Partial Molar Volume of 18-Crown-6 Complex Ions with Alkali-Metal Ions in Methanol

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The sedimentation potential (SP), molar conductivities and partial molar volumes at infinite dilution of salts (NaCl, KCl and CsCl) in methanol containing 18-Crown-6 (18 C 6) have been measured. By combining SP, transference numbers and limiting partial molar volumes of salts containing 18 C 6, single-ion volumes at infinite dilution of $[18\text{ C }6\text{-M}^+]$ complex ion and Cl^- ion have been evaluated. The single-ion partial molar volume of chloride ion is in fair agreement with that observed for alkali-metal-salts in methanol not containing 18 C 6. This fact suggests clearly that the charge of the alkali-metal ion trapped in the 18 C 6 cavity is effectively shielded by 18 C 6. The biggest volume change is shown for the 18 C 6 complex ion with K^+ among all the alkali-metal ions studied.

1 INTRODUCTION

The details about many characteristics of crown ethers have been reevaluated¹⁾ since its existence was discovered by Pedersen.²⁾ It was shown that the most important characteristic is that crown ethers interact with certain cations, especially alkali- and alkaline-earth-metal ions to form stable complexes.³⁻⁸⁾ These properties have resulted in considerable interest in crown ethers and their applications in solution chemistry.⁹⁻¹³⁾

When a solution of electrolyte is placed in an accelerating field, an electrical signal is produced in the solution as result of differences in the movement of the cation and anion in the applied field. This potential is called the sedimentation potential (SP)¹⁴⁾ and up to now has been measured for electrolytes in various solvents.¹⁵⁻¹⁷⁾ Nowadays, SP measurements have been demonstrated in order to apply as an ion sensor capable of detecting specific ion by means of 18-Crown-6 (18 C 6) as a crown ethers.¹⁸⁾ That is to say, the SP of alkali-metal salts (NaCl, KCl and CsCl) in various solvents containing 18 C 6 has been detected with SP measuring apparatus.¹⁸⁾ As the results, the significant differences between SP of alkali-metal salts in methanol containing 18 C 6 and that in methanol

not containing 18 C 6 are observed. That is due to the complex formation between 18 C 6 and the alkali-metal ions. From a viewpoint of solution chemistry, it is so interesting to study the factors influencing complex formation between 18 C 6 and alkali-metal ions and the behavior of the 18 C 6 complex ions in methanol, respectively. By the way, SP is the only physical quantity capable of dividing the partial molar volume of an electrolyte into its ionic constituents without relying on any kind of extrathermodynamic or semiempirical relationship. To divide the partial molar volume of an electrolyte, such as the 18 C 6 complexes with alkali-metal ions, $[18\text{ C }6\text{-M}^+]\text{Cl}$, into its constituent ions by means of SP, we need to know the transference number of the 18 C 6 complex ions, $[18\text{ C }6\text{-M}^+]$, and the partial molar volume of 18 C 6 complexes, $V_2^\infty([18\text{ C }6\text{-M}^+]\text{Cl})$, at the infinite dilution.

In this work, in order to obtain the information about solvation behavior of $[18\text{ C }6\text{-M}^+]$ in methanol, SP of alkali-metal salts in methanol containing 18 C 6 is measured. Secondly, the limiting conductivities of alkali-metal salts in methanol containing 18 C 6 is determined in order to calculate the corresponding transference number for the 18 C 6 complex ions. In this case, it is assumed that the association between the 18 C 6 complex ion and chloride ion is negligible and 18 C 6 forms 1:1 complexes with alkali-metal ions. Thirdly, the partial molar volume of the 18 C 6 complexes with alkali-metal ions by the density measurement is

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determined. From SP, the transference number and the partial molar volume of the 18 C 6 complexes with alkali-metal ions obtained at above, the partial molar volume of the 18 C 6 complexes with alkali-metal ions is divided into the single-ion partial molar volumes of the 18 C 6 complex ions and that of the chloride ion. In addition, the results obtained from this experiments will be evaluated with electron spectroscopy for chemical analysis (ESCA). On the basis of the results obtained, the behavior of the 18 C 6 complex ions and chloride ion in methanol will be discussed in details.

