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Kinetics and mechanism of the dissociation of a sodium-calix[4]arene ester complex in nonaqueous solution

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The kinetics and mechanism for the dissociation of sodium ion complexes of a calix[4]arene ester **1** were studied in nonaqueous solution by a dynamic ^{1}H NMR. Life times τ_c of the Na^+-**1** complexes and activation parameters $\Delta_d H^‡$ and $\Delta_d S^‡$ for the dissociation process were determined in five organic solvents. In methanol, the life time (8.8×10^{-3} s) of the sodium complex at 25 °C was 440 times larger than that of crown ether (18C6) and was *ca.* 40 times less than that of cryptands (C211 and C222). The activation parameters for the dissociation process, $\Delta_d H^‡$ of 67, 64, 57, 57, and 46 kJ mol^{-1}, and $\Delta_d S^‡$ of −22, −29, −7.7, −13, and −33 J mol^{-1} K^{-1} were determined in deuteriated nitromethane, acetonitrile, acetone, methanol, and dimethylformamide, respectively. It was observed that the activation enthalpies tend to decrease with increasing the electron-donating ability of solvents as indicated by the Gutmann donor number, while the activation enthalpies do not correlate to the donor number and all the values are negative. These results suggest that in the activated state of the Na^+-**1** complex, additional solvent molecules bind to the sodium ion encapsulated by ethoxycarbonylmethoxy groups in **1**, and the disruption of the bonding between a sodium ion and the oxygens in the OCH_2CO moieties plays a major contribution in the dissociation process. In acetonitrile, the life times of the Na^+-**1** complexes were not affected by the concentration of the free ligand of **1**, suggesting that the dissociation proceeds *via* a unimolecular dissociation not a bimolecular exchange between free and complexed **1**.

Introduction

Calixarenes prepared by the condensation of *p*-alkylphenol and formaldehyde are an interesting class of host molecules, which are characteristic of cyclic oligomers made up by phenol units.[1] Much attention has been paid to the design of calixarene derivatives with selective binding properties for particular ions and neutral molecules in solution. Functional modification of the lower rim of parent calix[*n*]arenes has led to a variety of ionophoric compounds.[2–7] It has been shown that ester and amide derivatives of calix[*n*]arenes have remarkable complexing abilities toward alkali-metal ions in a similar manner as crown ethers and cryptands.[7] Among a large number of ionophoric calix[*n*]arenes, particularly interesting is the calix[4]arene ester **1**. This calix[4]arene ester is known to have selective complexing ability toward sodium ions and acts as a Na^+ carrier in bilayer membranes as well as bulky liquid membranes.[7–10] To the best of our knowledge, the calix[4]arene ester **1** is the first example of a synthetic Na^+ carrier which is active in phospholipid bilayer membrane.[8,10] From the dynamic ^{23}Na NMR study in a vesicle system, we have found that the transport rates of sodium ions by **1** across phospholipid bilayers are comparable to the rates by an antibiotic ionophore, monensin.[8] The actual mechanism of the transport of sodium ions by **1** involves the formation and dissociation of the sodium complexes at a water/membrane interface. For a deeper understanding of the mechanism of the selective Na^+ transport by **1** across the bilayer membrane, it is of importance to characterize the kinetics and mechanism of the ion exchange reaction on Na^+-**1** complexes in solution.

Up until now, only a few reports have addressed the kinetics and mechanism of the formation and dissociation of alkali-metal ion complexes of calix[4]arenes in solution.[11–14] Previously, we have studied the dissociation kinetics of the Na^+-**1** complex in a chloroform–methanol mixture by an analysis of ^{23}Na longitudinal magnetization recovery curve and ^{1}H NMR spectroscopy.[11] We have found that the calix[4]arene ester **1** forms a sodium complex with a 1 : 1 stoichiometry and the dissociation of the Na^+-**1** complex proceeds *via* an unimolecular dissociation mechanism in the chloroform–methanol mixture. More recently, Israëli and Detellier have studied the dissociation kinetics of the Na^+-**1** complex in a chloroform–acetonitrile mixture by an analysis of the ^{23}Na NMR line widths.[13] They have reported a 2 : 1 (**1**/Na^+) complex as an intermediate in the pathway of the exchange of sodium ions between the 1 : 1 complex in the mixture solution.[13] However, there has been no systematic data for the kinetics of sodium ion exchange on the Na^+-**1** complex in various organic solutions. In this paper, lifetimes of the Na^+-**1** complex and activation parameters of the dissociation reaction in deuteriated nitromethane, acetonitrile, acetone, methanol, and dimethylformamide are presented. In addition, it is demonstrated that the dissociation of the Na^+-**1** complexes in acetonitrile follows an unimolecular dissociation mechanism not a bimolecular exchange mechanism. By comparison of the formation and the dissociation rates in acetonitrile, the kinetic factors which affect the sodium selectivity of **1** is discussed.

