Absorption Spectra of Methylene Blue Adsorbed on Homoionic Bentonites Suspended in Water

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The changes of the spectra of dyes added to some colloidal solutions are well-known as metachromasy. When some powdered materials usually used as adsorbents are suspended in water and dye solutions are added to them, color changes of the dye are also frequently observed if the dyes have the possibility ready to be adsorbed by those materials. In order to investigate if any relations exist between the trend of color changes of the dyes adsorbed and the surface structures of powdered materials used, the experiments have been carried out by using some kinds of clay minerals and silica gel, etc.[1] An interesting phenomenon has been observed in montmorillonite-methylene blue system; that is, the spectrum of the dye adsorbed on montmorillonite changes gradually with lapse of time after mixing of them. Furthermore this color change is influenced remarkably according to the kinds of added cation[2]. In order to clarify this phenomenon more thoroughly, the absorption

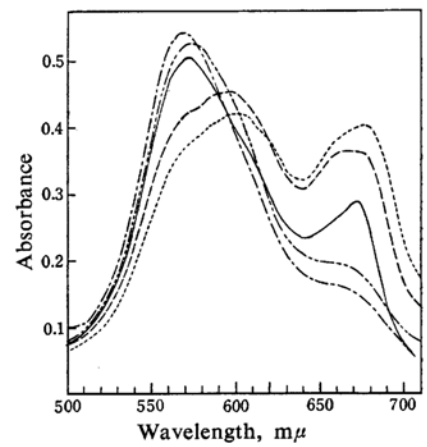

Fig. 1. Absorption spectra of methylene blue adsorbed on homoionic bentonites, after an hour from mixing.

—— Na-; -·-·- Ca-; -··· H-; ---- K-; ------ NH_4-bentonite

1) C. Sato, "Advances in Clay Science" Vol. 2, Edited by the Clay Research Group of Japan, Gihodo, Tokyo (1960), p. 69.

2) C. Sato, ibid. Vol., 3, in press; N. E. Vedeneeva, *Chem. Abstr.*, **49**, 4405^b (1955).

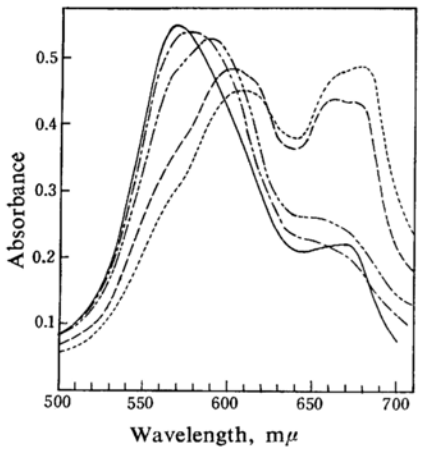

Fig. 2. Absorption spectra of methylene blue adsorbed on homoionic bentonites, after 2 days from mixing.
—— Na-; -·-·- Ca-; -··- H-; ---- K-; ------ NH_4-bentonite

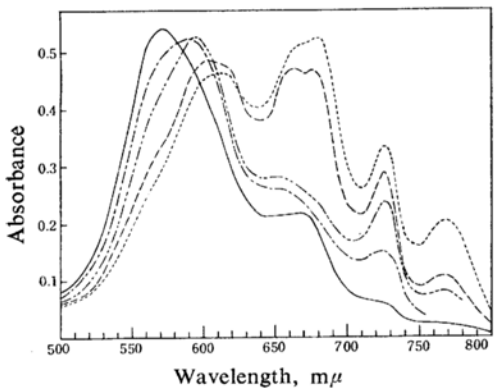

Fig. 3. Absorption spectra of methylene blue adsorbed on homoionic bentonites, after 7 days from mixing.
—— Na-; -·-·- Ca-; -··- H-; ---- K-; ------ NH_4-bentonite

spectra of methylene blue adsorbed on homoionic bentonites suspended in water and having exchangeable cations of hydrogen, sodium, potassium, ammonium and calcium, have been observed.

Homoionic bentonite suspensions were prepared according to the method of Slabaugh, etc.[3] In each run 10 ml. of this suspension (0.13%) was divided into two equivalent parts, to one of which was added 0.5 ml. of the dye solution of a definite concentration, 1.74×10^{-4} mol./l., and to the other was added the equivalent amount of distilled water. Then the absorption spectrum of the former was measured with reference to the latter with a spectrophotometer, after about an hour from the addition of dye. Furthermore, the change of spectrum of the above system with longer lapse of time was also examined. The results obtained are indicated in Figs. 1, 2 and 3.

As seen in the figures, in potassium and ammonium bentonites, the band at 570 mμ decreases its intensity remarkably, and the broad bands at 600~620 mμ and 660~680 mμ, especially the latter, increase their absorbance markedly, with lapse of time. The bands at 725 mμ and 770 mμ become also apparent gradually. But in hydrogen and calcium bentonites the above change appears considerably slowly and in sodium one any change is scarcely observed in the spectrum which shows a strong band at 570 mμ and a weak one at 670 mμ. According to the view reported in literature[4] for the interpretation of absorption spectrum of methylene blue dissolved in water, it may be presumed that in ammonium and potassium clays a greater part of dye adsorbed initially in associated form on the outer surface of clay particle migrates easily to the firm binding of the unassociated dye ion on the interlayer surface, but in sodium, calcium and hydrogen clays, especially in sodium type, this migration is impeded. It is also assumed that these differences by the kinds of exchangeable cations may result from the correlation between the arrangement of water molecules adsorbed on interlayer surface and surrounding the hydrated cation, and the size of methylene blue ion. But any quantitative interpretation has not been attempted yet. The interpretation of appearance of the bands at 725 and 770 mμ has also been left unsolved.

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3) W. H. Slabaugh and R. H. Siegel, *J. Phys. Chem.*, **60**, 1105 (1956).

4) M. Schubert and A. Levine, *J. Am. Chem. Soc.*, **77**, 4197 (1955).