Proton-Ligand Constants of 2-Carboxy-2′-hydroxy-3′,5′-dimethylazobenzene-4-sulphonic & 2-Carboxy-2′-hydroxy-3′,5′-dichloroazobenzene-4-sulphonic Acids & Stability Constants of Their Chelates with Fe(III)

(Miss) ALKA BOKARE, B. K. DESHMUKH & R. B. KHARAT
Department of Chemistry, Nagpur University, Nagpur 440010

Received 5 *May* 1975; *accepted* 16 *August* 1975

The stepwise proton ligand constants of 2-carboxy-2′-hydroxy-3′,5′-dimethyl- and 2-carboxy-2′-hydroxy-3′,5′-dichloro-azobenzene-4-sulphonic acids and the stability constants of their Fe(III) complexes have been determined at 25°, 35° and 45° and μ=0·2*M* (KNO_3) in ethanol-water (50%, v/v) employing Irving-Rossotti titration technique. The values of overall changes in Δ*G*, Δ*H* and Δ*S* accompanying complex formation have also been evaluated.

IN continuation of our earlier work[1,2] on 2-carboxy-2′-hydroxy-3′,5′-dimethylazobenzene-4-sul phonic acid (CHDMAS) and 2-carboxy-2′-hydroxy-3′,5′-dichloroazobenzene-4-sulphonic acid (CHDCAS) as the new reagents for spectrophotometric determination of Pd(II), Cu(II) and Ni(II), we report in this note stepwise proton-ligand stability constants of CHDMAS and CHDCAS and the stability constants of their chelates with Fe(III) at 25°, 35° and 45° determined potentiometrically.[3,4]. The computational methods, viz interpolation at half $\bar{n}$ values and interpolation at various $\bar{n}$ values were also applied to obtain the stepwise proton ligand stability constants and metal-ligand stability constants.

$Fe(NO_3)_3.9H_2O$ was dissolved in doubly distilled water and standardized employing a known method. The solutions of the ligands were prepared in ethanol-water (50%, v/v) and were standardized potentiometrically.

A Beckman *p*H-meter with a glass-calomel electrode assembly was employed for potentiometric titrations at 25°, 35° and 45° ± 0·2° under nitrogen atmosphere.

The following CO_2-free solutions (100 ml) having 1:1 water: ethanol ratio were prepared and titrated against standard carbonate-free NaOH solution:

For Fe(III)-CHDMAS system: (i) 10 ml HNO_3 (0·1*M*), (ii) 10 ml HNO_3 (0·1*M*) + 50 ml ligand (0·01*M*), and (iii) 10 ml HNO_3 (0·1*M*) + 50 ml ligand (0·01*M*) + 10 ml metal (0·01*M*), titrated against 0·5*M* NaOH solution; *for Fe(III)-CHDCAS system*: (i) 10 ml HNO_3 (0·2*M*), (ii) 10 ml HNO_3 (0·2*M*) + 50 ml ligand (0·008*M*), and (iii) 10 ml HNO_3 (0·2*M*) + 50 ml ligand (0·008*M*) + 8 ml metal (0·01*M*), titrated against 1·0*M* NaOH solution. The concentrations of the common components in solutions (i), (ii), and (iii) for a system were identical. Potassium nitrate (AR, BDH) was used for maintaining the desired ionic strength (μ=0·2*M*). The metal ligand ratio was kept at 1:5 to fulfil the maximum coordination number of the metal.

From the titration curves it is observed that the metal ligand curve is well separated from the ligand titration curve which proves that the liberation of protons is due to chelation.

To calculate the proton ligand constants, the values of $\bar{n}_A$ at different *p*H values were calculated from the acid and ligand titration curves, using the equation of Irving and Rossotti[4,5]. Since SO_3H group present in both ligands dissociates at all *p*H, log K_1^H corresponding to OH group and log K_2^H corresponding to COOH group were calculated and the results are presented in Table 1.

