Pakistan J. Sci. Ind. Res., Vol. 13, No. 3, October 1970

SPECTROPHOTOMETRIC STUDIES OF COPPER(II) AND CHROMIUM(III) IONS WITH TAURINE

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(Received September 17, 1969)

The association of Cu^{2+} and Cr^{3+} with taurine was investigated spectrophotometrically in aqueous solutions. For copper–taurine system, one complex having two moles of coordinated taurine with one mole of copper nitrate is indicated. While for chromium–taurine system one complex having three moles of coordinated taurine with one mole of chromium nitrate is indicated.. Possible structure of the complexes is also suggested.

Spectrophotomerty has been successfully employed to study metal complexes of proteins[1] peptides[2] and amino acids.[3,4] In this paper studies of copper(II) and chromium(III) ions with 2-aminoethane sulphonic acid made according to the Jobs' method of continuous variation[5] and modified molar ratio method,[6] respectively, are reported.

Procedure

Stock solution of copper nitrate was prepared by dissolving A.R. grade chemical (E. Merck Co. Ltd.) in pyrogen-free water. The exact strength of the solution determined idiometrically[7] was 0.52M.

Chromium nitrate was prepared by heating for 2 hr chromium carbonate with appropriate amount of nitric acid. Chromium nitrate thus obtained was checked to see that no free acid or carbonate is present. It was then diluted by adding distilled water. Chromium in the solution was determined gravimetrically.[8] The strength of the solution thus determined was 0.34M.

Solutions of 2-aminoethane sulphonic acid (Eastman Organic Chemical, U.S.A.) and potassium nitrate (B.D.H. Analytical grade) (0.1 molar) were prepared in distilled water.

The working solutions of copper nitrate and chromium nitrate were prepared by diluting their standard solutions to 0.1 molarity and adding the required amount of buffer (sodium acetate–acetic acid). The pH of copper nitrate solution thus prepared was kept at 5.25 while for chromium it was at 4.45.

Two series of mixtures, one for the system copper nitrate–taurine and the other for chromium nitrate–taurine were prepared in which the mole fraction of the components were varied and the total molarity was kept constant (see Tables 1 and 2). Again two series of mixtures of the respective systems were prepared following the modified molar ratio method. This was done by adding varying quantity of taurine in nine volumetric flasks containing 4 ml metal nitrate solution and 2 ml potassium nitrate solution. Water was added to make the total volume 20 ml in each case. The ionic strength of these solutions was calculated by using the expression,

$$\mu = \tfrac{1}{2}\Sigma C_i Z_i^2$$

where C_i is the ionic concentration in g-moles per litre and Z_i is the valency of the ion. It came out to be 0.1.

Before taking the optical density measurements the mixtures were heated on a water bath to accelerate the reaction. Optical density was measured on Bausch and Lomb, Spectronic 20, spectrophotometer. Beckman pH meter model G was used to measure pH of the solution mixtures.

Results and Discussion

Optical densities for the system copper nitrate–taurine, plotted at different wavelength using the Job's method, show one peak at 800 mμ (see Fig. 1), while optical density–wavelength plot of the system chromium nitrate–taurine gave two peaks, one at 425 mμ and the other at 575 mμ (see Fig. 2). Plots for the blanks are also shown in the figures.

The data summarized in Tables 1 and 2 indicate that for both the systems the measured optical densities are greater than that of the metal solutions without taurine. If there is no complex formation, the resulting plot should be linear. But the maxima obtained by plotting difference in optical densities against mole fractions of copper nitrate in the mixtures clearly indicate the formation of a complex at 1:2 copper to taurine ratio (see Fig. 3). Also a similar plot for chromium nitrate–taurine show complexing at 1:3 ratio (see Fig. 4).

Results obtained using modified molar ratio method, plots of which are shown in Figs. 5 and 6, further support the complexes formed at 1:2 ratio in case of copper and at 1:3 ratio in case of chromium. A small shoulder at 1:0.5 ratio in Fig. 5 and at 1:2 ratio in Fig. 6 is also present. It is perhaps due to weak interactions at these ratios and is therefore absent in the Job's plots.

