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The Viscosity Coefficients of 18-Crown-6–Alkali Metal-ion Complexes

Fumio KAWAIZUMI,* Isao YAJIMA, Hiroyasu NOMURA, and Yutaka MIYAHARA
Department of Chemical Engineering, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464

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The viscosities of LiCl, KCl, and CsCl have been measured in water and aqueous solutions containing 0.398 mol/dm^3 of 18-crown-6 (CR) at 25 °C. The *B*-coefficients of the alkali metal chlorides in water have been obtained using the theoretical values of the *A*-coefficients. The viscosity coefficients of 18-crown-6 itself have been determined in water and methanol. In systems containing crown ether, the viscosity increment due to the complex formed in solutions, $\Delta\eta_{[CR\text{-}M^+]Cl^-}$, has been evaluated by subtracting from the observed viscosity the increment attributed to non-coordinated crown ether and alkali metal chlorides in solutions. The two complex ions, [CR-K$^+$] and [CR-Cs$^+$], have nearly the same values of the *B*-coefficients, and these values are, in turn, approximately equal to that of 18-crown-6 in water. Measurements done on KCl in methanol containing 18-crown-6 have led to the finding that in methanol, 18-cown-6 and the [CR-K$^+$] ion take effectively the same *B*-value.

Macrocyclic polyether, crown ether, is known to form stable complexes with alkali or alkaline earth metal ions. The complex formation is characterized by the selectivity of certain crown ethers towards specific cations. A number of investigators[1–9] have endeavored to clarify the origin of the specificity observed in the interactions between crown ethers and metal ions in solutions. The metal ion is trapped in the central cavity of the crown ether by ion-dipole forces, and the ratio of the ionic radius of the cation to the dimension of the crown-ether cavity seems to be the most important factor governing the specificity of the complex formation, though an exception to the correlation of the cationic size with the hole size of crown ethers has been reported very recently.[8]

The effective volumes can presumably be expected to be different for the crown ether-cation complex and non-coordinated crown ether. When solute species flow in viscous media, the volume of solutes should affect the dragging resistance forces. Further, in spite of being a macroscopically measurable quantity, the viscosity of solutions has been found to give information on molecular interactions in solutions.

The purpose of this study is to determine the concentration dependence of the viscosity of solutions of three kinds of alkali chlorides (LiCl, KCl, and CsCl) in aqueous solutions containing 18-crown-6, and then to assess the contributions attributed to the crown ether-alkali metal-ion complexes. 18-Crown-6 has a very high solubility in water, which is an important factor in carrying out any viscometric study. The complex formation of an alkali metal ion with 18-crown-6 has been well confirmed for K$^+$ and Cs$^+$ ions in water, but this is not the case for Li$^+$. Therefore, as will be described in a later section, our experimental results for LiCl will be discussed from a standpoint different from that used for KCl and/or CsCl.

In order to compare the solvent effects, measurements have also been done for KCl in methanol and that containing 18-crown-6.

Experimental

Specimens and Solvents. The 18-crown-6 (abbreviated hereafter as CR) was purchased from the Nakarai Chemicals Co., Ltd. It was purified in a manner similar to the procedure proposed by Gokel and Cram;[10] about 50 g of CR were placed in an Erlenmeyer flask, into which 250 cm^3 of acetonitrile were then poured. The slurry was stirred and heated in a water bath held at 70 °C. A glass tube containing a drying agent was attached to the flask to prevent the penetration of humidity. The solution was then filtered. This process was repeated three times. After being stirred vigorously, the solution was allowed to cool to the ambient temperature. After the deposition of a fine white precipitate, the solution was kept in a refrigerator for 12 h. The precipitate was then collected by filtration. From the precipitate (CR-acetonitrile complex), acetonitrile was eliminated by heating at 35 °C under reduced pressure; then the product was kept in a vaccum for 48 h.

Guaranteed-grade chlorides were heated at 110—130 °C for more than 24 h; they were subsequently used without further purification.

Distilled and then deionized water was used as a solvent. The methanol was purified first by dehydrating it by means of a molecular sieve; then it was distilled by an ordinary procedure.

