



Proton NMR Study of the Ligand Interchange of the Ba^{2+} -18-Crown-6 Complex in Binary Acetonitrile-Water Mixtures

ALI REZA FAKHARI

Department of Chemistry, Tarbiat Modarres University, Tehran, Iran.

MOJTABA SHAMSIPUR*

Department of Chemistry, Razi University, Kermanshah, Iran

(Received: 13 March 1997; accepted: 1 August 1997)

Abstract. The exchange kinetics of the Ba^{2+} -18-crown-6 complex were studied in different acetonitrile-water mixtures by proton NMR line-shape analysis. While in 50% acetonitrile solution (and at all temperatures studied) the exchange of 18-crown-6 between the free and complexed sites proceeds via a dissociative pathway, in other binary mixtures containing >50% acetonitrile both the dissociative and bimolecular mechanisms contribute to the ligand interchange. The exchange rates and the activation parameters E_a , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger for the ligand exchange have been determined and the possible parameters controlling the exchange rate and mechanism are discussed.

Key words: 18-Crown-6, Ba^{2+} ion, mixed solvent, exchange kinetics, NMR.

1. Introduction

For a better understanding of the pronounced selectivities of macrocyclic ligands towards alkali and alkaline earth cations [1] it is necessary to investigate their mechanisms of association and dissociation. Although there is a wealth of information about the thermodynamic and structural studies of the complexation of macrocyclic ligands with metal ions in different solvent media, their kinetic and mechanistic studies have received less attention and hence are still poorly understood [2, 3]. In recent years, alkali metal NMR has been used to investigate the kinetics and mechanism of several alkali-macrocycle systems under different experimental conditions [3–12]. However, due to the low sensitivity and natural abundance of alkaline earth nuclei, their NMR cannot be used for such exchange kinetics studies.

We have recently used the dynamic proton NMR method to investigate the exchange of 18-crown-6 with its alkaline earth and some transition metal complexes, and the mechanism of ligand exchange [13, 14]. In this paper, we use proton NMR

* Author for correspondence.

line-shape analysis to determine the kinetic parameters and the mechanism for the chemical exchange of 18-crown-6 between the free and 1 : 1 complex with barium ion in different binary water-acetonitrile mixtures.

2. Experimental

The macrocyclic polyether 18-crown-6 (18C6, Merck) was precipitated as its acetonitrile complex [15]. The resulting crystals were isolated and kept under vacuum at room temperature for several days to drive off the acetonitrile. Reagent grade barium perchlorate (Merck) of the highest purity available was used without any further purification except for vacuum drying over P₂O₅. Deuteriated acetonitrile (CD₃CN, Fluka) and water (D₂O, Fluka) were used to prepare the solvent mixtures by weight.

The proton NMR spectra were recorded on a Joel JNM-EX90 FTNMR spectrometer operating at a field of 21.15 kG (a frequency of 90 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. Throughout the whole temperature range used, it was found that 10 min thermostating prior to data collection was adequate for each sample to reach the equilibrium temperature. Thus, each sample tube was left in the probe for at least 10 min before measurements. At all temperatures used, the accuracy of the temperature measurements was ± 0.1 °C. In all experiments, TMS was used as an internal standard. Sealed samples were used throughout. In the case of all samples used, 17–20 transients were collected.

Line widths of the free and complexed 18C6 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 Bloch equations [16]. Equations used were of similar format to those used by Cahen *et al.* [17]. A non-linear least-squares program based on Powell's technique [18] was used to fit 100–150 points of the spectral data to the exchange equations in order to extract the τ values for each system at several temperatures.

3. Results and Discussion

The exchange of 18C6 with its 1 : 1 complex with Ba²⁺ ion in different binary acetonitrile-water mixtures was examined by use of a ¹H NMR technique at three different metal ion to ligand mole ratios. Sample spectra are shown in Figure 1. It is well known that, due to its good size complementarity with the cavity of the macrocycle, the Ba²⁺ ion forms quite a stable 1 : 1 complex both in water ($\log K_f = 3.87$) [19] and, especially, in acetonitrile solution ($\log K_f > 5$) [20]. Thus, in the mixed solvents used, the exact population of free and complexed crown can be directly obtained from the barium ion to 18C6 mole ratios. Moreover, in all solvent mixtures used, upon complexation with Ba²⁺ ion, the single proton NMR signal of