2 EXPERIMENTAL PROCEDURE

2.1 Reagents

18 C 6 (Aldrich, stated purity 99.5%) was kept in an evacuated desiccator and was used with no further purification. Methanol (Merck, stated purity 99.8%, water content 0.005%) was kept over a thermally activated 3 A molecular sieve prior to use. Alkali-metal salts (NaCl, KCl and CsCl) purchased from Wako Junyaku (99.5%) and were dried for three days at 393 K in a vacuum oven. All reagents were kept in a vacuum desiccator with P_2O_5 .

2.2 SP measurements

SP of alkali-metal salts (MCl) in methanol containing 18 C 6 (0.05 M) was measured at 298 K at the acceleration of 5.0 G using the same apparatus and procedure as reported previously.¹⁶⁻¹⁸⁾

2.3 Conductivity measurements

Resistance measurements were carried out using a Beckman model RC-18 A conductivity bridge at a frequency of 1 kHz. Two Jones type conductivity cells with cell constants $0.4883 \pm 0.001 \text{ cm}^{-1}$ and $0.7689 \pm 0.001 \text{ cm}^{-1}$ were calibrated with aqueous KCl solutions as recommended previously. An oil thermostat maintained the temperature at $298.15 \pm 0.003 \text{ K}$. Temperature control was monitored at $\pm 0.001 \text{ K}$ near the cell with a platinum resistance probe connected to an ASL model F 250 thermometer, which was calibrated by Isotech (England). The whole system was placed in a room in which the temperature was kept constant within $\pm 0.5 \text{ K}$. Various solution of MCl in methanol containing 18 C 6 were prepared by weighting and added to cells where their resistance was measured. For all values of specific conductivi-

ty, K_0 , that corresponding to the solvent was subtracted.

2.4 Density measurements

The densities to obtain the limiting partial molar volumes of 18 C 6 (0.05 M) complexes with alkali-metal salts were also measured at 298.15 K with a vibrating-tube densitometer (A. Paar, model DMA 60/602) of $8 \times 10^{-6} \text{ g} \cdot \text{cm}^{-3}$.

3 RESULTS AND DISCUSSION

3.1 SP of alkali-metal salts

If a significant difference exists in the effective volume of a cation and an anion in solution, the responses of cation and anion to an externally applied accelerating field should be different. This difference in the motion of dissolved ions lead to an appearance of an electric potential, known as the sedimentation potential (SP). If the partial molar volume and the transference number of an electrolyte are available, the partial molar volume of the electrolyte can be divided into cationic and anionic parts by means of SP data. For that purpose, variation of SP (●) with concentration of alkali-metal salts in methanol containing 18 C 6 (0.05 M) is compared with those (···) of not containing 18 C 6 in Fig. 1. As is shown in Fig. 1, the absolute numerical values of SP are small at high salt concentration, approaching a certain value at about 0.001 M. This limiting value is generally referred to as the SP. The significant differences between SP (●) of alkali-metal salts in methanol containing 18 C 6 and those (···) of not containing 18 C 6 are observed in Fig. 1. This fact can be explained as follows. 18 C 6 traps alkali-

Fig. 1 Sedimentation potential of alkali-metal salts in methanol containing 18 C 6 (●) and that not containing 18 C 6 (···).

metal ion in its cavity and forms the 18 C 6 complexes with alkali-metal ions, $[18\text{C}6\text{-M}^+]\text{Cl}$ (M^+ is Na^+ , K^+ , Cs^+ , respectively). At that case, the complex formation constant, $\log K_{\text{ML}}^+$, between 18 C 6 and alkali-metal ions in methanol is 4.32, 6.10 and 4.62 for Na^+ , K^+ and Cs^+ , respectively.¹⁹⁾ Therefore, when alkali-metal salts, MCl , is dissolved in methanol containing 18 C 6, the ratio of the 18C6 complexes with alkali-metal ions, $[18\text{C}6\text{-M}^+]\text{Cl}$, which occupy in the solution is about 100 percent.¹⁹⁾ Consequently, SP (●) of alkali-metal salts in methanol containing 18 C 6 is equal to measure that of $[18\text{C}6\text{-M}^+]\text{Cl}$ in methanol. While, SP in alkali-metal salts (⋯) in methanol not containing 18 C 6 is equal to measure that of MCl in methanol. SP is generally proportional to the difference in molecular weight between cation and anion in the solvent.¹⁴⁻¹⁶⁾ The anion of both compounds are the same. The molecular weight of $[18\text{C}6\text{-M}^+]$ is higher than that of M^+ . Therefore, a big differences between SP (●) for the complexed state and that (⋯) of uncomplexed state are observed. Among all the alkali-metal salts studied, KCl shows the biggest difference of SP. This is a consequence of having the highest complex formation constant.¹⁹⁾