Experimental

p-tert-Butylcalix[4]arene was purchased from Acros Organics. The calix[4]arene ester **1** (Fig. 1) was synthesized by the literature method.[7] Sodium thiocyanate, potassium thiocyanate and lithium chloride were of analytical reagent grade quality

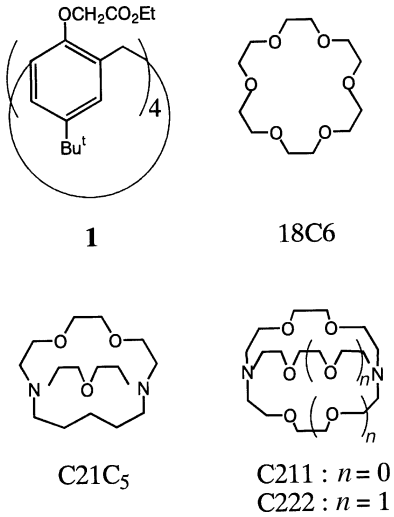

Fig. 1 Ligand structures.

and dried under vacuum at 80 °C for 24 h prior to use. Nitromethane-d_3 (>99%), acetonitrile-d_3 (>99%), acetone-d_6 (99.8%), methanol-d_4 (99.8%), dimethylformamide-d_7 (99.5%), and chloroform-d (99.8%) were purchased from Merck. All solvents were stored over 4 Å molecular sieves. ^{1}H NMR spectra were measured on Varian XL-200 at 200 MHz and Bruker XL-400 at 400 MHz. The chemical shifts of ^{1}H NMR spectra were referred to 1% TMS which was added to the deuteriated solvents. The temperature calibration was made with a thermocouple inserted in a nonspining tube containing deuteriated solvents. The error on the temperature was estimated to be 0.5 K. The temperature-dependent ^{1}H NMR spectra were subjected to complete line shape analyses[15] to obtain the temperature variation of the life times, τ_c, of alkali-metal ion complexes.

Results and discussion

Change in ^{1}H NMR spectra in the presence of sodium ions

Fig. 2 shows the typical data for changes in the ^{1}H NMR spectra of **1** upon addition of NaSCN in chloroform at 25 °C. In the absence of NaSCN, ^{1}H NMR spectra of **1** afforded a simple pattern characterizing the C_{4v} symmetry. The AB splitting signals arising from bridging methylene protons observed at 3.14 and 4.88 ppm show that **1** forms a cone structure in chloroform. From the NOE experiment, the signals at 3.14 and 4.88 ppm were assigned to the equatorial and axial protons of the bridging methylene, respectively. When microliter aliquots of deuteriated chloroform solution of NaSCN was added to the solution of **1**, new signals immediately generated. The intensity of these signals increased with increasing the amounts of NaSCN added, while the signals of the uncomplexed **1** became small and completely diminished at the concentration ratio of $R = [Na^+]/[\mathbf{1}] = 1$. It should be noted that the spectra at $R = 1$ becomes a simple pattern again, where the spectrum is assigned to the cone conformation of complexed **1** with a C_{4v} symmetry. When more NaSCN up to $R = 2$ was added, no further spectral change occurred. Thus, it is concluded that **1** forms a 1 : 1 complex with sodium ions and exists as a free and a 1 : 1 complexed species in chloroform. Except for the difference in temperature, similar spectral behavior as shown Fig. 2 was observed in the five solvents studied.

