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Potentiometric Study of Thermodynamic Parameters of Complexing of Lithium Ion-Basic Aprotic Solvents and Sodium Ion-Macrocyclic Polyethers in Acetonitrile

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Formation constants of the 1 : 1 complexes of lithium ion in acetonitrile (AN) with DMF, DMSO, DMA, and HMPA and of sodium ion in AN with 15-crown-5 (15C5), 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6), and cryptand 211 (Cryp 211), were determined at 10, 25, and 40 °C by potentiometric methods with a cation-sensitive glass electrode. From the change of the formation constants with temperature, thermodynamic parameters ΔG°_{298}, ΔH°_{298}, and $-T\Delta S^\circ_{298}$, were obtained. ΔG°_{298}, ΔH°_{298}, and $-T\Delta S^\circ_{298}$, all in kJ mol^{-1}, for Li$^+$-solvent complexes were, respectively, -7.9, $-9._0$, $+1._1$ for DMF, -9.7, $-10._1$, $+0._5$ for DMSO, -10.0, $-9._9$, $-0._1$ for DMA, and -18.9, $-15._8$, $-3._1$ for HMPA, and those for Na$^+$-macrocyclic polyether complexes, -28.4, $-24._1$, $-4._5$ for 15C5, -27.2, $+1._6$, $-28._7$ for 18C6, -28.6, $-14._3$, $-14._2$ for DB18C6, and -51.9, $-53._8$, $+2._1$ for Cryp 211. Some features about the roles of enthalpy and entropy terms in complexing have been discussed.

In the previous papers,$^{1-5)}$ we reported the successive formation constants of complexes of several univalent cations in acetonitrile (AN) with other donor solvents. They were obtained potentiometrically at 25 °C by using a univalent cation-sensitive glass electrode (Beckman 39047). In this paper, intending to understand the complexing phenomena in more detail, we have determined at several different temperatures the formation constants of lithium ion in AN with some basic aprotic solvents and obtained the values of ΔG°_{298}, ΔH°_{298}, and $-T\Delta S^\circ_{298}$ for the reaction shown by Eq. 1:

$$\mathrm{Li_S^+} + \mathrm{D} = \mathrm{Li_D^+}, \tag{1}$$

where $\mathrm{Li_S^+}$ is the lithium ion solvated only by AN and $\mathrm{Li_D^+}$ that complexed by one molecule of solvent D. We have also obtained similar thermodynamic parameters for the complexing (Eq. 2) of the sodium ion in AN with some macrocyclic polyethers by a potentiometric method:

$$\mathrm{Na_S^+} + \mathrm{L} = \mathrm{Na_L^+}, \tag{2}$$

where $\mathrm{Na_S^+}$ is the sodium ion solvated only by AN and $\mathrm{Na_L^+}$ that complexed by macrocyclic polyether L. The general construction of the cell used for the measurements was as follows:

$$\mathrm{Ag}\left|\begin{matrix}5\times10^{-3}\ \mathrm{M\ AgNO_3}+\\ 10^{-2}\ \mathrm{M\ Et_4NClO_4(AN)}\end{matrix}\right\|\begin{matrix}5\times10^{-2}\ \mathrm{M}\\ \mathrm{Et_4NClO_4(AN)}\end{matrix}\Bigg\| \begin{matrix}10^{-3}\ \mathrm{M\ M^+ClO_4^-}+10^{-2}\ \mathrm{M}\\ \mathrm{Et_4NClO_4(AN+D\ or\ L)}\end{matrix}\left|\begin{matrix}\text{Cation-sensitive}\\ \text{glass electrode}\end{matrix}\right.$$

(Cell I)

where M$^+$ was $\mathrm{Li_S^+}$ for reaction (1) and Na$^+$ for reaction (2).