3.2 Conductivity of 18 C 6 complexes

In analyzing the conductivity data for 18 C 6 complexes, however, it is assumed that the association between a cation and anion is negligible under these highly dilute experimental conditions and that 18 C 6 forms 1 : 1 complexes with alkali-metal ions in this work. The equilibrium equation is given by : ²⁰⁾

where L stands for 18 C 6 and M is either Na, K, or Cs. α is the fraction of free alkali-metal ions that are not in the complexed state. Λ_{Total} is the total molar conductivity when alkali-metal salts are dissolved in methanol containing 18 C 6. $\Lambda([\text{MCl}])$ and $\Lambda([\text{ML}]\text{Cl})$ represent the conductivity of the alkali-metal salts and that of the complex. Λ_{Total} is obtained from the resistance measured with the conductivity bridge and the cell constant. α can be obtained from the complex

Fig. 2 Molar conductivity, $\Lambda([\text{MCl}]\text{Cl})$ as function of concentration $\sqrt{C_1}$ for $[\text{ML}]\text{Cl}$.

formation constant, K_{ML}^+ , which is defined as,²⁰⁾

$$K_{\text{ML}}^+ = \frac{[\text{ML}^+]}{[\text{M}^+][\text{L}]} = \frac{[1 - \alpha]}{\alpha[\text{L}]} \quad (2)$$

The corresponding values of $\Lambda([\text{MCl}])$ ^{17, 21)} and K_{ML}^+ ¹⁹⁾ in methanol have been taken from the literature. Therefore, the molar conductivities of complex $[\text{ML}]\text{Cl}$, $\Lambda([\text{MCl}]\text{Cl})$, can be calculated from equation (1). A plot of $\Lambda([\text{MCl}]\text{Cl})$ vs. $[\text{MCl}]^{1/2}$ is shown in Fig. 2. The value of $\Lambda([\text{MCl}]\text{Cl})$ at infinite dilution, $\Lambda^\infty([\text{ML}]\text{Cl})$ was calculated by extrapolation using a least-squares fit. The results obtained are given below.

$$\Lambda^\infty([\text{NaL}]\text{Cl})/\text{S cm}^2\text{mol}^{-1} = 92.85 \pm 0.19,$$

$$\Lambda^\infty([\text{KL}]\text{Cl})/\text{S cm}^2\text{mol}^{-1} = 92.42 \pm 0.21,$$

$$\Lambda^\infty([\text{CsL}]\text{Cl})/\text{S cm}^2\text{mol}^{-1} = 95.49 \pm 0.11$$

Since we have known the value of the ionic molar conductivity at infinite dilution for chloride ion in methanol,²¹⁾ the corresponding values for complex ions ML^+ can be determined :

$$\Lambda^\infty(\text{NaL}^+) = 40.49/\text{S cm}^2\text{mol}^{-1}; \Lambda^\infty(\text{KL}^+) =$$

$$40.06/\text{S cm}^2\text{mol}^{-1}; \Lambda^\infty(\text{CsL}^+) = 43.13/\text{S cm}^2\text{mol}^{-1}$$

The value for $\Lambda^\infty(\text{KL}^+)$ is in agreement with that of Takeda,²¹⁾ $39.9/\text{S cm}^2\text{mol}^{-1}$. Moreover, the transference numbers, t_+ and t_- for complex ion and chloride ion are calculated by using the following equation.

$$t_+ = \Lambda^\infty(\text{ML}^+)/\Lambda^\infty([\text{ML}]\text{Cl}), \quad t_- = 1 - t_+ \quad (3)$$

3.3 Limiting partial molar volume for 18 C 6 complexes

In a liquid mixture of methanol, 18 C 6 and

alkali-metal salts MCl, equilibrium equation on molality is expressed as follows.²²⁾

here M^+ , L , and α are presented in the above paragraph. m stands for molality and the subscript E and L represent electrolyte and 18 C 6, respectively. When alkali-metal salts are dissolved in methanol containing 18 C 6, the total apparent molar volume, V_ϕ , can be expressed as follows.²²⁾

$$V_\phi = \frac{m_E m_E + m_L m_L}{m_{total} d} + \frac{10^3 (d_0 - d)}{m_{total} d} \quad (5)$$

Where m_E and m_L are the molalities of the MCl and crown ether (L), respectively, d_0 and d are the densities of the solvent and the solution, respectively. M_E and M_L are the molecular weights of MCl and L . m_{total} is $m_E + m_L$. The value of V_ϕ can be calculated by measuring d and d_0 with the densitometer.