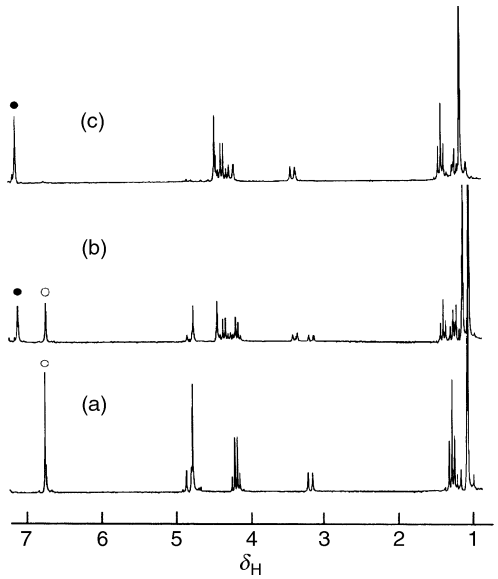

Fig. 2 Change in ^{1}H NMR spectra of **1** (5 mM) upon additions of NaSCN in $CDCl_3$: (a) $R = [Na^+]/[\mathbf{1}] = 0$, (b) $R = 0.5$ and (c) $R = 1$. Open and closed circles indicate the aromatic protons in free and complexed **1**, respectively.

Dynamic ^{1}H NMR spectra

As can be seen from Fig. 2(b), most well-resolved signals of the free and complexed species of **1** are the signals in the aromatic proton regions. Thus, we measured the temperature dependence of the NMR signals of the aromatic protons of **1** in five solvents at *ca.* $R = 0.5$. Fig. 3 shows typical data for experimental and calculated ^{1}H NMR spectra of **1** at $R = 0.6$ in acetone. Two signals at −10 °C show the signals of aromatic protons resulting from free (higher field) and complexed species (lower field) of **1**. With increasing the temperature, two signals became coalesced, indicating that the sodium ion exchange on the Na^+-**1** complex takes place and the exchange rate increases with increase in temperature. By the lineshape analysis for two-site exchange[15] between the free and complexed **1**, the life times τ_c of the sodium complexes were obtained. In acetone, the life times of the sodium complex decreased from 96 to 0.58 ms in the range of −10 to 50 °C. For other solvent systems, the lineshape analysis of temperature-dependent ^{1}H NMR spectra was also undertaken and the life times of the sodium complexes in these solvents were obtained.

Life times of the sodium complex and activation parameters for the dissociation reaction

Fig. 4 shows the temperature dependence of the life times τ_c of the sodium complexes in five solvents. The life times are significantly influenced by the temperature and the nature of the solvents. For the exchange of sodium ion, we assumed a two-jump model, where two different sites correspond to the complex and (Na^+-**1**) and the other is the solvated sodium ions:

$$Na^+\text{-}\mathbf{1} \underset{}{\overset{k_d}{\rightleftharpoons}} Na^+ + \mathbf{1} \qquad (1)$$

Eqn. 1 is meant to represent the general situation of the dissociation reaction and not to imply any specific mechanism of the dissociation. The activation parameters $\Delta_d H^\ddagger$ and $\Delta_d S^\ddagger$ for the dissociation of the complex were calculated by the Eyring equation [eqn. (2)] in which all symbols have their usual meaning.

$$k_d = \frac{1}{\tau_c} = \frac{k_B T}{h} \exp\left(\frac{-\Delta_d H^\ddagger}{RT} + \frac{\Delta_d S^\ddagger}{R}\right) \qquad (2)$$

The life times of the complex and the activation parameters for the dissociation are summarized in Table 1, together with the data earlier reported for Na^+-18C6,[16,17] Na^+-C21C_5,[18] Na^+-C211,[19,20] Na^+-C222,[19,20] and Na-monensin.[21] The values of τ_c at 25 °C exhibit 3300-fold variation among the five

