Bull. Chem. Soc. Jpn. Vol. 79, No. 2, 291–293 (2006)

# Determination of the Solubility Product of $CH_3COONa$ in Propylene Carbonate and Standard Gibbs Energies of Ion Transfer Using a Poly(acrylamide) Membrane Ion-Selective Electrode Based on Benzo-15-crown-5

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A Benzo-15-crown-5 modified poly(acrylamide) membrane coated platinum electrode is successfully used to determine the solubility product of $CH_3COONa$ in propylene carbonate. The standard Gibbs energies of $Na^+$ and $CH_3COO^-$ transfer from water to propylene carbonate are obtained. The datum of $CH_3COO^-$ is reported for the first time.

The thermodynamic study of electrolyte solutions is an important aspect in solution chemistry.[1] The solubility products of electrolytes, and the activities and Gibbs energies of ions, etc. in dipolar aprotic solvents are quite different from those in aqueous systems. Molar Gibbs energies of single ion transfers between pure and mixed solvents and the thermodynamic properties of ions in dipolar aprotic solvents have been extensively studied and reviewed.[2–10] The determination of the solubility products of electrolytes in various solvents plays an important role in these studies. Ion-selective electrodes are very useful tools for detecting the activity changes and other thermodynamic properties of ions, but these studies have mainly been performed in aqueous solution.

In order to study the thermodynamic properties of ions in nonaqueous solutions, a number of ion-selective electrodes based on a non-plasticized poly(acrylamide) (PAA) membrane have been developed in our laboratory. A benzo-15-crown-5 modified PAA membrane coated platinum electrode (PAA-B15C5 electrode), for example, can show a Nernstian response to $Na^+$ and $Ca^{2+}$ in some dipolar aprotic solvents as a result of the activity change due to both the ion concentration and solvent effect.[11,12] The construction and applications of this kind of electrode have been reviewed,[13] and the fundamental physical properties of the PAA membrane used as the matrix of the electrode have been investigated voltammetrically.[14]

Potentiometric titration has widely been used in studying various types of reactions, e.g. precipitation, complex formation, and redox reactions, in nonaqueous solutions because of its accuracy and convenience. In this paper, a PAA-B15C5 electrode was used as a $Na^+$ indicator electrode in the titration of $Na^+$ with $F^-$ and $CH_3COO^-$ in PC solutions. Figure 1 shows, for example, a typical titration and dynamic response curve of $NaClO_4$ with $Bu_4NF{\cdot}3H_2O$, and Figure 2 shows those of $NaClO_4$ with $CH_3COOBu_4N$ in a propylene carbonate (PC) solution at 25 °C.

Using these titration curves, the solubility products of NaF and $CH_3COONa$ in PC were obtained by the following method. When a $Na^+$ indicator electrode is used in the titration, for example, Eq. 1 will hold. The $a_{Na^+}$ can be calculated by Eq. 2;

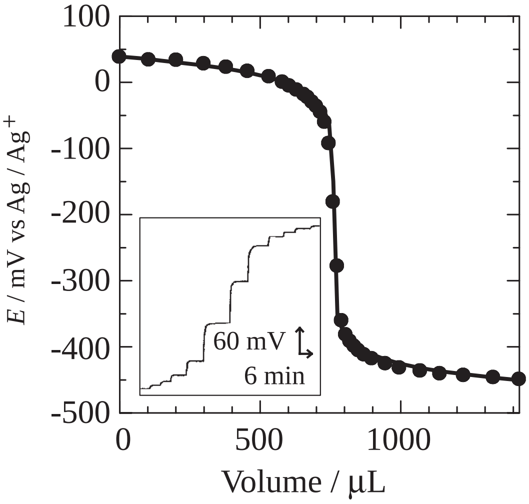

Fig. 1. Titration curve for 10 mL of 2 mM $NaClO_4$ versus 25 mM $Bu_4NF{\cdot}3H_2O$ in a propylene carbonate solution with the PAA-B15C5 electrode. (●) and (—) show the measured and calculated values, respectively. The inset shows the dynamic response curve. One step on the curve corresponds to one drop of the titrant.