The marked increase in the optical density of copper nitrate and chromium nitrate solutions in the presence of taurine is an indication of metal

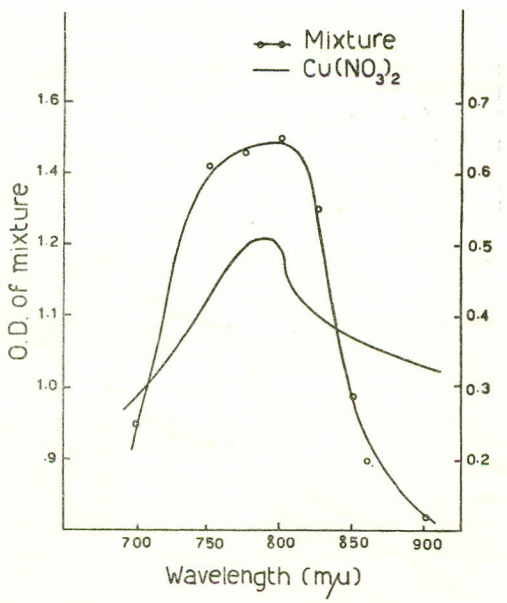


Fig. 1.—Plot showing optical density versus wavelength for the system copper nitrate–taurine at pH 5.25.

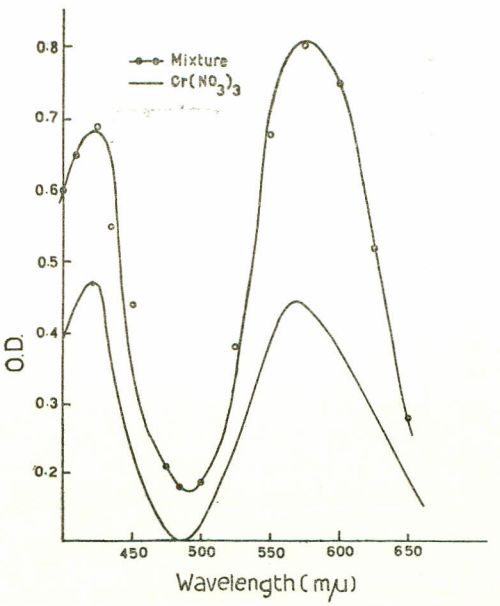


Fig. 2.—A plot of optical density against wavelength for the system, chromium nitrate–taurine at pH 4.45.

TABLE 1

pH=5.25; wavelength used=800 mμ.

Expt.	$Cu(NO_3)_2$ taken ml	Taurine soln added ml	Optical Density	
			Blank	Mixture
1	1.0	9.0	0.142	0.420
2	2.0	8.0	0.420	0.430
3	3.3	6.7	0.490	1.350
4	4.0	6.0	0.762	1.500
5	5.0	5.0	0.795	1.850
6	6.0	4.0	0.815	1.900
7	7.0	3.0	0.890	1.990
8	8.0	2.0	0.920	2.000
9	9.0	1.0	0.930	2.000

TABLE 2

pH=4.45

Expt.	$Cr(NO_3)_3$ soln taken ml	Taurine soln added ml	Optical density measured at 425 mμ		Optical density measured at 575 mμ	
			Blank	Mixture	Blank	Mixture
1	1.0	9.0	0.160	0.250	0.155	0.180
2	2.0	8.0	0.290	0.450	0.330	0.360
3	2.5	7.5	0.470	0.650	0.450	0.590
4	4.0	6.0	0.640	0.780	0.670	0.800
5	5.0	5.0	0.760	0.920	0.700	0.980
6	6.0	4.0	0.950	1.200	0.860	1.200
7	7.0	3.0	1.200	1.500	1.150	1.500
8	8.0	2.0	1.350	1.700	1.330	1.700
9	9.0	1.0	1.400	1.800	1.420	1.800

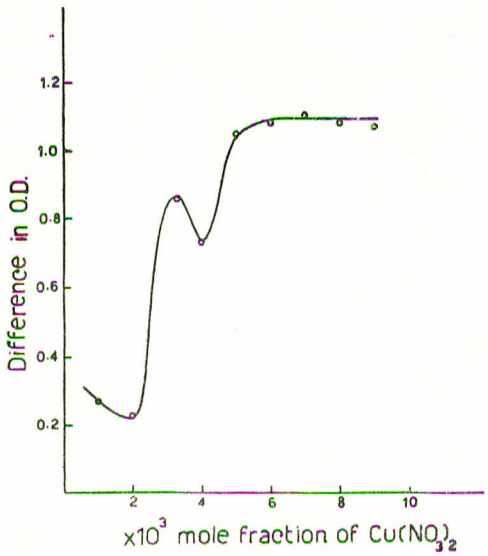


Fig. 3.—Difference in optical density plotted against mole fraction of copper nitrate.