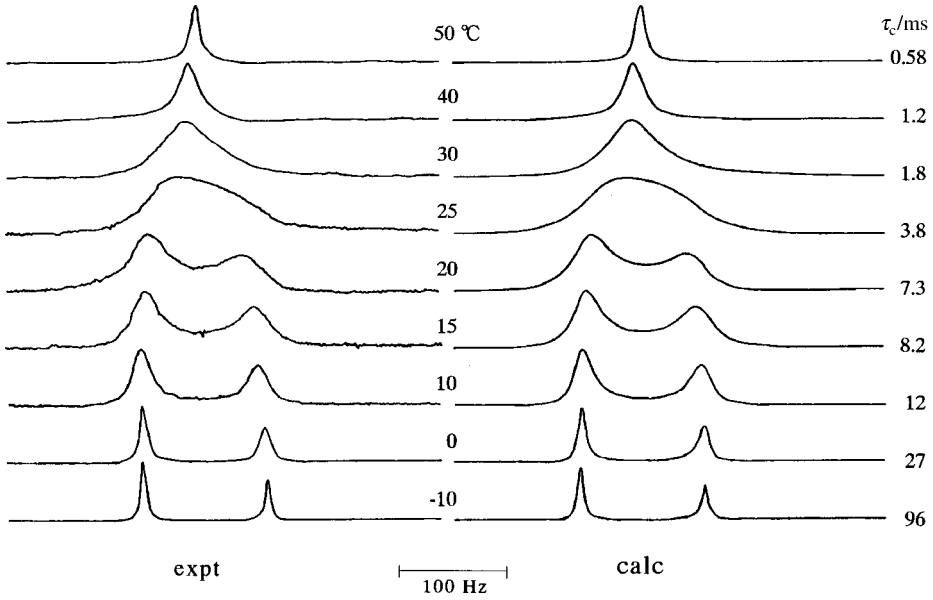

Fig. 3 Typical experimental and calculated data for the temperature-dependent ^{1}H NMR spectra of the aromatic protons of **1** (5 mM) at $R = 0.6$ in acetone.

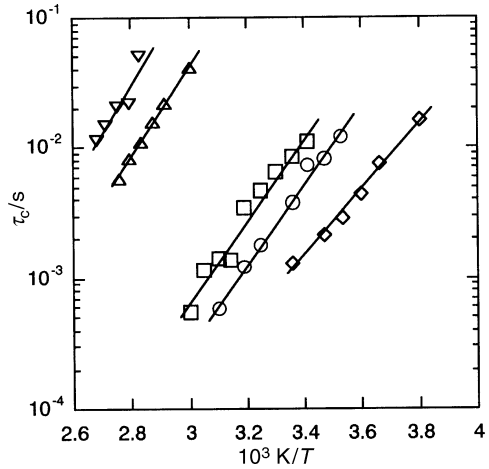

Fig. 4 Plots of the life times τ_c of the Na^+-**1** complexes *vs.* the inverse of the temperature in five solvents: nitromethane (▽), acetonitrile (△), methanol (□), acetone (○) and DMF (◇).

solvents. In the case of nitromethane and acetonitrile, the life times of the complexes at 25 °C are determined by the extrapolation of the linear τ_c *vs.* $1/T$ plot to the temperature. It is seen that the life times tend to decrease with increasing the electron-donating ability of solvents. In methanol, the life time (8.8×10^{-3} s) of the sodium complexes at 25 °C was 440 times larger than that of crown ether (18C6) and was *ca.* 40 times less than that of cryptands (C211 and C222). It is of interest to note that the life time of the Na^+-**1** complex is of similar order to that of the sodium complex of an antibiotic ionophore, monensin.[21]

Fig. 5 shows a plot of $\Delta_d H^‡$ and $\Delta_d S^‡$ *vs.* the Gutmann donor number[22] of the solvents. It is seen that the activation enthalpies tend to decrease with increasing the donor number, while the activation entropies hardly depend on solvents and all the values are negative. These findings suggest that in the activated state of the Na^+-**1** complex, additional solvent molecules coordinate to the sodium ion encapsulated by ethoxycarbonylmethoxy groups in **1**, and the activated complex

Table 1 Life times of sodium complexes and activation parameters[a] for the dissociation of sodium complexes in nonaqueous solution

