Spectrophotometric Study on the Interaction of Chromium(III) with Alizarinsulfonic Acid

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(Received August 13, 1962)

The interaction of metal ions with alizarinsulfonic acid has been studied by a number of workers[1-6], but little seems to have been done as regards the chromium(III) complexes. Preliminary experiments show that chromic chloride does not react with alizarinsulfonic acid at room temperature. However, on heating the mixture at about 80°C for nearly half an hour a red color develops, indicating the probable existence of the complex. The work described here deals with the spectrophotometric studies on the composition of the red product obtained at 80°C.

Chromic chloride (A. R.) was dissolved in redistilled water and the concentration was determined by the usual methods. The solution of alizarinsulfonic acid (sodium salt) was prepared by dissolving a known amount in acetate buffer of pH 3.1. Absorption experiments were carried out with a Bausch and Lomb 'Spectronic 20'. Measurements of pH were made with a Beckman pH-meter model G.

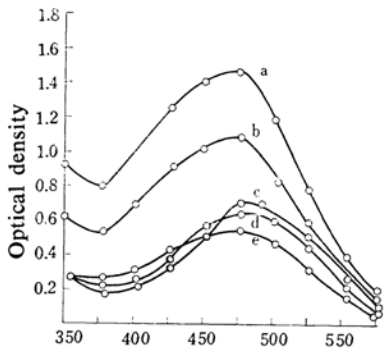

Fig. 1

a) 1 : 1 ratio of the reactants at pH 3.1
b) 1 : 2 ratio of the reactants at pH 3.1
c) 1 : 3 ratio of the reactants at pH 3.1
d) 2 : 1 ratio of the reactants at pH 3.1
e) 3 : 1 ratio of the reactants at pH 3.1

Vosburgh and Cooper's[7] method was employed to determine the number of complexes formed. The reactants were mixed in different molar ratios (1 : 1, 1 : 2, 1 : 3, 2 : 1, 3 : 1), heated on a water bath for about half an hour, cooled to room temperature and their optical densities were measured. All the mixtures gave a maximum at 475 mμ (Fig. 1) showing thereby the formation of only one complex.

The Job's method of continuous variation[8] was followed for determining the composition of the complex. Solutions of chromic chloride and sodium alizarinsulfonic acid of two different concentrations, M/3000 and M/4000, were mixed according to the method of continuous variation and the optical densities measured at 475 mμ. In order to account for the absorption of alizarinsulfonic acid, the mixtures of water (in place of chromic chloride) and alizarinsulfonic acid were taken, heated on a water bath to 80°C, cooled and their optical densities were measured. The chromic chloride solutions prepared under exactly similar conditions showed almost negligible absorption at 475 mμ. A curve was plotted between the

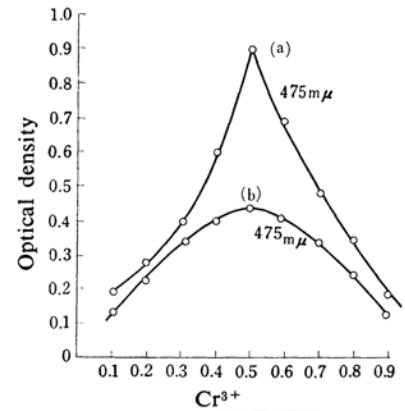

Fig. 2

a) For M/3000 of the reactants at pH 3.1
b) For M/4000 of the reactants at pH 3.1

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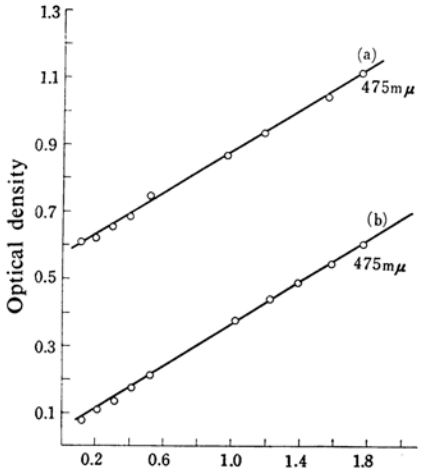
difference in optical density of complex and alizarinsulfonic acid and the ratio $Cr^{3+}/(Cr^{3+}+$ alizarinsulfonic acid). The results are depicted in Fig. 2.

The results were also confirmed by the slope ratio[9] and the molar ratio methods[9]. Two sets of experiments were performed for the slope ratio method. In the first set the concentration of sulfonic acid (taken in excess) was kept constant while the concentration of chromic chloride was varied. In the other set the mixtures were prepared by mixing the reagents just in the reverse manner. The optical densities of the mixtures in the two sets were measured under exactly similar conditions as described above and curves drawn between the optical density of the solution and the volume of the reactant (Fig. 3) to be varied. In the

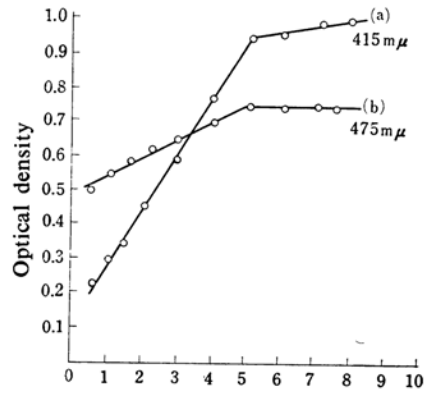


Volume of the reactants (variable) (a)

Fig. 3

a) $CrCl_3$ variable
b) Alizarin variable

case of molar ratio method the optical densities of the following two sets of mixtures were measured: (i) 5 cc., alizalinsulfonic acid of 0.5×10^{-3} M mixed with 0.5 cc., to 8.0 cc., chromium(III) chloride 0.5×10^{-3} M, total volume made upto 20 cc. by adding required amount of buffers; (ii) reagent mixed in just the reverse manner as given under (i). The results are shown in Fig. 4.

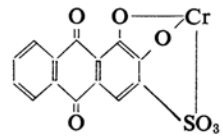


Volume of the reactants (variable), cc.

Fig. 4

a) Alizarin variable
b) $CrCl_3$ variable

The Vosburgh and Cooper's method shows the existence of one complex with an absorption maximum at 475 mμ. By applying the Job's method at two different concentrations of the reactants, peaks are obtained corresponding to the molar ratio 1:1 (Fig. 2). The results obtained by the Job's method find support from the slope ratio and molar ratio methods. Hence the probable composition of the complex may be written as:



Dey and Mukherji[6] determined the stability constant and free energy of the red alizarinsurfonic acid complex by considering two concentrations of the reactants which gave the same optical density. No such attempt was made here in view of the inert nature of the chromium complex[10] and the slowness with which the reaction is expected to reach equilibrium. The composition put forward here, therefore, refers only to the product formed by the interaction of chromic chloride and alizarinsulfonic acid at 80°C.

Thanks are due to Professor Akhlaq R. Kidwai for providing facilities and C.S.I.R. for the award of a fellowship to one of us (R. H.)

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