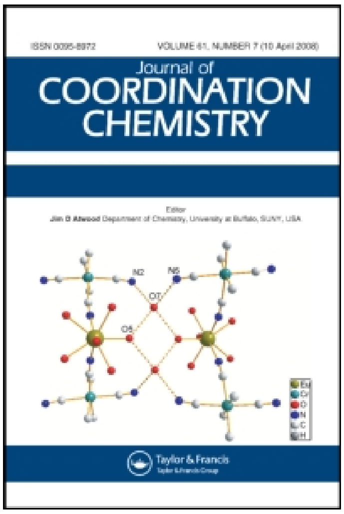

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NMR STUDY OF EXCHANGE KINETICS OF THE LITHIUM ION WITH CRYPTAND C222 IN BINARY ACETONITRILE-NITROMETHANE MIXTURES

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The exchange kinetics of the lithium ion with cryptand C222 were studied in acetonitrile-nitromethane mixtures by lithium-7 NMR line-shape analysis. In all solvent mixtures used, and over the entire temperature range studied, the chemical exchange of the Li^+ ion between the solvated and complexed sites was found to occur *via* a bimolecular mechanism. The activation parameters E_a, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ for the exchange have been determined. The free energy barrier for the exchange process appears to be nearly independent of the binary mixture composition. The results confirm the preferential solvation of the lithium ion with acetonitrile in the binary mixed solvent systems used.

Keywords: C222; Li^+; mixed-solvent; ^{7}Li NMR; exchange kinetics; bimolecular mechanism

INTRODUCTION

It is well known that macrobicyclic polyethers (cryptands), first synthesized by Lehn and co-workers,[1] are able to form very stable and selective complexes (cryptates) with a wide variety of metal ions.[2-4] The stability and lability of metal cryptates is dependent on the structure of the cryptand, the type and number of its donor atoms, the nature of the metal ion and the solvent properties. Among these factors, the ability of solvent molecules to solvate ions and thus to compete

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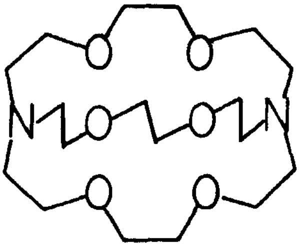
with the donating groups of the cryptands for the coordination sites of the central cation plays an important role, both thermodynamically and kinetically. The influence of solvent properties, especially dielectric constant and donating ability, on the thermodynamics and kinetics of the metal cryptate formation has been studied in detail.[3-5]

There has been recent increasing interest in the study of complexation reactions in binary mixed solvent systems and their interpretation in terms of the solute's preferential solvation by one of the mixed solvent components.[6-8] Although there are some reports on the thermodynamics of metal cryptate formation in the binary mixed solvent systems,[9-16] kinetic studies in these solvent systems are quite sparse.[12,13,17] In the last decade, we have employed multinuclear NMR line-shape analysis for the study of the complexation kinetics of macrocyclic ligands with different metal ions in nonaqueous.[18-23] and mixed solvents.[7],[24] In this paper we report a lithium-7 NMR study of the exchange kinetics of the Li^+ ion with cryptand C222 (**I**) in binary acetonitrile-nitromethane mixtures. Acetonitrile and nitromethane are solvents of similar dielectric constant (*i.e.*, $\epsilon_{AN} = 37.5$ and $\epsilon_{NM} = 35.6$), but of quite different donor numbers (*i.e.*, $DN_{AN} = 14.1$ and $DN_{NM} = 2.7$).[25] In acetonitrile, the ionic association of the lithium salt is quite small.[26] Similar condition may prevail in nitromethane, which has about the same dielectric constant as acetonitrile.



I

EXPERIMENTAL

Reagent grade cryptand C222 (Merck, **I**) and lithium perchlorate (Merck) were purified and dried as described before.[27],[28] Spectroscopic grade acetonitrile (AN, Merck) and nitromethane (NM, Reidel) were used to prepare the solvent mixtures by weight. The concentration of all lithium perchlorate solutions used was 0.01 M.