Complexing of the Lithium Ion in AN with Other Aprotic Solvents. The formation constant, K_1 in mol^{-1} dm^3, for reaction (1) is defined by

$$K_1 = \frac{(\mathrm{Li_D^+})}{(\mathrm{Li_S^+})[\mathrm{D}]}, \tag{3}$$

where $(\mathrm{Li_S^+})$ and $(\mathrm{Li_D^+})$ are the activities of $\mathrm{Li_S^+}$ and $\mathrm{Li_D^+}$, respectively, and [D] is the concentration of solvent D. The values of K_1 at 10, 25, and 40 °C were determined by the same method as those in the previous papers.$^{1-5)}$ From the relation between $R\ln K_1$ and $1/T$, ΔH°_{298} was obtained using the SALS program of the Tokyo University Computer Center. The value of $-T\Delta S^\circ_{298}$ was obtained with the following relation:

$$-RT\ln K_1 = \Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298}. \tag{4}$$

Complexing of the Sodium Ion in AN with Macrocyclic Polyethers. The formation constant, K in mol^{-1} dm^3, for the 1 : 1 complexing of the sodium ion in AN with a macrocyclic polyether L (Eq. 2) is defined by

$$K = \frac{(\mathrm{Na_L^+})}{(\mathrm{Na_S^+})_\mathrm{L}[\mathrm{L}]}, \tag{5}$$

where $(\mathrm{Na_S^+})_\mathrm{L}$ and $(\mathrm{Na_L^+})$ are the activities of $\mathrm{Na_S^+}$ and $\mathrm{Na_L^+}$, respectively, and [L] is the concentration of L. Here, the activity coefficient of the sodium ion is assumed not to change on complexation. Then we may write Eq. 5 as follows:

$$K = \frac{[\mathrm{Na_L^+}]}{[\mathrm{Na_S^+}]_\mathrm{L}[\mathrm{L}]}, \tag{6}$$

There exist following relations:

$$[\mathrm{Na_L^+}] = [\mathrm{Na_S^+}]_\mathrm{init} - [\mathrm{Na_S^+}]_\mathrm{L}, \tag{7}$$

$$[\mathrm{L}] = C_\mathrm{L} - [\mathrm{Na_L^+}], \tag{8}$$

where $[\mathrm{Na_S^+}]_\mathrm{init}$ and $[\mathrm{Na_S^+}]_\mathrm{L}$ are the concentrations of $\mathrm{Na_S^+}$ before and after the addition of L to Cell I, and C_L shows the total concentration of L added. Equation 6 can then be written as follows:

$$K = \frac{[\mathrm{Na_S^+}]_\mathrm{init} - [\mathrm{Na_S^+}]_\mathrm{L}}{[\mathrm{Na_S^+}]_\mathrm{L}\{C_\mathrm{L} - [\mathrm{Na_S^+}]_\mathrm{init} + [\mathrm{Na_S^+}]_\mathrm{L}\}}. \tag{9}$$

Here, $[\mathrm{Na_S^+}]_\mathrm{init}$ and $[\mathrm{Na_S^+}]_\mathrm{L}$ are related with the electrode potentials, E_init before the addition of L and E_L after the addition of L, by the following equation:

$$E_\mathrm{L} = E_\mathrm{init} + \frac{RT}{F}\ln\frac{[\mathrm{Na_S^+}]_\mathrm{L}}{[\mathrm{Na_S^+}]_\mathrm{init}}. \tag{10}$$

To obtain K, the sodium ion in AN was titrated with a solution of L in AN up to about three times the equivalence point and the potential change during the titration was plotted. K-values which precisely fitted with the titration curves were obtained by successive approximation method. From the values of K at 10, 25, and 40 °C, values of ΔG°_{298}, ΔH°_{298}, and $-T\Delta S^\circ_{298}$ for Eq. 2 were obtained as above.

Experimental

The apparatus and experimental techniques were the same as those described before,[1,2] except that more effort was made to keep all parts of the cell assembly, including the reference electrode, precisely (within ±0.2 °C) at the desired temperatures.