Apparatus and Measurements. In contrast to the case of the determination of the molecular weight of polymers, the use of an Ubbelohde viscometer of a conventional type is improper for the present purpose, since the degree of variation of the viscosity upon the addition of solutes with respect to the viscosity of pure solvent is relatively small. Therefore, an improved Ubbelohde viscometer with a sufficient efflux time at a low shear rate was designed and used. It has four successive bulbs, and the solution flows through a long capillary tube wound in a spiral form. The efflux times for water at 25 °C are 554, 887, and 1,377 s for the second, third, and fourth bulbs respectively. In addition, to determine the viscosity coefficient with a high degree of precision, measurements of the viscosity were carried out at approximately twenty different concentrations of salts in water as well as in aqueous solvents containing 18-crown-6 (the concentration of CR was 0.398 mol/dm^3), which have also served as solutions to determine the viscosity coefficients of non-coordinated 18-crown-6 in water. The concentration ranges of the salts investigated are much wider than in ordinary viscometric measurements.[11] On the other hand, in methanol, on account of the low solubility of KCl, experiments on KCl have been limited to concentrations far lower than in aqueous media (for KCl in methanol, up to *ca.* 0.03 mol/dm^3). The concentration of CR in methanol for KCl was 0.02085 mol/dm^3. Sample solutions were prepared by weight, and the concentrations of the solute were converted into volumetric concentration scales using the density data of solutions.

The densities were measured by means of a Digital Precision Density Meter, type DMA-02C, manufactured by the

Anton Paar Co., Ltd. The numerical values of density necessary were interpolated from the mathematical expression of the density-volumetric concentration relation obtained by the least-squares fitting of the experimental data.

All measurements were done at 25±0.05 °C.

Results and Discussion

Viscosity of LiCl, KCl, CsCl, and 18-Crown-6 in Water. The concentration dependence of the relative viscosity of dilute electrolyte solutions have been expressed in terms of the Jones-Dole equation:[12]

$$\eta_{\rm rel} = 1 + Ac^{1/2} + Bc, \tag{1}$$

or:

$$\psi \equiv (\eta_{\rm rel} - 1)/c^{1/2} = A + Bc^{1/2}, \tag{2}$$

where c is the molarity. The B-coefficient has often been determined as a slope of the relation of Eq. 2 by plotting the data obtained in relatively dilute concentrations. However, our measurements, carried out up to rather high concentration ranges (for LiCl, to 0.65, and for KCl and CsCl, to 0.9—1 mol/dm^3), require a modified form of Eqs. 1 and 2:

$$\eta_{\rm rel} = 1 + Ac^{1/2} + Bc + Dc^2, \tag{3}$$

or:

$$\psi = A + Bc^{1/2} + D(c^{1/2})^3. \tag{4}$$

The simultaneous determination of the parameters A, B, and D by means of simple least-squares fitting of the experimental data to the third-order equation of $c^{1/2}$ failed, for the analysis gave a negative value of A for the case of LiCl, a fact contradictory to the theory.[13,14] Therefore, the coefficients B and D have been determined in the following way: first, the A-coefficient was calculated according to the theory proposed by Falkenhagen.[13,14] Then, Eq. 4 was rearranged into the expression shown below:

$$(\eta_{\rm rel} - 1 - Ac^{1/2})/c = B + Dc. \tag{5}$$

Using the calculated values of A-coefficients, the left-hand side of Eq. 5 was evaluated; meanwhile, the coefficients B and D have been obtained from the most suitable plot of the relation of Eq. 5. As an example, the case for CsCl is illustrated in Fig. 1. The unmerical values of the B- and D-coefficients thus obtained are summarized in Table 1, along with the values of the A-coefficient calculated and used. Our B-coefficients are in excellent agreement with the values given by Kaminsky[15] and Isono.[16] Differences exist, however, in the values of D. These differences seem to arise from the differences in the concentration ranges concerned in the measurements. Isono,[16] aiming to ascertain correlations between B- and D-coefficients, has carried out measurements in highly concentrated solutions (up to 3.5, 5.9, and 3.7 mol/dm^3 for KCl, CsCl, and LiCl respectively).

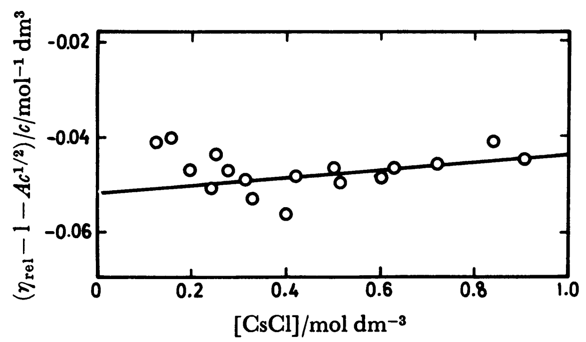

Fig. 1. Plot of $(\eta_{\rm rel}-1-Ac^{1/2})/c$ against molar concentration c of CsCl in water at 25 °C.

