

Ionic association of lithium salts in propylene carbonate/1,2-dimethoxyethane mixed systems for lithium batteries

Masashi Ishikawa, Shi-Qi Wen and Yoshiharu Matsuda*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2557, Ube 775 (Japan)

(Received January 18, 1993; accepted February 15, 1993)

Abstract

The ionic association constants of lithium perchlorate, lithium trifluoromethylsulfate, lithium hexafluorophosphate, and lithium tetrafluoroborate have been determined experimentally (by Shedlovsky's method) in various mixtures of propylene carbonate and 1,2-dimethoxyethane as typical electrolyte systems for rechargeable lithium batteries. The association constants vary extensively for different mixing ratios of propylene carbonate to 1,2-dimethoxyethane and for different species of salts. These values are compared with the theoretical values as predicted by the Fuoss and Bjerrum equations. On the basis of this comparison and some physical properties of the solution, the variation in the ionic association constants may be ascribed to the change of ionic association species, i.e., a contact ion-pair and a solvent-separated ion-pair.

Introduction

The application of a high conductive lithium salt/organic solvent system as the electrolyte is requisite for obtaining excellent performance from rechargeable lithium batteries [1]. It is well known that the conductivity of the electrolyte solution is much influenced by the permittivity and the viscosity of the solution [2]. A high permittivity facilitates the dissociation of the salt and a low viscosity promotes the motion of ions in the solution. In this context, considerable efforts have so far been devoted to the development of lithium salt/aprotic organic solvent systems [3–6]. As for the tactics of this development, mixed systems consisting of two solvents, i.e., a high-permittivity solvent and a low-viscosity solvent, have been used for the cells, because few solvents satisfy simultaneously the above two physical properties [3–6].

The authors have reported on the characteristics of some mixed-electrolyte systems consisting of a high-permittivity solvent and a low-viscosity solvent for primary and secondary lithium batteries [7–16]. As was expected, high conductivities were observed in the mixed-solvent systems, and the electrode characteristics were also excellent in the mixed-electrolyte systems [10, 13, 14, 16–18]. Because sufficient dissociation of salts is essential to give high-conductive electrolytes for the batteries, the ionic association constant of the salts is an important parameter in evaluating the electrolyte properties [3, 11, 17]. Nevertheless, no systematic study of the ionic association constant of salts in the electrolytes for lithium batteries has been reported to date, but there have

*Author to whom correspondence should be addressed.

been some reports on the qualitative evaluation of the behaviour of ions in the electrolytes for these cells [11, 15–19].

In the present work, the ionic association constants of lithium perchlorate (LiClO_4), lithium trifluoromethylsulfate (LiCF_3SO_3), lithium hexafluorophosphate (LiPF_6), and lithium tetrafluoroborate (LiBF_4) have been systematically investigated in various mixtures of propylene carbonate (PC) and 1,2-dimethoxyethane (DME), as typical electrolyte systems for rechargeable lithium batteries. The high-permittivity solvent used here was PC and the low-viscosity solvent was DME.

Experimental

High purity PC and DME (Mitsubishi Petrochemical, battery grade) were used as the solvent. Extrapure grade lithium salts, LiClO_4 (Ishizu Pharmaceutical), LiCF_3SO_3 (Central Grass), LiPF_6 (Morita Chemical Industries), and LiBF_4 (Morita Chemical Industries) were used as the electrolytic salts after drying under reduced pressure at appropriate temperatures (80–170 °C) for 24 h. The conductivity of the solution was measured by an impedance bridge method (10 kHz a.c.) at 30 °C. The cell constant of the conductivity cell was 0.410 cm^{-1} . The dielectric constant of the solvent was determined by a bridge method using 10 kHz a.c. at 30 °C [20]. The viscosities of the solvent and the solution were measured with a modified Ostwald viscometer at 30 °C [20].

