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# The Viscosities of Aqueous Solutions Containing Metal Complexes. II. *trans*-1,2-Cyclohexanediaminetetraacetato Complexes[*1]

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The viscosities of aqueous solutions containing metal chelate formed with *trans*-1,2-cyclohexanediaminetetraacetic acid ($H_4$cydta) were measured with a Cannon-Fenske capillary viscometer. Measurements were made in a Shibata viscosity bath maintained at 25±0.01°C. The Jones-Dole viscosity $B$-coefficient of the cydta$^{4-}$ chelates is larger than that of the corresponding ethylenediaminetetraacetato (edta$^{4-}$) chelates, as may be expected. The $B$-value of the Co(III) chelate [Co cydta]$^-$ is much smaller than that of any of the divalent metal cydta$^{4-}$ chelates studied. This fact, the same as in the case of the edta$^{4-}$ chelates, may indicate that the Co(III) chelate has a marked stable hexa-coordinated structure, while divalent metal chelates do not have such a stable hexa-coordinated structure as the Co(III) chelate.

In part I of this series,[1)] the viscosities of aqueous solutions containing several cobalt complexes were measured with a capillary viscometer. The results showed that there was a distinct difference between the $B$-coefficients of Co(II) and Co(III) chelates formed with ethylenediaminetetraacetic acid ($H_4$ edta); this suggested that there might be a marked difference between the structures of [Co edta]$^{2-}$ and [Co edta]$^-$ ions. In order to confirm this, a viscosity study was made of aqueous solutions of metal chelates formed with 1,2-cyclohexanediaminetetraacetic acid ($H_4$ cydta), whose structure is very similar to that of $H_4$edta.

## Experimental

**Measurements.** The viscosity $B$-coefficients of Co(III) and eleven divalent metal chelates were determined with a Cannon-Fenske capillary viscometer with an efflux time of *ca.* 240 sec for distilled water. The viscosities and densities of the solutions were measured in a Shibata viscosity bath maintained at 25±0.01°C.

**Complexes.** Potassium (cyclohexanediaminetetraacetato)cobaltate(III) trihydrate was obtained as red-violet crystals following the method in the literature.[2)] However, divalent metal chelates were not isolated as crystals. Instead, solutions of these chelate were made up using metal nitrate (or chloride) and $K_4$cydta stock solutions. The concentrations of the metal nitrate (or chloride) solutions were determined by chelatometric titrations. The concentration of the $K_4$cydta stock solution, made from Dotite $H_4$cydta and potassium hydroxide, was also determined by chelatometric titration.

**Calculations.** For each of the chelates studied, the variations in the viscosity with the solute concentration was expressed by the Jones-Dole equation:[3)]

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

where $\eta$ and $\eta_0$ are the viscosities of the solution and of water respectively; and where $A$ and $B$ are constants characteristic of the solute. Only the $B$-coefficient will be discussed in this paper, for the $B$-coefficient seems to be a manifestation of the hydrated ionic volume; this is supported by the linearity of the $BC$ term in the concentration. On the other hand, the $A$-coefficient, which is thought to represent the amount of the interionic electrostatic forces, will not be discussed here, for the $A$-values are very small compared with the $B$-values and are almost independent of the metal included in the chelate.

## Results and Discussion

The viscosity and density data for $K_2$[Cu cydta] (+2$KNO_3$) and K[Co cydta] are listed in Tables 1 and 2. Table 3 contains the $B$-values of cydta$^{4-}$ complex anions at 25°C, together with the stability constants for these complex ions reported by Anderegg.[4)]

The solubility of the lead chelate, which was the least soluble in water of the metal chelates studied, was only 0.01 mol/$l$; thus, the $B$-value of

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1) M. Yasuda, This Bulletin, **41**, 139 (1968).

2) F. P. Dwyer and F. L. Garvan *J. Am. Chem. Soc.*, **83**, 2610 (1961).

3) G. Jones and M. Dole, *ibid.*, **51**, 2950 (1929).

4) G. Anderegg, *Helv. Chim. Acta*, **46**, 1833 (1963).

TABLE 1. VISCOSITY AND DENSITY DATA FOR $K_2$[Cu cydta] (+2$KNO_3$)*

| $C$ | $d$ | $\eta/\eta_0$ |
|---|---|---|
| 0.0600 | 1.01855 | 1.05201 |
| 0.0300 | 1.00816 | 1.02639 |
| 0.0200 | 1.00474 | 1.01846 |
| 0.0150 | 1.00278 | 1.01392 |

* The $B$-value of the complex ion is obtained by subtracting a relatively small correction for the $K^+$ and $NO_3^-$ ions. The $B$-values given by Gurney were used for these ions; $B_{K^+}=-0.007$, $B_{NO_3^-}=-0.046$. R.W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York (1953).

TABLE 2. VISCOSITY AND DENSITY DATA FOR K[Co cydta]

| $C$ | $d$ | $\eta/\eta_0$ |
|---|---|---|
| 0.04401 | 1.00802 | 1.02405 |
| 0.03081 | 1.00474 | 1.01639 |
| 0.02427 | 1.00323 | 1.01287 |
| 0.01592 | 1.00109 | 1.00814 |

TABLE 3. $B$-COEFFICIENTS AND STABILITY CONSTANTS ($k$) OF *trans*-1,2-CYCLOHEXANEDIAMINETETRAACETATO CHELATES

| Metal | $B$ | log $k$⁴⁾ |
|---|---|---|
| $Cu^{2+}$ | 0.92 | 21.95 |
| $Zn^{2+}$ | 0.98 | 19.32 |
| $Ni^{2+}$ | 1.01 | 19.4* |
| $Co^{2+}$ | 1.03 | 19.57 |
| $Cd^{2+}$ | 1.13 | 19.88 |
| $Mn^{2+}$ | 1.15 | 17.43 |
| $Mg^{2+}$ | 1.20 | 10.97 |
| $Ca^{2+}$ | 1.21 | 13.15 |
| $Sr^{2+}$ | 1.24 | 10.54 |
| $Ba^{2+}$ | 1.27 | 8.64 |
| $Pb^{2+}$ | ~1.0 | 20.33 |
| $Co^{3+}$ | 0.54 | —— |

* J. H. Holloway and C. N. Reilly, *Anal. Chem.*, **32**, 249 (1960).