The relative viscosities of aqueous solutions of 18-crown-6 measured in the concentrations less than 0.4 mol/dm^3 can be represented in terms of an equation similar to Eq. 3:

$$\eta_{\rm rel} = 1 + B'c + D'c^2, \tag{6}$$

where the term corresponding to $Ac^{1/2}$ in Eq. 3 is dropped, for this term refers to interionic interaction and is unnecessary for non-electrolytic solute. The plot of $(\eta_{\rm rel}-1)/c$ against c has led to the following values of the B'- and D'-coefficients:

$$B' = 0.846 \text{ dm}^3/\text{mol} \text{ and } D' = 0.559 \text{ (dm}^3/\text{mol})^2.$$

Below, this B' value will be compared with the corresponding values of the [CR-M$^+$] ions.

Viscosity of LiCl, KCl, and CsCl in Aqueous Solutions Containing 18-Crown-6. The effects of an added solute on the relative viscosity should be expressed as:

$$\eta_{\rm rel} = 1 + \Delta\eta_{\rm solute}, \tag{7}$$

where $\Delta\eta_{\rm solute}$ refers to the resultant variation in the relative viscosity of the solution due to the added solute. Aqueous solutions containing both 18-crown-6 and an electrolyte were prepared by introducing the electrolyte into the aqueous solutions containing 18-crown-6. First, the following relation has been considered as a starting equation for the data analysis:

$$\eta_{\rm rel} = (1 + \Delta\eta_{\rm CR}) + \Delta\eta_{\rm electrolyte}. \tag{8}$$

Mention should be made of the fact that the $\eta_{\rm rel}$ of the above equation is not related to the viscosity of the aqueous solutions containing 18-crown-6 to which the electrolyte is added, but to the viscosity of pure water.

Table 1. Viscosity coefficients of extended Jones-Dole equation for LiCl, KCl, and CsCl in water at 25 °C

	$A^{\rm a)}$ [dm^3/mol]$^{1/2}$	B [dm^3/mol]			D [dm^3/mol]^2	
LiCl	0.0065	0.137	0.1425$^{\rm b)}$	0.134$^{\rm c)}$	0.0065	0.013$^{\rm c)}$
KCl	0.0050	−0.0137	−0.0140$^{\rm b)}$	−0.015$^{\rm c)}$	0.0033	0.008$^{\rm c)}$
CsCl	0.0049	−0.0517	−0.052$^{\rm b)}$	−0.060$^{\rm c)}$	0.0077	0.013$^{\rm c)}$

a) Values calculated from theory. b) Values reported by M. Kaminsky.[15] c) Values reported by T. Isono.[16]

Equation 8 is equivalent to the assumption of a superposition of effects due to the crown ether and the electrolyte; in other words, there are no interactions between 18-crown-6 and electrolytic solutes in solutions. In actuality, however, such a crude assumption does not hold, and an attempt to represent experimental results in terms of Eq. 8 was unsuccessful for any kind of chloride investigated.

For KCl and CsCl, a complex formation with 18-crown-6 occurs.[1] We, therefore, have transformed Eq. (8) into the following form and analyzed the data related with KCl and CsCl:

$$\eta_{\text{rel}} = 1 + \Delta\eta_{\text{CR}} + \Delta\eta_{\text{MCl}} + \Delta\eta_{[\text{CR-M}^+]\text{Cl}^-}, \tag{9}$$

where $\Delta\eta_{[\text{CR-M}^+]\text{Cl}^-}$ represents the variation in the solution viscosity due to the chloride of the crown ether-cation complex, [CR-M$^+$]Cl$^-$, formed in the solutions. Furthermore, considering the complex [CR-M$^+$]Cl$^-$ as an ordinary salt, we impose the following relation on $\Delta\eta_{[\text{CR-M}^+]\text{Cl}^-}$:

$$\Delta\eta_{[\text{CR-M}^+]\text{Cl}^-} = A(c_{[\text{CR-M}^+]\text{Cl}^-})^{1/2} + Bc_{[\text{CR-M}^+]\text{Cl}^-} \tag{10}$$

