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The Complexing of the Lithium Ion in Acetonitrile with Other Solvents. Investigation by the Use of a Cation-sensitive Glass Electrode

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The complexing of the lithium ion with other popular solvents has been studied in acetonitrile (AN) using a monovalent cation-sensitive glass electrode. A method similar to that developed to study the complexing of the sodium ion was employed.1) Mono- and di-solvated species were formed for methanol, pyridine, formamide, methylfomamide, and HMPA. Tri-solvated species were also formed for DMF, DMA, and DMSO. In general, the complexing of the lithium ion with these solvents was more pronounced than that of the sodium ion. The formation constants for the mono-solvated lithium ion were 4.5 for methanol, 5.2 for pyridine, 16 for DMF, 20 for formamide, 25 for methylformamide, 49 for DMSO, 62 for DMA, and 2.1×10^3 for HMPA. When water was the complexing solvent, the equilibrium potential could not be obtained, probably because of the hydrolysis of the hydrated lithium ion. Prior to these experiments, the cation-sensitive glass electrode was confirmed to respond to the lithium-ion activity in different solvents by comparing its behavior with that of a lithium-amalgam electrode.

In the previous paper,1) the author and his collaborators reported a potentiometric method which used a monovalent cation-sensitive glass electrode to obtain the formation constants of the complexing of the sodium ion in acetonitrile (AN) with several popular solvents. In this experiment, a similar method has been used to determine the formation constants (the so-called hybrid formation constants), β_x, of the complexing of the lithium ion in AN with other solvents (Eqs. (1) and (2)):

$$\mathrm{Li_s^+} + x\mathrm{D} = \mathrm{Li_{\mathit{x}D}^+} \tag{1}$$

$$\beta_x = \frac{(\mathrm{Li_{\mathit{x}D}^+})}{(\mathrm{Li_s^+})[\mathrm{D}]^x} \tag{2}$$

In Eqs. (1) and (2), $\mathrm{Li_s^+}$ shows the lithium ion solvated only by AN, and $\mathrm{Li_{\mathit{x}D}^+}$, that complexed by x molecules of the D solvent. $(\mathrm{Li_s^+})$ and $(\mathrm{Li_{\mathit{x}D}^+})$ are the activities of $\mathrm{Li_s^+}$ and $\mathrm{Li_{\mathit{x}D}^+}$ respectively, and [D], the concentration of the free (uncomplexed) solvent, D.

Prior to the determination of the formation constants, the glass electrode was verified to respond with a Nernstian slope to the activity of the lithium ion in different solvents. This was done by comparing the response of the glass electrode, immersed in solutions of the 10^{-3}M lithium ion in different solvents, with the response of a lithium amalgam electrode immersed in the same solutions. The formation constants were determined by the emf measurement of Cell I, in the compartment (C) of which the D solvent was titrated to a solution of 10^{-3}M $\mathrm{LiClO_4}$+10^{-2}M $\mathrm{Et_4NClO_4}$, originally in pure AN:

Ag|0.005M $\mathrm{AgNO_3}$(AN)‖0.1M $\mathrm{Et_4NPic}$(AN)‖
(A) (B)
10^{-3}M $\mathrm{LiClO_4}$ + 0.01M $\mathrm{Et_4NClO_4}$(AN–D)|glass electrode
(C)
Cell I

(D denotes the solvents added)

The following relations were used:

$$R \equiv \left\{\frac{(\mathrm{Li_s^+})_{\mathrm{AN}}}{(\mathrm{Li_s^+})_{\mathrm{AN-D}}} - 1\right\}/[\mathrm{D}]$$

$$= \beta_1 + \beta_2[\mathrm{D}] + \beta_3[\mathrm{D}]^2 + \cdots \tag{3}$$

$$(R-\beta_1)/[\mathrm{D}] = \beta_2 + \beta_3[\mathrm{D}] + \cdots \tag{4}$$

$$(\mathrm{Li_s^+})_{\mathrm{AN}}/(\mathrm{Li_s^+})_{\mathrm{AN-D}} = 10^{(\mathrm{E_{AN}}-\mathrm{E_{AN-D}})/59} \tag{5}$$