Complex	Solvent	D_N[b]	ε[b]	Counter anion	τ_c/s (298 K)	$\Delta_d H^‡$/kJ mol^{-1}	$\Delta_d S^‡$/J mol^{-1} K^{-1}	$\Delta_d G^‡$/kJ mol^{-1} (298 K)
Na^+-**1**								
	Nitromethane	2.7	35.9	NCS^-	4.0	67 ± 14	−22 ± 39	77 ± 26
	Acetonitrile	14.1	37.5	NCS^-	0.71	64 ± 1	−29 ± 4	73 ± 2
	Acetone	17.0	20.7	NCS^-	3.8×10^{-3}	57 ± 3	−7.7 ± 9	59 ± 6
	Methanol	19.0	32.6	NCS^-	8.8×10^{-3}	57 ± 4	−13 ± 14	61 ± 8
	DMF	26.6	36.7	NCS^-	1.2×10^{-3}	46 ± 3	−33 ± 10	56 ± 6
Na^+-18C6								
	Methanol[c]	19.0	32.6	NCS^-	1.3×10^{-5}	53.6	27.8	45.3
	Methanol[c]	19.0	32.6	NCS^-	2.7×10^{-5}	38.1	−30.1	47.1
Na^+-$C21C_5$[e]								
	Methanol	19.0	32.6	ClO_4	5.5×10^{-4}	44.9	−31.9	54.4
Na^+-C211[f]								
	Methanol	19.0	32.6	Cl^-	0.40			
Na^+-C222[f]								
	Methanol	19.0	32.6	Cl^-	0.35			
Na-monensin[g]								
	Methanol	19.0	32.6	Monensin$^-$	1.5×10^{-2}	43.1	−66.0	62.7

[a] Quoted errors represent one standard deviation obtained from a linear regression analysis of the temperature dependence of experimental τ_c data through eqn. (2). [b] Ref. 22. [c] Ref. 16. [d] Ref. 17. [e] Ref. 18. [f] Ref. 19, 20. [g] Ref. 21.

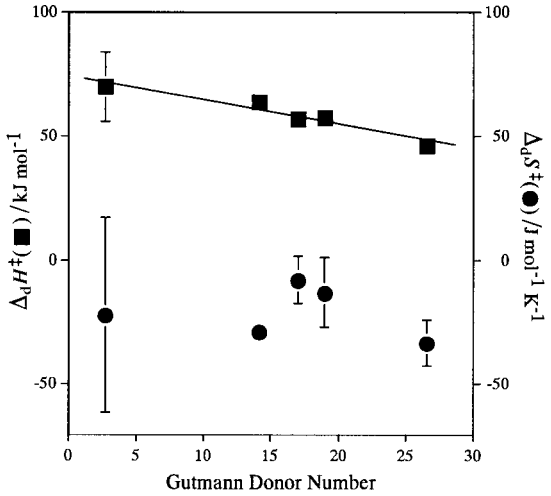

Fig. 5 Plots of $\Delta_d H^\ddagger$ and $\Delta_d S^\ddagger$ for the dissociation reaction of Na^+-**1** *vs.* the Gutmann donor number of solvents.

is stabilized by the electron-donating nature of the solvent. This indicates that the enthalpy term (the disruption of the bonding between Na^+ and **1**) plays a major contribution on the dissociation in comparison with the entropy term. The rearrangement of the binding groups prior to dissociation should not be a major barrier to the dissociation. In this system, the enthalpy–entropy compensation effects were not observed in contrast to the case of (dibenzo18C6-Na^+)[23] and (18C6-Na^+)[24] systems: the $\Delta_d G^\ddagger$ tends to decrease with increasing the donor number of solvents. This may have resulted from the small flexibility of the binding sites (ester moieties) of the complex, in which the molecular motion is suppressed by the template effect by sodium ion.[25] Since there is no correlation between $\Delta_d S^\ddagger$ and the donor number, it is suggested that the conformation of the Na^+-**1** complex in the activated states is less affected by solvents.