The actual contributions of $\Delta\eta_{\text{CR}}$, $\Delta\eta_{\text{MCl}}$, and $\Delta\eta_{[\text{CR-M}^+]\text{Cl}^-}$ are dependent upon the amounts of the respective species present in the solutions. From the experimental concentrations and the stability constants, K, of the complex ions [CR-M$^+$], the equilibrium concentrations of each solute species, [M$^+$], [CR], and [CR-M$^+$], can be calculated. The stability constants of 18-crown-6-alkali metal ion complexes have been reported by Frensdorff[17] and by Izatt *et al.*[18] The values given by these authors are similar for the complex ion [CR-K$^+$] ($\log K$=2.06[17] and 2.03[18]), while a certain difference exists for [CR-Cs$^+$] ($\log K$=0.8[17] and 0.99[18]). We have used Frensdorff's values, which are concentration-equilibrium constants. After subtracting the amounts attributed to $\Delta\eta_{\text{CR}}$ and $\Delta\eta_{\text{MCl}}$, the resultant $\Delta\eta_{[\text{CR-M}^+]\text{Cl}^-}$ has been found to be expressed in the form of the equation:

$$\frac{\Delta\eta_{[\text{CR-M}^+]\text{Cl}^-}}{(c_{[\text{CR-M}^+]\text{Cl}^-})^{1/2}} = A_{[\text{CR-M}^+]\text{Cl}^-} + B_{[\text{CR-M}^+]\text{Cl}^-}(c_{[\text{CR-M}^+]\text{Cl}^-})^{1/2} \tag{11}$$

The results of the analysis of the data of CsCl carried out in this way are shown in Fig. 2. The straight line in Fig. 2 seems to support our approach. The final results of the $A_{[\text{CR-M}^+]\text{Cl}^-}$ and $B_{[\text{CR-M}^+]\text{Cl}^-}$ coefficients obtained, respectively, as the intercept and the slope of the relation of Eq. 11, are given in Table 2, which also includes the value of the B-coefficient of 18-crown-6.

As was mentioned in the last part of the introductory section of this paper, the stability constant of the complex ion [CR-Li$^+$] has not been reported. Consequently, the analysis of our viscosity data for LiCl along the lines adopted for KCl and CsCl, namely, the analysis of the data using Eqs. 9 to 11, is impossible at present. However, as we have seen in the foregoing discussion, the simple additivity relation, as expressed in terms of Eq. 8, was unsuccessful in reproducing the experimental data for LiCl.

For the comparison of the B-coefficient of [CR-M$^+$]Cl$^-$ with that of 18-crown-6, the contribution from the Cl$^-$ ion should be considered. Somewhat different values have been assigned to the values of the B-coefficient of the Cl$^-$ ion on the basis of different criteria for the division: −0.007,[15] 0.014,[19] and −0.033.[20] In any case, the effect of the complex ion [CR-M$^+$] is overwhelming. This fact enables us to compare the B values of Table 2. The complex ions [CR-K$^+$] and [CR-Cs$^+$] have similar values of the B-coefficients, and these values are near the B'-coefficient of the non-coordinated 18-crown-6 in water. Generally speaking, a direct comparison of the viscosity coefficient for an electrolyte with that for a nonelectrolyte is not free from disputation. This is because the concentration dependences of solution viscosities are expressed in different forms for electrolytes and nonelectrolytes. However, from the results given in Table 2, we can say that the dragging resistances of [CR-K$^+$] and [CR-Cs$^+$] complex ions are approximately the same as that of non-coordinated 18-crown-6 in water.

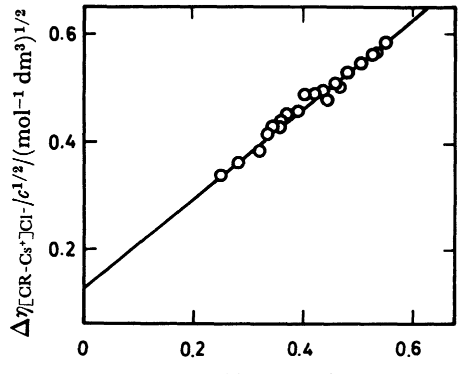

Fig. 2. Concentration dependence of $\Delta\eta_{[\text{CR-Cs}^+]\text{Cl}^-}/(c_{[\text{CR-Cs}^+]\text{Cl}^-})^{1/2}$ plotted against $(c_{[\text{CR-Cs}^+]\text{Cl}^-})^{1/2}$ for [CR-Cs$^+$]Cl$^-$ complex in water at 25 °C. The symbol c attached to the vertical axe means here $c_{[\text{CR-Cs}^+]\text{Cl}^-}$.