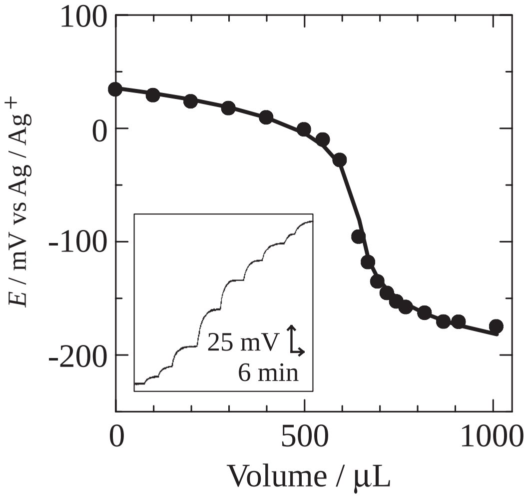

Fig. 2. Titration curve for 10 mL of 2 mM $NaClO_4$ versus 25 mM $CH_3COOBu_4N$ in a propylene carbonate solution with the PAA-B15C5 electrode. (●) and (—) show the measured and calculated values, respectively. The inset shows the dynamic response curve. One step on the curve corresponds to one drop of the titrant.

Published on the web February 10, 2006; DOI 10.1246/bcsj.79.291

here, $f_{\mathrm{Na}^+}$ is calculated by the Debye–Hückel equation. The constant $k$ can be calculated by substituting the titration results into Eq. 1, and then $K_{\mathrm{sp}}$ is calculated by Eq. 3, where $E$ at the equivalent point is expressed as $E_{\mathrm{ep}}$. The electrode potential after the equivalent point, $E_{\mathrm{after}}$, can be calculated by Eq. 4, in which $K_{\mathrm{sp}}$ is obtained by Eq. 3 and $a_{\mathrm{X}^-}$($\mathrm{X}^- = \mathrm{F}^-$ and $\mathrm{CH_3COO^-}$) calculated by Eq. 5. The reliability of the above procedure is confirmed by the fact that the theoretical curve is consistent with the experimental curves shown in Fig. 1 and Fig. 2.

$$E = k + (RT/zF)\ln a_{\mathrm{Na}^+} \quad (z = 1), \tag{1}$$

$$a_{\mathrm{Na}^+} = f_{\mathrm{Na}^+} c_{\mathrm{Na}^+}, \tag{2}$$

$$E_{\mathrm{ep}} = k + (RT/zF)\ln (K_{\mathrm{sp}})^{1/2}, \tag{3}$$

$$E_{\mathrm{after}} = k + (RT/zF)\ln K_{\mathrm{sp}}/a_{\mathrm{X}^-}, \tag{4}$$

$$a_{\mathrm{X}^-} = f_{\mathrm{X}^-} c_{\mathrm{X}^-}. \tag{5}$$

The solubility product of NaF in PC, $\mathrm{p}K_{\mathrm{sp,NaF}}$, was obtained by this method using the PAA-B15C5 electrode to be 12.6 (RSD = 7.8%, $n = 4$). The solubility product of $\mathrm{CH_3COONa}$ in PC, $\mathrm{p}K_{\mathrm{sp,CH_3COONa}}$, was determined to be 10.4 (RSD = 3.6%, $n = 3$).

When the solvation energies of a chemical species i in a reference solvent R and another solvent D are expressed by $\Delta G^0_{\mathrm{sv}}(\mathrm{i, R})$ (denotes the Gibbs energy change in the process of the dissolution of i in R) and $\Delta G^0_{\mathrm{sv}}(\mathrm{i, D})$, respectively, the difference between the two is expressed by $\Delta G^0_{\mathrm{t}}(\mathrm{i, R} \rightarrow \mathrm{D})$, as shown in Eq. 6, and is defined as the Gibbs energy of i transfer from solvent R to D:

$$\Delta G^0_{\mathrm{t}}(\mathrm{i, R} \rightarrow \mathrm{D}) = \Delta G^0_{\mathrm{sv}}(\mathrm{i, D}) - \Delta G^0_{\mathrm{sv}}(\mathrm{i, R}). \tag{6}$$

