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# The Viscosities of Aqueous Solutions Containing Metal Complexes. I. Luteo-type Co(II) and Co(III) Complexes and Ethylenediaminetetraacetato Complexes*[1]

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The viscosities of aqueous solutions containing cobalt complexes formed with ammonia, ethylenediamine (en), propylenediamine (pn), 2, 2′-bipyridine (bip), 1, 10-phenanthroline (phen), and ethylenediaminetetraacetic acid ($H_4$edta) were determined with a Cannon-Fenske capillary viscometer. Measurements were made in a Shibata viscosity bath maintained at 25± 0.01°C. The Jones-Dole viscosity $B$-coefficients of Co(III) complex cations formed with $NH_3$, en, pn, bip, and phen increase in that order. There is no significant difference between the $B$-coefficients of $[Cobip_3]^{3+}$ and $[Cobip_3]^{2+}$, or $[Cophen_3]^{3+}$ and $[Cophen_3]^{2+}$. On the other hand, a pronounced difference is found between the $B$-coefficients of $[Coedta]^-$ and $[Coedta]^{2-}$. This might suggest that there is a marked difference in the structure of $[Coedta]^-$ and $[Coedta]^{2-}$ anions.

The viscosities of aqueous electrolyte solutions have been accurately measured by many authors, but very few data are available for the metal complexes. Charles,[1] who measured the viscosities of the ethylenediaminetetraacetic acid and Schiff base chelates, showed that significant information concerning the configuration and the degree of solvation of the metal chelates could be obtained by viscosity measurements. It was felt that a thorough study on the viscosity of the metal complexes might supply useful information regarding the structure of the complexes. A study was therefore made of the viscosities of aqueous solutions containing cobalt complexes.

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*[1] Presented at the Symposium on Coordination Chemistry of the Chemical Society of Japan, Tokyo, Dec., 1966.

[1] R. G. Charles, *J. Am. Chem. Soc.*, **78**, 3946 (1956); **81**, 1793 (1959).

## Experimental

**Complexes.** Co(III) complexes such as $[Co(NH_3)_6]Cl_3$,⁽²⁾ $[Coen_3]Cl_3\cdot 3H_2O$,⁽³⁾ $[Copn_3]Cl_3$,⁽⁴⁾ $K[Coedta]\cdot 2H_2O$,⁽⁵⁾ and $[Cophen_3]Cl_3\cdot 7H_2O$,⁽⁶⁾ were prepared following the literature method. The first four complexes were obtained by oxidizing a solution of a mixture of cobalt(II) chloride and ligand with hydrogen peroxide; the last one, by oxidizing with chlorine. An analogous procedure (*i. e.* oxidization with chlorine) was used for the preparation of $[Cobip_3]Cl_3\cdot 3H_2O$, which was originally obtained from cobalt(III) sulfate and bipyridine.⁽⁷⁾ All these well-known complexes were checked by analysis of chloride ion and/or water contents. But Co(II) complexes such as $[Cobip_3]Cl_2$, $[Cophen_3]Cl_2$ and $Na_2[Coedta]$, were not isolated as crystals. Instead, solutions of these chelates were made up with the standard $CoCl_2$ solution, the weighed amount of ligand and distilled water. The concentration of the $CoCl_2$ stock solution was determined by the chelatometric titration.

**Measurements.** Viscosities were determined with a Cannon-Fenske capillary viscometer having efflex time *ca.* 240 sec for distilled water. Measurements were made in a Shibata viscosity bath maintained at 25±0.01°. Efflex times, measured with a stopwatch to the 0.1 sec, were easily reproducible to 0.2 sec. Densities of the solutions were also determined in the same constant temperature bath used for the viscosities.