where $(\mathrm{Li_s^+})_{\mathrm{AN}}$ and $(\mathrm{Li_s^+})_{\mathrm{AN-D}}$ are the activities of $\mathrm{Li_s^+}$ in pure AN and in the mixture of AN and D respectively. $\mathrm{E_{AN}}$ and $\mathrm{E_{AN-D}}$ show the potentials of the glass electrode in mV obtained in pure AN and in the AN–D mixture respectively. Assumptions similar to those in the previous paper1) were made: (i) the (D) solvent in AN–D mixtures is monomeric; (ii) the activity of AN does not change upon the addition of D and is equal to unity; (iii) the salt-effect activity coefficient of the lithium ion, as calculated by the Debye-Hückel equation, is equal in pure AN and in AN–D mixtures; (iv) the amount of (D) solvent consumed by the solvation of the ions of an indifferent electrolyte is negligible and (v) the liquid-junction potential between the solutions in the salt bridge (B) and the compartment (C) in Cell I does not change upon the addition of D.

By this method, such formation constants for D as methanol, pyridine, DMF, formamide, methylformamide, DMSO, DMA, and HMPA were obtained. In general, the complexing of the lithium ion occurs to a fairly greater extent than that of the sodium ion. The formation constants for the hydration of the lithium ion in AN, however, could not be determined because of a peculiar behavior of the electrode potential which is probably due to the hydrolysis of the lithium ion, as will be described later.

Apparatus and Reagents

Apparatus. Most of the apparatus and experimental techniques for the determination of formation constants are the same as those in the previous report.1) The assembly of Cell I is that Shown in Fig. 1 of Ref. (1), except that in the compartment (C) 10^{-3}M $\mathrm{LiClO_4}$ was used instead of 10^{-3}M $\mathrm{NaClO_4}$. The lithium-amalgam electrode was constructed by modifying the one used by Matsuura *et al.*2); the lithium amalgam was prepared by electrolyzing 10^{-2}M $\mathrm{LiClO_4}$ in AN, and the concentration of lithium in the amalgam was determined to be 6.58×10^{-2}M by titration with perchloric acid. The potential of the amalgam electrode was measured with a voltameter equipped with a voltage follower with an input impedance of $10^{11}\Omega$. For the acid-base titration in AN containing a small amount of water, a pH glass electrode, Hitachi-Horiba 1026, was used.

Reagents. Unhydrated lithium perchlorate was dried before use at 250 °C under a vacuum. The tetraethylammonium picrate, tetraethylammonium perchlorate, acetonitrile, and pyridine were the same as those in the previous work.[1] The DMF, DMSO, PC, and HMPA were purified by the conventional methods. The methylformamide was used after the purification of an analytical reagent-grade substance by fractional crystallization. The formamide was a chromatographic product. The lithium tetraphenylborate was prepared by passing an aqueous solution of sodium tetraphenylborate through a column of amberlite IR 120 exchange resin in the Li^+-form. It was dried at 50 °C under a high vacuum. The tetrabutylammonium tetraphenylborate was prepared by the method of Accascina *et al.*[3] The procedure of Cundiff and Markunas[4] was used to prepare the tetrabutylammonium hydroxide solution in a benzene–methanol (3: 2) mixture. The other solvents and reagents were of an analytical reagent grade and were used without further purification.

Results

Response of the Glass Electrode to the Activity of the Lithium Ion in Different Solvents. The glass electrode used in the present study showed a slope of 57 mV to the lithium ion between 10^{-4}M and 10^{-2}M in AN–0.01M Et_4NClO_4. If corrected for the change in the salt-effect activity coefficient, the response towards pa_{Li}^{+} is very near the Nernstian slope of 59 mV.

