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# Temperature Dependence of Walden Product of 18-Crown-6-K$^+$ Complex in Water

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**Synopsis.** Limiting ionic molar conductivities of the 18-crown-6-K$^+$ complex in water were determined at 15 and 35 °C. Walden product values of the complex at 15, 25, and 35 °C are nearly identical within experimental errors of conductance measurements. Solvation properties of the complex in water were discussed in detail.

From a viewpoint of solution chemistry, it is interesting to study solvation properties of crown ether-alkali metal ion complexes as well as medium effects on stabilities of the complexes. It has been carried out by various methods and the information on solute-solvent interactions regarding the crown ether complexes has been reported. For example, density and speed-of-sound measurements suggested that hydration number of K$^+$ in 18-crown-6 (18C6) is zero.1) The data for entropies of transfer from water to methanol of the 18C6-K$^+$ complex indicate that the complex in water undergoes hydrophobic hydration.2) It was concluded from the results of viscosity measurements that the dragging resistance of the 18C6-K$^+$ complex is nearly the same as that of the free 18C6 in water.3) It was reported from conductance study that the 18C6-K$^+$ complex acts as a structure breaker in water.4,5) In a series of our conductance studies,4–7) limiting ionic molar conductivity at 25 °C of the 18C6-K$^+$ complex in a given solvent was compared with that of $(n\text{-}C_4H_9)_4N^+$ since they have almost the same size, and Walden products of the complex at 25 °C in various solvents were discussed.

In this work, in order to obtain more detailed information about solvation behavior of the 18C6-K$^+$ complex in water, limiting ionic molar conductivities of the complex in water were determined at 15 and 35 °C, and temperature dependence of Walden products for the complex was investigated.

## Experimental

18-Crown-6 and extremely pure potassium chloride were obtained from Nisso Co., Ltd. and Merck Japan Ltd., respectively. The 18C6 was recrystallized three times from acetonitrile and, prior to use, dried at 70 °C in a vacuum oven. The potassium chloride was used without further purification. Conductivity of water was less than $2\times10^{-7}\ \Omega^{-1}\ \text{cm}^{-1}$. Conductance measurements were made on a Fuso conductivity apparatus, model 362 A, in a water bath thermostated at 10, 15, 20, 25, 35, 45±0.01 °C. Two cells were used with cell constants of 0.059707 and 0.093938 cm$^{-1}$.

The experimental procedures to obtain formation constants and limiting ionic molar conductivities of the 18C6-K$^+$ complex were described in the previous paper.7) For each conductance measurement system, total concentrations of KCl and 18C6 were kept below $5\times10^{-3}$ and $3\times10^{-2}$ mol dm$^{-3}$, respectively.

Table 1. $\log K_{ML^+}$ values of the 18C6-K$^+$ complex and $\Lambda°$ values of the 18C6 complex with potassium chloride in water at various temperatures

| Temp/°C | $\log (K_{ML^+}/\text{mol}^{-1}\ \text{dm}^3)$ | $\Lambda°/\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ |
|---|---|---|
| 10 | 2.288±0.008 | — |
| 15 | 2.253±0.012 | 81.2±0.5 |
| 20 | 2.135±0.011 | — |
| 25 | 2.034±0.004 | 101.7±0.3[4)] |
| 35 | 1.940±0.004 | 124.2±0.5 |
| 45 | 1.790±0.020 | — |

## Results and Discussion

Formation constant ($K_{ML^+}$) and limiting ionic molar conductivity ($\lambda°$) of the 18C6-K$^+$ complex were obtained in the same manner described in the previous study.7) M$^+$ and L designate an alkali metal ion and a crown ether, respectively. It is assumed that the association between a cation and an anion is negligible and that 18C6 forms a 1:1 complex with K$^+$. Corrections for viscosity changes due to solute were neglected. The $\log K_{ML^+}$ values of the 18C6-K$^+$ complex and the limiting molar conductivity ($\Lambda°$) values of the 18C6 complex with potassium chloride in water at various temperatures are listed in Table 1.