Results and discussion

Figure 1 shows the limiting molar conductivities (Λ^∞) of LiClO_4 as a function of DME content (vol.%) in the solution. The molar conductivities increase with DME concentration because of a lowering of the solvent viscosity [11, 16]. From the limiting molar conductivities and the viscosities of the LiClO_4 solution, the Walden products ($\Lambda^\infty \eta$, where η represents viscosity of the solution) of the LiClO_4 solution were also obtained. These products are shown in Fig. 1 as a function of DME content. The Walden products decrease with increase in DME concentration. Because the Walden products are known to be constant if the Stokes' radii of the cation and the anion do not change [21], the observed variation of the Walden products with an increase in DME content may be ascribed to the corresponding change in Stokes' radii of the cation and/or anion [9]. Therefore, the result suggests that the interaction between the solvents (PC or DME) and lithium cations and/or between the solvents and perchlorate anions may change with variation in the mixing ratio of DME to PC [9, 16]. Based on the above discussion, it is supposed that when the ions (lithium cation and perchlorate anion) associate together and result in an ion-pair, the interaction between the ions and the solvents will change with a variation in DME content [16]. As for the interaction between a solvent and an ion-pair, a contact ion-pair and a solvent-separated ion-pair are well known [16, 22, 23].

In order to investigate this interaction, the ionic association constant (K_s) of LiClO_4 in various PC/DME electrolyte systems was determined by conductmetry. The K_s values were evaluated from the data of the conductivities, according to the Shedlovsky's extrapolation method [24], on a NEC personal computer N88 basic programme. The Shedlovsky's equation used in the calculation is [24, 25]:

$$1/(\Lambda S) = 1/\Lambda^\infty + K_s C A S f^2 / \Lambda^{\infty 2} \quad (1)$$

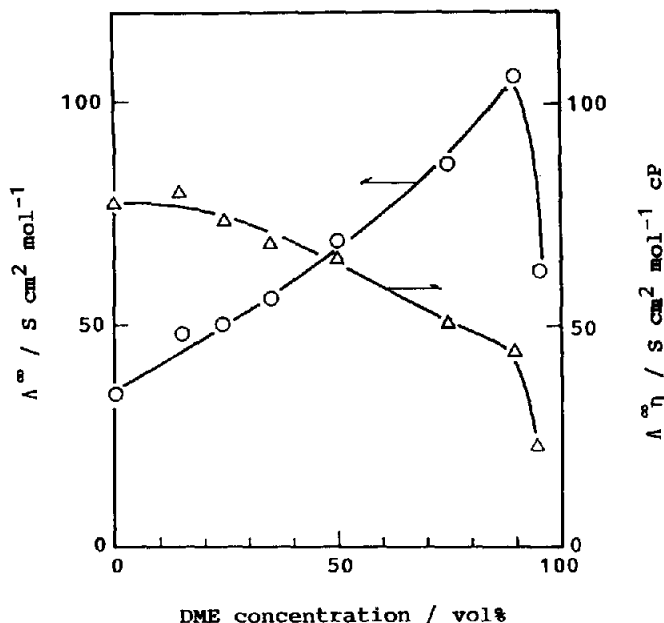


Fig. 1. (○) Limiting molar conductivities (A^∞) and (△) Walden products ($A^\infty \eta$) for LiClO_4 in PC/DME at 30 °C.

where A , A^∞ and C are the molar conductivity, the limiting molar conductivity, and the concentration of LiClO_4 , respectively; S is the Shedlovsky's function [24], and f is a mean activity coefficient calculated from the Debye-Hückel limiting law. Figure 2 shows the plot of the logarithm of the K_s value of LiClO_4 versus DME concentration (vol.%) in a PC/DME mixed solvent. The K_s values are almost constant in the low DME concentration region, $\sim 0\% < \text{DME}\% < 50\%$, and reach a minimum value at 75%. Then, the K_s values increase remarkably in the high concentration region. At first sight, such variation in the K_s value, is not consistent with the usual rule; it has been believed that the ionic association constant increases gradually with decrease in the dielectric constant [11], which corresponds with the increase in DME concentration.

In order to explain the unusual variation in the ionic association constant (Fig. 2), a theoretical simulation of the ionic association constants was carried out using the Fuoss [26] and Bjerrum equations [21, 27]; these are expressed by eqn. (2) and eqn. (3), respectively,

$$K_F = 4\pi N_A d^3 \exp(b)/3000 \quad (2)$$

$$K_B = (1.322 \times 10^6 \int_2^b x^{-4} \exp(x) dx) / \epsilon^3 \quad (3)$$

where N_A is the Avogadro constant and b is a function given by eqn. (4).

$$b = 550.8 / (d\epsilon) \quad (4)$$

In these equations, the dielectric constant (ϵ) and the contact distance of ions in ion association (d) are important parameters for the evaluation of the ionic association constant, K_F or K_B using the Fuoss or Bjerrum equations.

