

# Thermodynamics of Cu(II)-Chromotrope-2R Chelate in Aqueous Medium

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The composition, stability and thermodynamic parameters of the chelate formed between Cu(II) and phenylazochromotropic acid (Chromotrope 2R) has been investigated spectrophotometrically in aqueous medium. The red-violet chelate has  $\lambda_{max}$  at 580 nm against a reagent blank. The composition as determined by different methods is 1:1 at  $pH = 6.0 \pm 0.1$ . The mean value of  $\log K$  and free energy of formation of the chelate are found to be  $4.56 \pm 0.1$  and  $-6.24 \pm 0.2$  kcal/mole respectively at 25°C. The enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) calculated by van't Hoff's isochore and Gibbs-Helmholtz equations are  $-17.92 \pm 0.02$  kcal/mole and  $-39.82 \pm 0.02$  e.u. respectively.

**P**HENYLZACHROMOTROPIC acid (abbreviated as CTR in this paper) has extensively being used as a chelating agent in the photometric studies of various inorganic ions<sup>1-7</sup>. In spite of large amount of work done on the chromogenic properties of this reagent, no work on its copper chelate is on record. The present studies deals with the investigation of copper(II)-CTR chelate regarding its composition, stability and thermodynamic parameters like  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  associated with the formation of chelate in aqueous medium.

## Experimental

Standard solutions of copper sulphate (Analar, BDH) and CTR (BDH) were prepared in CO<sub>2</sub> free double distilled water. The copper content was estimated as usual. Absorbance measurements were made on the Perkin-Elmer model 139 UV-Visible spectrophotometer using 1 cm matched quartz cells. The cell compartment was fitted with a jacket through which water was circulated from a thermostat. pH measurements were made on Beckman pH meter model H2.

The measurements were performed at  $25 \pm 0.1^\circ\text{C}$ . The solutions were kept in a constant temperature bath for 30 minutes previous to measurements. The pH of all the solutions was adjusted to  $6.0 \pm 0.1$  by hexamine-perchloric acid buffer and the ionic strength was maintained 0.1 by the addition of sodium perchlorate.

It was found that the order of addition of reactants has no significant effect on absorbance. The development of colour is instantaneous and remains constant for about 24 hrs.

## Results and Discussion

**Nature of the chelate formed:** The method of Vosburgh and Cooper<sup>8</sup> was followed. Mixtures containing copper(II) and CTR in different proportions were prepared and absorbances measured at

various wavelengths. The observations show that CTR has  $\lambda_{max}$  at 510 nm and the chelate has  $\lambda_{max}$  at 580 nm against a reagent blank. This confirms that only one chelate is formed under conditions of study. The chelate is stable in the pH range 5.0 to 11.0. However, pH  $6.0 \pm 0.1$  was selected for subsequent studies. Hexamineperchloric acid buffer was used for maintaining the pH.

**Composition and stability constant:** The mole-ratio 1:1 of copper: CTR was established by three different methods viz., method of continuous variation mole-ratio method and the slope ratio method. The stability constant of the chelate is calculated by the method of Banerji and Dey, mole-ratio method and the method using molecular extinction coefficient. The values obtained by three different methods are in close agreement and the mean value of  $\log K$  and free energy of formation are  $4.56 \pm 0.1$  and  $6.24 \pm 0.2$  kcal/mole respectively at 25°C.

**Adherence to Beer's law:** The colour system obeys Beer's law upto a concentration range of 5.2 ppm of copper. The molecular extinction coefficient and Sandell's sensitivity<sup>9</sup> are 7250 and 0.008  $\mu\text{g}$  of copper/cm<sup>2</sup> respectively.

**Thermodynamic functions:** The values of free energy of formation ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were calculated using Van't Hoff's equation, Van't Hoff's Isochore and Gibbs-Helmholtz equation respectively and are recorded in Table 1.

The formation of cupric chelate with CTR is a spontaneous process which is evident from Gibb's free energy value. The negative value of  $\Delta H$  ensures that the reaction is exothermic and metal-ligand bond is stronger than the ligand-solvent bond. The negative value of  $\Delta S$  indicate that products are more ordered than the reactants.

TABLE I. THERMODYNAMIC FUNCTIONS OF THE CHELATE AT DIFFERENT TEMPERATURES

$\lambda_{max} = 580 \text{ nm}; \mu = 0.1; \text{pH} = 6.0 \pm 0.1$   
 $\Delta H = -17.92 \pm 0.02 \text{ kcal/mole}$

Temp., °C	log K	$\Delta G$ kcal/mole	$\Delta S$ e.u.
15	4.88	-6.44	-39.84
20	4.65	-6.24	-39.84
25	4.43	-6.05	-39.82
30	4.21	-5.84	-39.81
Mean value $\Delta S = 39.82 \pm 0.02$			

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