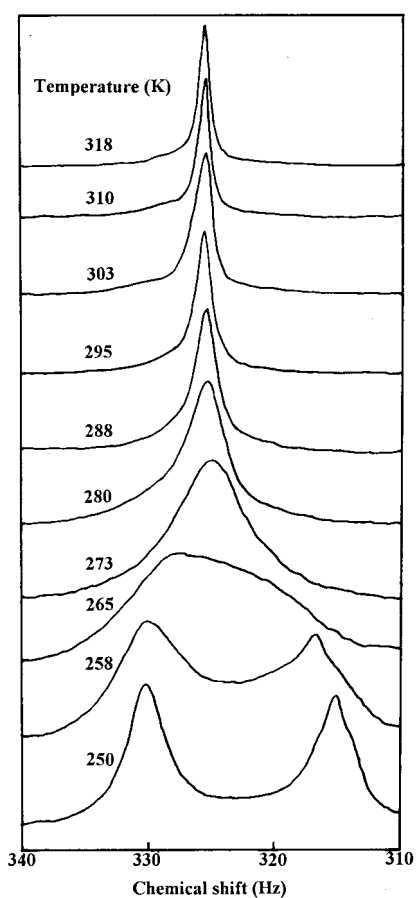


Figure 1. ¹H NMR spectra at various temperatures for 0.02 M 18C6 in 90% AN solution with a Ba²⁺-18C6 mole ratio of 0.54.

the crown ether shows suitable shift changes for the application of dynamic NMR methods. A sample computer fit of the proton NMR spectrum is shown in Figure 2 and all the resulting τ values obtained are collected in Table I.

The first ²³Na NMR studies of the dissociation kinetics of the Na⁺-DB18C6 complex in different solvents [21, 22] indicated that the major mechanism responsible for the exchange of sodium ion between the solvated and complexed sites is a dissociative pathway:



However, in 1983 Schmidt and Popov [23] reported the first evidence of a bimolecular metal exchange mechanism for the K⁺-18C6 system in 1,3-dioxolane using ³⁹K NMR spectroscopy:

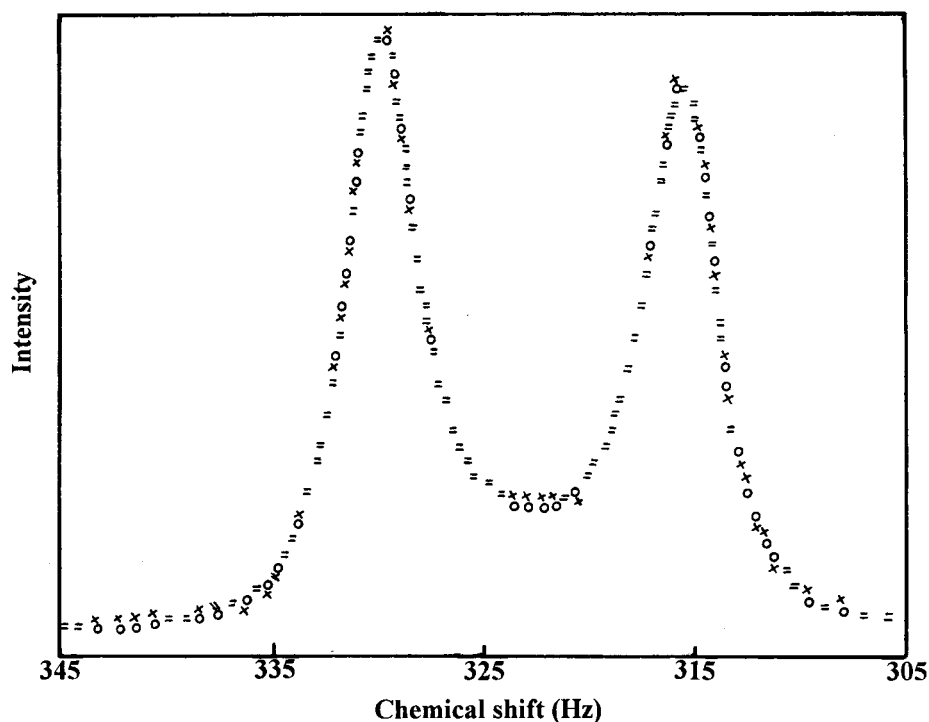
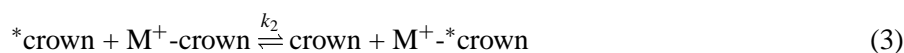


