Kinetic Studies on Complexation Reactions of Lithium Ion with Cryptand C211 in Ionic Liquids by Using ^{7}Li NMR

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Kinetic studies on complexation reactions of Li^{I} with cryptand C211 in *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)-ammonium bis(trifluoromethylsulfonyl)imide (DEMETFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (EMITFSI) have been carried out using ^{7}Li NMR. It was found that the reaction rates in both solutions depend on concentrations of free Li^{I} and that their kinetic parameters are almost same. From these results, it is proposed that the Li^{I} complexation reactions in DEMETFSI and EMITFSI solutions proceed though bimolecular mechanism.

Recently, ionic liquids (ILs) have been paid attention as environmentally benign alternatives to conventional organic solvents, because ILs have attractive properties such as thermal stability, nonflammability, high ionic conductivity, and wide electrochemical potential windows,[1] and hence ILs are expected to be used as media in various fields, e.g., media for syntheses of organic compounds,[2] extraction media for metal ions (M^{n+}),[3] and electrolytes for electrochemical devices such as capacitors[4] and batteries.[5]

In order to develop these applications, especially extraction of M^{n+}, basic data on reactivities of metal complexes in ILs are necessary. However, little information is available concerning data on dynamic properties such as complexation reactions of M^{n+} and ligand-exchange reactions in ILs.[6] Hence, as a part of acquisition of basic data on reactivities of M^{n+} in ILs, we have studied complexation reactions of Li^{I} with cryptand C211 in ILs, because there are many data on the complexation reactions of M^+ such as Li^+, Na^+, and Cs^+ with cryptands in aqueous and nonaqueous solutions,[7–9] and the kinetic data in ILs can be compared with those in conventional solvents.

We used DEMETFSI and EMITFSI as ILs. DEMETFSI was purified by stirring with active carbon in water for 3 days, followed by filtration of active carbon. DEMETFSI phase was separated and a small amount of water in DEMETFSI was removed with evaporation in vacuo at 80 °C for 12 h. EMITFSI was also dried in vacuo at 80 °C for 12 h and used without further purification. LiTFSI was used as lithium salt having the same anion as that in DEMETFSI and EMITFSI, and dried in vacuo at 80 °C for 12 h before use. C211 was dried in vacuo at room temperature for 3 days and used without further purification. Sample solutions for ^{7}Li NMR measurements were prepared by dissolving LiTFSI (0.24 mol kg^{-1}) and appropriate amount of C211 (molar rations of C211 to LiTFSI, [C211]/[LiTFSI] = 0.0–1.0) into ILs. ^{7}Li NMR spectra were measured by using a JEOL-JNM-LA300WB NMR spectrometer in temperature range of 25–140 °C.

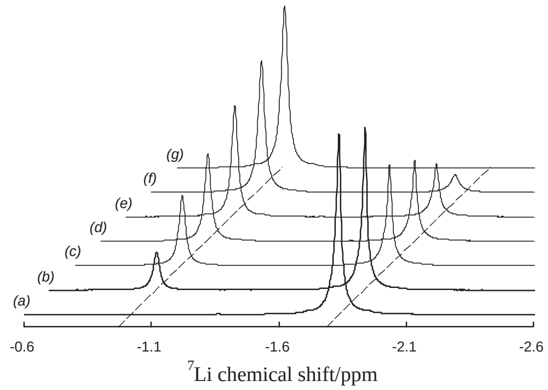

Figure 1. ^{7}Li NMR spectra of DEMETFSI solutions containing LiTFSI (0.24 mol kg^{-1}) and C211 ([C211]/[LiTFSI] = 0.0 (a), 0.2 (b), 0.4 (c), 0.5 (d), 0.6 (e), 0.8 (f), and 1.0 (g)). External standard of chemical shift: 1.0 mol dm^{-3} LiCl aqueous solution.

Figure 1 shows ^{7}Li NMR spectra of DEMETFSI solutions containing LiTFSI (0.24 mol kg^{-1}) and C211 ([C211]/[LiTFSI] = 0.0–1.0). In DEMETFSI solution without C211 ([C211]/[LiTFSI] = 0.0), one signal assigned to free Li^{I} was observed at -1.83 ppm. For DEMETFSI solution containing LiTFSI and C211 with [C211]/[LiTFSI] ≥ 0.2, a new signal was observed at -1.02 ppm and the area ratio of this signal to the signal of free Li^{I} increased with an increase in [C211]/[LiTFSI]. Furthermore, in DEMETFSI solution of [C211]/[LiTFSI] = 1.0, the signal observed at -1.83 ppm disappeared and only one signal was observed at -1.02 ppm. Same phenomena were also observed in EMITFSI solutions containing LiTFSI and C211. These results indicate that the signal observed at -1.02 ppm is assigned to the complexed Li^{I} and that only 1:1 complex ($Li^+\cdot$C211) is formed in DEMETFSI and EMITFSI solutions. This proposal is supported by the fact that stability constants for the complex formation of $Li^+\cdot$C211 in organic solvents are very large, e.g., stability constant in methanol is $10^{8.04}$.[10]

