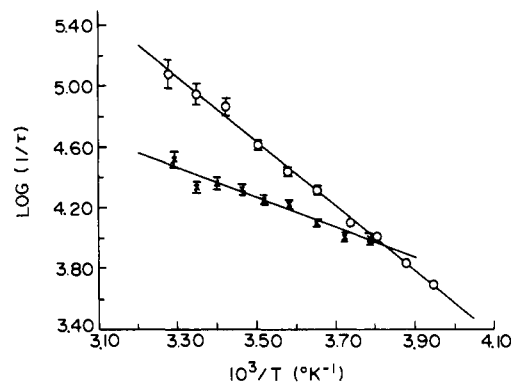


Figure 2. Plots of $\log 1/\tau$ vs. reciprocal temperature for the complexed Na^+ ion in methanol and in propylene carbonate solutions: (O) MeOH (NaSCN), (x) PC (NaBPh₄).

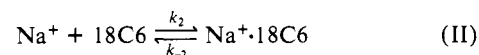
values observed in the respective neat solvents. In fact, there appears to be a linear relationship between solvent composition and the activation energy for solvent reorganization. Table II lists values of E_r observed in the mixed solvents and predicted in these systems by using the relationship

$$E_{r,A}X_A + E_{r,B}X_B = E_{r,\text{mixture}} \quad (3)$$

where $E_{r,i}$ = activation energy in solvent i and X_i = mole fraction of the solvent i . Within the experimental error the predicted and observed values for E_r are the same.

In the MeOH–THF mixture, the relaxation rate, $1/T_2$, for the uncomplexed cation is greater than those observed in the neat solvent components, which is probably due to the fact that both types of solvent molecules enter into the primary solvation shell of the ion, thus distorting the symmetry around it. This distortion may also be causing the increase in the observed relaxation rates in the PC–THF mixtures, compared to neat THF, but it is necessary to separate this effect from that of increased viscosity upon addition of PC.

Kinetic Results. The exchange of sodium ion between the solvated and complexed sites may proceed via two mechanisms as proposed by Shchori et al.,³ the bimolecular exchange process (I) and the dissociative mechanism (II).



The mean lifetime, τ , is then expressed by

$$1/\tau = 2k_1[\text{Na}^+]_{\text{tot}} + k_{-2}[\text{Na}^+]_{\text{tot}}/[\text{Na}^+]_f \quad (4)$$

where $[\text{Na}^+]_{\text{tot}}$ and $[\text{Na}^+]_f$ refer to the total sodium salt concentration and the uncomplexed sodium ion concentration, respectively. The contributions of these two mechanisms to the exchange process may be determined at a given temperature from a plot of $1/(\tau[\text{Na}^+]_{\text{tot}})$ vs. $1/[\text{Na}^+]_f$.

A plot of $\log 1/\tau$ vs. inverse temperature is essentially the Arrhenius plot if either mechanism is predominant. Figure 2 illustrates such plots for NaSCN with 18C6 in MeOH and for NaBPh₄ with 18C6 in PC solution. The Arrhenius activation energies determined from these plots are listed in Table II. The influence of the solvent on the activation energy is readily apparent.

A. Neat Solvents. Plots of $1/(\tau[\text{Na}^+]_{\text{tot}})$ vs. $1/[\text{Na}^+]_f$ for the neat solvent systems are shown in Figure 3. The predominant

(12) Deverell, C. *Prog. Nucl. Magn. Reson. Spectrosc.* **1969**, *4*, 278.

(13) Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.

(14) Lin, J. D.; Popov, A. I. *J. Am. Chem. Soc.* **1981**, *103*, 3773.

(15) Wu, Y. C.; Freidman, H. L. *J. Phys. Chem.* **1966**, *70*, 501.