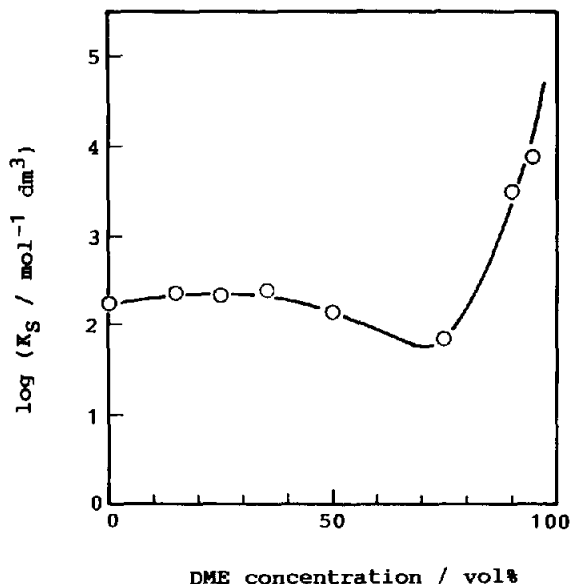


Fig. 2. Logarithm of ionic association constant (K_s) of LiClO_4 evaluated by the Shedlovsky method in PC/DME at 30 °C.

As for the dielectric constant, it is well known that the actual dielectric constant in the vicinity of ions is smaller than that in the bulk of the solution. This is due to the dielectric saturation effect in the vicinity of ions [28]. Therefore, for the precise simulation of the ionic association constants by theoretical equations (eqns. (2) and (3)), the correction factor (c^*) was introduced into the equations, i.e., $1/\epsilon_0 = 1/\epsilon + c^*$. Here, ϵ_0 is the dielectric constant in the vicinity of ions, and ϵ is the dielectric constant in the bulk of the solution. In the present case, the best-fit c^* value from the experimental data was determined as 2.3×10^{-2} and the resulting ϵ_0 value was applied to both equations (eqns. (2) and (3)).

Another important parameter in the theoretical equations is the contact distance of ions in ion association, d . This is known to be 3.0 Å and ~ 8.0 Å for the contact ion-pair ($\text{Li}^+ \text{ClO}_4^-$) and the solvent-separated (PC or DME) ion-pair (Li^+ solvent ClO_4^-), respectively [9].

Figure 3 shows the dependence of the logarithm of the K_s values (evaluated experimentally by Shedlovsky's method) on the reciprocal values of the dielectric constant ($1/\epsilon$) in the PC/DME solvent. Figure 3 also displays theoretical lines that indicate the relation between the ionic association constant and the dielectric constant as predicted by the Fuoss equation (eqn. (2), dashed lines) and the Bjerrum equation (eqn. (3), solid lines) in the presence of a contact ion-pair ($d = 3.0$ Å) and a solvent-separated ion-pair ($d = 8.0$ Å) [9]. Obviously, the ion-pair of LiClO_4 changes from a contact ion-pair to a solvent-separated ion-pair with a decrease in the dielectric constant (an increase in DME concentration). This tendency may be ascribed to the large donor number of DME, compared with that of PC [29, 30], i.e., because the interaction between the lithium cation and DME is stronger than that between the lithium cation and PC, adding sufficient amount of DME to PC results in a change in the ion-pair from ($\text{Li}^+ \text{ClO}_4^-$) to ($\text{Li}^+ \text{DME ClO}_4^-$) [9].