On the other hand, the total apparent molar volumes, V_ϕ , can be expressed in a similar way as those for the conductivity in equation (1):²²⁾

$$V_\phi = \frac{m_E}{m_{total}} \alpha V_\phi(E) + \frac{m_L - m_E(1-\alpha)}{m_{total}} V_\phi(L) + \frac{m_E}{m_{total}} (1-\alpha) V_\phi([ML] Cl) \quad (6)$$

where $V_\phi(E)$, $V_\phi(L)$, and $V_\phi([ML] Cl)$ are the partial molar volume of MCl, 18 C 6, and 18 C 6 complex, respectively. From equation (6), V_ϕ is also represented as follows.²²⁾

$$V_\phi = \frac{m_E}{m_{total}} \alpha V_\phi(E) + \frac{m_L - m_E(1-\alpha)}{m_{total}} V_\phi(L) + \frac{m_E}{m_{total}} (1-\alpha) [V_2^\infty([ML] Cl) + b' \sqrt{(1-\alpha) m_E}] \quad (7)$$

Where b' are an empirical constant. $V_2^\infty([ML] Cl)$ is the partial molar volume of 18 C 6 complexes with alkali-metal ions at infinite dilution. Here, $V_\phi(L)$ is calculated from density data in the same way as equation (5). And α is calculated from equation (2). The value of $V_\phi(E)$ is also reported previously.¹⁷⁾

In order to obtain $V_2^\infty([ML] Cl)$ ($L = 18 C 6$, $M = Na^+$, K^+ , Cs^+) from equation (7), Y and X are written as equation (8), and then equation (7) is given as follows.

Fig. 3 Partial molar volume, Y as function of $X = \sqrt{(1-\alpha) m_E}$ for molality m_E of [MCl].

$$Y = \frac{V_\phi - \frac{m_E}{m_{total}} \alpha V_\phi(E) - \frac{m_L - m_E(1-\alpha)}{m_{total}} V_\phi(L)}{\frac{m_E}{m_{total}} (1-\alpha)} \quad (8)$$

$$X = \sqrt{(1-\alpha) m_E} \quad (9)$$

Y of equation (9) has been plotted as function of X . The result is shown in Fig. 3. As is shown in Fig. 3, the apparent molar volumes of $V_2^\infty([18 C 6-M^+] Cl)$ can be determined by extrapolation of the linear Y vs. X plot to the intercept. $V_2^\infty([18 C 6-M^+] Cl)/cm^3 mol^{-1}$ obtained from Fig. 3 is as follows.

$$V_2^\infty([18 C 6-Na^+] Cl) = 232.00 \pm 0.4$$

$$V_2^\infty([18 C 6-K^+] Cl) = 249.0 \pm 0.5$$

$$V_2^\infty([18 C 6-Cs^+] Cl) = 259.5 \pm 0.4$$

3.4 Ionic partial molar volume

SP of alkali-metal salts generated in methanol containing 18 C 6 using our apparatus is expressed as follows:¹⁴⁻¹⁶⁾

$$SP = 0.005 \times 10^{-6} [t_+ (m_+ - V_+^0 d_0) - t_- (m_- - V_-^0 d_0)] x_0 \quad (10)$$

where t_+ , m_+ and V_+^0 are the transference number, the molecular weight and the partial molar volume of cation, respectively. Similarly, t_- , m_- and V_-^0 are these of anion. d_0 is the density of the solvent, and x_0 is the distance between electrodes. Since V_2^∞