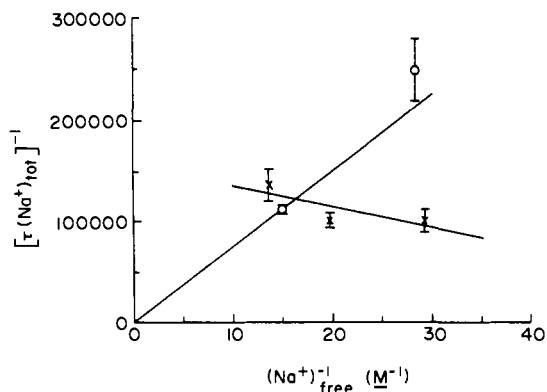


Figure 3. Plots of $[\tau(\text{Na}^+)_{\text{tot}}]^{-1}$ vs. $[\text{Na}^+]_{\text{free}}^{-1}$ for the complexed Na^+ ion: (O) MeOH, (X) PC.

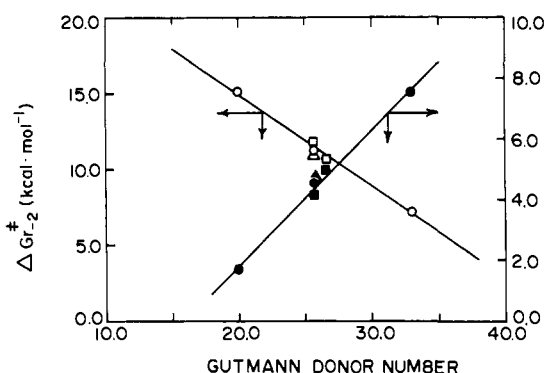


Figure 4. Plots of ΔG_{-2}^{\ddagger} (open symbols) and of $\log(k_{-2})$ (closed symbols) vs. Gutmann donor number of $\text{Na}^+\cdot 18\text{C}6$ and Na^+ -substituted $18\text{C}6$ in THF, MeOH, DMF, and H_2O : (O, ●) $18\text{C}6$; (□, ■) $\text{DB}18\text{C}6$; (▲, ▲) $\text{DC}18\text{C}6$ (present work and ref 3, 17).

exchange mechanism in methanol is the dissociative process (the intercept is zero). This is not unusual in that Shchori and co-workers³ found it to be the predominant mechanism for the Na^+ ion exchange with $\text{DC}18\text{C}6$ and with $\text{DB}18\text{C}6$ in this solvent.

In propylene carbonate solutions, however, the predominant exchange process occurs via the bimolecular mechanism. Previously, we reported⁸ the observation of this mechanism for NaSCN with $18\text{C}6$ in tetrahydrofuran solutions. The strong ion pairing of NaSCN and of its $18\text{C}6$ complex reduced the charge-charge repulsion of the two sodium ions in the transition state of the bimolecular process, thereby allowing this mechanism to predominate. However, in propylene carbonate solutions NaBPh_4 (and probably its complex with $18\text{C}6$) does not form contact ion pairs.¹⁶ It is likely that the high dielectric constant of this solvent is able to reduce the charge-charge repulsion in the transition state to allow this mechanism to predominate.

It was pointed out above that Cox and co-workers⁵ have reported a correlation between the dissociation rate constant of alkali metal-cryptand complexes and the Gutmann donor number of the solvent. Figure 4 is a plot of $\log k_{-2}$ and of ΔG_{-2}^{\ddagger} vs. Gutmann donor number for all systems in which the predominant exchange mechanism is the dissociative one. As can be seen, the correlation is quite good. Since, according to the Eyring theory, $\log k \propto \Delta G_{-2}^{\ddagger}$, it is reasonable that ΔG_{-2}^{\ddagger} and the Gutmann donor number should also correlate well. No such correlation is found for ΔG_1 . In those two cases where the bimolecular exchange process is predominant no such correlation exists. Schmidt and Popov⁷ also reported similar rates regardless of solvent for K^+ ion exchange with $18\text{C}6$ via the bimolecular process.

The correlations of ΔG_{-2}^{\ddagger} and not ΔG_1^{\ddagger} , with the Gutmann donor number may be explained as follows. The free energy diagram for the dissociative step of these two mechanisms may

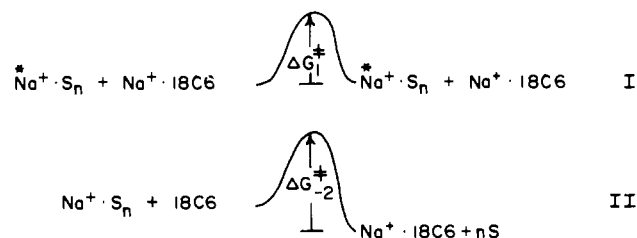


Figure 5. Activated free energy profiles for the bimolecular exchange (I) and the dissociation (II) mechanisms.

be expressed as shown in Figure 5. It seems reasonable that the solvating ability of a solvent will influence the magnitude of ΔG_{-2}^{\ddagger} . The Gutmann donor number scale has been shown¹⁶ to correlate well with sodium-23 chemical shifts. It appears that this empirical scale is also useful in sodium ion-crown ether complexation kinetics for the dissociative mechanism.