In order to confirm that the glass electrode can respond to the difference in the activity of the lithium ion in different solvents, the emf of Cell II was compared with that of Cell III. Because the reference electrode and the salt bridge in both cells are the same as each other (and as those used in Cell I), a comparison of the emf's of Cells II and III is equivalent to a comparison of the potentials of the glass electrode and the amalgam electrode.

$$\mathrm{Ag|0.005M\ AgNO_3(AN)\|0.1M\ Et_4NPi(AN)\|}$$
$$\mathrm{10^{-3}M\ LiClO_4 + 0.01M\ Et_4NClO_4(D)|Glass\ Electrode}$$

Cell II

$$\mathrm{Ag|0.005M\ AgNO_3(AN)\|0.1M\ Et_4NPi(AN)\|}$$
$$\mathrm{10^{-3}M\ LiClO_4 + 0.01M\ Et_4NClO_4(D)|Li(Hg)}$$

Cell III

(D denotes AN, methanol, DMF, and DMSO)

The results are shown in Fig. 1. From these results, it may be considered that the glass electrode used in the present experiment responds to the activity of the lithium ion in those different solvents.

Complexing of the Lithium Ion in AN with Other Solvents. From the emf measurement of Cell I, the values of the formation constants (β_x) were calculated by using Eqs. (3) to (5). The results are summarized in Table 1. Figures 2 to 6 show some examples of the R–[D] and $(R-\beta_1)/[D]$–[D] relations used to obtain the formation constants.

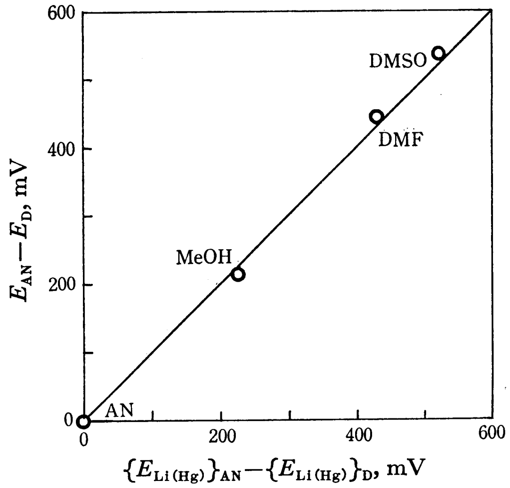

Fig. 1. Relations between potentials of the ion-sensitive glass electrode and those of the lithium amalgam electrode in various solvents, both referred to the values in AN.

When water was the complexing solvent, the equilibrium potential could not be obtained. As is shown in Fig. 7, Curve A, when water was added to the AN solution of the lithium ion, the potential shifted first to the more negative direction, but then back to the less negative direction, and it did not attain a constant value even after 60 min. (When the other solvents in Table 1 were the complexing solvents, equilibrium potentials were usually obtained soon after their addi-

TABLE 1. COMPLEX FORMATION CONSTANTS OF LITHIUM ION WITH OTHER SOLVENTS IN AN

Solvent	Upper mol added (M)	β_1	β_2	β_3
PC	0.4	<0.3		
H_2O		? [1.8]	? [1.8]	?
Methanol	1.0	4.3 4.6 [1.1]	6.4 7.0 [0.4]	
Pyridine	0.2	5.1 5.3 [0.7]	2.7 2.7 [0.5]	
DMF	0.4	16 16 [2.5]	1.0×10^2 1.1×10^2 [2.1]	61 71 [1.2]
Formamide	0.2	19 20	91 89	
Methyl-formamide	0.25	25 25	2.4×10^2 2.6×10^2	
DMSO	0.3	49 49 [6.0]	9.6×10^2 9.8×10^2 [11]	3.1×10^3 3.2×10^3 [14]
DMA	0.4	60 63 [5.3]	8.8×10^2 8.5×10^2 [11]	2.1×10^3 1.6×10^3 [6.4]
HMPA	0.04	2.0×10^3 2.2×10^3 [29]	3.0×10^5 3.1×10^5 [3.1×10^2]	[1.2×10^3]

Values in brackets are those in the case of the sodium ion. Abbreviation: PC=propylene carbonate; DMF=dimethylformamide; DMSO=dimethyl sulfoxide; DMA=dimethylacetoamide; HMPA=hexamethylphosphoramide. (at 25 ±0.1 °C)

