

## The Viscosities of Aqueous Solutions Containing Metal Complexes. IV. Nitrilotriacetato Complexes

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**Synopsis.** Viscosity  $B$ -coefficients of bivalent metal complexes formed with nitrilotriacetic acid ( $H_3nta$ ) were determined with Cannon-Fenske capillary viscometers at  $25 \pm 0.01^\circ C$ . The  $B$ -coefficients obtained are smaller for metal chelates having larger stability constants, and larger for metal chelates having smaller stability constants.

The viscosities of aqueous electrolyte solutions have been measured by many authors, but few data are available for the metal complexes. In the previous papers of this series, the viscosity  $B$ -coefficients were reported for metal complexes formed with several amino polycarboxylic acid.<sup>1-3</sup> The results showed valuable information concerning the metal complexes. For example, it was shown that for a particular ligand a bivalent metal ion with a greater affinity for the ligand generally formed a chelate with a smaller  $B$ -value. In order to extend these conclusions further, a viscosity study was made of aqueous solutions of bivalent metal chelates formed with nitrilotriacetic acid.

### Experimental

Viscosity measurements were made using Cannon-Fenske capillary viscometers with efflux times of *ca.* 240–320 s for distilled water. The time of flow was measured with a stopwatch graduated to 0.1 s. All measurements were made at  $25 \pm 0.01^\circ C$ . Solutions of metal chelates were made up using metal nitrate (or chloride) and  $K_3nta$  stock solutions.

For each of the 1 : 1 chelates studied, the variation in the relative viscosity  $\eta_{rel}$  with the solute concentration  $c$  was expressed by the Jones-Dole equation:<sup>4)</sup>

$$\eta_{rel} = \frac{\eta}{\eta_0} = 1 + A\sqrt{c} + Bc, \quad (1)$$

where  $\eta$  and  $\eta_0$  are viscosities of solution and water, respectively.  $A$  is a constant depending on the ion-ion interaction between the solute ions, and  $B$  is a constant depending on the size of the ion and on the interaction between the ion and the surrounding solvent molecules.  $A$  and  $B$  are called the Jones-Dole viscosity  $A$ - and  $B$ -coefficients. These constants were fully discussed by Gurney,<sup>5)</sup> who showed the  $B$ -coefficient of the electrolyte was composed additively of contributions from each of the solute species present in the solution. So  $B$ -values of the complex ions were obtained by subtracting a relatively smaller correction for the coexisting species.

### Results and Discussion

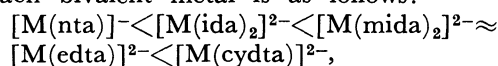
In each case the  $A$ -coefficient was found to be zero within experimental error. The same was also found, for example, in ethylenediaminetetraacetato chelates<sup>6)</sup>  $[M(edta)]^{2-}$  and *trans*-1,2-cyclohexanediaminetetraacetato chelates<sup>2)</sup>  $[M(cydtta)]^{2-}$ . The  $B$ -coefficients of the nitrilotriacetato chelates obtained here at  $25^\circ C$  are listed in Table 1, together with stability constants reported by Schwarzenbach *et al.*<sup>7)</sup> For metal ions

TABLE 1.  $B$ -VALUES, STABILITY CONSTANTS  $k$ , AND AVERAGE RADII  $r$  OF NITRILOTRIACETATO COMPLEXES

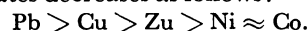
Metal	$B$ dm <sup>3</sup> mol <sup>-1</sup>	log $k^{7)}$	$r$ Å
Cu <sup>2+</sup>	0.52	12.96	4.4
Ni <sup>2+</sup>	0.63	11.54	4.6
Co <sup>2+</sup>	0.61	10.4	4.6
Zn <sup>2+</sup>	0.62	10.66	4.6
Pb <sup>2+</sup>	0.50	11.39	4.3
Mg <sup>2+</sup>	0.71	7.0	4.8
Ca <sup>2+</sup>	0.74	8.2	4.9

studied, the stability constants of nitrilotriacetato chelates are sufficiently large, and so even for magnesium chelate, which is the least stable, the estimated error due to dissociation of the complex is less than 0.01 in  $B$ -value.

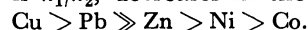
Larger  $B$ -values seem to indicate more free carboxylato groups of the ligand, which will make the chelates less stable. As seen from Table 1, the more stable the chelate is, in general, the smaller is its  $B$ -value. This was already seen in the case of amino polycarboxylato chelates studied previously.<sup>2,3,6)</sup> It is interesting to compare the  $B$ -values of amino polycarboxylato chelates for a particular metal ion. The order of the  $B$ -value for each bivalent metal is as follows:



where  $H_2ida$  is iminodiacetic acid and  $H_2mida$  is *N*-methyliminodiacetic acid. This order meets our expectations. However, there seems to be no special relation between the  $B$ -values of *nta*-chelate and those of  $(ida)_2$ -chelate, although a linear relationship<sup>2)</sup> was found between  $B$ -values of *edta*- and *cydtta*-chelates. This might be due to the fact that  $[M(nta)]^-$  and  $[M(ida)_2]^{2-}$  chelates do not have such similar structures, whereas  $[M(edta)]^{2-}$  and  $[M(cydtta)]^{2-}$  do. The difference between  $B$ -values of  $[M(nta)]^-$  and  $[M(ida)_2]^{2-}$  chelates decreases as follows:



In this connection it is interesting to note that the ratio of the 1st and 2nd stability constants of iminodiacetato chelates, that is  $k_1/k_2$ , decreases in the order:<sup>8)</sup>



This means that lead and copper form relatively unstable 1 : 2 chelates compared with the corresponding 1 : 1 chelate and so that  $[Pb(ida)_2]^{2-}$  and  $[Cu(ida)_2]^{2-}$  chelates may have relatively large  $B$ -values.

Since the  $A$ -value of each chelate was within experimental error of zero, we may calculate the volume of the hydrated chelate  $v_h$  from Eq. 2, because its radius is large compared with that of the solvent molecules:<sup>2)</sup>

$$v_h = \frac{4000 B}{6.02} (\text{Å}). \quad (2)$$

Thus the average radius of the chelate  $r$  can be obtained from its  $B$ -coefficient, and is also listed in Table 1. This varies from 4.3 Å for the lead chelate to 4.9 Å for the calcium chelate. The variation may be in part due to the difference in effective ionic radii of metal ions, but cannot be wholly explained by this difference. For example, though the effective ionic radii of octahedral  $Mg^{2+}$  and  $Ca^{2+}$  are 0.86 and 1.14 Å, respectively,<sup>9)</sup> both average radii of the chelates calculated are about the same. As we discussed previously,<sup>2)</sup> the larger average radius may be ascribed to the larger extent of free carboxylato groups of nitrilotriacetic acid ligand which do not attach to the metal ion.

#### References

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