**Calculations.** According to Jones and Dole,⁽⁸⁾ the viscosities of aqueous electrolyte solutions have the following relation with the solute molarity, $C$:

$$\frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC$$

where $\eta$ and $\eta_0$ are viscosities of solution and water, respectively; $A$ and $B$ are constants charactereistic of the solute. The square-root term was attributed to the interionic electrostatic forces and the experimental values of A were found to be positive in every case studied. The coefficient $B$ of the electrolytes is composed additively of contributions from each of the solute species present in the solution. And Gurney⁽⁹⁾ divided the $B$-coefficient of $-0.014$ for KCl equally between $K^+$ and $Cl^-$ ions (thus $B_{K^+}=B_{Cl^-}=-0.007$). Although his division of the $B$-coefficient of KCl into individual ionic values is a rather arbitrary process, it is regarded as a good approximation. The contributions depend on the size of the ions and on the interaction between the ions and the surrounding solvent.

When $((\eta/\eta_0)-1)/\sqrt{C}$ was plotted against $\sqrt{C}$, a straight line was obtained for each of the complexes studied. The slope of the resulting straight line gives the value of $B$-coefficient and the intercept gives the value of $A$-coefficient. The $B$-value of the complex ions is obtained by subtracting a relatively small correction for the ions present in the solution.

## Results and Discussion

A part of the viscosity and density data for $[Coen_3]Cl_3$ and $CoCl_2$ are listed in Tables 1 and 2. Table 3 contains the $B$-values of the complex ions at 25°C obtained in this study, together with those reported by Kaminsky⁽¹⁰⁾ and by Charles⁽¹⁾. The trivalent $[Co(NH_3)_6]^{3+}$ ion, having a much smaller radius than that of any of the other complex ions studied, is expected to form an ion pair much more easily with the anion, chloride ion. Accordingly, the $B$-value of this complex ion is the least accurate.

TABLE 1. VISCOSITY AND DENSITY DATA FOR $[Coen_3]Cl_3$

| $C$ | $d$ | $\eta/\eta_0$ |
|---|---|---|
| 0.01500 | 0.99924 | 1.01009 |
| 0.03981 | 1.00317 | 1.02484 |
| 0.07606 | 1.00798 | 1.04427 |
| 0.1305 | 1.01630 | 1.07536 |
| 0.1858 | 1.02426 | 1.10700 |

TABLE 2. VISCOSITY AND DENSITY DATA FOR $CoCl_2$

| $C$ | $d$ | $\eta/\eta_0$ |
|---|---|---|
| 0.02302 | 0.99953 | 1.01216 |
| 0.06906 | 1.00526 | 1.03146 |
| 0.1381 | 1.01312 | 1.05885 |
| 0.2302 | 1.02374 | 1.09683 |

TABLE 3. THE $B$-VALUES OF COBALT COMPLEXES (25°C)

| Complex | $B$ | Complex | $B$ |
|---|---|---|---|
| $[Co(NH_3)_6]^{3+}$ | 0.17 | $[Co(H_2O)_6]^{2+}$ | 0.38 (0.36*) |
| $[Coen_3]^{3+}$ | 0.56 | $[Cobip_3]^{2+}$ | 1.37 |
| $[Copn_3]^{3+}$ | 0.88 | $[Cophen_3]^{2+}$ | 1.61 |
| $[Cobip_3]^{3+}$ | 1.31 | $[Coedta]^{2-}$ | 0.85 (0.88**) |
| $[Cophen_3]^{3+}$ | 1.53 | $[Coedta]^{-}$ | 0.41 |

* Ref. 10 (at 35°C)
** Ref. 1 (at 30°C)

According to Kaminsky, the temperature coefficient of $B$ is negative for the strongly hydrated ions such as $Li^+$, $Be^{2+}$, $Mg^{2+}$, $Fe^{2+}$, and $Ce^{3+}$, as seen from Table 4. Therefore, the $B$-value of 0.38 obtained for $[Co(H_2O)_6]^{2+}$ ion at 25° is very reasonable, compared with the Kaminsky's value of 0.36 at 35°.