Figure 2. Computer fit of ^1H NMR spectrum obtained with a 0.02 M solution of 18C6 in 90% AN containing Ba^{2+} ion with a cation to crown mole ratio of 0.54 at 250 K: (x) experimental point; (o) calculated point; (=) experimental and calculated points are the same within the resolution of the plot.



These two mechanisms describe all the metal exchange systems studied to date [3–12]. Moreover, in the case of the excess crown ether coexisting in solution with the complex, a bimolecular mechanism for the ligand exchange should also be considered [13, 14, 24]:



The general expression for mean lifetime, τ , in terms of these two mechanisms (i.e., mechanisms 1 and 3) is [13]:

$$1/\tau = k_{-1}[\text{crown}]_t/[\text{crown}]_f + 2k_2[\text{crown}]_t \quad (4)$$

where $[\text{crown}]_t$ is the total concentration and $[\text{crown}]_f$ is the concentration of uncomplexed 18C6. According to Equation (4), at a given temperature, a plot of $1/\tau[\text{crown}]_t$ vs. $1/[\text{crown}]_f$ determines the contributions of the two mechanisms

Table I. Mean lifetimes, τ , and calculated rate constants for the ligand interchange of the Ba^{2+} -18C6 complex in different acetonitrile-water mixtures at various temperatures.

wt% AN	T (°K)	MR ^a	τ (s)	MR	τ (s)	MR	τ (s)	k_{-1} (s ⁻¹)	k_2 (M ⁻¹ s ⁻¹)
90	303	0.22	4.21×10^{-4}	0.54	3.85×10^{-4}	0.87	1.95×10^{-4}	433	4.6×10^3
	295	0.22	7.73×10^{-4}	0.54	6.99×10^{-4}	0.87	3.14×10^{-4}	299	2.1×10^4
	288	0.22	1.45×10^{-3}	0.54	1.29×10^{-3}	0.87	5.52×10^{-4}	177	1.1×10^4
	280	0.22	3.63×10^{-3}	0.54	3.37×10^{-3}	0.87	1.90×10^{-3}	40	5.4×10^{-3}
	273	0.22	6.34×10^{-3}	0.54	6.20×10^{-3}	0.87	4.21×10^{-3}	25	2.9×10^{-3}
	265	0.22	1.33×10^{-2}	0.54	1.30×10^{-2}	0.87	7.03×10^{-3}	11	1.4×10^3
	258	0.22	2.63×10^{-2}	0.54	2.60×10^{-2}	0.87	1.53×10^{-2}	4	7.7×10^2
	250	0.22	6.22×10^{-2}	0.54	5.36×10^{-2}	0.87	3.29×10^{-2}	2	3.3×10^2
80	310	0.22	8.47×10^{-4}	0.56	6.57×10^{-4}	0.88	3.07×10^{-4}	298	2.1×10^4
	303	0.22	1.62×10^{-4}	0.56	8.93×10^{-4}	0.88	4.51×10^{-4}	216	1.2×10^4
	295	0.22	2.00×10^{-3}	0.56	1.61×10^{-3}	0.88	7.74×10^{-4}	114	9.4×10^3
	288	0.22	4.01×10^{-3}	0.56	2.56×10^{-3}	0.88	1.31×10^{-3}	70	5.0×10^3
	280	0.22	6.32×10^{-3}	0.56	5.01×10^{-3}	0.88	1.85×10^{-3}	56	2.1×10^3
	273	0.22	1.05×10^{-2}	0.56	8.23×10^{-3}	0.88	3.06×10^{-3}	34	1.3×10^3
	265	0.22	1.71×10^{-2}	0.56	1.37×10^{-2}	0.88	4.07×10^{-3}	28	4.3×10^2
70	308	0.22	7.22×10^{-4}	0.56	5.32×10^{-4}	0.87	2.20×10^{-4}	463	2.3×10^4
	303	0.22	1.33×10^{-3}	0.56	8.64×10^{-4}	0.87	3.52×10^{-4}	301	1.2×10^4
	298	0.22	1.48×10^{-3}	0.56	9.68×10^{-4}	0.87	3.72×10^{-4}	292	9.4×10^3
	293	0.22	2.17×10^{-3}	0.56	1.37×10^{-3}	0.87	4.66×10^{-4}	247	4.4×10^3
	288	0.22	2.78×10^{-3}	0.56	1.91×10^{-3}	0.87	5.76×10^{-4}	20.5	2.2×10^3
	283	0.22	3.58×10^{-3}	0.56	2.50×10^{-3}	0.87	7.02×10^{-4}	1.71	1.1×10^3
50	303	0.26	2.22×10^{-3}	0.61	1.13×10^{-3}	—	—	342	—
	295	0.26	2.82×10^{-3}	0.61	1.45×10^{-3}	—	—	268	—
	288	0.26	3.63×10^{-3}	0.61	1.86×10^{-3}	—	—	208	—
	280	0.26	4.62×10^{-3}	0.61	2.34×10^{-3}	—	—	160	—
	273	0.26	6.01×10^{-3}	0.61	3.20×10^{-3}	—	—	121	—
	265	0.26	1.40×10^{-2}	0.61	4.40×10^{-3}	—	—	87	—