It should be noted that there is no correlation between the dielectric constants of the solvent and the life times of the sodium complexes. Shinkai *et al.* have reported that **1** complexes with sodium picrate to form solvent-separated ion pairs in THF.[26] Considering the small dielectric constant (7.6) of THF, in the other solvents studied (>20.7), it is not likely that the SCN anion forms an ion pair with a sodium cation. From the X-ray analysis data of a tetraester analogue (a potassium complex of *p-tert*-butylcalix[4]arene tetraamide),[27] it has been shown that the potassium ion is completely encapsulated by the cavity constructed by the four phenolic and the four carbonyl oxygen atoms of the calix[4]arene. In addition, it has been shown that the values of the ^{23}Na spin-lattice relaxation rates of the Na^+-**1** complexes in chloroform–methanol mixture were not affected by counter anions, such as Br^- and SCN^-.[11] On the basis of these findings together with the dielectric constant data, it is suggested that the ion-paring effect is negligible on the stability of the Na^+-**1** complex in the solvent systems studied.

The dissociation mechanism of the sodium complexes in acetonitrile

At the condition of the ratio $R = [Na^+]/[\mathbf{1}] < 1$, the concentration of free sodium ions should be very small compared to the concentration of complexed sodium ions because the stability constant of the Na^+-**1** complex in acetonitrile is very large (>10^6).[7,28] Thus, it may be taken into account the possibility of two dissociation mechanisms for the Na^+-**1** complexes:

$$Na^+\text{-}\mathbf{1} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Na^+ + \mathbf{1} \qquad (3)$$

$$Na^+\text{-}\mathbf{1}^* + \mathbf{1} \overset{k_2}{\rightleftharpoons} \mathbf{1}^* + Na^+\text{-}\mathbf{1} \qquad (4)$$

The first is refereed to as the unimolecular dissociation mechanism. The second is the bimolecular cation exchange by the free ligand, which is known as the associative exchange mechanism. From these equations, the life time of the Na^+-**1** complex is expressed as follows:

$$\frac{1}{\tau_c} = k_1 + k_2[\mathbf{1}]_{free} \qquad (5)$$

Therefore, we can determine the relative contribution of the two dissociation mechanisms by the measurements of $[\mathbf{1}]_{free}$ dependence on the life times of the Na^+-**1** complex. Fig. 6 shows the concentration dependence of $[\mathbf{1}]_{free}$ on the ^1H NMR spectra in the aromatic protons of **1** in acetonitrile. The signals at 7.08 and 7.42 ppm are ascribed to the free and complexed species of **1**, respectively. It should be noted that the chemical shift and the linewidth of the complexed signal is less affected by the increase in the concentration of $[\mathbf{1}]_{free}$. Over the range of the concentration ratio ($[\mathbf{1}]_{free}/[\mathbf{1}]_{complex}$) from 0.1 to 4, the life times of the Na^+-**1** complexes were almost constant ($1/\tau_c = 1.4 \pm 0.3\ s^{-1}$) within the experimental error. This result indicates that the unimolecular dissociation is dominant in the dissociation of the Na^+-**1** complexes in acetonitrile.

Recently, Israëli and Detellier have reported the formation of a 2 : 1 complexes (**1**/Na^+) in a chloroform–acetonitrile mixture based on the ^{23}Na NMR linewidth analysis.[13] They have proposed that the outer-sphere 2 : 1 complex is an intermediate in the pathway of the exchange of sodium ions between 1 : 1 complexes in solution. If the formation of the 2 : 1 complexes takes place before the formation of the 1 : 1 complexes, it is anticipated that the life time of the 1 : 1