All NMR measurements were carried out on a JEOL FX90Q FT-NMR spectrometer with a field strength of 21.3 kG. At this field, lithium-7 resonates at 34.77 MHz. The temperature of the probe was adjusted with a temperature control unit using liquid nitrogen at low temperatures and a heating element at high temperatures. To reach the equilibrium temperature, each sample was left in the probe for at least 15 mins before measurements. At all temperatures used, the accuracy of the temperature measurements was ±0.1°C.

The line widths of the free and complexed Li^+ ion were measured by fitting a Lorentzian function to their spectra. A complete line-shape analysis technique was used to determine the mean lifetime, τ, for the exchange processes, using the modified Block equations.[29] Equations used were of similar format to those used by Cahen *et al.*[30] A non-linear least-squares program based on the Powell's technique[31] was used to fit 100-200 points of data to the exchange equations in order to extract τ values for the exchange system at several temperatures.

RESULTS AND DISCUSSION

The exchange kinetics of complexation of C222 with the Li^+ ion was studied in different AN-NM mixtures by ^7Li NMR line-shape analysis at different temperatures. In all solvent systems used, the concentration of the lithium perchlorate salt was kept constant at 0.01 M and three solutions with C222 to Li^+ ion mol ratios <1 were prepared. ^7Li NMR spectra were obtained at several different temperatures. Sample spectra are shown in Figure 1. Under the same conditions, the ^7Li NMR spectra of the solvated and complexed sites (*i.e.*, 0.01 M solutions of $LiClO_4$ with respective ligand to metal ion mol ratios of 0 and about 1.1) were obtained and the line widths were measured by fitting a Lorentzian function to the spectra. The broadening of the resonance lines of Li^+ ion in the solvated shell and in the cryptate form, even at very low temperatures, was found to be approximately equal. This observation, which originates from similar symmetry of the electrical field gradients in both sites, implies that the small Li^+ ion should be located in the centre of the cavity of the cryptand, as reported for the crystalline state of the alkali cryptates.[32]

Line-shape analysis of the spectra was carried out by computer fitting of the spectra to the NMR exchange equations in order to extract τ values (the mean lifetime of lithium ion) at different temperatures for each solvent system. A sample computer fit of the ^7Li NMR spectrum is shown in Figure 2 and all the resulting τ values are collected in Table I.