^a MR = $[\text{Ba}^{2+}]/[\text{18C6}]$.

to the exchange process. Such plots for Ba^{2+} -18C6 in 90% and 50% acetonitrile are shown in Figures 3 and 4, respectively. The corresponding plots in 80% and 70% acetonitrile show a pattern more or less similar to those observed in 90% acetonitrile.

As can be seen from Table I and Figures 3 and 4, while in 50% AN solution (and at all temperatures used) the exchange of 18C6 between the free and complexed

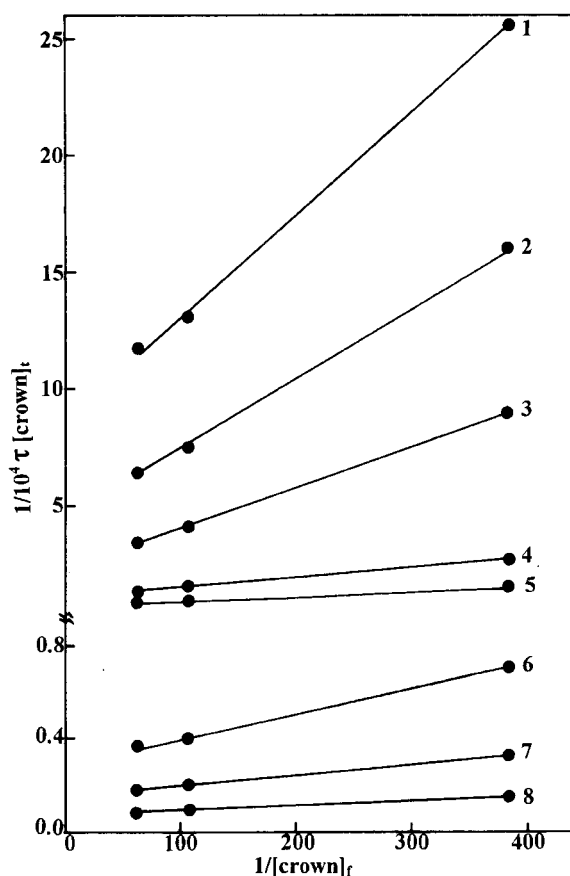


Figure 3. Plots of $1/\tau[\text{crown}]_f$ vs. $1/[\text{crown}]_f$ for the Ba^{2+} -18C6 complex in 90% AN at various temperatures (K): (1) 303, (2) 295, (3) 288, (4) 280, (5) 273, (6) 265, (7) 258, (8) 250.