The $B$-value for $[Co(NH_3)_6]^{3+}$ ion is much smaller than that for $[Co(H_2O)_6]^{2+}$ ion, as seen

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2) "Inorganic Syntheses," Vol. 2, p. 216 (1946).
3) "Inorganic Syntheses," Vol. 2, p. 221 (1946).
4) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, **1951**, 68.
5) F. P. Dwyer, E. C. Gyarfas and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).
6) P. Pfeiffer and B. Werdelmann, *Z. anorg. Chem.*, **263**, 31 (1950).
7) F. Blau, *Monath.*, **10**, 372 (1889).
8) G. Jones and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
9) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Company, Inc., New York (1953).
10) M. Kaminsky, *Discussions Faraday Soc.*, **24**, 171 (1957).

from Table 3. This might suggest that the water molecules coordinated to the metal ion have a greater interaction with the surrounding molecules of solvent than the ammonia molecules, much more tightly bound to the metal ion, have.

The *B*-values of Co(III) complex cations formed with $NH_3$, en, pn, bip, and phen, all of which might be called as the luteo-Co(III) ions, increase considerably in that order, as may be expected. The *B*-value of Co(II) chelate of bip (or phen) is almost the same to that of corresponding Co(III) chelate. Moreover, the chelate derived from the bulky ligand, such as bip or phen has a rather large ionic radius, so it may be assumed that such a chelate ion has no large interaction with the solvent molecules. Accordingly, it might be considered that the Co(II) and Co(III) chelates of bip or phen have the similar structure one another.

TABLE 4. *B*-VALUES AND DEPENDENCE ON TEMPERATURE[10]

| *t*°C | $Be^{2+}$ | $Mg^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Ce^{3+}$ |
|---|---|---|---|---|---|
| 15 | 0.4345 | 0.4091 | — | — | 0.5841 |
| 25 | 0.3923 | 0.3852 | 0.4160 | — | 0.5765 |
| 35 | 0.3444 | 0.3625 | 0.3955 | 0.360 | 0.5573 |
| 42.5 | 0.3105 | 0.3472 | — | — | 0.5427 |

On the other hand, as seen from Table 3, the *B*-value of the $[Coedta]^-$ chelate is only 0.41, much smaller than the *B*-value of 0.85 of $[Coedta]^{2-}$. In this connection, it is especially interesting to compare these *B*-values with those of EDTA-complexes reported by Charles (Table 5). The *B*-value of the $[Coedta]^-$ is much smaller than that of any other divalent metal chelates given in Table 5. Further, it is easily seen from Table 5, which contains also the values of stability constants reported by Schwarzenbach *et al.*,[11] that metals with a greater affinity for the ligand generally form chelates with smaller *B*-values. These facts might suggest that Co(III) chelate has a stable hexa-coordinated structure, but that divalent metal chelates, having not so stable hexa-coordinated structure as the Co(III) chelate, are present as a penta-coordinated structure or as a mixture of the penta- and hexa-coordinated structures.

TABLE 5. *B*-VALUES AND STABILITY CONSTANTS (*k*) OF ETHYLENEDIAMINETETRAACETATO COMPLEXES

| Metal | *B* | log *k* |
|---|---|---|
| $Cu^{2+}$ | 0.82 | 18.80 |
| $Ni^{2+}$ | 0.86 | 18.62 |
| $Co^{2+}$ | 0.88 | 16.31 |
| $Zn^{2+}$ | 0.88 | 16.50 |
| $Mn^{2+}$ | 0.91 | 14.04 |
| $Cd^{2+}$ | 0.98 | 16.46 |
| $Pb^{2+}$ | 0.83 | 18.04 |
| $Mg^{2+}$ | 0.88 | 8.69 |
| $Ca^{2+}$ | 1.07 | 10.70 |
| $Sr^{2+}$ | 1.13 | 8.63 |
| $Ba^{2+}$ | 1.17 | 7.76 |

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[11] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954).