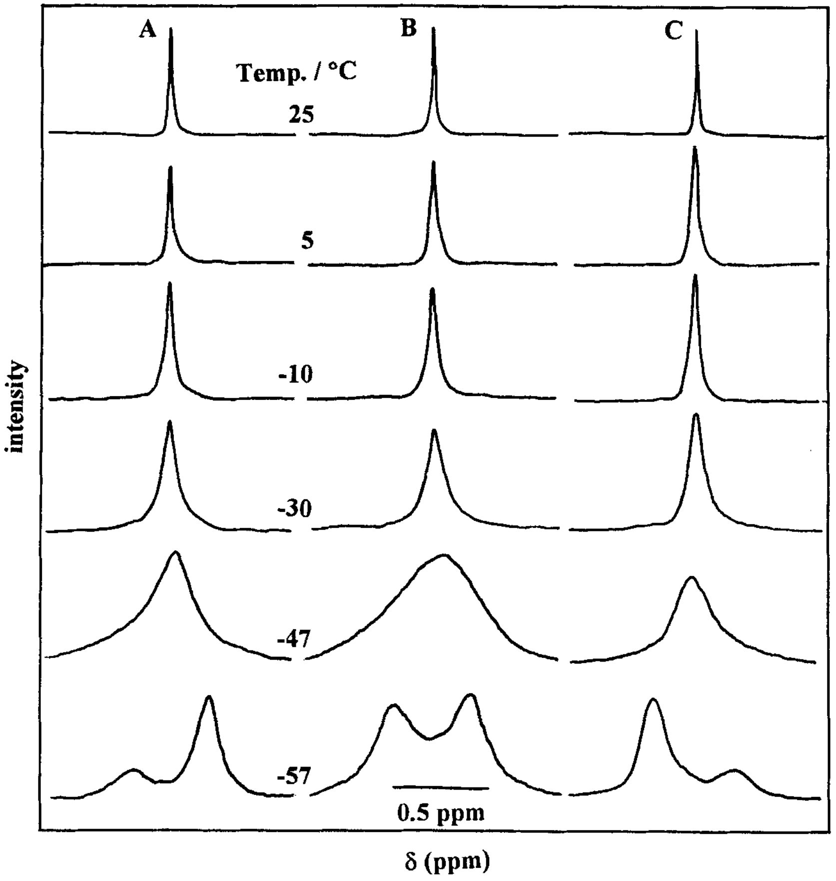


FIGURE 1 ^{7}Li NMR spectra at various temperatures for 0.01 M $LiClO_4$ in 60% AN solution with $[C222]/[Li^+]$ mol ratios of 0.3 (A), 0.5 (B) and 0.7 (C).

As Shchori *et al.*[33] proposed, the lithium ion may exchange between the solvated and cryptate sites by either a bimolecular mechanism (*1*) or a dissociative pathway (*2*):

$$^*Li^+ + Li^+C222 \xrightleftharpoons{k_1} {}^*Li^+C222 + Li^+ \qquad (1)$$

$$Li^+ + C222 \xrightleftharpoons[k_{-2}]{k_2} Li^+\,C222 \qquad (2)$$

The general expression for τ, in terms of the above mechanisms is[24]

$$1/\tau = 2\,k_1\,[Li^+]_{tot} + k_{-2}\,[Li^+]_{tot}/[Li^+]_{free} \qquad (3)$$

where $[Li^+]_{tot}$ and $[Li^+]_{free}$ represent the total concentration and the concentration of uncomplexed lithium ion, respectively. According to (*3*), at a given temperature, a plot of $1/\tau[Li^+]_{tot}$ *vs.* $1/[Li^+]_{free}$ determines the contribution of the two mechanisms to the exchange process. It is noteworthy that, since the stability constant of the Li^+C222 complex in the solvent mixtures used is greater than 10^4,[3-5] the free lithium ion concentration, $[Li^+]_{free}$, can be directly obtained from the [C222]/[Li^+] mol ratios used. Such plots for different solvent systems studied at −10°C are shown in Figure 3. Similar plots were obtained over entire temperature range studied.

As can be seen from Figure 3, in all AN-NM mixtures used, the $1/\tau[Li^+]_{tot}$ value is independent of $1/[Li^+]_{free}$. This observation implies that the exchange of the Li^+ ion between the solvated and complexed sites for the Li^+C222 complex proceeds solely *via* a bimolecular mechanism. In a previous study,[20] we observed the predominance of a dissociative pathway for the Li^+C222 complex in acetonitrile solution, where a 0.04 M concentration of $LiClO_4$ was employed. However, by reducing the salt concentration to 0.01 M in this solvent, the exchange mechanism is changed to a bimolecular pathway. Such a concentration dependence of the exchange mechanism has already been reported in the literature.[23],[34]

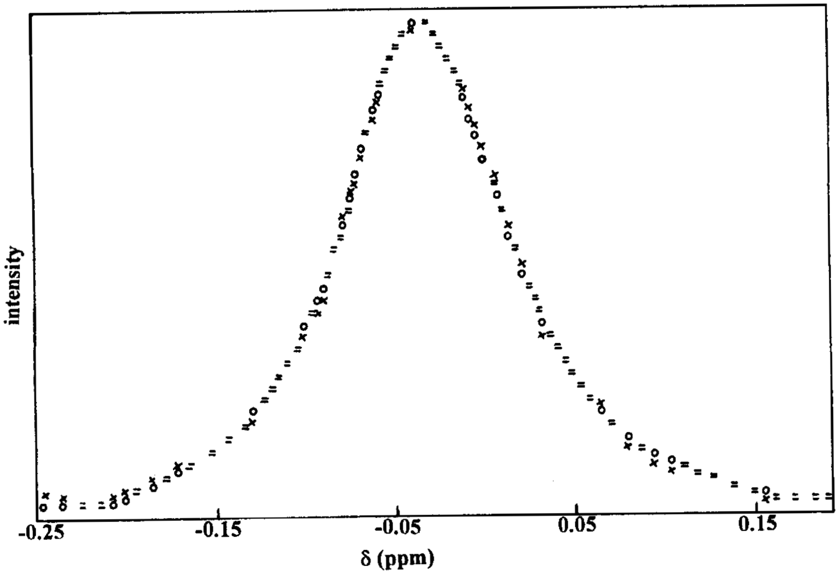


FIGURE 2 Computer fit of ^7Li NMR spectrum obtained with a 0.01 M solution of $LiClO_4$ in 60% AN containing C222 with a ligand to cation mol ratio of 0.5 at −30°C: (×) experimental point; (∘) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.