Figure 2 shows temperature dependence of ^{7}Li NMR spectra of DEMETFSI solutions containing LiTFSI and C211 with [C211]/[LiTFSI] = 0.5. Both signals sharpen till 80 °C, and then broad with an increase in temperature. Hence, this broadening phenomenon is attributed to the exchange between Li^{I} complexed with C211 and free Li^{I}. Similar behavior was also observed in EMITFSI solution. Kinetic data for complexation reactions in DEMETFSI and EMITFSI solutions were obtained by using two-site model of NMR line-broadening method.[11] The apparent first-order rate constants (k_{obs}) of complexation reactions were obtained from τ_c values ($k_{\mathrm{obs}} = 1/\tau_c$), which are the mean lifetime of Li^{I} of complexed site and were evaluated from the best-fitting of NMR lineshapes.

Figure 3 shows plots of the k_{obs} values against the concentrations of free Li^{I} ($[\mathrm{Li^I}]_{\mathrm{free}}$) for DEMETFSI system. The plots are found to give good linear relationships, that is, $k_{\mathrm{obs}} = k_s[\mathrm{Li^I}]_{\mathrm{free}}$.

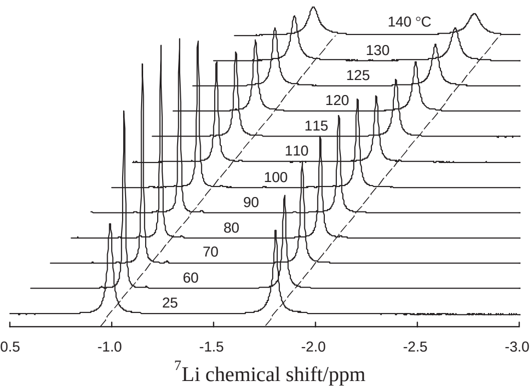

Figure 2. ^{7}Li NMR spectra of DEMETFSI solution containing LiTFSI ($0.24\,\mathrm{mol\,kg^{-1}}$) and C211 ($[\mathrm{C211}]/[\mathrm{LiTFSI}] = 0.5$). External standard of chemical shift: $1.0\,\mathrm{mol\,dm^{-3}}$ LiCl aqueous solution.

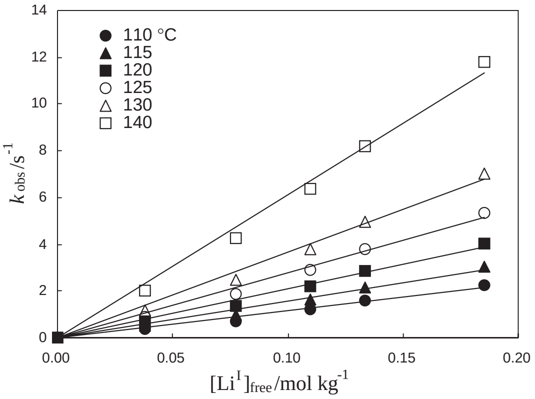

Figure 3. $[\mathrm{Li^I}]_{\mathrm{free}}$ dependence of k_{obs} for complexation reactions of $\mathrm{Li^I}$ by C211 in DEMETFSI solutions containing LiTFSI ($0.24\,\mathrm{mol\,kg^{-1}}$) and C211 ($[\mathrm{C211}]/[\mathrm{LiTFSI}] = 0.2$–$0.8$) at various temperatures.

Similar behavior was also observed in EMITFSI system. The dependence of k_{obs} on $[\mathrm{Li^I}]_{\mathrm{free}}$ suggests that the present complexation reactions proceed via the following bimolecular mechanism proposed by Shchori et al.[12]

$$^*\mathrm{Li}^+ + \mathrm{Li}^+\cdot\ \mathrm{C211} \rightleftarrows \mathrm{Li}^+ + {}^*\mathrm{Li}^+\cdot\ \mathrm{C211}$$

Second-order rate constants (k_{s}) were obtained from the slopes in Figure 3. The kinetic parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for k_{s} were obtained from the semi-logarithmic plots of the k_{s} values vs. the reciprocal temperature. The resulting $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are $69.8 \pm 0.4\,\mathrm{kJ\,mol^{-1}}$ and $-44.5 \pm 1.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for DEMETFSI system, and $70.6 \pm 0.2\,\mathrm{kJ\,mol^{-1}}$ and $-41.4 \pm 0.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for EMITFSI system. From these activation parameters, the k_{s} values at 25 °C were evaluated as 1.77×10^{-2} and $1.83 \times 10^{-2}\,\mathrm{s^{-1}\,mol^{-1}\,kg}$ for DEMETFSI and EMITFSI systems, respectively. The kinetic parameters for each solution are found to be almost same, regardless of difference in cations in ILs. This suggests that the complexation reactions of $\mathrm{Li^I}$ in DEMETFSI and EMITFSI are not affected by cations in ILs.