$=V_+^0+V_-^0$,¹⁴⁻¹⁶⁾ by combining the SP measured, the transference number obtained from equation (3) and the partial molar volume obtained, the limiting partial molar volume V_2^∞ ([18 C 6-M⁺] Cl) has been split into cationic and anionic contributions, $V_+^0/\text{cm}^3\text{mol}^{-1}$, $V_-^0/\text{cm}^3\text{mol}^{-1}$, respectively. The results obtained are shown in Table 1 along with SP values, the transference numbers of [18C6-M⁺] and the partial molar volume $V_2^\infty/\text{cm}^3\text{mol}^{-1}$ obtained. As is shown in Table 1, the partial molar volumes of the 18 C 6-complex ions with alkali-metal ions, V_+^0 ([18 C 6-M⁺]), increase with increasing molecular weight, while the partial molar volume of chloride ion, $V_-^0(\text{Cl}^-)$, hardly changes. Besides, when the partial molar volume of V_+^0 ([18 C 6-M⁺]) is compared with that of V_2^∞ (18 C 6) ($223.87 \pm 0.47/\text{cm}^3\text{mol}^{-1}$) obtained in this work, the change rate of V_+^0 ([18 C 6-M⁺]) against the partial molar volume of alkali-metal ions is the biggest for V_+^0 ([18 C 6-K⁺]) among V_+^0 ([18 C 6-M⁺]). On the contrary, V_+^0 ([18 C 6-Na⁺]) is the smallest. Moreover, $V_-^0(\text{Cl}^-)$ is in fair agreement with that in methanol not containing 18 C 6.¹⁷⁾ In order to clarify this fact, the intensity of photoelectron from the same solution used in this work was measured with ESCA (Shimadzu Co., Ltd., ESCA-1000) equipped at Kagoshima Univ. Before measuring the intensity of photoelectron from the solution, the solution of alkali-metal salts (concentration is 0.01 M) in methanol not containing 18 C 6 and those in methanol containing 18 C 6 (concentration is 1.0 M) are dried with an infrared desiccator. The six samples of crystalline thin film are made of the solutions. The intensity of photoelectron against binding energy for the six samples, is measured with ESCA. The intensity of photoelectron of alkali-metal ions from three samples containing 18 C 6 among six samples shown in Fig. 4 (a)-(c). (a) is NaCl in methanol containing 18 C 6, (b) and (c) are KCl and CsCl

in the same solvent. Although no results from three samples not containing 18 C 6 is shown for want of space, the intensity of photoelectron of alkali-metal ions from three samples containing 18 C 6 is much smaller than that of the same ions from three samples not containing 18 C 6. Besides, as is shown in Fig. 4 (a)-(c), the intensity of photoelectron from K⁺ ion is the smallest among alkali-metal ions. When rearranging the results mentioned above, the results demonstrate clearly that 18 C 6 traps selectively K⁺ ion in its cavity, and the charge of K⁺ ion is effectively shielded by 18C6.¹⁹⁻²²⁾

4 CONCLUSIONS

We have made detailed measurements of conductance and the partial molar volume of the 18 C 6 complexes with alkali-metal ions and SP of alkali-metal salts in methanol containing 18 C 6. By combining the transference number, the partial molar volume and SP, single-ion volumes at infinite dilution of the 18 C 6 complexes have been obtained. Moreover, intensity of photoelectron from alkali-metal for the same solutions used measurements of SP have been also observed with ESCA. It is clarified that when 18 C 6 forms the 18 C 6-complexes with alkali-metal ions, the change rate of V_+^0 ([18 C 6-M⁺]) against the partial molar volume of alkali-metal ions is the biggest for V_+^0 ([18C6-K⁺]) with K⁺ ion among those studied, while that for $V_-^0(\text{Cl}^-)$ hardly changes. This demonstrates clearly that 18 C 6-complex formation with K⁺ ion is stronger than that with the other ions, and its charge being effectively shielded by 18 C 6.

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Table 1 Ionic partial molar volumes of 18C6-complex ions with alkali-metal and that of chloride ions at 298K.

[18C6-M ⁺] Cl	SP (μV)	t_+	V_2^∞ ($\text{cm}^3\text{mol}^{-1}$)	V_+^0 ($\text{cm}^3\text{mol}^{-1}$)	V_-^0 ($\text{cm}^3\text{mol}^{-1}$)
[18C6-Na ⁺] Cl	0.28	0.436	232.0	223.1	8.92
[18C6-K ⁺] Cl	0.61	0.427	249.0	239.9	9.06
[18C6-Cs ⁺] Cl	1.33	0.452	259.5	250.5	9.05

Fig. 4 Photoelectron spectrum of alkali metal from thin film made of alkali-metal salts (0.01 M) in methanol contained 18 C 6 (1.0 M). Thin film ; (a) NaCl, (b) KCl, (c) CsCl.

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