The $\log K_{ML^+}$ value at 25 °C determined in this study is in good agreement with those by Izatt *et al.*8) (2.03±0.10, by calorimetric titration) and Stover9) (2.029±0.028, by isotachophoresis); however, it is slightly lower than those by Frensdorff10) (2.06±0.04, using cation-selective electrode by potentiometry) and Høiland *et al.*1) (2.0476±0.0015, using cation-exchange membrane by potentiometry). The $\log K_{ML^+}$ *vs.* $T^{-1}$ plots in Fig. 1 show a linear relationship. Enthalpy change ($\Delta H$) and entropy change ($\Delta S$) were calculated from these data by using equations, $\Delta G=-RT\ln K_{ML^+}$ and $\Delta G=\Delta H-T\Delta S$, $\Delta G$ being free energy change. The $\Delta H$ and $\Delta S$ values are

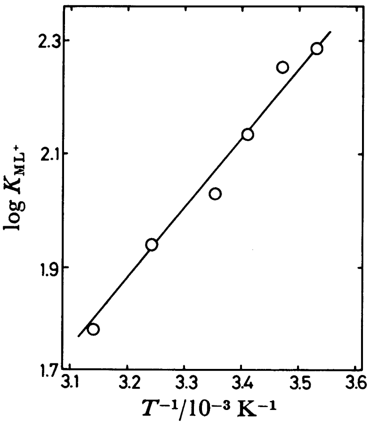

Fig. 1. $\log K_{ML^+}$ *vs.* $T^{-1}$ plots for the 18C6-K$^+$ complex in water.

Table 2. $\lambda^\circ/\Omega^{-1}\,\mathrm{cm^2\,mol^{-1}}$ and Walden products in water at various temperatures

| Temp/°C | $\eta_o$/cP*[12] | 18C6-K$^+$ |  | $(n\text{-}C_4H_9)_4N^+$ |  | Cl$^-$ |
|---|---|---|---|---|---|---|
|  |  | $\lambda^\circ$ | $\lambda^\circ\eta_o$ | $\lambda^\circ$[13] | $\lambda^\circ\eta_o$ | $\lambda^\circ$ |
| 10 | 1.306 | — | — | 12.56 | 0.1640 | — |
| 15 | 1.138 | $19._8$ | $0.22_5$ | — | — | $61.4_1$[12] |
| 25 | 0.8903 | $25._3$[4] | $0.22_5$ | 19.31 | 0.1719 | 76.39[13] |
| 35 | 0.7194 | $32._0$ | $0.23_0$ | — | — | $92.2_1$[12] |
| 45 | 0.5963 | — | — | 30.40 | 0.1813 | — |

* $\eta_o$ denotes viscosity of water, 1 P=0.1 Pa s.

$-25.01\ \mathrm{kJ\,mol^{-1}}$ and $-44.34\ \mathrm{J\,K^{-1}\,mol^{-1}}$, respectively; they agree well with those by Izatt *et al.*[8] ($\Delta H=-25.9\ \mathrm{kJ\,mol^{-1}}$, $\Delta S=-47.6\ \mathrm{J\,K^{-1}\,mol^{-1}}$). Values of $\log K_{\mathrm{ML^+}}$ at 25 °C ($2.140\pm0.022$), $\Delta H$ ($-23.43\pm0.83\ \mathrm{kJ\,mol^{-1}}$), and $\Delta S$ ($-37.60\pm3.22\ \mathrm{J\,K^{-1}\,mol^{-1}}$) determined by Michaux and Reisse[11] ($\log K_{\mathrm{ML^+}}$: using electrode by potentiometric titration, $\Delta H$ and $\Delta S$: by calorimetric measurement) are relatively larger than those by us.

Thus, conductometry is a very accurate and reliable method for obtaining formation constants and thermodynamic parameters of crown ether-metal ion complexes.