If the species i is an electrolyte, $\mathrm{MX}_n$, and its solubility products in solvent R and D are expressed by $K_{\mathrm{sp}}{}^{\mathrm{R}}$ and $K_{\mathrm{sp}}{}^{\mathrm{D}}$, respectively, the value of $\Delta G^0_{\mathrm{t}}(\mathrm{i, R} \rightarrow \mathrm{D})$ can be calculated from the solubility products of $\mathrm{MX}_n$ in the respective solvent by Eq. 7:

$$\Delta G^0_{\mathrm{t}}(\mathrm{i, R} \rightarrow \mathrm{D}) = RT \ln(K_{\mathrm{sp}}{}^{\mathrm{R}}/K_{\mathrm{sp}}{}^{\mathrm{D}}). \tag{7}$$

The molar Gibbs energies of NaF transfer from water (The solubility of NaF in water is 4.1 g/100 mL at 25 °C. The solubility product of NaF in water, $K_{\mathrm{sp}}{}^{\mathrm{W}}$, is calculated to be 0.31 by the solubility and activity coefficient,[15] and it agrees with the reference.[16]) to PC at 25 °C were calculated by Eq. 7 to be $\Delta G^0_{\mathrm{t}}(\mathrm{NaF, W} \rightarrow \mathrm{PC}) = 69.0\,\mathrm{kJ\,mol^{-1}}$.

The molar Gibbs energies of $\mathrm{CH_3COONa}$ transfer from water (The solubility of $\mathrm{CH_3COONa}$ in water is 50.0 g/100 mL at 25 °C. The solubility product of $\mathrm{CH_3COONa}$ in water, $K_{\mathrm{sp}}{}^{\mathrm{W}}$, is calculated to be 90.6 by the solubility and activity coefficient.[17]) to PC at 25 °C were calculated by Eq. 7 to be $\Delta G^0_{\mathrm{t}}(\mathrm{CH_3COONa, W} \rightarrow \mathrm{PC}) = 70.5\,\mathrm{kJ\,mol^{-1}}$.

However, if species i is a single ion, the value of $\Delta G^0_{\mathrm{t}}(\mathrm{i, R} \rightarrow \mathrm{D})$ cannot be obtained by purely thermodynamic means. It is necessary to introduce some extra-thermodynamic assumptions. Various extra-thermodynamic assumptions have been proposed.[7] Based on these assumptions, a number of standard molar Gibbs energies of ion transfer from water to solvent D, $\Delta G^0_{\mathrm{t}}(\mathrm{i, W} \rightarrow \mathrm{D})$, have been obtained. Many such data have been compiled by Marcus.[8] If $\Delta G^0_{\mathrm{t}}(\mathrm{M, W} \rightarrow \mathrm{D})$ or $\Delta G^0_{\mathrm{t}}(\mathrm{X, W} \rightarrow \mathrm{D})$ is known for the electrolyte $\mathrm{MX}_n$, the standard molar Gibbs energy of transfer of the counter ion, $\Delta G^0_{\mathrm{t}}(\mathrm{X, W} \rightarrow \mathrm{D})$ and $\Delta G^0_{\mathrm{t}}(\mathrm{M, W} \rightarrow \mathrm{D})$, can be calculated by Eq. 8.

$$\begin{aligned} &\Delta G^0_{\mathrm{t}}(\mathrm{MX}_n, \mathrm{W} \rightarrow \mathrm{D}) \\ &\quad = \Delta G^0_{\mathrm{t}}(\mathrm{M, W} \rightarrow \mathrm{D}) + n\Delta G^0_{\mathrm{t}}(\mathrm{X, W} \rightarrow \mathrm{D}) \\ &\quad = RT \ln(K_{\mathrm{sp}}{}^{\mathrm{W}}/K_{\mathrm{sp}}{}^{\mathrm{D}}). \end{aligned} \tag{8}$$

Here, the solubility product of $\mathrm{MX}_n$ in water, $K_{\mathrm{sp}}{}^{\mathrm{W}}$, can be found in a thermodynamic database and the solubility product of $\mathrm{MX}_n$ in solvent D, $K_{\mathrm{sp}}{}^{\mathrm{D}}$, can be obtained by the method described above.