sites for the Ba^{2+} -18C6 complex proceeds via a dissociative mechanism; in the binary mixtures containing >50% acetonitrile both the dissociative and bimolecular mechanisms contribute to the ligand exchange; the contributions of the two mechanisms could be obtained graphically. The results agree well with the influence of the solvent properties on the exchange kinetics of the Na^+ -18C6 system (as studied by ^{23}Na NMR) by Strasser and Popov [4]. They observed that, in solvents with both high donor numbers and high dielectric constants the predominant mechanism is the dissociative one, while in solvents of low donor number but relatively high dielectric constant a bimolecular mechanism tends to predominate. Thus, it is not unexpected that the addition of a high percentage of water, as a solvent of both high donor number and high dielectric constant (i.e., $\text{DN} = 33$ and $\epsilon = 78$) [25], to acetonitrile with $\text{DN} = 14.1$ and $\epsilon = 37.5$ [26] will change the predominant bimolecular exchange mechanism for the Ba^{2+} -18C6 system to a dissociative pathway.

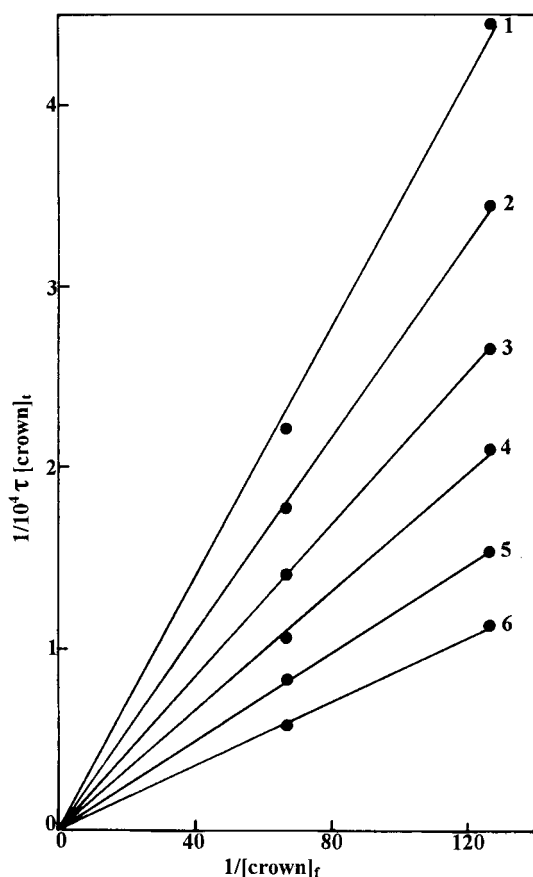


Figure 4. Plots of $1/\tau[\text{crown}]_i$ vs. $1/[\text{crown}]_f$ for the Ba^{2+} -18C6 complex in 50% AN at various temperatures (K): (1) 303, (2) 295, (3) 286, (4) 280, (5) 273, (6) 258.

When either mechanism is dominant, a plot of $\ln k$ vs. inverse temperature gives an Arrhenius plot. Sample Arrhenius plots for both bimolecular and dissociative mechanisms are shown in Figure 5. Activation energies, E_a , for the release of 18C6 from its complex with the Ba^{2+} ion complex in all solvent mixtures used were determined from the slopes of such linear plots, and the activation parameters ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger were calculated by using Eyring's transition-state theory [27]. Results of these calculations are summarized in Table II.

The data given in Table II indicate that, in the case of the dissociative mechanism, the activation energy decreases by increasing the water content of the solvent mixture, while an opposite behavior is observed for the bimolecular pathway. The results suggest that the activated complex in the dissociative mechanism should be a solvated complex (solvent : Ba^{2+} : 18C6), in which the water molecules with higher donating abilities are preferred over acetonitrile by the active species. Since the dissociation process can be assumed as the result of a series of stepwise barium-

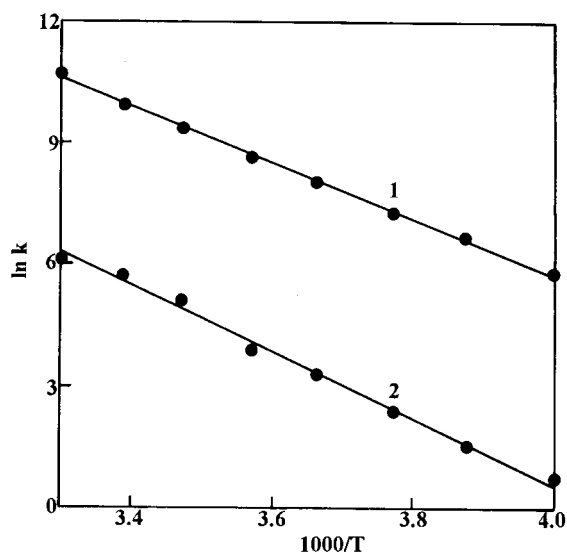


Figure 5. Arrhenius plots of $\ln k$ vs. inverse temperature for the Ba^{2+} -18C6 in 90% AN: (1) bimolecular mechanism, (2) dissociative mechanism.