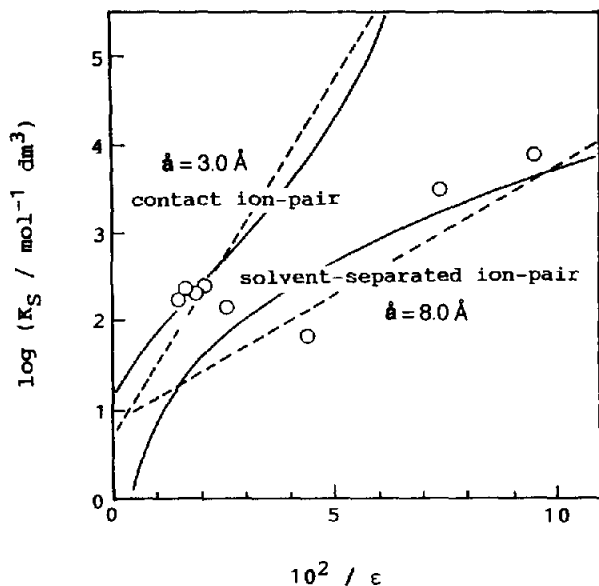


Fig. 3. Plot of logarithm of ionic association constant (K_s) of LiClO_4 vs. reciprocal of dielectric constant (ϵ) of PC/DME at 30 °C; (—) and (---) are predicted by the Bjerrum equation and the Fuoss equation, respectively.

For the other lithium salts (LiCF_3SO_3 , LiPF_6 , and LiBF_4), the dependence of K_s values on the dielectric constants in the PC/DME systems was also investigated. Unfortunately, accurate d values in both cases of a contact ion-pair (Li^+ anion) and a solvent-separated ion-pair (Li^+ solvent anion), where the anion is CF_3SO_3^- , PF_6^- , or BF_4^- , are not known. Nevertheless, since the Stokes' radii of these anions are known to be within $\pm 0.5 \text{ \AA}$ of the radius of ClO_4^- [9], we can use the prescribed values $d = 3.0$ and 8.0 \AA in the presence of a contact ion-pair and a solvent-separated ion-pair, respectively, as the tools for judging which (contact or solvent-separated) ion-pair is present in the solution.

Figures 4 to 6 show the dependence of the logarithm of the K_s values (which are evaluated experimentally in the case of LiCF_3SO_3 , LiPF_6 and LiBF_4 as salts, respectively) on the $1/\epsilon$ value in the PC/DME systems. Figure 4 to 6 also display theoretical lines that indicate the relation between the ionic association constant and the dielectric constant as predicted by the Fuoss equation (eqn. (2), dashed lines) and the Bjerrum equation (eqn. (3), solid lines) in the presence of a contact ion-pair ($d \approx 3.0 \text{ \AA}$) and a solvent-separated ion-pair ($d \approx 8.0 \text{ \AA}$) [9]. In every case, the ion-pair of the lithium salt changes from a contact ion-pair to a solvent-separated ion-pair with an increase in DME concentration, although some differences are observed in the association constants with the various species of the salts. It is generally known that the order of the crystallographic radii of anions is $\text{CF}_3\text{SO}_3^- > \text{ClO}_4^- \approx \text{PF}_6^- > \text{BF}_4^-$ [9, 16]. The strict evaluation of the Stokes' radii of these anions at the each DME concentration in PC/DME systems is not easy, however, because the interaction among PC, DME and the anion may change in a complex manner with variation in the DME content in the PC/DME systems [9, 16]. In addition, in the case of CF_3SO_3^- , which

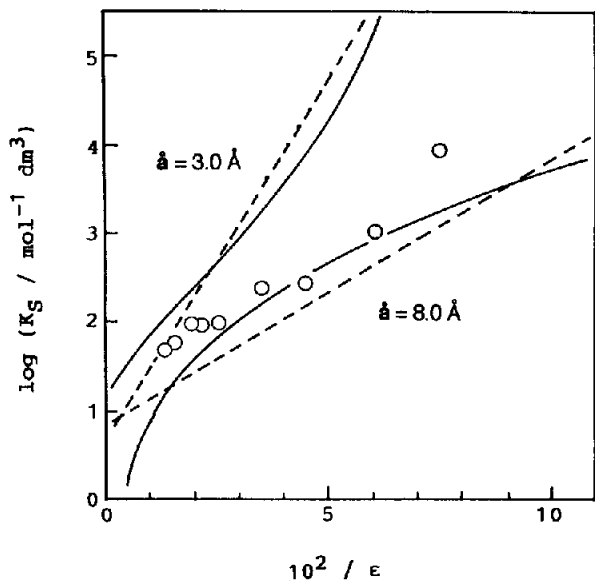


Fig. 4. Plot of logarithm of ionic association constant (K_s) of LiCF_3SO_3 vs. reciprocal of dielectric constant (ϵ) of PC/DME at 30 °C; (—) and (---) are predicted by the Bjerrum equation and the Fuoss equation, respectively.