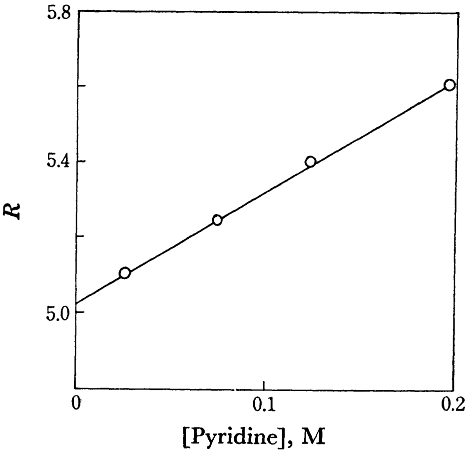

Fig. 2. R-[Pyridine] relation.

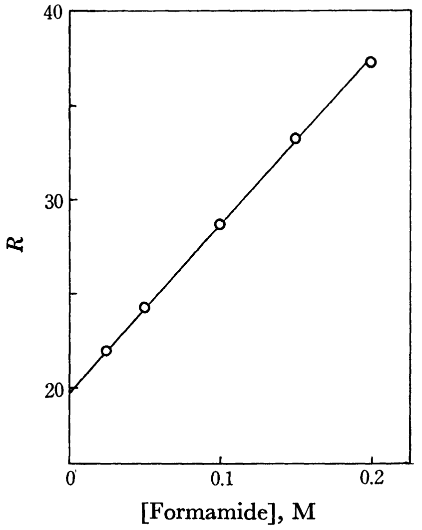

Fig. 3. R-[Formamide] relation.

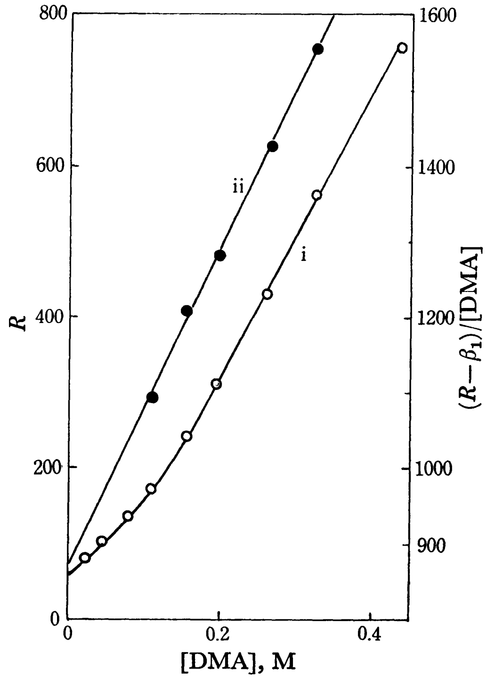

Fig. 4. R-[DMA] (Curve i) and $(R-\beta_1)$/[DMA]-[DMA] (Curve ii) relations.

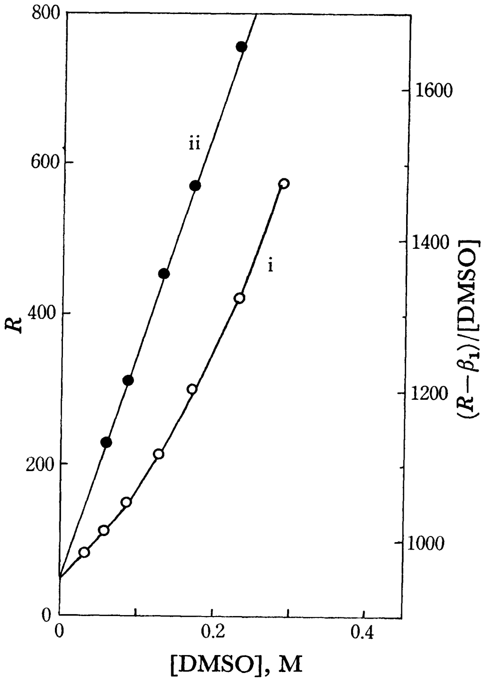

Fig. 5. R-[DMSO] (Curve i) and $(R-\beta_1)$/[DMSO]-[DMSO] (Curve ii) relations.