As can be seen from Table 2, $\lambda^\circ$ values at 15 and 35 °C of the 18C6-K$^+$ complex are nearly equal to and larger than those at 25 and 45 °C of $(n\text{-}C_4H_9)_4N^+$, respectively; both mobilities of the 18C6-K$^+$ complex and $(n\text{-}C_4H_9)_4N^+$ gradually increase with an increase in temperature. This indicates that the 18C6-K$^+$ complex is more mobile than $(n\text{-}C_4H_9)_4N^+$ in water as reported previously.[4] The explanation for the results was offered in the preceding paper.[4] Walden product values of the 18C6-K$^+$ complex in water at 15, 25, and 35 °C are nearly identical within experimental errors of conductance measurements (Table 2). This may reflect the effects caused by the following two factors. (1) There exist possible interactions between the central potassium ion and water molecules on two axial sides of the 18C6 plane, and between ether oxygen atoms of the 18C6 and water molecules *via* hydrogen bonding. The interactions may be weakened with an increase in temperature. Thus, the 18C6-K$^+$ complex is more mobile than expected at a higher temperature. This would cause a positive temperature coefficient of Walden product of the 18C6-K$^+$ complex in water. (2) The 18C6-K$^+$ complex acts as a structure breaker in an aqueous solution.[4,5] Since hydrogen-bonded structure of water gradually disappears at a higher temperature, the 18C6-K$^+$ complex is less mobile than expected. This would cause a negative temperature coefficient of Walden product. These two factors compensate each other, resulting in no temperature dependence of Walden product of the 18C6-K$^+$ complex.

Values of $\lambda^\circ(K^+)/\lambda^\circ(18C6\text{-}K^+)$ for $CH_3OH$, $CH_3CN$, DMF, DMSO, propylene carbonate, and water are 1.31, 1.41, 1.24, 1.46, 1.34, and 2.90, respectively. These were calculated from the data in Ref. 4. If the radii of moving entities of K$^+$ and 18C6-K$^+$ complex in the nonaqueous solvents (*i.e.*, effective radii) are considered to be 2.9 and 4.9 Å, respectively, the $\lambda^\circ(K^+)/\lambda^\circ(18C6\text{-}K^+)$ value is about 1.6 ($\lambda^\circ=0.819/\eta_o r$, $r$ being radius). The former was evaluated from Stokes' radii of K$^+$ in the nonaqueous solvents, and the latter is the crystal ionic radius itself evaluated from the crystal ionic radius of K$^+$ and the 18C6 volume. Experimental $\lambda^\circ(K^+)/\lambda^\circ(18C6\text{-}K^+)$ values of the nonaqueous solvents are very much closer to the calculated value (1.6) compared to that of water (2.90). This indicates that the 18C6-K$^+$ complex is not so much strongly solvated in the nonaqueous solvents as K$^+$. From the fact that there is no large difference in Walden products of the 18C6-K$^+$ complex among these solvents (including water)[4] and that the Walden product value of K$^+$ for water is very much larger than those for the other solvents,[4] the considerably high $\lambda^\circ(K^+)/\lambda^\circ(18C6\text{-}K^+)$ value of water is attributed completely to the role of K$^+$ as a structure breaker in water. This is supported by the data that the $\lambda^\circ(K^+)/\lambda^\circ(18C6\text{-}K^+)$ value of water decreases with an increase in temperature ($\lambda^\circ(K^+)$[12]$=59.6_6$ at 15 °C and $88.2_1$ at 35 °C). From the fact that the 18C6-K$^+$ complex in water shows no temperature dependence of Walden product, whereas Walden product of K$^+$ in water decreases with an increase in temperature, the negative temperature coefficient of the $\lambda^\circ(K^+)/\lambda^\circ(18C6\text{-}K^+)$ value for water may be caused entirely by the decrease of iceberg structure in water at a higher temperature.

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