TABLE 2. VISCOSITY COEFFICIENTS OF 18-CROWN-6 AND THOSE ASSIGNED TO 18-CROWN-6-ALKALI METAL-ION COMPLEXES IN AQUEOUS SOLUTIONS AT 25 °C

	A [dm^3/mol]$^{1/2}$		*B* [dm^3/mol]
18-crown-6	—		0.846[b]
[CR-K$^+$]Cl$^-$	0.118	0.0082[a]	0.87
[CR-Cs$^+$]Cl$^-$	0.12		0.83

a) Theoretical value calculated using conductivity data reported in Ref. 9. b) B'-coefficient of Eq. 6.

A theoretical evaluation of the A-coefficient is possible for the [CR-K$^+$]Cl$^-$ complex from the reported value of the limiting molar conductivity of the complex.[9] Our experimental A-coefficient of the [CR-K$^+$]Cl$^-$ complex is more larger than the theoretical one. A comparison of the experimental and theoretical A-coefficients for the [CR-Cs$^+$]Cl$^-$ complex is impossible because of the lack of conductivity data for this complex.

Viscosity Coefficients in Methanol Systems. As has already been mentioned in the Experimental section of this paper, viscosity measurements in methanol

TABLE 3. VISCOSITY COEFFICIENTS OF 18-CROWN-6, KCl, AND [CR-K$^+$]Cl COMPLEX IN METHANOL AT 25 °C

	A [dm^3/mol]$^{1/2}$	B [dm^3/mol]
18-crown-6	—	0.44$^{c)}$
KCl	0.024, 0.0173$^{a)}$	0.736, 0.7635$^{d)}$
[CR-K$^+$]Cl$^-$	0.039, 0.0208$^{b)}$	0.86

a) Theoretical value found in H. Falkenhagen, "Theorie der Electrolyte," S. Hirzel, Stuttgart (1971), Chap. 10. b) Theoretical value calculated using conductivity data reported by Y. Takeda.[9] c) B'-coefficient of Eq. 6. d) Value given by G. Jones and H. J. Fornwalt.[21]

systems have been carried out in relatively low concentration ranges. In such circumstances, the D- or D'-coefficient of Eq. 3 or Eq. 6 need not be taken into account. For KCl in methanol, the A- and B-coefficients have been determined simultaneously from the least-squares plotting of Eq. 2, without paying any attention to the theoretical values of A. On the contrary, the experimental data on 18-crown-6 in methanol and KCl in CR-methanol systems have been treated in a way analogous to that in the aqueous media described above. The numerical values of the viscosity coefficients in methanol systems obtained are shown in Table 3. Our B-coefficient for KCl in pure methanol is a little smaller than that in the literature,[21] while our experimental value of the A-coefficient is larger than the theoretical one. In our results, a small experimental B-coefficient is compensated for by a large experimental A-coefficient. The comparison of Tables 2 and 3 shows that the dragging resistance of 18-crown-6 is smaller in methanol than in water. For the discussion of B-coefficient of the complex ion [CR-M$^+$], the contribution from the Cl$^-$ ion, B_{Cl^-}, should be subtracted. The principle of the assignment of the B-coefficient of a salt into its constituent ionic B values has not been well established for the data in nonaqueous solvents. Criss and Mastroianni[22] evaluated the ionic B-coefficients in methanol on the assumption that $B_{K^+}=B_{Cl^-}$, as in water.[15] Following their results, we can obtain 0.48~0.49 dm^3/mol as the value of $B_{[CR\text{-}K^+]}$. This value is approximately identical with that of non-coordinated 18-crown-6 in methanol. The results shown in Tables 2 and 3 lead to the conclusion that the hydrodynamic volume of the complex ion [CR-K$^+$] remains effectively the same as that of the non-coordinated 18-crown-6, irrespective of the solvent media surrounding the complex ion. Further measurements will be required, however, to discuss whether or not the conclusion obtained in this work is applicable to other solvent systems.

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