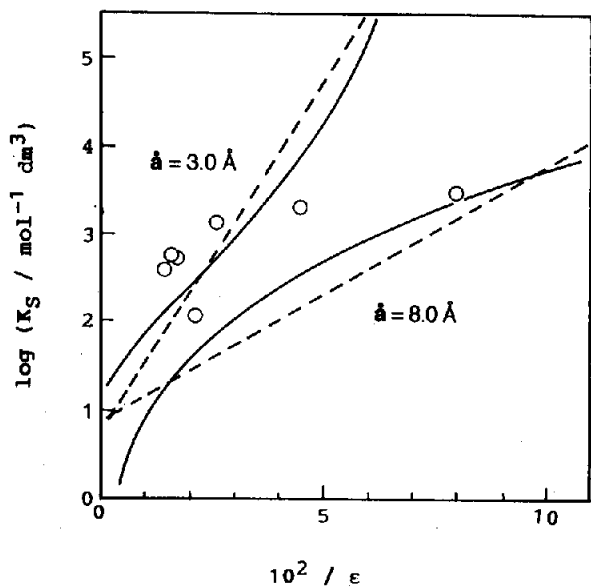


Fig. 5. Plot of logarithm of ionic association constant (K_s) of LiPF_6 vs. reciprocal of dielectric constant (ϵ) of PC/DME at 30 °C; (—) and (---) are predicted by the Bjerrum equation and the Fuoss equation, respectively.

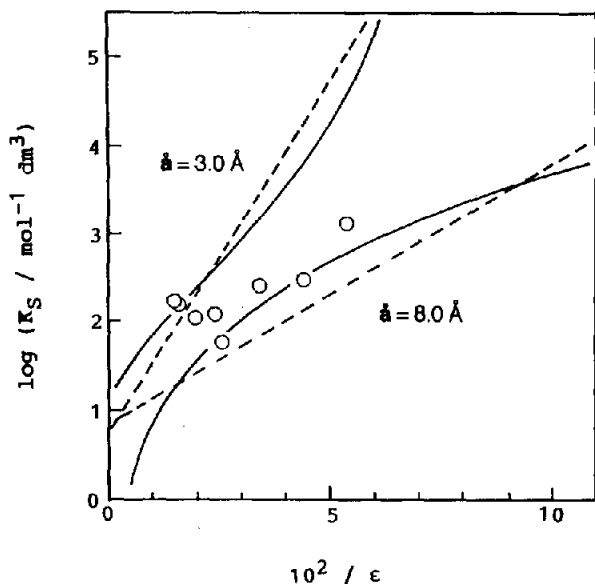


Fig. 6. Plot of logarithm of ionic association constant (K_s) of LiBF_4 vs. reciprocal of dielectric constant (ϵ) of PC/DME at 30 °C; (—) and (---) are predicted by the Bjerrum equation and the Fuoss equation, respectively.

is not a spherical anion, an accurate evaluation of the Stokes' radii of the anion is difficult. Therefore, a theoretical simulation on the experimental data at each DME content in PC/DME by theoretical equations cannot be performed. Using the method reported here, however, the complicated situation becomes a simple one; the overall trend in the variation of the state of the ion-pair can be determined.

In conclusion, the present study has provided a clear picture of the change from contact ion-pair to solvent-separated ion-pair of lithium salts (especially, LiClO_4) with increase in the DME concentration, i.e., with decrease in the dielectric constant of the solvent. This interpretation can account for the unusual variation in the K_s value. For example, in Fig. 1, the K_s value does not increase gradually with increase in DME concentration (i.e., a decrease in the dielectric constant). Further, this study has suggested that in the region of high DME concentration the amount of lithium ions, which are available for the electrode reaction in rechargeable lithium batteries, would decrease due to the formation of solvent-separated ion-pairs.