The metal-ligand stability constants (Table 2) were obtained from the analysis of metal-ligand formation curves drawn between $\bar{n}$ (average number of ligands attached per metal ion) and *p*L (free ligand exponent). The values of $\bar{n}$ and *p*L were calculated from Eqs. (1) and (2).

$$\bar{n} = \frac{(V'''-V'')(N^\circ+E^\circ)}{(V^\circ+V')\,\bar{n}_A \cdot T_M} \qquad \ldots(1)$$

$$p\mathrm{L} = \log_{10}\left[\frac{\sum_{n=0}^{n=j}\beta_n^H\left(\frac{1}{\text{antilog } p\mathrm{H}}\right)^n}{(T_L-\bar{n}\,T_M)} \cdot \frac{V^\circ+V'''}{V^\circ}\right] \qquad \ldots(2)$$

where T_M=[metal]$_{total}$, N°=strength of alkali, E°=[HNO_3], V°=total initial volume of solution and V', V'' and V''' volumes of alkali required corresponding to solutions (i), (ii), and (iii) for each ligand at the fixed *p*H.

The values of the overall changes in the free energy (Δ*G*), enthalpy (Δ*H*) and entropy (Δ*S*) have been calculated at 25°, 35° and 45° and μ=0·2*M* (KNO_3) using the temperature coefficient and Gibbs-Helmoltz equations[7] and are given in Table 3.

The substitution of an electron donating methyl groups in CHDMAS by an electron withdrawing

TABLE 1 — PROTON-LIGAND STABILITY CONSTANTS OF CHDMAS AND CHDCAS AT DIFFERENT TEMPERATURES (μ=0·2*M*)

Temp. °C	log K_1^H	log K_2^H	log β^H
	CHDMAS		
25	12·10	4·40	16·50
35	12·00	4·30	16·30
45	11·80	4·20	16·00
	CHDCAS		
25	8·90	3·80	12·70
35	8·70	3·75	12·45
45	8·65	3·60	12·25

TABLE 2 — STABILITY CONSTANTS OF Fe(III)-COMPLEXES AT μ=0·2*M*

Temp. °C	Stability constants		
	log K_1	log K_2	log β
	Fe(III)-CHDMAS SYSTEM		
25	14·30	10·45	24·80
35	14·20	10·30	24·50
45	14·05	10·20	24·25
	Fe(III)-CHDCAS SYSTEM		
25	10·60	8·15	18·75
35	10·30	7·80	18·10
45	10·08	7·45	17·53

TABLE 3 — ΔG, ΔH AND ΔS VALUES OF THE COMPLEXATION REACTION AT $\mu = 0{\cdot}2M$

Temp. °C	ΔG kcal mole^{-1}	ΔH kcal mole^{-1}	ΔS kcal deg^{-1} mole^{-1}
	Fe(III)-CHDMAS SYSTEM		
25	−33·83		
35	−34·53	−12·06	+73·0
45	−35·30		
	Fe(III)-CHDCAS SYSTEM		
25	−25·57		
35	−25·52	−25·06	+1·5
45	−25·51		

chloro groups as in CHDCAS results in the formation of weaker complexes due to the lowering of the basicity of the ligand. The chelation may be taking place through carboxylic oxygen, hydroxylic oxygen and one of the nitrogens of azo group.

We thank Prof. R. H. Sahasrabudhey, Head, Department of Chemistry, Nagpur University, for providing necessary research facilities and CSIR, New Delhi, for the award of a junior research fellowship to one of us (B.K.D.).

References

1. SHARMA, O. P. & KHARAT, R. B., *Indian J. Chem.*, **13** (1975), 848.
2. SHARMA, O. P. & KHARAT, R. B., unpublished work.
3. BJERRUM, J., *Metal amine formation in aqueous solution* (P. Haase & Sons, Copenhagen,), 1941, 298.
4. CALVIN, M. & WILSON, K. W., *J. Am. chem. Soc.*, **67** (1945), 2003.
5. IRVING, H. & ROSSOTTI, H. S., *J. chem. Soc.*, (1953), 3397.
6. IRVING, H. & ROSSOTTI, H. S., *J. chem. Soc.*, (1954), 2904.
7. YATSIMIRSKII, K. B. & VASI'L'EV, V. P., *Instability constants of complex compounds* (D. Van Nostrand, New York), 1960, 63.