One would not expect the solvent to have a large influence on the magnitude of ΔG_1^{\ddagger} for the bimolecular exchange mechanism. In fact, in those two systems in which this mechanism has been found to predominate, i.e., $\text{NaSCN}\cdot 18\text{C}6$ in tetrahydrofuran⁸ and $\text{NaBPh}_4\cdot 18\text{C}6$ in PC solutions, the free energy barrier has been found to be approximately $10.5 \text{ kcal}\cdot\text{mol}^{-1}$. As discussed above, Schmidt and Popov⁷ have reported a solvent-independent free energy barrier for the bimolecular exchange mechanism for K^+ ion complexation with $18\text{C}6$. With the exception of 1,3-dioxolane solutions, the free energy of activation for this process is always approximately $10.0 \text{ kcal}\cdot\text{mol}^{-1}$. This result is interesting in that on a charge density basis one would expect K^+ ions to have a lower free energy barrier for this mechanism than Na^+ ions. This is what is observed.

Although one would not expect such good correlation between ΔG_{-2}^{\ddagger} and donor number in all solvents, the trend does allow us to make reasonable conclusions concerning these systems. According to Figure 4, if the dissociative mechanism is predominant in propylene carbonate solutions, the free energy of activation, ΔG_{-2}^{\ddagger} , would be approximately $18 \text{ kcal}\cdot\text{mol}^{-1}$. This would be the largest observed value for the $\text{Na}^+\cdot 18\text{C}6$ decomplexation process. However, the high dielectric constant allows the bimolecular process to occur with a much lower free energy of activation. In high dielectric constant and high donor number solvents, such as water, the predominant mechanism is the dissociative one due to the lower ΔG_{-2}^{\ddagger} , even though the high dielectric constant favors the bimolecular process. This is due to the fact that ΔG_1^{\ddagger} for the bimolecular process appears to be solvent independent.

If we assume that ion pairing is negligible, predictions concerning the predominant mechanism in a given solvent may be made on the basis of the trends discussed above. The predominant mechanism will be the dissociative one in solvents which have both high donor numbers and high dielectric constants. The predominant mechanism will be the bimolecular process in solvents which have low donor numbers but high dielectric constants. In solutions of either low donor number and low dielectric constant or high donor number and low dielectric constants the mechanism will likely be determined by the extent of ion pairing. Tetrahydrofuran solutions with either NaBPh_4 or NaSCN salts exchanging with $18\text{C}6$ are examples of this last case.

It is interesting to compare our results in MeOH with those of the $18\text{C}6$ analogues reported by Shchori and co-workers.^{3b} The forward rate constant for the $\text{Na}^+\cdot 18\text{C}6$ complex is much larger than that for $\text{DC}18\text{C}6$ or $\text{DB}18\text{C}6$ probably due to the higher flexibility of the cavity of $18\text{C}6$ compared to that of its analogues. The trend in the magnitudes of the stability of these complexes follows the reverse trend in dissociation rate constants. The activation energy for the dissociative process is highest for the most stable and lowest for the least stable complex. The activation entropies follow the reverse trend with the result that the free energies of activation, ΔG_{-2}^{\ddagger} , are all very similar.