For example, from Marcus,[8] the Gibbs energy of $\mathrm{F}^-$ transfer from water to PC, $\Delta G^0_{\mathrm{t}}(\mathrm{F^-, W} \rightarrow \mathrm{PC})$, is 56. So, the Gibbs energy of $\mathrm{Na}^+$ transfer from water to PC can be calculated by Eq. 8, $\Delta G^0_{\mathrm{t}}(\mathrm{Na^+, W} \rightarrow \mathrm{PC}) = RT \ln(K_{\mathrm{sp}}{}^{\mathrm{W}}/K_{\mathrm{sp}}{}^{\mathrm{PC}}) - \Delta G^0_{\mathrm{t}}(\mathrm{F^-, W} \rightarrow \mathrm{PC})$, to be $13.0\,\mathrm{kJ\,mol^{-1}}$, and thus the transfer activity coefficient ($\ln \gamma_{\mathrm{t}} = \Delta G^0_{\mathrm{t}}/RT$) of $\mathrm{Na}^+$ from water to PC, $\gamma_{\mathrm{t}}(\mathrm{Na^+, W} \rightarrow \mathrm{PC})$, can be calculated to be $10^{-2.3}$. The results agree well with the datum in the reference ($10^{-2.5}$).[8]

By this method the Gibbs energy of $\mathrm{CH_3COO^-}$ transfer from water to PC was calculated by Eq. 8, $\Delta G^0_{\mathrm{t}}(\mathrm{CH_3COO^-, W} \rightarrow \mathrm{PC}) = RT \ln(K_{\mathrm{sp}}{}^{\mathrm{W}}/K_{\mathrm{sp}}{}^{\mathrm{PC}}) - G^0_{\mathrm{t}}(\mathrm{Na^+, W} \rightarrow \mathrm{PC})$, to be $57.5\,\mathrm{kJ\,mol^{-1}}$. Then, the transfer activity coefficient of $\mathrm{CH_3COO^-}$ from water to PC, $\gamma_{\mathrm{t}}(\mathrm{CH_3COO^-, W} \rightarrow \mathrm{PC})$, can be calculated to be $10^{10.1}$. The relationships between the standard Gibbs energy of $\mathrm{CH_3COO^-}$ transfer from water to several solvents and the acceptor number are shown in Fig. 3. In this figure, the data besides that of PC are quoted from the reference.[8] In ion solvation, the solvent molecules approach a cation with their negative charge and approach an anion with their positive charge. So, the anion solvation is closely related to the electron pair acceptability or Lewis acidity of solvents and tends to become stronger with the increase in acceptor number.[7] So, in Fig. 3 it is reasonable that $\Delta G^0_{\mathrm{t}}(\mathrm{CH_3COO^-})$ becomes lower with the increase in acceptor number.

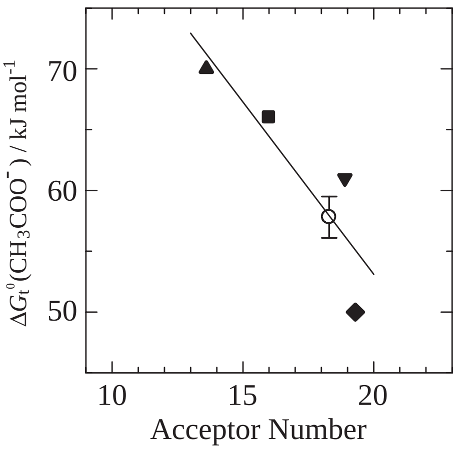

Fig. 3. Standard Gibbs energies of transfer of the acetate ion from water to other solvents plotted against the acceptor number of solvents. ▲[a]: *N*,*N*-Dimethylacetamide, ■[a]: *N*,*N*-dimethyl formamide, ▼[a]: acetonitrile, ◆[a]: dimethyl sulfoxide, ○[b]: PC (a: Data are from Ref. 8; b: The datum is from this work).