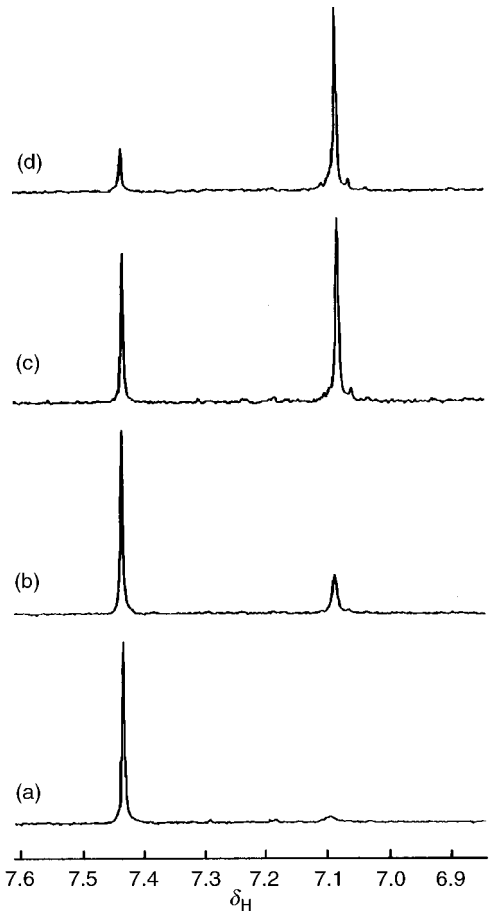

Fig. 6 ^1H NMR spectra (25 °C) of the aromatic protons of **1** at different ratios of $[\mathbf{1}]_{free}/[\mathbf{1}]_{complex}$ in acetonitrile: (a) 0.1, (b) 0.4, (c) 1.1 and (d) 4.0. $[\mathbf{1}]_{total} = 5$ mM.

complex should decrease with increasing $[\mathbf{1}]_{free}$, as a result of the increase in contribution of the bimolecular dissociation [see eqn. (5)]. However, the decrease in the life time of the Na^+-**1** complex was not observed in the range of $[\mathbf{1}]_{free}/[\mathbf{1}]_{complex}$ from 0.1 to 4.

Kinetic factors affecting the ion selectivity of 1 in acetonitrile

Fig. 7 shows the temperature dependence on the life times of Li^+, Na^+, and K^+ complexes in acetonitrile. The life times of the complexes were obtained by the line shape analysis of the temperature-dependent ^1H NMR spectra in **1**-LiCl, **1**-NaSCN, and **1**-KSCN systems. The order of the life times is Na^+-**1** (0.71 s) > Li^+-**1** (1.0×10^{-2} s) > K^+-**1** (3.3×10^{-4} s) at 25 °C, where except for the case of Li^+-**1**, the values are obtained by the extrapolation of the linear τ_c *vs.* $1/T$ plot to the temperature.

Table 2 summarized the rate constants of the dissociation and formation reaction including activation parameters for the dissociation process, together with the data earlier reported for the Na^+-18C6[16] and Na^+-$C21C_5$ [18] complexes. The dissociation rate constants ($k_1 = 1/\tau_c$) are 100, 1.4 and 3030 s^{-1} for the Li^+, Na^+, and K^+ complex, respectively. Since the unimolecular dissociation is dominant in acetonitrile, the formation rate constants k_{-1} can be calculated by $k_{-1} = k_1 \times K$. Recently, the accurate values of stability constants K in acetonitrile have been reported by Daniel de Namor *et al.*[28] by potentiometric titrations: $10^{6.20}$ (Li^+ complex), $10^{7.68}$ (Na^+ complex), and $10.^{4.04}$ (K^+ complex). By using these data, the values of k_{-1} were calculated as follows: 1.5×10^8, 6.7×10^7 and 3.3×10^7 $dm^3\ mol^{-1}\ s^{-1}$ for the Li^+, Na^+ and K^+ complexes, respectively. The variation in k_{-1} is within one order, while the variation in k_1 is much larger than that in k_{-1} by a factor of *ca.* 2100. This suggests that the sodium selectivity of **1** is mainly responsible for the difference in the dissociation rate constants, not for the difference in the formation rate constants.

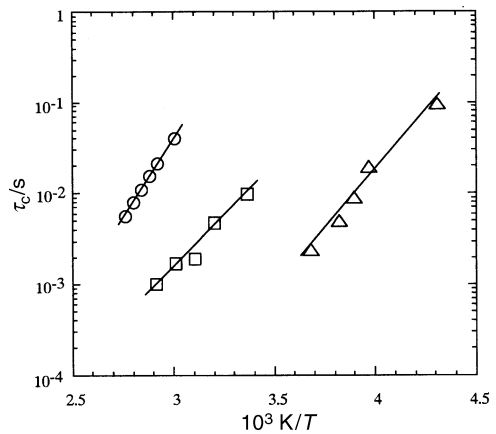

Fig. 7 Plots of the life times τ_c of the alkali-metal ion complexes of **1** *vs.* the inverse of the temperature in acetonitrile: Li^+ complex (□), Na^+ complex (○) and K^+ complex (△).