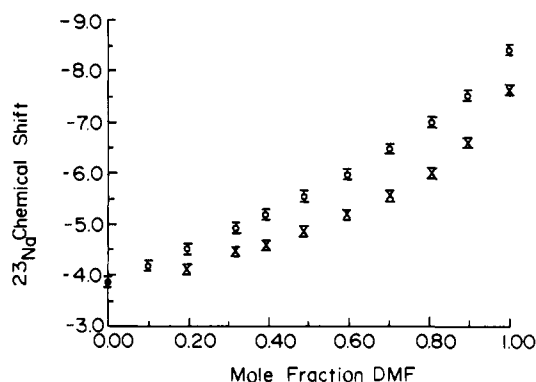
Shchori et al. have postulated that the major barrier to dissociation of these complexes is the energy needed for the conformational rearrangement of the complex. This postulation seems

(16) Erlich, R. H.; Roach, E.; Popov, A. I. *J. Am. Chem. Soc.* **1970**, *92*, 4989.

Table III. Kinetic Parameters for Sodium Ion Exchange with Crown Ethers at 25 °C.

solvent	salt	crown	K^a	k_f^b	k_d^c	E_a^d	$\Delta H^{\ddagger d}$	$\Delta S^{\ddagger e}$	$\Delta G^{\ddagger d}$	mech ^f
MeOH	NaSCN	18C6	21000.	7.6×10^8	$3.65 (0.07) \times 10^4$	9.7 (0.3) ^g	9.1 (0.3)	-7.2 (1.0)	11.23 (0.02)	II
MeOH ^h	NaSCN	DC18C6 ⁱ	4800.	2.6×10^8	5.2×10^4	8.3	7.7	-11.1	11.0	II
MeOH ^h	NaSCN	DB18C6	23000.	3.2×10^8	1.4×10^4	11.7	11.1	-2.3	11.8	II
PC	NaBPh ₄	18C6	$>10^4$ ^j	$>1.30 \times 10^9$	$1.30 (0.07) \times 10^{5b}$	4.6 (0.5)	4.0 (0.5)	-21.7 (1.7)	10.48 (0.04)	I
THF-MeOH (0.6-0.4) ^k	NaBPh ₄	18C6			$3.56 (0.09) \times 10^3$	9.84 (0.3)	9.24 (0.03)	-11.3 (1.0)	12.61 (0.03)	II
THF-PC (0.8-0.2)	NaBPh ₄	18C6			$9.15 (0.13) \times 10^2$	10.26 (0.1)	9.66 (0.1)	-12.6 (0.4)	13.41 (0.02)	II
THF-PC (0.4-0.6)	NaBPh ₄	18C6			$5.00 (0.23)^b \times 10^4$	9.13 (0.4)	8.53 (0.4)	-8.4 (1.4)	4.04 (0.03)	I

^a Reference 13. ^b M⁻¹ s⁻¹. ^c s⁻¹. ^d Kcal/mol⁻¹. ^e E.u. ^f See text for description of mechanisms. ^g Standard deviation estimates. ^h Reference 3. ⁱ Isomer B, cis-anti-cis. ^j Reference 14. ^k Respective mole fractions of the two solvents.

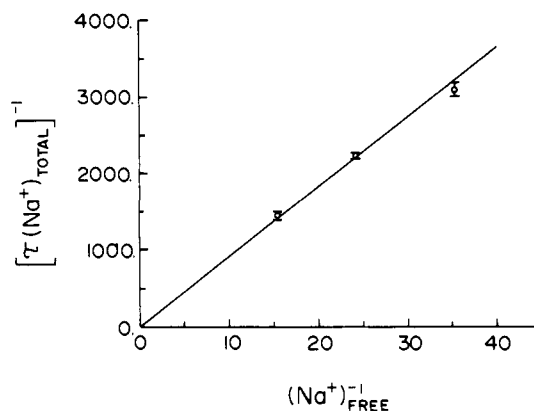
**Figure 6.** Sodium-23 chemical shift vs. composition of the THF-MeOH mixture: (O) 0.10 M NaClO₄, (X) 0.10 M NaBPh₄.

reasonable despite the solvent influence on the activation energy for dissociation of Na⁺·18C6. If we assume that the transition state is similar for the three complexes, it would reasonably follow that the most rigid complex would have the higher activation energy and most positive free energy of activation. This is indeed the case since one would normally predict the flexibility order of the complexes to be DB18C6 < 18C6 ~ DC18C6 with DB18C6 being the more rigid. The results seem to indicate that the DC18C6·Na⁺ complex is slightly more flexible than the 18C6·Na⁺ complex.