Table II. Activation parameters for the ligand exchange in the Ba^{2+} -18C6 complex in different acetonitrile-water mixtures.

Exchange mechanism	Activation parameter	Solvent composition (%AN)			
		50	70	80	90
Dissociative	E_a (kJ mol^{-1})	23.9 ± 0.2	29.6 ± 2.9	37.3 ± 2.9	66.2 ± 1.9
	ΔH^\ddagger (kJ mol^{-1})	21.5 ± 0.2	27.1 ± 2.9	34.9 ± 2.8	63.9 ± 1.9
	ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$)	-125 ± 1	-108 ± 10	-86 ± 10	10 ± 6
	$\Delta G^{\ddagger a}$ (kJ mol^{-1})	58.7 ± 0.1	59.3 ± 0.2	60.5 ± 0.2	60.9 ± 0.1
Bimolecular	E_a (kJ mol^{-1})	—	87.2 ± 3.6	58.5 ± 3.0	57.5 ± 0.9
	ΔH^\ddagger (kJ mol^{-1})	—	84.8 ± 3.6	56.1 ± 3.1	55.2 ± 0.09
	ΔS^\ddagger ($\text{J mol}^{-1} \text{K}^{-1}$)	—	115 ± 12	19 ± 10	16 ± 3
	$\Delta G^{\ddagger a}$ (kJ mol^{-1})	—	50.5 ± 0.1	50.4 ± 0.1	50.4 ± 0.1

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

oxygen bond ruptures accompanied by barium-solvent bond formation [28], an increase in the donicity of the solvent mixture is expected to decrease the activation energy of the system. On the other hand, the predominance of a bimolecular mechanism requires the existence of a well isolated sandwich complex $18\text{C}6 : \text{Ba}^{2+} : 18\text{C}6$ in the transition state, which is much less solvated than the initial $\text{Ba}^{2+} - 18\text{C}6$ complex. Thus, the preferential solvation of the initial complex by the water

molecules may lead to an increase in the E_a by the increasing amount of water in the mixed solvent.

From Table II is readily seen that, in the cases where both the dissociative and bimolecular mechanisms prevail, a transition state resulting from the close approach of two 18C6 molecules (i.e., 18C6 : Ba²⁺ : 18C6) is energetically favored compared to a transition state resulting from the partial release of Ba²⁺ ion from its 18C6 complex (i.e., H₂O : Ba²⁺ : 18C6); the ΔG^\ddagger values for the bimolecular mechanisms are some 10 kJ mol⁻¹ less positive than those for the dissociative pathway. It is noteworthy that the predominance of the bimolecular mechanism over the dissociative pathway is mainly of entropic origin. We have previously observed similar results for the Ba²⁺-18C6 system in methanol [14]. The occurrence of a bimolecular exchange is associated with the release of some solvent molecules, in going from the initial complex to the transition state, which results in positive values of ΔS^\ddagger . While, in the dissociative pathway, the partial release of Ba²⁺ ion from its 18C6 complex during the course of transition state formation will be expected to result in a much higher degree of solvent organization in the transition state compared to the initial complex, resulting in negative ΔS^\ddagger values. As expected, the ΔS^\ddagger values for the dissociative mechanism becomes more negative by increasing the water content of the solvent mixtures used.