Kinetic data for complexation reactions of $\mathrm{Li^I}$ with C211 in *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), etc. have been reported by Popov et al.[7a] According to their reports, the k_{obs} values at 25 °C for DMSO and DMF systems are 2.32×10^{-2} and $1.30 \times 10^{-2}\,\mathrm{s^{-1}}$, respectively, which are larger than those (4.43×10^{-3} and $4.58 \times 10^{-3}\,\mathrm{s^{-1}}$ at $[\mathrm{Li^I}]_{\mathrm{free}} = 0.25\,\mathrm{mol\,kg^{-1}}$) for DEMETFSI and EMITFSI systems. They also proposed that the complexation reaction in DMSO proceeds through the following dissociative mechanism.[7b,12]

$$\mathrm{Li}^+ + \mathrm{C211} \rightleftarrows \mathrm{Li}^+\cdot\ \mathrm{C211} \qquad (1)$$

The k_{obs} values and mechanism reported by Popov et al. are different from those for the present reaction systems. This is considered to be due to the differences in the chemical forms of free $\mathrm{Li^I}$ species in DMSO and ILs (DEMETFSI and EMITFSI). In DMSO with high dielectric constant and donicity, the free $\mathrm{Li^I}$ species should exist as solvated Li^+ ions, while the free $\mathrm{Li^I}$ species in DEMETFSI and EMITFSI are coordinated by two TFSI anions, $[\mathrm{Li(TFSI)_2}]^-$.[13] Hence, the free $\mathrm{Li^I}$ species with negative charge in DEMETFSI and EMITFSI should more easily associate with $\mathrm{Li}^+\cdot\mathrm{C211}$ than those with positive charge in DMSO. From this viewpoint, it should be reasonable that the complexation reactions of $\mathrm{Li^I}$ with C211 proceed through the bimolecular mechanism in DEMETFSI and EMITFSI, and via the dissociative mechanism in DMSO.

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References and Notes

1 a) M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391. b) *Green Industrial Applications of Ionic Liquids*, ed. by R. D. Rogers, K. R. Seddon, S. Volkov, Kluwer Academic Publishers, **2000**. c) *Ionic Liquids in Synthesis*, ed. by P. Wasserscheid, T. Welton, Wiley-VCH, **2003**.
2 T. Welton, *Chem. Rev.* **1999**, *99*, 2071.
3 a) S. Chun, S. V. Dzyuba, R. A. Bartsch, *Anal. Chem.* **2001**, *73*, 3737. b) H. Luo, S. Dai, P. V. Bonnesen, *Anal. Chem.* **2004**, *76*, 2773.
4 T. Sato, G. Masuda, K. Takagi, *Electrochim. Acta* **2004**, *49*, 3603.
5 a) S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, N. Kihira, M. Watanabe, N. Terada, *J. Phys. Chem. B* **2006**, *110*, 10228. b) H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, *J. Power Sources* **2006**, *160*, 1308. c) T. Sato, T. Maruo, S. Marukane, K. Takagi, *J. Power Sources* **2004**, *138*, 253.
6 a) C. F. Weber, R. Puchta, N. J. R. van Eikema Hommes, P. Wasserscheid, R. van Eldik, *Angew. Chem., Int. Ed.* **2005**, *44*, 6033. b) P. Illner, S. Kern, S. Begel, R. van Eldik, *Chem. Commun.* **2007**, 4803.
7 a) Experimental conditoion: $[\mathrm{LiClO_4}] = 0.50\,\mathrm{M}$, $[\mathrm{C211}] = 0.25\,\mathrm{M}$: Y. M. Cahen, J. L. Dye, A. I. Popov, *J. Phys. Chem.* **1975**, *79*, 1292. b) M. Shamsipur, A. I. Popov, *J. Phys. Chem.* **1986**, *90*, 5997.
8 a) J. M. Ceraso, P. B. Smith, J. S. Landers, J. L. Dye, *J. Phys. Chem.* **1977**, *81*, 760. b) S. F. Lincoln, I. M. Brereton, T. M. Spotswood, *J. Am. Chem. Soc.* **1986**, *108*, 8134.
9 a) E. Mei, A. I. Popov, J. L. Dye, *J. Am. Chem. Soc.* **1977**, *99*, 6532. b) M. Shamsipur, A. I. Popov, *J. Phys. Chem.* **1987**, *91*, 447.
10 B. G. Cox, H. Schneider, J. Stroka, *J. Am. Chem. Soc.* **1978**, *100*, 4746.
11 S. F. Lincoln, *Prog. React. Kinet.* **1977**, *9*, 1.
12 E. Shchori, J. Jagur-Grodzinski, Z. Luz, M. Shporer, *J. Am. Chem. Soc.* **1971**, *93*, 7133.
13 Y. Umebayashi, T. Mitsugi, S. Fukuda, T. Fujimori, K. Fujii, R. Kanzaki, M. Takeuchi, S. Ishiguro, *J. Phys. Chem. B* **2007**, *111*, 13028.