Nakarai's reagent grade dibenzo-18-crown-6 (DB18C6) was purified by extraction with chloroform and recrystallization from ethanol. 18-Crown-6 (18C6), 15-crown-5 (15C5), and cryptand 211 (Cryp 211) were the Merck products and were used without further purification. Hexamethylphosphoric triamide (HMPA) was a products of Johoku Chemical Industry Co. Ltd. and was purified by distilling three times under vacuum, first from barium oxide, second by the addition of small amount of sodium metal, and last without additives.[6] This HMPA was used within an hour after the purification. Other solvents and reagents were the same as those used in the previous reports.[1,2]

Results and Discussion

Before running the present experimental work, the cation-sensitive glass electrode was confirmed to respond in a Nernstian way to the activities of sodium and lithium ions in AN at 10, 25, and 40 °C. The value of the activity coefficient y used was calculated from the Debye-Hückel equation, $\log y = -AI_c^{1/2}/[1+BaI_c^{1/2}]$ ($A=1.82(\varepsilon T)^{-3/2}\times 10^6$ mol$^{-1/2}$ dm$^{3/2}$ (deg K)$^{3/2}$, $B=5.03(\varepsilon T)^{-1/2}\times 10^{10}$ dm$^{1/2}$ mol$^{-1/2}$ (deg K)$^{1/2}$, $a=5\times 10^{-9}$ dm, and I_c=ionic strength). As the dielectric constant at 10, 25, and 40 °C, respectively, 39.1, 36.7, and 34.3 were used.[7] The density of HMPA was measured to be 1.03_3, 1.02_1, and 1.00_7 g cm^{-3} at 10, 25, and 40 °C, respectively. For the densities of other solvents, we referred to literature values.[8]

Complexing of the Lithium Ion in AN with Other Aprotic Solvents. The values of K_1 for the complexing of N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), N,N-dimethylacetamide (DMA), and HMPA are shown in Table 1. Each value is the average of more than four determinations. Maximum concentrations of solvent D added to Cell I were 0.08 M for DMF, 0.045 M for DMSO, 0.05 M for DMA, and 0.005 M for HMPA. The relation between $R \ln K_1$ and $1/T$ for each solvent is linear, as shown in Fig. 1, and makes possible to obtain ΔH°_{298} and $-T\Delta S^\circ_{298}$. These values, calculated by using the SALS program and Eq. 4, are also shown in Table 1. It is interesting to note that, in each case, the enthalpy term plays an important role and the role of the entropy term is relatively small in determining the free energies. These results seem to be reasonable if the complexation reaction of Eq. 1 is considered to be the exchange of one solvated AN molecule with one molecule of added solvent D.

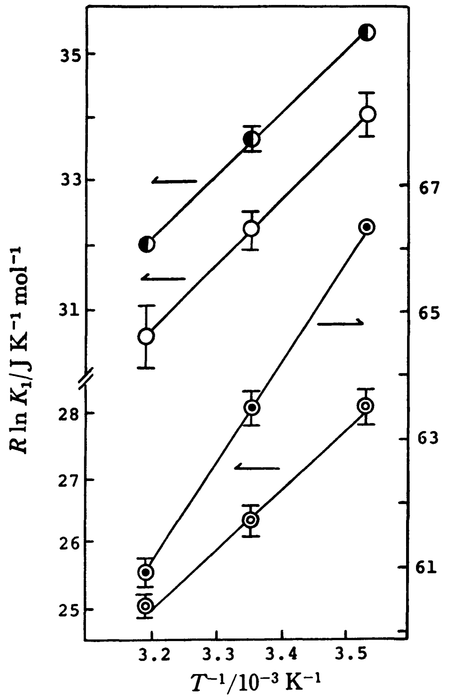

Fig. 1. Relation between $R \ln K_1$ for the reaction $Li^+ + D = Li_D^+$ and $1/T$.
D=DMF (◎), DMSO (○), DMA (◐), and HMPA (⊙).

