

## Spectral Changes of Dyes in Colloidal Solutions of Hydrous Oxides

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from the next nearest ones.<sup>2</sup> It has not only one but three sets of equivalent sites; hence even in disordered states we must take care of three parameters for the 15 sites, i.e.,  $\mu_1$  for the central site,  $\mu_2$  for each of its first shell sites and  $\mu_3$  for each of the six sites taken from second shell (see Fig. 1.)

It is still quite easy to prove that the disordered distribution is always a solution of

$$\sum_{\lambda} c_{\lambda} \sum_{(h)} \ln \mu_{\lambda i} - r_h (D \ln(\theta_h/1 - \theta_h) - C) = 0.$$

We see that when  $\theta_h = \theta$  the parameter of the  $i$ th site has the same value no matter to which sublattice it belongs, i.e.,  $\mu_{\lambda i} = \mu_i$  ( $\lambda = 1, \dots, l$ ). It follows that

$$\sum_{\lambda} c_{\lambda} \sum_{(h)} \ln \mu_{\lambda i} = \sum_{\lambda} c_{\lambda} \sum_{(h)} \ln \mu_i = r_h \sum_i \ln \mu_i,$$

when  $\theta_h = \theta$ . Therefore the  $m$  equations of the above set reduce to the equation

$$\sum_i \ln \mu_i - D \ln(\theta/1 - \theta) + C = 0.$$

The latter can always be satisfied because of the arbitrariness of  $C$ .

<sup>1</sup> Y-Y Li, J. Chem. Phys. 17, 447 (1949).

<sup>2</sup> Some results of an approximation using this group have been published in the article by Y-Y Li, Phys. Rev. 76, 972 (1949).

## Spectral Changes of Dyes in Colloidal Solutions of Hydrous Oxides

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RECENT publications have shown that dyes which do not follow Beer's law will exhibit spectral changes when mixed with colloidal solutions. This effect is attributable to the existence of an equilibrium between two or more forms of the dye, one of which is preferentially adsorbed by the micelles.<sup>1,2</sup> It appears to be generally accepted that dyes that follow Beer's law exhibit only slight spectral change in colloidal solutions although it has been shown that native albumin forms complexes with simple dye anions.<sup>3</sup>

We have obtained some results with dyes that follow Beer's law which indicate that single dye ions that are bound by hydrous oxides show a spectral absorption curve distinctly different from that of the free ion. The addition of salts causes the displacement of the bound dye and the absorption spectrum is shifted back toward that of the free dye ion.

The spectral change of Orange I caused by colloidal hydrous alumina is shown in Fig. 1. The molar extinction coefficient at 475  $m\mu$  shows a decrease of about 40 percent in the presence of the hydrous oxide and the absorption maximum is shifted some 30  $m\mu$  toward the violet. The displacing ability and hence the affinity for competing anions to form complexes with the hydrous alumina may be measured by the extent of the reversal of the absorption spectrum towards that for the free dye. In the case of sulphate ions, complete displacement of the dye was observed when the total concentration of sulphate was comparable to that for dye.

When dye and sol are mixed, the greater part of the spectral change takes place within a few minutes. This rapid process is followed by a slow uptake of the dye by the colloidal particle suggesting penetration of the micelles by the dye ions. About ten to twenty hours were required to reach the equilibrium values given in the figure.

That the sorbed dye ions on the surface are in mobile equilibrium with the ions in the bulk of the solution is shown by the rapid response of the colloidal solution to temperature changes. An increase of a few degrees caused an increase of several percent in the

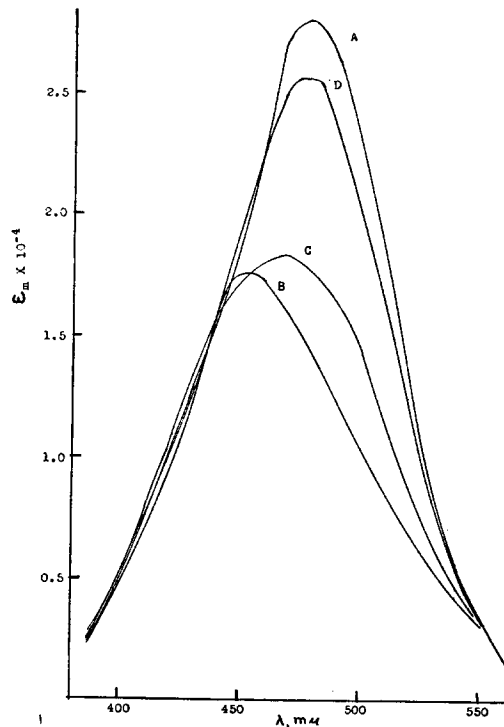


FIG. 1. Molar Extinction Coefficient of  $2.0 \times 10^{-4}$  M Orange I. (A) Dye and acetate buffer at pH 4.0. (B) Dye and colloidal solution of hydrous alumina peptized by HCl, pH 3.9;  $Al_2O_3$  content 0.880 g/liter. (C) Same as (B) in presence of 0.01M KCl. (D) Same as (B) in presence of 0.01M KAc. Addition of 0.01M  $K_2SO_4$  to (B) gave curve identical with (A).

optical density, indicating a desorption process. Bringing the colloidal solution back to its original temperature brought the optical density back to its former value within a few minutes.

In the case of dyes which do not follow Beer's law, the gradual changes in the intensity, position and shape of absorption bands generally indicate an increase in the proportions of the polymeric form of the dye. This is brought on by the colloidal particles combining with the polymeric dye molecules as a result of electrostatic and van der Waals forces. The spectral changes which we have observed with simple dye anions in the presence of hydrous oxides, however, is consistent with the postulate of chemical bonding as suggested previously by one of us.<sup>4</sup>

The use of suitable dye ions to study changes in colloidal solutions of hydrous oxides offers several advantages over the usual procedure employing e.m.f. measurements. It should be noted that a "suitable dye ion" is one whose spectral characteristics are not altered by the salt and pH changes involved in a particular investigation. Some of these advantages are the following:

1. Increase in sensitivity of detecting changes. For example, the colloidal solution whose effect on Orange I is given in Fig. 1, showed a change of about a 0.1 of a pH unit upon the addition of the salts, whereas, the optical density of the system was altered considerably.

2. It should be possible to investigate readily those systems whose dispersed particles are not quite large enough to be considered micellar, and yet are outside the crystalline range.

3. Several methods are available for determining the extinction coefficient for the sorbed dye ions, thus making it possible to express quantitatively the exchange processes that occur in colloidal solutions in terms of number of molecules.

<sup>1</sup> Merrill and Spencer, J. Am. Chem. Soc. 70, 3683 (1948).

<sup>2</sup> Michaelis and Granick, J. Am. Chem. Soc. 67, 1212 (1945); also see S. E. Sheppard and A. L. Geddes, J. Chem. Phys. 13, 63 (1945).

<sup>3</sup> Klotz, Triwush, and Walker, J. Am. Chem. Soc. 70, 2935 (1948).

<sup>4</sup> A. W. S. Thomas, *Colloid Chemistry* (McGraw-Hill Book Company, Inc., New York, 1934).