values from the linear relationships which hold for the alkaline earths, the variation of ΔS^0 with temperature is also abnormally large. The reason for the unique behavior of Mn(II) in this case is not apparent.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE, NAGOYA UNIVERSITY]

Stability of Zinc and Cadmium Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline

BY KAZUO YAMASAKI AND MOTOO YASUDA

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The stability constants of zinc and cadmium complexes with 2,2'-bipyridine and 1,10-phenanthroline were determined by the *p*H titration method at 25°. The stepwise stability constants log k_1, log k_2 and log k_3 and the over-all constant log K for Cd- and Zn-bipyridine complexes were found to be 4.5, 3.5, 2.5, 10.5 and 5.4, 4.4, 3.5, 13.3, respectively. The values of log k_2 and log k_3 for Cd- and Zn-phenanthroline complexes were 5.2, 4.2 and 5.9, 4.8, respectively.

Stability constants of bivalent metal complexes of 2,2'-bipyridine[1] and 1,10-phenanthroline[2] have been reported by several authors. The ferrous complex,[3] in particular, has been studied because of its importance from the standpoint of analytical chemistry. During spectrochemical studies of several bipyridine and phenanthroline complexes[4] we have determined the stability constants of zinc and cadmium complexes with bipyridine and phenanthroline by the titration method of Bjerrum,[5] and compared them with data previously determined by other methods.

Experimental

Method and Apparatus.—By means of potentiometric *p*H determinations the acid dissociation constants of bipyridine and phenanthroline were determined in 0.1 *M* potassium nitrate solution at 25°. Fifty ml. of 0.001 *M* ligand solution was titrated with standard nitric acid solution. Similar measurements were then made on solutions in which the metal being investigated was maintained at a concentration of about 2–5 × 10^{-4} *M* and that of the ligand 5–10 × 10^{-4} *M*. In all cases a very large excess of KNO_3 over all other ionic species present was added to maintain the ionic strength at about 0.1. A glass electrode combined with a thermionic amplifier was used. The *p*H values in duplicate titrations agreed within 0.01 *p*H unit.

Materials.—2,2'-Bipyridine and 1,10-phenanthroline employed were reagents prepared by the Osaka Government Industrial Research Institute and G. F. Smith Co., U.S.A., respectively. Nitrates of both metals were analytical grade.

Results

The acid dissociation constants determined are: bipyridine, $-\log k = 4.44$; phenanthroline, 4.92. The $-\log k$ value reported by Krumholz[6] at 25° and ionic strength of 0.33 is 4.43 for bipyridine. The $-\log k$ value for phenanthroline determined by Lee, *et al.*,[3] under the same conditions as ours is 4.91.

The data for bipyridine and phenanthroline complexes are given in Table I. The first formation constant, k_1, of the phenanthroline complexes could not be determined for both metals; only k_2 and k_3 were determined. This difficulty occurs because the mixed solution of metal ion, ligand and nitric acid behaves as a strong acid.

TABLE I

Complex	log k_1	log k_2	log k_3	log K	Author
Cd–bipyridine	4.5	3.5	2.5	10.5	Present study
	..	...	...	10.47	Douglas, *et al.*[1]
Zn–bipyridine	5.4	4.4	3.5	13.3	Present study
Cd–phenanthroline	..	5.2	4.2	.....	Present study
	..	...	...	15.20	Douglas, *et al.*[1]
Zn–phenanthroline	..	5.9	4.8	.....	Present study
	6.43	~5.8	~4.8	~17.0	Kolthoff, *et al.*[2]

The values obtained here agree well with those of other authors determined by different methods.

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