It is interesting to note that, in the solvent systems which show the bimolecular mechanism, the free energy of activation, ΔG^\ddagger , is largely independent of the solvent mixture composition, although the ΔH^\ddagger and ΔS^\ddagger values do depend on the nature of the solvent. These results are not very surprising, since in a bimolecular exchange mechanism the initial and the final states are identical and, therefore, one would not expect the solvent to have a large influence on the magnitude of ΔG^\ddagger . Similar results have already been reported in the literature [4, 7, 23]. On the other hand, in the cases where the dissociative exchange mechanism predominates, the free energy of activation depends on the solvent composition: the ΔG^\ddagger decreases with increasing mole fraction of water in the solvent mixture. The same kind of correlation between ΔG^\ddagger and the Gutmann donor number [26] of solvents has previously been reported for alkali metal complexes with crown ethers [4] and cryptands [5, 6, 29].

References

1. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
2. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
3. C. Detellier, H.P. Graves, and M.K. Briere: in *Isotopes in the Physical and Biomedical Sciences; Isotopic Applications in NMR Studies* (Eds. E. Buncler and J.R. Jones), Vol. 2, Ch. 4, Elsevier, Amsterdam (1991).
4. B.O. Strasser and A.I. Popov: *J Am. Chem. Soc.* **107**, 7921 (1985).
5. M. Shamsipur and A.I. Popov: *J Phys.* **90**, 5997 (1986).
6. M. Shamsipur and A.I. Popov: *J. Phys. Chem.* **91**, 447 (1987).
7. M. Shamsipur and A.I. Popov: *J. Phys. Chem.* **92**, 147 (1988).

8. H.D.H. Stover and C. Detellier: *J. Phys. Chem.* **93**, 3174 (1989).
9. S.F. Lincoln and T. Rodopoulos: *Inorg. Chim. Acta* **190**, 223 (1991).
10. K.M. Briere and C. Detellier: *Can. J. Chem.* **70**, 2536 (1992).
11. K.M. Briere and C. Detellier: *J. Phys. Chem.* **96**, 2185 (1992).
12. S.L. Whilbread, S. Politis, A.K.W. Stephens, J.B. Lucas, R. Dhillon, S.F. Lincoln, and K.P. Wainwright: *J. Chem. Soc., Dalton Trans.* 1379 (1996).
13. N. Alizadeh and M. Shamsipur: *J. Chem. Soc., Faraday Trans.* **92**, 4391 (1996).
14. N. Alizadeh and M. Shamsipur: *J. Solution Chem.* **25**, 1029 (1996).
15. G.W. Gokel, D.J. Cram, C.L. Liottla, H.P. Harris, and F.L. Cook: *Org. Synth.* **56**, 30 (1977).
16. J.A. Pople, W.G. Schneider, and H.J. Bernstein, *High Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York (1959), p. 218.
17. Y.M. Cahen, J.L. Dye, and A.I. Popov: *J. Phys. Chem.* **79**, 1292 (1975).
18. M.J.D. Powell: *Comput. J.* **42**, 96 (1962).
19. R.M. Izatt, R.E. Terry, B.L. Haymore, L.D. Hansen, N.K. Dailey, A.G. Avondet, and J.J. Christensen: *J. Am. Chem. Soc.* **98**, 7920 (1976).
20. A. Semnani and M. Shamsipur: *J. Electroanal. Chem.* **315**, 95 (1991).
21. E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer: *J. Am. Chem. Soc.* **95**, 7133 (1971).
22. E. Shchori, J. Jagur-Grodzinski, and M. Shporer: *J. Am. Chem. Soc.* **95**, 3842 (1973).
23. E. Schmidt and A.I. Popov: *J. Am. Soc.* **105** 1873 (1983).
24. J.C. Lockhart, M.B. McDonnell, M.N. Stuart Hill, and M. Todd: *J. Chem. Soc., Perkin Trans.* **2** 1915 (1989).
25. R.H. Erlich, E. Roach, and A.I. Popov: *J. Am. Chem. Soc.* **92**, 4989 (1970).
26. V. Gutmann and E. Wychera: *Inorg.Nucl. Chem. Lett.* **2**, 257 (1966).
27. S.H. Lin, K.P. Li, and H. Eyring: in *Physical Chemistry, an Advanced Treatise* (Eds. H. Eyring, D. Handerson, and W. Yost), Vol. vii, Academic Press, New York (1971), p. 1.
28. B.G. Cox and H. Schneider: *Pure Appl. Chem.* **62**, 2259 (1990).
29. B.G. Cox, J. Garcia-Rosas, and H. Schneider: *J. Am. Chem. Soc.* **103**, 1054 (1981).