If the complexation proceeds *via* a simple diffusion control reaction,[21,29,30] the formation rates should be increased in the order of K^+-**1** > Na^+-**1** > Li^+-**1** because the desolvation energy decreases with the increase of ion radius.[31] However, inverse behavior was observed in k_{-1}: $k_{-1}(Li^+\text{-}\mathbf{1}) > k_{-1}(Na^+\text{-}\mathbf{1}) > k_{-1}(K^+\text{-}\mathbf{1})$. In the formation process, the rate determining step should be the rearrangement of the binding groups to accommodate metal ions. The smaller ion may have access more easily to the binding cavity created by the ethoxycarbonylmethoxy groups in **1**. In the dissociation process, $\Delta_d H^\ddagger$ plays a major contribution in the energy barrier for the dissociation of M^+-**1**. The large variation (2100-fold) in k_1 could be explained by the difference in the electrostatic stability of the metal ion complex.

It is of interest to compare the rate constants in the Na^+-**1** system with the data reported for Na^+-18C6[24,32] and Na^+-$C21C_5$.[18] The formation rate constant of the Na^+-**1** is in the order of magnitude of the crown ether and the cryptand. The dissociation rate of the Na^+-**1** is rather close to that of the cryptand, and the rate is slower than that of the crown ether by a factor of 2700. Judging from these observations, the calix[4]arene ester **1** has the "open" system for incoming metal ions such as a crown ether, while the complexed **1** has the "closed" system for outgoing metal ions such as a cryptand.

Conclusion

The kinetics and mechanism of the dissociation of the sodium ion complexes of **1** in nonaqueous solution are summarized as follows.

(1) The life times of the Na^+-**1** complex tend to decrease with increasing the electron-donating ability of the solvent as indicated by Gutmann donor number.

(2) The enthalpy term (the disruption of the bonding between Na^+ and **1**) plays a major contribution on the dissociation process compared to the entropy term.

(3) It is suggested that in the activation state of the Na^+-**1** complex, additional solvent molecules bind to the sodium ion which is encapsulated by four ethoxycarbonylmethoxy groups in **1**.

(4) The dissociation of the Na^+-**1** complexes in acetonitrile proceeds *via* an unimolecular dissociation mechanism.

(5) The sodium selectivity of **1** is mainly responsible for the difference in the dissociation rate constants, not for the difference in the formation rate constants.

The calix[4]arene ester **1** can be characterized as the host molecule where the stability of the sodium complex in solution is intermediate between that of the sodium complexes of crown ether (18C6) and cryptands (C211 and C222). In addition, the calix[4]arene ester **1** has an intermediate behavior of kinetics between crown ether (18C6) and cryptand ($C21C_5$), formation of the complex occurs as for the crown ether, but dissociation of the complex occurs as for the cryptand.

Acknowledgements

The author thanks Mr E. Yamada for the measurement of ^1H

Table 2 Rate constants and activation parameters[a] for the dissociation of alkali-metal ion complexes in acetonitrile

Complex	k_1/s^{-1} (298 K)	$k_{-1}/dm^{-3}\ mol^{-1}\ s^{-1}$ (298 K)	$\Delta_d H^\ddagger$/kJ mol^{-1}	$\Delta_d S^\ddagger$/J mol^{-1} K^{-1}	$\Delta_d G^\ddagger$/kJ mol^{-1} (298 K)
Li^+-**1**	1.0×10^2	1.5×10^8	40 ± 5	−73 ± 14	62 ± 9
Na^+-**1**	1.4	6.7×10^7	64 ± 1	−29 ± 4	73 ± 2
K^+-**1**	3.0×10^3	3.3×10^7	46 ± 3	−29 ± 11	55 ± 6
Na^+-18C6	3.8×10^3[b]	2.3×10^7[c]	32 ± 2[b]	−65 ± 8[b]	53 ± 0.4[b]
Na^+-$C21C_5$[d]	84.8	1.0×10^7	58 ± 1	−14 ± 2	62 ± 1

[a] Quoted errors represent one standard deviation obtained from a linear regression analysis of the temperature dependence of experimental τ_c data through eqn. (2). [b] Ref. 24. [c] Calculated by using the stability constant in ref. 32. [d] Ref. 18.

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