## Experimental

Tetrabutylammonium fluoride ($Bu_4NF \cdot 3H_2O$) was purchased from Fluka Co., Ltd., and was used without further purification. Tetrabutylammonium acetate ($CH_3COOBu_4N$) was purchased from Aldrich. Tetraethylammonium perchlorate ($Et_4NClO_4$) was a polarographic grade product purchased from Nacalai Tesque and was dried at 65 °C for 3 h under high vacuum with $P_2O_5$. Acetonitrile (AN) was purchased from Wako and was purified by fractional distillation twice under atmospheric pressure after the removal of water with molecular sieves, first with the existence of $P_2O_5$, and second with $CaH_2$. Propylene carbonate was obtained from Merck and was purified according to the reported method.[18] The water content of the solvent measured by Karl Fischer titration was 0.01% for AN and 0.003% for PC, respectively.

The PAA-benzo-15-crown-5 electrode, which had been confirmed to respond to $Na^+$ in PC and AN thermodynamically, was used as an indicator electrode, and was constructed by the method described in previous reports.[11,12]

The PAA-benzo-15-crown-5 electrode was used as an indicator electrode in the precipitation titration of $Na^+$ with $F^-$ in PC by Cell 1. The emfs were measured with a pH meter and recorded using a chart recorder (LR4110E, Yokokawa Denki Co.). All compartments of Cell 1 were prepared freshly each time. Steady-state potentials were read to 0.1 mV.

$$\begin{aligned}&\mathrm{Ag}|10\,\mathrm{mM\ AgNO_3} + 10\,\mathrm{mM\ Et_4NClO_4\ (AN)}\|\\&\quad 50\,\mathrm{mM\ Et_4NClO_4\ (D)}\|c\ \mathrm{mM\ NaClO_4\ (+P)}\\&\quad + 10\,\mathrm{mM\ Et_4NClO_4\ (PC)|PAA\text{-}B15C5|Pt} \cdots \text{Cell 1,}\end{aligned} \tag{9}$$

where P = $Bu_4NF \cdot 3H_2O$ and $CH_3COOBu_4N$; $Bu_4NF \cdot 3H_2O$ and $CH_3COOBu_4N$ PC solution were added by a Gilmont S-1200 microburet.

## References

1 W. Ronald Fawcett, *Liquids, Solution, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details*, Oxford University Press, New York, **2004**.

2 A. J. Bard, *Electroanalytical Chemistry*, Marcel Dekker, Inc., New York, **1975**, Vol. 8.

3 V. Gutmann, *The Donor–Acceptor Approach to Molecular Interactions*, Plenum press, New York and London, **1978**.

4 K. Burger, *Solvation, Ionic, and Complex Formation Reactions in Non-Aqueous Solvents*, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, **1983**.

5 G. Gritzner, *Pure Appl. Chem.* **1988**, *60*, 1743.

6 *Chemistry of Nonaqueous Solutions*, ed. by G. Mamantov, A. I. Popov, VCH Publishers, New York, **1994**.

7 K. Izutsu, *Electrochemistry in Nonaqueous Solutions*, Wiley-VCH, Weinheim, **2002**.

8 Y. Marcus, *Ion Solvation*, John Wiley & Sons, Inc., New York, **1985**.

9 Y. Marcus, *Ion Properties*, Marcel Dekker, New York, **1997**.

10 Y. Marcus, *The Properties of Solvents*, John Wiley & Sons, Inc., New York, **1998**.

11 T. Nakamura, C. Hayashi, K. Izutsu, *Anal. Chim. Acta* **1994**, *292*, 305.

12 T. Nakamura, H. Mongi, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2449.

13 J. Ren, T. Nakamura, *Rev. Polarogr.* **2005**, *51*, 3.

14 X. Ji, B. Jin, J. Ren, J. Jin, T. Nakamura, *J. Electroanal. Chem.* **2005**, *579*, 25.

15 R. A. Robinson, R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, **1970**, p. 492.

16 W. J. Hamer, Y. C. Wu, *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.

17 O. D. Bonner, *J. Solution Chem.* **1988**, *17*, 999.

18 K. Izutsu, I. M. Kolthoff, T. Fujinaga, M. Hattori, M. K. Chantooni, Jr., *Anal. Chem.* **1977**, *49*, 503.