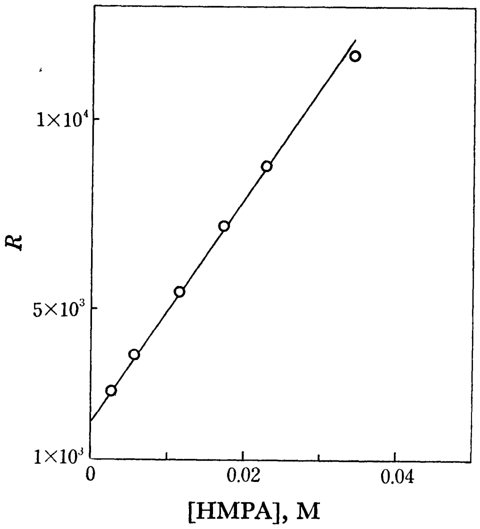

Fig. 6. R-[HMPA] relation.

tion. As example is shown in Fig. 7, Curve B, for DMSO.) Because of this behavior, hydration constants could not be obtained by the present experiment.

Discussion

From the results in Fig. 1, it seems reasonable to consider that the glass electrode can respond to the activity of the lithium ion in solvents of different species or compositions.

The formation constants in Table 1 show that the complexing of the lithium ion in AN with other solvents is generally more extensive than in the case of the sodium ion. For DMF, DMA, and DMSO, a complexing up to three solvent molecules was observed. For HMPA, however, no tri-solvated complex was formed in spite of the quite large values of β_1 and β_2. This may be

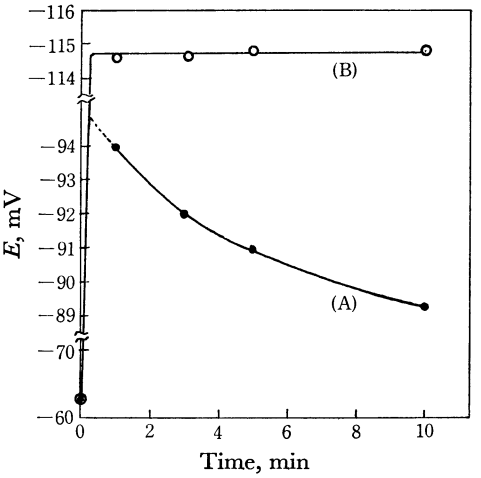

Fig. 7. Potential curves of the ion-sensitive glass electrode after the addition of complexing solvent to the AN solution of 10^{-3} M $LiClO_4$ and 10^{-2} M Et_4NClO_4.
(A) H_2O, 200 µl/50 ml, (B) DMSO, 200 µl/50 ml.

because of the steric effect in the reactions between large HMPA molecules and the small lithium ion. The solvation of PC, which has a weak basic character but a large dielectric constant, occurred only weakly. From these results, it can be said that, except for the case of pyridine, the complexing of the lithium ion in AN with other solvents is more pronounced when the solvent basicity increases. The solvation of pyridine, which has a strong basic character but a small dielectric constant, occurred to only a small extent, as in the case of the sodium ion.

The values of β_1 in Table 1 seem to be reliable enough within ±10% for pyridine, DMF, DMSO, and HMPA. For protic solvents, such as methanol, formamide, and methylformamide, the reliability might be somewhat less because the junction potentials between the compartments (B) and (C) of Cell I may change during titration to a somewhat larger extent than in the case of the dipolar aprotic solvents, in which the change of the junction potential is quite small.[5]

In order to elucidate the peculiar potential change observed when water was the complexing solvent, some experiments were carried out:

(1) The lithium ion in AN has been found conductometrically to associate with the perchlorate ion, though to an extent somewhat smaller than that of the ion association between the sodium ion and the perchlorate ion.[6,7] The addition of water to the AN solution may cause the dissociation of the ion association (though the possibility of this is very small, considering the small change in the dielectric constant by the addition of water[8]) and the increase in the lithium-ion activity (the shift of the potential to a less negative direction). In order to investigate the influence of this reaction, measurements were carried out by changing the concentration of the indifferent electrolyte, Et_4NClO_4, from 0 M to 0.1 M. However, the phenomena shown in the Curve A, Fig. 7, were observed in all concentrations. The tetraphenylborate may be completely dissociated in AN, considering the case of the sodium ion.[7] Therefore, instead of the $LiClO_4$ and Et_4NClO_4 in the above experiments, $LiBPh_4$ and Bu_4NBPh_4 were used, and similar measurments were carried out. However the results did not change. From these experiments, the peculiar phenomena in Fig. 7 do not seem to be due to the effect of ion association.