TABLE I Mean lifetimes and calculated rate constants for the Li^+C222 exchange system in different AN-NM mixtures as a function of temperature.

solvent composition/ % AN	*temp./ °C*	*MR*[a]	τ*/s*	*MR*	τ*/s*	*MR*	τ*/s*	*k/dm*^{3}*mol*$^{-1}$*s*$^{-1}$
100	25	0.3	5.35×10^{-4}	0.5	5.27×10^{-4}	0.7	5.41×10^{-4}	9.4×10^4
	5	0.3	9.7×10^{-4}	0.5	8.96×10^{-4}	0.7	9.05×10^{-4}	5.5×10^4
	−10	0.3	1.34×10^{-3}	0.5	1.30×10^{-3}	0.7	1.33×10^{-3}	3.8×10^4
	−25	0.3	2.22×10^{-3}	0.5	2.18×10^{-3}	0.7	2.23×10^{-3}	2.3×10^4
80	25	0.3	3.93×10^{-4}	0.5	4.25×10^{-4}	0.7	4.23×10^{-4}	1.2×10^5
	5	0.3	6.11×10^{-4}	0.5	5.97×10^{-4}	0.7	6.15×10^{-4}	8.2×10^4
	−10	0.3	9.01×10^{-4}	0.5	8.95×10^{-4}	0.7	9.11×10^{-4}	5.5×10^4
	−30	0.3	1.82×10^{-3}	0.5	1.80×10^{-3}	0.7	1.80×10^{-3}	2.8×10^4
60	5	0.3	4.85×10^{-4}	0.5	4.75×10^{-4}	0.7	5.15×10^{-4}	1.0×10^5
	−10	0.3	6.85×10^{-4}	0.5	6.92×10^{-4}	0.7	6.90×10^{-4}	7.2×10^4
	−30	0.3	1.32×10^{-3}	0.5	1.35×10^{-3}	0.7	1.36×10^{-3}	3.7×10^4
	−47	0.3	2.83×10^{-3}	0.5	2.76×10^{-3}	0.7	3.02×10^{-3}	1.7×10^4
40	5	0.3	3.47×10^{-4}	0.5	3.40×10^{-4}	0.7	3.91×10^{-4}	1.5×10^5
	−10	0.3	4.63×10^{-4}	0.5	4.49×10^{-4}	0.7	4.54×10^{-4}	1.1×10^5
	−30	0.3	8.57×10^{-4}	0.5	8.53×10^{-4}	0.7	8.49×10^{-4}	5.9×10^4
	−50	0.3	2.20×10^{-3}	0.5	2.27×10^{-3}	0.7	2.19×10^{-3}	2.2×10^4
20	−10	0.3	3.49×10^{-4}	0.5	3.40×10^{-4}	0.7	3.32×10^4	1.4×10^5
	−30	0.3	7.09×10^{-4}	0.5	7.02×10^{-4}	0.7	7.15×10^{-4}	7.0×10^4
	−40	0.3	1.03×10^{-3}	0.5	1.00×10^{-3}	0.7	1.10×10^{-3}	4.8×10^4
	−50	0.3	1.61×10^{-3}	0.5	1.59×10^{-3}	0.7	1.58×10^{-3}	3.1×10^4
0	25	0.3	1.21×10^{-3}	0.5	1.10×10^{-3}	0.7	1.31×10^{-3}	4.1×10^4
	5	0.3	3.36×10^{-3}	0.5	3.41×10^{-3}	0.7	3.42×10^{-3}	1.5×10^4
	−5	0.3	6.61×10^{-3}	0.5	6.57×10^{-3}	0.7	6.65×10^{-3}	7.5×10^3
	−15	0.3	1.13×10^{-2}	0.5	1.13×10^{-2}	0.7	1.07×10^{-2}	4.5×10^3
	−25	0.3	1.86×10^{-2}	0.5	1.76×10^{-2}	0.7	1.82×10^{-2}	2.8×10^3

[a] MR = $[C222]/[Li^+]$; 0.01 M $LiClO_4$.