B. Mixed Solvents. Since the results described above clearly indicate the important influence of the donor properties of solvents on the kinetics of complexation reactions, the studies were extended to some binary solvent mixtures. It is well-known that properties of solvents in mixtures cannot be predicted from their behavior in the neat state and that it is particularly difficult to anticipate how the donor properties will be affected by the presence of another solvent.¹⁸

As a preliminary investigation into the solvent mixtures, sodium-23 chemical shifts were obtained for NaBPh₄ and NaClO₄ as a function of solvent composition. The results are shown in Figure 6. The influence of the anion on the sodium chemical shifts is readily apparent. As mentioned above other workers have concluded that NaBPh₄ does not form contact ion pairs in neat PC or THF solutions. It appears that while NaClO₄ may not be ion paired in PC (since it has the same chemical shift as NaBPh₄) this salt is certainly ion paired in THF. The curves for NaBPh₄ in the PC-THF mixtures are not monotonic as a function of solvent composition. This trend may indicate that while contact ion pairing does not occur in the neat solvents, it exists in the solvent mixtures—particularly at the high THF composition region where the S-shaped wiggle is seen.

The kinetic analysis of the data was carried out as described above for neat solvents. For example, the results for the 20–80 mol % PC-THF mixture are shown in Figure 7. It is seen that in this case dissociative mechanism is predominant, as is the case for the neat solvents, and the value of the kinetic parameters (Table III) falls between those found in the neat solvents.

**Figure 7.** Plot of $[\tau(\text{Na}^+)_{\text{tot}}]^{-1}$ vs. $(\text{Na}^+)_{\text{free}}^{-1}$ for the NaBPh₄·18C6 complex in 20–80 mol % PC-THF mixture.

For the PC-THF mixtures, the results indicate dissociative mechanisms for the 20–80 mol % mixtures (as in pure THF) but bimolecular mechanisms for the mixtures rich in PC (40–60 mol %). The kinetic parameters were calculated and are shown in Table III.

There are two interesting observations which may be made concerning the PC-THF mixture results. First, in the PC-rich mixture where the bimolecular mechanism predominates, the free energy of activation, ΔG_1^{\ddagger} , is approximately 11 kcal·mol⁻¹. These data support the independence of ΔG_1^{\ddagger} of the solvent since this is the magnitude of ΔG_1^{\ddagger} , observed in all systems studied thus far in which this mechanism predominates.

The second interesting observation is that in the THF-rich mixture, the value observed for ΔG_{-2}^{\ddagger} does not fall between that seen in THF (15 kcal·mol⁻¹) and that predicted for PC (18 kcal·mol⁻¹) based on the model presented above. Two explanations are likely. One is, of course, that ΔG_{-2}^{\ddagger} predicted for PC solutions is incorrect and/or the model breaks down at this point. Another possibility concerns the possibility of a pairing in this solvent mixture. As noted above, the sodium-23 chemical shift curve is not monotonic in PC-THF solutions, and an inflection point occurs at high THF composition. It is possible, therefore, that ion pairing may be occurring which results in a decrease in ΔG_{-2}^{\ddagger} . More work is necessary in order to clarify these issues.

Conclusions

The dissociative mechanism has been found to predominate for NaSCN·18C6 exchange in methanol while the bimolecular process predominates for NaBPh₄·18C6 in propylene carbonate solutions. A correlation has been found between the free energy of activation for the dissociative step of the dissociative mechanism and the Gutmann donor number of the solvent.

The study of complexation kinetics in mixed solvent systems provides additional information concerning solvent influence on exchange mechanisms.

Acknowledgment. The authors gratefully acknowledge the support of this work by National Science Foundation Grant CHE-8515474 and the help of Dr. T. V. Atkinson with computational methods.

Registry No. Na⁺, 17341-25-2; 18-crown-6, 17455-13-9.

(17) Liesegang, G. W.; Farrow, M. M.; Vazquez, F. A.; Purdie, N.; Eyring, E. M. *J. Am. Chem. Soc.* **1977**, *99*, 3240.

(18) Kinsinger, J. B.; Tannahill, M. M.; Greenberg, M. S.; Popov, A. I. *J. Phys. Chem.* **1973**, *77*, 2444.