Studies on Complexes of Cr^{2+}, VO^{2+}, MoO_2^{2+} & WO_2^{2+} with Amino Acids

WAHID U. MALIK, RAMESH BEMBI & (MRS) YASMEEN ASHRAF
Department of Chemistry, University of Roorkee, Roorkee

Received 14 *July* 1975; *accepted* 4 *October* 1975

Complexes of Cr^{2+}, VO^{2+}, MoO_2^{2+} and WO_2^{2+} with glycine, histidine, lysine arginine and β-alanine have been studied spectrophotometrically and by conductometric and amperometric titrations. Cr(II) forms 1:1 complex with histidine and 1:2 complex with glycine in solution. MoO_2^{2+} and WO_2^{2+} form complexes of the type $[M(A)_2].2H_2O_2$ where A = arginine, lysine or histidine for M = MoO_2^{2+} and A = arginine or lysine for M=WO_2. VO_2^{+} forms the complexes $[VO(histidine)_2].2H_2O$ and $[VO(alanine)(H_2O)_4].\frac{1}{2}(SO_4)$. IR spectra of the solid complexes show coordination of the amino acids through the carboxylic and amino groups. In the case of arginine, coordination takes place through the α-amino as well as the terminal NH group. With histidine, the heterocyclic ring nitrogen is involved in coordination. Magnetic measurements show the complexes of VO^{2+} to be paramagnetic (one unpaired electron) and those of MoO_2^{2+} and WO_2^{2+} to be diamagnetic.

DURING our investigations[1-4] on the metal-protein interaction, it was observed[5] that the metals are probably linked through the nitrogen of arginine, guanidine or lysine residues. In view of the importance of metal-protein interactions in biological systems and the fact that molybdenum is an essential component of at least five different enzymes[6-8], we have prepared the complexes of MoO_2^{2+} and some other metal ions with glycine, histidine, lysine, arginine and β-alanine and studied their physicochemical properties.

Vanadyl sulphate, sodium tungstate and ammonium molybdate were BDH (AR) products. Chromous chloride was prepared by the method of Lingane and Pecsok[9].

Glycine, histidine, arginine and β-alanine were BDH products and their purity was checked by TLC.

Spectrophotometric studies were carried out on a Bausch and Lomb spectronic 20 spectrophotometer. Conductometric titrations were carried out using a Toshniwal conductivity bridge (type CLOI/0·1 A) with a dip-type cell. Amperometric titrations were carried out with the help of a Toshniwal manual polarograph (type CLO-2) in conjunction with a Pye 'Scalamp' galvanometer. A d.m.e. with drop time of 3·4 sec and capillary characteristic $m^{2/3}\,t^{1/6} = 1{\cdot}877$ was used. Magnetic measurements were carried out by Gouy's method. Infrared spectra (KBr) of the amino acids and their complexes were recorded on Beckman IR 20 spectrophotometer.

Preparation of the complexes — The complexes were prepared by mixing the solutions (0·01*M*) of the metal salt and the amino acid in the stoichiometric ratio and adjusting the *p*H to 4·5 in the case of vanadyl complexes and 2·0 in the case of molybdate and tungstate complexes. The precipitates obtained were centrifuged, washed with water, ethanol and dried *in vacuo* over anhydrous calcium chloride. Complexes of Cr(II) could not be isolated in solid state due to rapid oxidation of Cr(II) to Cr(III) during isolation.

For analysis, the complexes were decomposed by boiling with a 1:2 mixture of HNO_3 and HCl. The metal content was then determined by the usual methods[10-12].

Cr(II) forms a blue 1:1 complex with histidine and bluish-violet 1:2 complex with glycine in the *p*H range 2·5-5·0, as shown by mole-ratio and continuous variation methods. Amperometric titrations carried out at the plateau (−0·2 V) of the anodic wave of Cr(II) also confirmed these stochiometric ratios.

Ammonium molybdate forms 1:2 complexes with arginine, histidine and lysine while sodium tungstate forms 1:2 complexes with arginine and lysine at *p*H 2·0. These stoichiometric ratios were determined by conductometric titrations. Amperometric titrations (at −1·0 V and −0·8 V, the plateau of the second waves of ammonium molybdate and sodium tungstate, in 1*M* HCl, respectively) confirmed the above ratios. At *p*H 2·0, tungstate and molybdate exist as polymeric species[13] in equilibrium with small amounts of WO_2^{2+} and MoO_2^{2+} and the equilibrium shifts to the unpolymerized species below this *p*H. The reactions with amino acids would, therefore, take place with WO_2^{2+} and MoO_2^{2+}.