(2) The hydrolysis of the lithium ion may cause behavior such as is shown in Fig. 7 if the hydrogen ion liberated by hydrolysis shifts the potential of the glass electrode to a less negative direction. Curve 1 in Fig. 8 is a acid-base titration curve obtained by titrating 10^{-3}M $LiClO_4$ in 1.2 v/v % aqueous AN–0.01M Et_4NClO_4 with Bu_4NOH (0.176M in benzene–methanol (3:2)). The pH glass electrode was a Hitachi-Horiba 1026 electrode. The titration curve of the lithium ion indicates the possibility of the lithium ion being hydrolyzed considerably in AN containing a small amount of water. The hydrolysis of the sodium ion also occurs, but to a much smaller extent; Curve 2 is the titration curve of 10^{-3} M $NaClO_4$ under the same conditions, while Curve 3 is that of the blank solution. Curve 4 in Fig. 8 is the titration curve of acetic acid with Bu_4NOH in the same solution as that of Curve 3. From Curves 1 and 4, the lithium ion can be considered as an acid, the strength of which is roughly of the same order of magnitude as that of acetic acid. When a similar titration of acetic acid was carried out by using a mono-valent cation sensitive glass electrode, Beckman 39047, Curve 5 was obtained. In this curve, the potential is almost constant before the equivalent point, but the potential change to a negative direction occurs near the equivalent; after the equivalent point, the potential changes slowly to a less negative direction.

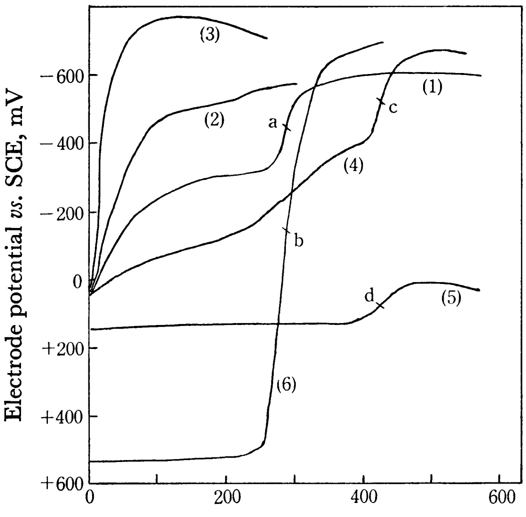

Fig. 8. Titration curves with benzene–methanol (3:2) solution of tetrabutylammoniumhydroxide (0.18 M). Curves (1) 10^{-3} M $LiClO_4$+10^{-2} M Et_4NClO_4+667 mM H_2O in 50 ml AN solution, (2) 10^{-3} M $NaClO_4$+10^{-2} M Et_4ClO_4+667 mM H_2O in 50 ml AN solution, (3) 10^{-2} M Et_4NClO_4+667 mM H_2O in 50 ml AN solution (blank), (4), (5) 10^{-2} M Et_4NClO_4+1.44 mM CH_3COOH+667 mM H_2O in 50 ml AN solution, and (6) 10^{-3} M $HClO_4$+667 mM H_2O in AN solution. The letters a,b, c, and d are the equivalent end point, respectively. For the glass electrodes used, see text.

From this, it seems reasonable to conclude that the cation-sensitive glass electrode can respond to the hydrogen ion liberated by the hydrolysis of the lithium ion in AN containing a small amount of water. Curve 6 was obtained by titrating 10^{-3} M $HClO_4$ in 1.2 v/v % aqueous AN with Bu_4NOH. From these experimental results, the peculiar behavior observed when water is the complexing solvent seems to be caused by the hydrolysis of the lithium ion and the response of the cation-sensitive glass electrode to the hydrogen ion liberated.

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