[Pb cydta]$^{2-}$ is the least accurate.

Now it may be very interesting to compare the $B$-values of the cydta$^{4-}$ chelates with those of the edta$^{4-}$ chelates, reported by Charles⁵⁾ and by the present author.¹⁾ Their relation is shown in Fig. 1; the ordinates are the $B$-values of the cydta$^{4-}$ chelates, and the abscissas, those of the edta$^{4-}$ chelates. The rather good agreement of all the points except those for $Mg^{2+}$ and $Mn^{2+}$ chelates with the straight line may indicate that Mcydta$^{n-}$ and Medta$^{n-}$ chelates have similar structures.

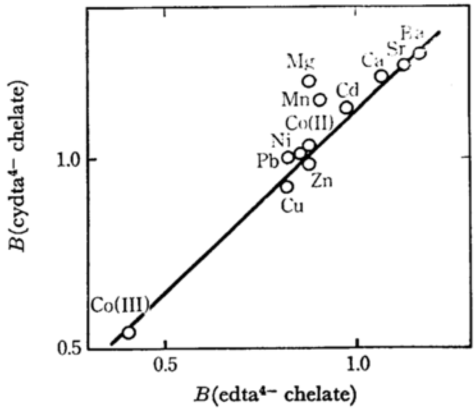

Fig. 1. Relation between the B-coefficients of cydta$^{4-}$ and edta$^{4-}$ Chelates

Next, Einstein's equation,⁶⁾ derived for the viscosity of the solution, must be taken into account. According to Einstein, the viscosity of a solution which contains, in suspension, rigid spherical particles which are large compared with the size of the solvent molecules is given by the following equation;

$$\eta=\eta_0(1+2.5\,\phi) \tag{2}$$

where $\phi$ is the volume-fraction occupied by the particles.

If it is assumed that his theory can be applied to large molecules in solution,*2 Eq. (3) is obtained from Eqs. (1) and (2);

$$A\sqrt{C}+BC=2.5\,\phi \tag{3}$$

The volume fraction, $\phi$, may then be expressed by:

$$\phi=CV \tag{4}$$

where $V$ is the molar volume of the solute, including an attached solvent (in $l$/mol). Further the $A\sqrt{C}$ term is very small in comparison with $BC$, and so it can safely be neglected. Accordingly, we obtain:*3

$$B=2.5\,V \tag{5}$$

Eq. (5) leads to:

$$v_h=\frac{4000\,B}{6.02}\,\text{Å}^3 \tag{6}$$

where $v_h$ is the volume of the hydrated solute. Thus, the average radius can be calculated from the $B$-coefficient. The values obtained for the Co(II) and Co(III) chelates of edta$^{4-}$ and cydta$^{4-}$ are listed in Table 4.

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5) R. G. Charles, *J. Am. Chem. Soc.*, **78**, 3946 (1956).

6) A. Einstein, *Ann. Phys.*, **19**, 289 (1906); **34**, 591 (1911).

*2 This was confirmed by Fuoss and Tuan and by Stokes and Mills for C($CH_2OH$)$_4$, $Bu_4N^+$, $Ph_4B^-$, *etc.*

*3 This relation was derived by Stokes and Mills; R. H. Stokes and R. Mills, "Viscosity of Electrolytes and Related Properties," Pergamon Press, Oxford (1965).

TABLE 4. $B$-COEFFICIENTS AND AVERAGE RADII ($r$) OF THE Co CHELATES

| | $[\text{Co edta}]^{2-}$ | $[\text{Co edta}]^{-}$ | $[\text{Co cydta}]^{2-}$ | $[\text{Co cydta}]^{-}$ |
|---|---|---|---|---|
| $B$ | 0.85 | 0.41 | 1.03 | 0.54 |
| $r$(Å) | 5.1 | 4.0 | 5.5 | 4.4 |

As may be seen from Table 4, the radius of the Co(III) chelate is about 1 Å smaller than that of the corresponding Co(II) chelate. Co–N interatomic distances have been measured for several Co(II) and Co(III) complexes derived from ligands with nitrogen donors. Since there are few data available on the Co(II)–N interatomic distance, it may be improper to draw a conclusion concerning the difference between the Co(II)- and Co(III)–N distances. However, it may be safely assumed that there is no marked difference between them. Further, since the cydta$^{4-}$ chelates have very large stability constants, it may be assumed that there is no apprreciable change in the viscosity of the solution due to the dissociation of the chelate. Accordingly, the large difference between $B$-coefficients of Co(III) and divalent metal chelates may imply that the structure of the Co(III) chelate is different from that of divalent metal chelates, as with the edta$^{4-}$ chelates. Thus, it may be assumed that the Co(III) chelate has a markedly stable hexa-coordinated structure, but that the divalent metal cydta$^{4-}$ chelates, not having so stable a hexa-coordinated structure as the Co(III) chelate, are present as a penta-coordinated chelate or as an equilibrium mixture of hexa- and penta-coordinated structures.