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Potentiometric Studies on the Complex Formation of Fe(II), Co(II), Ni(II), Cu(II) & Zn(II) with 3-Mercapto-propane-1,2-diol & 2-Diethyl-aminoethanethiol Hydrochloride

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Complex formation by Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-mercaptopropane-1, 2-diol (MPD) and 2-diethylamino-ethanethiol hydrochloride (DAET) has been studied potentiometrically at different ionic strengths ($\mu = 0.05, 0.10, 0.15$ and 0.20 *M* $NaClO_4$) at 20 ± 0.5°C and only at $\mu = 0.10$ *M* at 30 ± 0.5°C and 40 ± 0.5°C in aqueous medium using Calvin-Bjerrum *p*H titration technique as modified by Irving and Rossotti. The thermodynamic stability constants and thermodynamic parameters (ΔG, ΔH and ΔS) have been calculated in the above systems. The orders of stabilities have been found to be: Fe(II) > Co(II) ≈ Ni(II) < Cu(II) > Zn(II) for MPD complexes and Fe(II) > Co(II) < Ni(II) < Cu(II) > Zn(II) for DAET complexes.

Polynuclear complexes of 3-mercaptopropane-1, 2-diol (MPD) with Zn(II) and Ni(II) have been reported[1]. No work seems to have been carried out on mononuclear complexes of MPD and 2-diethylaminoethanethiol hydrochloride (DAET) with metal ions of first transition series. In view of this, we report here the results of our studies on the potentiometric determination of thermodynamic stability constants and related thermodynamic parameters of the complexes formed by Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) with MPD and DAET.

The solutions of DAET and metal sulphates (AR) were prepared by direct weighing in conductivity water. The solutions of MPD and perchloric acid (0.04 *M*) were prepared from stock solutions by diluting with conductivity water. Potentiometric titrations were carried out with a Philips *p*H meter (PR 9405) using Calvin-Bjerrum[2,3] technique as modified by Irving and Rossotti[4]. Three solutions were prepared and titrated against standard alkali (0.4 *M*) using the techniques mentioned above, A: 4×10^{-3} *M* perchloric acid, B: A + 3×10^{-3} *M* ligand and C: B + 5×10^{-4} *M* metal ion. The total volume was kept at 50 ml and an appropriate amount of sodium perchlorate (2 *M*) was added to maintain the desired ionic strengths.

The *p*H ranges investigated for M(II)-MPD and M(II)-DAET systems (M = Fe, Co, Ni, Cu and Zn) were 3.2-8.8, 5.4-8.6, 5.6-8.8, 2.6-4.4 and 6.2-8.7; 3.4-

Table 1—Stability Constants and Thermodynamic Parameters of Some Bivalent Transition Metals with MPD and DAET

Metal ion	Ligand	Log *K*	20±0.5°C					30±0.5°C	40±0.5°C	20±0.5°C		30±0.5°C
			$\mu = 0.05$	0.10	0.15	0.20	0.0	0.1	0.1	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (cal deg^{-1}) mol^{-1})
H^+	MPD	log K_1^H	11.33	11.24	11.09	10.91	11.50	11.26	10.74			
		log K_2^H	9.66	9.57	9.48	9.32	9.77	9.36	9.17			
		log β_2^H	20.99	20.81	20.57	20.23	21.27	20.62	19.91			
	DAET	log K_1^H	11.01	10.83	10.36	10.14	11.30	10.53	10.44			
		log K_2^H	8.05	7.94	7.80	7.72	8.16	7.70	7.66			
		log β_2^H	19.06	18.77	18.16	17.86	19.46	18.23	18.10			
Fe^{2+}	MPD	log K_1	13.50	13.37	13.08	12.97	13.65	13.17	12.84	17.94	5.71	40.34
	DAET	log K_1	12.00	11.38	11.28	11.00	12.35	11.30	11.24	23.20	4.57	61.45
		log β_2	17.96	17.29	16.77	16.45	18.50	17.06	16.93			
Co^{2+}	MPD	log K_1	9.56	9.50	9.41	8.87	9.75	9.34	9.22	12.74	4.57	26.95
	DAET	log K_1	5.05	4.56	3.85	3.64	5.50	4.23	4.20	6.11	4.15	6.47
Ni^{2+}	MPD	log K_1	9.53	8.73	8.66	8.10	9.75	8.40	8.31	11.71	5.08	21.87
	DAET	log K_1	7.26	6.96	6.81	6.60	7.47	6.74	6.63	17.20	9.14	26.59
		log β_2	13.20	12.82	12.37	11.76	13.67	12.28	11.89			
Cu^{2+}	MPD	log K_1	17.90	17.82	17.75	17.26	18.10	17.49	17.42	23.90	4.57	63.76
	DAET	log K_1	15.90	15.80	15.69	15.60	16.00	15.50	15.09	21.20	7.62	44.80
Zn^{2+}	MPD	log K_1	10.26	10.03	10.00	8.99	10.50	9.94	9.63	23.74	9.14	48.16
		log β_2	18.03	17.70	17.50	15.46	18.60	17.55	16.91			
	DAET	log K_1	9.61	9.51	9.41	8.69	9.85	9.15	8.85	23.81	15.23	28.30
		log β_2	17.93	17.75	17.54	16.14	18.30	16.86	16.35			

Overall Standard Deviation = ±0.01-0.09.

8.8, 8.6-9.8, 6.8-9.2, 2.6-4.0 and 5.0-7.4 respectively. The proton-ligand stability constants (log K_n^H) of MPD and DAET and stepwise formation constants (log K_n) of their chelates with Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) were determined at $20 \pm 0.5°$, $30 \pm 0.5°$ and $40 \pm 0.5°$C (Table 1) using the well known computational techniques[5,6]. In Fe(II)-, Co(II)-, Ni(II)- and Cu(II)-MPD systems and Co(II)- and Cu(II)-DAET systems, the formation of 1:1 complexes has been indicated whereas in Zn(II)-MPD, Fe(II)-, Ni(II)- and Zn(II)-DAET systems the formation of both 1:1 and 1:2 complexes has been observed. In the case of MPD the formation curve is incomplete at the lower portion; therefore, the value of log K_1^H was obtained by extrapolation. Table 1 shows that stability constant values decrease with increase in temperature; thus, lower temperature is favourable for complex formation. Metal-ligand stability constants also decrease with an increase in ionic strength of the medium. The thermodynamic functions (ΔG, ΔH and ΔS) were evaluated by using standard equations[7] (Table 1).

The stability orders have been found to be:

M(II)-MPD complexes

Fe(II) > Co(II) ≈ Ni(II) < Cu(II) > Zn(II) and

M(II)-DAET complexes

Fe(II) > Co(II) < Ni(II) < Cu(II) > Zn(II) which are in accordance with the Irving-Williams order[8]. Abnormally high stability of Fe(II) complexes could be due to very high crystal field stabilization energy for the low-spin complex formation.

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