To obtain reliable ΔH°_{298}, K_1 at each temperature should be determined at least within errors of several percent. The present potentiometric method could give such K_1-values for the complexing of lithium ion with

Table 1. THERMODYNAMIC PARAMETERS FOR THE COMPLEXING OF LITHIUM ION IN ACETONITRILE WITH OTHER APROTIC SOLVENTS

Ligand D	K_1/mol^{-1} dm^3 (T/K)	$-\Delta G^\circ_{298}$ / kJ mol^{-1}	$-\Delta H^\circ_{298}$ / kJ mol^{-1}	$T\Delta S^\circ_{298}$ / kJ mol^{-1}
DMF	29.5±1.1(283) 23.7±0.7(298) 20.3±0.4(313)	+7.85±0.07	+9.0±1.0	−1.1±1.0
DMSO	59.8±2.9(283) 50.0±3.1(298) 39.7±2.5(313)	+9.70±0.09	+10.1±1.9	−0.5±1.9
DMA	70.1±1.5(283) 57.3±1.5(298) 47.0±0.3(313)	+10.04±0.06	+9.9±0.5	+0.1±0.5
HMPA	(2.87±0.04)×10^3(283) (2.05±0.07)×10^3(298) (1.51±0.04)×10^3(313)	+18.91±0.08	+15.8±0.8	+3.1±0.8

TABLE 2. THERMODYNAMIC PARAMETERS FOR THE COMPLEXING OF SODIUM ION WITH SEVERAL MACROCYCLIC POLYETHERS

Ligand L	K/mol^{-1} dm^3 (T/K)	$\frac{-\Delta G^\circ_{298}}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H^\circ_{298}}{\text{kJ mol}^{-1}}$	$\frac{T\Delta S^\circ_{298}}{\text{kJ mol}^{-1}}$
15C5	$1.7_2\times10^5$(283) $9._5\times10^4$(298) $6._4\times10^4$(313)	+28.4±0.1	+24.1±2.0	+4.5±2.0
18C6	$5._4\times10^4$(283) $5._8\times10^4$(298) $5._7\times10^4$(313)	+27.2±0.1	−1.6±0.4	+28.7±0.4
DB18C6	$1.3_4\times10^5$(283) $1.0_1\times10^5$(298) $7._4\times10^4$(313)	+28.6±0.2	+14.3±2.3	+14.2±2.4
Cryp 211	$3.7_5\times10^9$(283) $1.2_3\times10^9$(298) $4.2_0\times10^8$(313)	+51.9±0.4	+53.8±0.9	−2.1±1.0

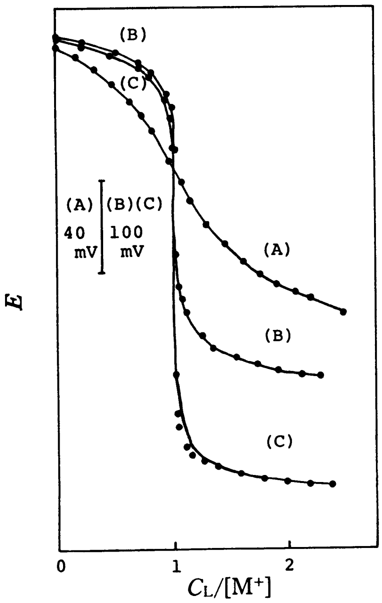

Fig. 2. Titration curves for the reaction $M^+ + L = M_L^+$: (A) M=Na and L=18C6; (B) M=Na and L=Cryp211; (C) M=Li and L=Cryp211 (at 25 °C).

basic aprotic solvents, as is apparent from Fig. 1 and Table 1. But the application of this method becomes somewhat difficult for the complexing of lower formation constants. We have run similar experiment for complexing of the sodium ion, but the precision of K_1 was not sufficiently good. Qualitatively, however, the smaller ΔG°_{298} for the sodium complexes could be attributed mainly to the smaller ΔH°_{298}. Work is now in progress for the complexing of other univalent cations.