Acknowledgements

The authors are grateful for financial support by a grant-in-aid (Scientific Research No. 04453081) from the Ministry of Education, Science and Culture, Japan, and from the Electric Technology Research Foundation of Chugoku.

References

- 1 G. E. Blomgren, in J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983, Ch. 2.

- 2 R. Jasinski, in P. Delahey and C. W. Tobias (eds.), *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 8, Wiley, New York, 1971, p. 253.
- 3 M. Fukuda and T. Iijima, *Prog. Batteries Solar Cells*, 1 (1978) 26.
- 4 H. Ikeda, T. Saito and H. Tamura, *Denki Kagaku*, 45 (1977) 314.
- 5 H. Ikeda, S. Ueno, T. Saito, S. Nakaido and H. Tamura, *Denki Kagaku*, 45 (1977) 391.
- 6 A. Morita, T. Iijima, T. Fujii and H. Ogawa, *J. Power Sources*, 5 (1980) 111.
- 7 Y. Matsuda and H. Satake, *J. Electrochem. Soc.*, 127 (1980) 877.
- 8 Y. Matsuda and H. Satake, *Denki Kagaku*, 47 (1979) 743.
- 9 Y. Matsuda, H. Nakashima, M. Morita and Y. Takasu, *J. Electrochem. Soc.*, 128 (1981) 2552.
- 10 Y. Matsuda, Y. Yamamoto and M. Morita, *Denki Kagaku*, 49 (1981) 653.
- 11 Y. Matsuda, M. Morita and K. Kosaka, *J. Electrochem. Soc.*, 130 (1983) 101.
- 12 Y. Matsuda, M. Morita and K. Kosaka, *Denki Kagaku*, 51 (1983) 119.
- 13 Y. Matsuda, M. Morita and S. Kanameda, *Denki Kagaku*, 52 (1984) 702.
- 14 Y. Matsuda, M. Morita, K. Yamada and K. Hirai, *J. Electrochem. Soc.*, 132 (1985) 2538.
- 15 Y. Matsuda, M. Morita and T. Yamashita, *J. Electrochem. Soc.*, 131 (1984) 2821.
- 16 Y. Matsuda, M. Morita and F. Tachibara, *Bull. Chem. Soc. Jpn.*, 59 (1986) 1967.
- 17 S. Tobishima, J. Yamaki and T. Okada, *Electrochim. Acta*, 29 (1984) 1471.
- 18 S. Tobishima and T. Okada, *J. Appl. Electrochem.*, 15 (1985) 317.
- 19 M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, 77 (1973) 3089.
- 20 C. K. Mann, in A. J. Bard (ed.), *Electroanalytical Chemistry*, Vol. 3, Marcel Dekker, New York, 1969, Ch. 2.
- 21 R. A. Robinson and R. H. Stokes (eds.), in *Electrolyte Solutions*, Butterworths, London, 2nd edn. (revised), 1965, p. 125.
- 22 R. Fernandez-Prini, in A. K. Covington and T. Dickinson (eds.), *Physical Chemistry of Organic Solvent Systems*, Plenum, London, 1973, Ch. 5.
- 23 I. R. Lantzke, in A. K. Covington and T. Dickinson (eds.), *Physical Chemistry of Organic Solvent Systems*, Plenum, London, 1973, Ch. 4.
- 24 R. M. Fuoss and T. Shedlovsky, *J. Am. Chem. Soc.*, 71 (1949) 1496.
- 25 I. Sakamoto, K. Masuda, S. Okazaki and T. Fujinaga, *Electrochim. Acta*, 26 (1981) 197.
- 26 R. M. Fuoss, *J. Am. Chem. Soc.*, 80 (1958) 5059.
- 27 R. L. Kay, D. F. Evans and S. M. A. Matesich, in J. F. Coetzee and C. D. Ritchie (eds.), *Solute-Solvent Interactions*, Vol. 2, Marcel Dekker, New York, 1976, p. 105.
- 28 R. Fernandez-Prini and J. E. Prue, *Trans. Faraday Soc.*, 62 (1966) 1257.
- 29 V. Gutmann (ed.), in *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978, p. 13.
- 30 V. Gutmann, *Electrochim. Acta*, 21 (1976) 661.