It is noteworthy that, in order for a bimolecular metal exchange mechanism to proceed in a metal-macrocycle system, the ligand should have a conformation such that the simultaneous arrival of a free cation and departure of a previously complexed cation can easily occur.[18-24] Due to its moderate flexibility and the large cavity for the Li^+ ion, the cryptand C222 seems able to provide a proper configuration for the bimolecular mechanism. In this case, the transition state can be assumed as a C222 molecule with two Li^+ ions approximately in the centres of the two poly (oxadiazacycloalkane) rings on the opposite sides of the cryptand. Evidence for the formation of such 2:1 M^+LM^+ adducts, where M^+ is an alkali metal cation and L is a multidentate ligand, are frequently reported in the literature.[35-39] Solvents of low donor numbers and relatively high dielectric constants such as nitromethane and acetonitrile are particularly well suited media for the formation of such dicationic complexes.

Arrhenius plots of ln k_1 *vs* 1/T for the Li^+C222 system in all solvent systems used are shown in Figure 4. Activation energies were determined from the slopes of the Arrhenius plots, and the activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ were calculated by using Eyring's transition-state theory.[40] The results of these calculations are summarized in Table II.

From the data given in Table II, it is obvious that the activation energy in pure nitromethane is about twice as that in pure acetonitrile solution. Such a sharp decrease in E_a with increasing donor number of the solvent reveals that solvents of higher donicity can more easily reduce the electrostatic repulsion of the two charged species brought together in the transition state, so that less activation energy is needed for the system. However, the contribution from strong

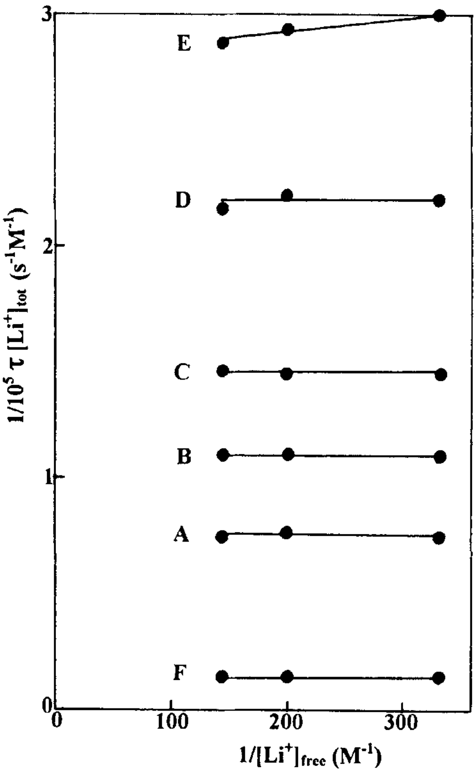


FIGURE 3 $1/\tau[Li^+]_{tot}$ *vs* $1/[Li^+]_{free}$ plots for Li^+C222 complex at −10°C (−5°C for 0% AN) in AN-NM mixtures: 100% AN (A); 80% AN (B); 60%AN (C); 40% AN (D); 20% AN (E); 0% AN (F).