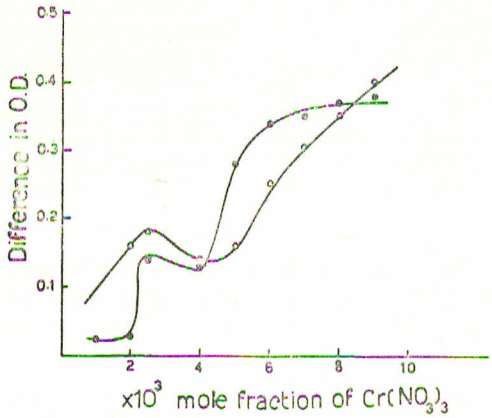


Fig. 4.—Difference in optical density plotted against mole fraction of chromium nitrate.

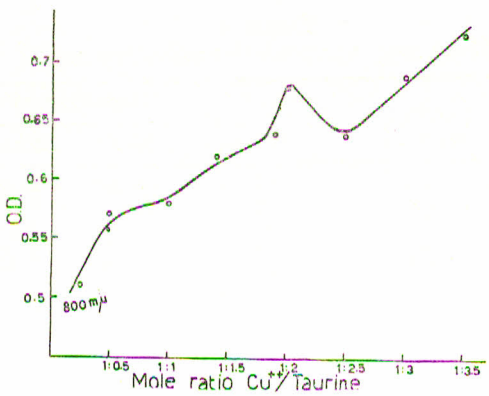


Fig. 5.—A plot of optical density against mole ratio for the system, copper nitrate–taurine.

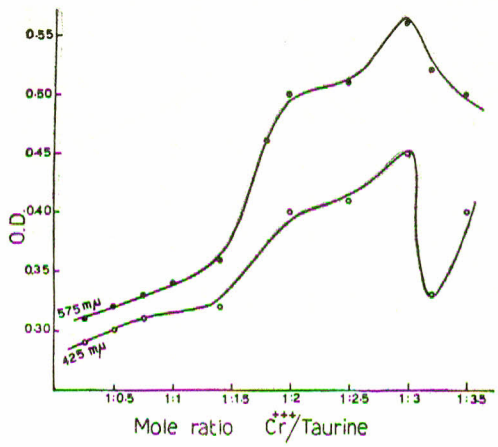


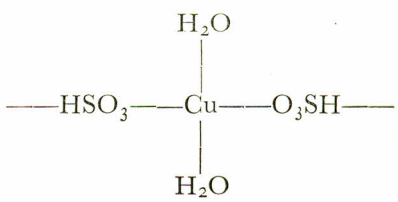
Fig. 6.—Plot showing optical density against mole ratio for the system, chromium nitrate–taurine.

ions association with taurine. This could possibly be due to the fact that the metal ion combines with taurine through oxygen atoms of the taurine molecule,

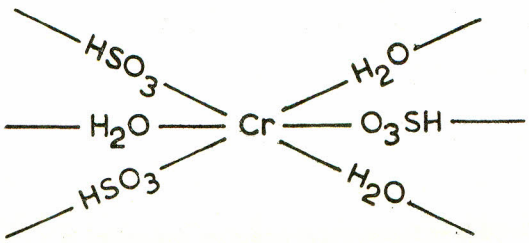
$$H_2N.CH_2.CH_2.SO_3H$$

This is also supported by the electrochemical studies of taurine.[10] The pK values of the sulphonate group in taurine molecule is >1, while pK value of the amino group is 9.06. Since our measurements were below pH 6, it is reasonably justified to assume that metal ion is bound primarily with oxygen atom of taurine molecule and not with nitrogen atom.

The maxima at 1:2 copper to taurine ratio corresponds to a complex compound containing two moles of coordinated taurine with one mole of copper nitrate. Again considering that copper having its coordination number four will give rise to a square planar complex; the possible structure of the complex will be:



Chromium having six coordination number will give rise to a complex whose structure will be:



Acknowledgement.—The authors would like to record their thanks to Miss Maimuna Nizam for drawing the figures and to Dr. Ahmed Kamal, Director of the P.C.S.I.R. Laboratories, Karachi, for providing the work facilities.

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