Complexing of the Sodium Ion in AN with Macrocyclic Polyethers. Thermodynamic parameters for the complexing of sodium ion in AN with such macrocyclic polyethers as 15C5, 18C6, DB18C6, and Cryp211 were determined by titrating sodium ion in 0.01 M Et_4NClO_4–AN with 0.01 M Et_4NClO_4–AN solution containing 0.02—0.04 M of macrocyclic ligands. Titrations were carried out at 10, 25, and 40 °C. Some examples of the titration results are shown in Fig. 2. Curve(A) is for the titration with 18C6 and Curve(B) for that with Cryp211. In each case, the formation constant K, which fitted well with the titration results, could be found by the successive approximation method; the solid curves were obtained from Eqs. 9 and 10 using such K values. Thus the assumption of the 1 : 1 complexing is proved to be reasonable. Curve(C) in Fig. 2 is for the titration of lithium ion with Cryp211 In this case, the formation constant of Li^+–Cryp211, is expected to be larger than 10^{10} from the potential jump at the equivalence point, but it is impossible to find a K-value which fits exactly with the experimental results. This may be due to the fact that the response of the glass electrode deviates somewhat from the Nernstian one at such low activities of lithium ion in the presence of Cryp211. The values of K of the sodium complexes are shown in Table 2. log K for the complexes of Na^+–DB18C6 and Na^+–18C6 at 25 °C were 5.00 and 4.76, respectively, in good agreement with the literature values of 4.8_5—5.0_0 for Na^+–DB18C6 and 4.5_5 for Na^+–18C6.[9]

The relations between $R \ln K$ and $1/T$ are plotted in

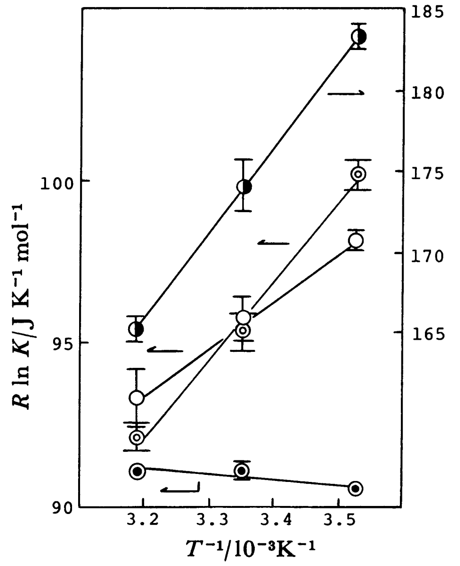

Fig. 3. Relation between $R \ln K$ for the reaction $Na^+ + L = Na_L^+$ and $1/T$.
L=15C5 (◎), 18C6 (⊙), DB18C6 (○), and Cryp 211 (◑).

Fig. 3, and thermodynamic parameters obtained by the SALS program and Eq. 4 are shown in Table 2. Except for the complex with Cryp211, the formation constants are approximately the same order of magnitudes, but it is interesting to note that the factors determining the free energies of complex formation are quite different from one complex to another. For the complex with 15C5 the enthalpy term plays a predominant role, while for the complex with 18C6 the entropy term is predominant. For the complex with DB18C6, the contributions from both factors are approximately the same. The small contribution of the enthalpy term for the 18C6 complex has been found by Popov$^{10)}$ in the calorimetric investigation of the lithium ion complexing ($\Delta H^\circ_{298} \approx 0$ and $-T\Delta S^\circ_{298} = 13.3$ kJ mol^{-1}). For Na$^+$–Cryp211, most of the free energy of formation was determined by the ethalpy term.

Because of the importance of complexes with macrocyclic polyethers, reports concerning the thermodynamic parameters of the complexing are recently increasing. Various methods, such as NMR,$^{10-12)}$ conductometry,$^{13,14)}$ potentiometry,$^{15)}$ and calorimetry,$^{10,16)}$ have been applied in several solvents. In order to discuss the mechanism of the complexing, however, the data are still too scarce. The present potentiometric method will be very convenient to obtain further information on this problem.

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