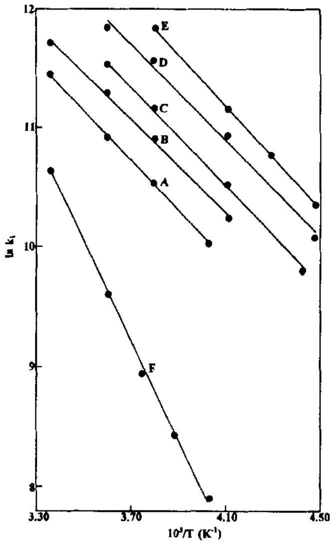


FIGURE 4 Plots of ln k_1 *vs* T^{-1} for Li^+C222 complex in AN-NM mixtures: 100% AN (A); 80% AN (B); 60% AN (C); 40% AN (D); 20% AN (E); 0% AN (F).

favourable interaction of the Li^+ ion with the cryptand donor atoms in counterbalancing the charge-charge repulsion in the transition state cannot be neglected. Moreover, since the activation energy varies over a broad range by changing the solvent from acetonitrile to nitromethane, it appears that it is not directly related to the energy required for a conformational rearrangement of the cryptand upon decomplexation. On the other hand, it is seen that the addition of only 20% (by wt) of acetonitrile to nitromethane will diminish the E_a drastically from 33.7 kJ mol^{-1} to 18.2 kJ mol^{-1}; further addition of acetonitrile does not

TABLE II Activation parameters for metal exchange in the Li^+C222 complex in AN-NM mixtures.

solvent composition/ % AN	E_a /kJ mol^{-1}	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J mol^{-1} K^{-1}	$\Delta G^{\ddagger a}$ /kJ mol^{-1}
100	17.3 ± 0.3	15.0 ± 0.3	−99 ± 1	44.5 ± 0.1
80	17.2 ± 0.6	15.0 ± 0.7	−97 ± 2	43.9 ± 0.1
60	17.8 ± 0.7	15.7 ± 0.7	−92 ± 3	43.0 ± 0.2
40	17.7 ± 0.6	15.6 ± 0.8	−89 ± 3	42.1 ± 0.1
20	18.2 ± 0.5	16.2 ± 0.5	−85 ± 1	41.5 ± 0.2
0	32.7 ± 0.9	30.4 ± 0.9	−51 ± 3	45.6 ± 0.1

[a] The standard deviation calculated by using the approximate equation $\sigma(\Delta G^{\ddagger}) \approx |\sigma(\Delta H^{\ddagger})\text{-}T\sigma(\Delta S^{\ddagger})|$; G. Binsch and H. Kessler, *Angew. Chem. Int. Ed. Engl.*, **19**, 411 (1980).

change the activation energy considerably. This observation clearly indicates the preferential solvation of the Li^+ ion with acetonitrile molecule in the binary mixtures, as noticed before.[41]

From Table II, it is seen that the free energy of activation is nearly independent of solvent not only throughout the range of binary mixtures used, but also in the pure solvents. As it was mentioned above, in the transition state of a bimolecular process, two positive ions must approach one another. Therefore, it is expected that the free energy of activation would be somewhat independent of solvent.[18,42-44] It is interesting to note that in pure acetonitrile and in its different mixtures with nitromethane not only $\Delta G^{\ddagger}$, but also $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are essentially constant. These findings indicate that, in these cases, the bimolecular exchange process is mainly controlled by the conformational changes of the cryptand during the concerted partial decomplexation of a Li^+ ion and partial complexation of a second Li^+ ion, which should be only slightly dependent on the binary mixture composition.[44,45] However, the slight increase in $\Delta S^{\ddagger}$ upon the increasing amount of NM in the solvent mixtures could be due to some decreased solvation of the Li^+ ion in the transition state.

On the other hand, Table II shows that the $\Delta H^{\ddagger}$ value in nitromethane is much larger than that in acetonitrile solution, most probably indicating the weak solvation of the Li^+ ion in the transition state in the former solvent. However, the large difference between the $\Delta H^{\ddagger}$ values in acetonitrile and nitromethane solutions is nearly compensated by the change in the corresponding $\Delta S^{\ddagger}$ values. In other words, a more positive $\Delta H^{\ddagger}$ value reflects a weaker transition state, a poorer overlap of the ligand and the cation and a sloppy geometry, which in turn requires a more positive $\Delta S^{\ddagger}$ value, and *vice versa*. Such a compensation effect is not uncommon when a given reaction is studied in a series of solvents.[7,30,46] The large negative values of $\Delta S^{\ddagger}$ such as those observed in this work are characteristic of bimolecular exchange processes.[24,44,45]

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