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Abstract

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PHYSICAL CHEMISTRY

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ON THE FEATURES OF THE ABSORPTION OF COLLOIDAL SOLUTIONS AND DRY LAYERS OF CERTAIN ORGANIC DYES

In the works of E. P. Kramalei (^{1}) it was shown that colloidal solutions of silver and gold, under certain conditions, exhibit in their absorption spectra, in addition to the usual colloidal band described by Mie theory, also a system of narrow bands similar to that which had previously been observed in the spectra of silver halides and thin metallic layers (^{2}). Further investigation of this question led to the supposition that a complex character of absorption may also be possible in a number of organic compounds, if one proceeds from the analogy in the properties of the easily mobile electrons of metals and the π-electrons that form conjugated bonds (^{3}). It could therefore be expected that in such polydisperse systems as colloidal solutions and dry layers of organic dyes, a corresponding character of the absorption spectra would be observed.

In connection with this, the absorption of a number of dyes was studied: erythrosine, methylene blue, fuchsin, and also the dyes 3-ethyl-5-(3′-ethylbenzoxazolinylidene-2′-ethylidene)-thiazolidinethione-(2)-one-(4), 3-methyl-1′-ethylthia-2′-quinocyanine iodide; 3,3′-diethylthiacarbocyanine iodide, containing no metals either in their structure or as impurities; the latter were synthesized at the Scientific Research Cinema and Photo Institute and are hereinafter denoted I, II, III. Such an investigation may provide new information on the features of adsorption of dyes on various substrates and on the mechanism of optical sensitization.

In contrast to the work of other authors, the measurements in the present work were carried out at the lowest possible dye concentrations (10^{-8}—10^{-6} mol/l) with intervals between observation points of 5 mμ, for which purpose a spectrophotometric setup possessing sufficiently high differential sensitivity was used (^{4}).

Colloidal solutions of the dyes were prepared by introducing small amounts of

Fig. 1

Figure 1: Fig. 1

true solutions in absolute alcohol into dehydrated benzene, or benzene solutions into distilled water. This method, known in the literature as the solvent-replacement method, was developed for dyes by M. V. Savost' yanova (^{5}).

According to the procedure we adopted, the dye solutions and the solvents were poured into glass cuvettes from the SF-4 set and placed in the apparatus on a common holder. The ratio of the intensities of light transmitted through the solvent (I_1) and through the dye solution (I_2) was measured for each wavelength with an accuracy up to 0.02%. To maintain differential conditions, absolute alcohol was added to the cuvette with benzene in such an amount that its quantity in both cuvettes would be the same. The measurements were carried out continuously, using only freshly prepared solutions. These measurements showed that in the absorption spectra of all the dyes studied, in addition to a broad band, there is also observed a system of rather narrow and well-defined bands. Apparently, in colloidal solutions, in addition to particles whose absorption obeys Mie theory (^{5}), there are also particles responsible for the narrow bands. On independent-

The existence of such particles is indicated by experiments on their separation from colloidal solutions and transfer into another medium.

The separation of particles of both types occurs most clearly during dark storage of the solutions. The experiments were carried out as follows. A colloidal solution of the dye was prepared in an amount considerably exceeding that required for a single measurement. The freshly prepared solution was poured into a cuvette and its absorption was measured. Further measurements of the absorption of the solution were then made at specified time intervals during its storage in the dark.

Fig. 1. Absorption spectra of colloidal solutions—erythrosin (**A**) and methylene blue (**B**). **1**—freshly prepared solutions, **2**—after storage in the dark for 6 h, **3**—after storage in the dark for 24 h, **4**—absorption of empty cuvettes (on the axes are plotted the ratios of the intensities of light passed through the solvent and through the dye solution)

In curves **1** (Fig. 1), the colloidal band is clearly manifested and, against its background, a weakly expressed structure. As the solution is stored, the spectral picture changes substantially: the structure becomes increasingly distinct, the intensity of the colloidal band decreases (curves **2**), and after storage for 24 h (curves **3**) mainly the structural bands are already manifested. Further storage of the solution does not lead to a decrease in absorption, but only to some redistribution (in intensities) of the narrow bands. At the same time, the external appearance of the initial solutions also changes. In the course of storage the colloidal particles become larger and settle to the bottom of the vessel;

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

the solution becomes decolorized. In such a decolorized solution the complex structure appears most distinctly.

Fig. 2. Absorption spectra of erythrosin: of sediment illuminated along its axis (**1**) and of the solution above it (**2**)

It was of interest to measure the absorption of the precipitate that had fallen out of the main solution. For this purpose, dark storage of the colloidal solution was carried out

was carried out in a measuring cuvette with a removable bottom. As soon as the solution became decolorized and the dye settled on the bottom, the solution was poured off, the bottom was removed and dried, and the absorption of the dry layer and of the decanted solution was measured. As is seen from Fig. 2, the absorption of dye particles deposited on the bottom is characterized by an ordinary colloidal band with a weakly expressed structure, whereas, when the solution is measured, a system of narrow bands is observed.

Fig. 3. Absorption spectra of colloidal solutions: erythrosin (**A**) and dye I (**B**): **1**—glass bottoms untreated; **2**—bottoms treated with gelatin; **3**—bottoms treated with paraffin.

To elucidate the conditions for the formation of the particles responsible for the complex structure, the colloidal solution of the dye poured, as usual, into cuvettes with carefully washed glass bottoms was measured; then these bottoms were replaced by others, on the inner side of which an extremely thin film of paraffin was applied (in the case of aqueous colloidal solutions), or a film of gelatin dried to constant weight (for benzene solutions), and repeated measurements were made.

From curves **1** in Fig. 3 it is seen that the particles producing the complex structure in the absorption spectrum appear optically only when the cuvette bottoms have not been treated in the manner indicated above, whereas the surface treatment has no effect on the appearance of the colloidal band. Hence it follows that colloidal particles are formed in the bulk, while particles of complex structure are formed upon adsorption of their components on glass. These particles apparently represent molecular complexes whose dimensions occupy an intermediate position between individual molecules and colloidal particles.

Fig. 4. Spectral absorption of methylene blue: **1**—dry layer before washing in solvent; **2**—the same layer after washing; **3**—the alcohol solution in which the

Fig. 4

Figure 4: Fig. 4

washing was carried out.

The adsorption mechanism of formation of such intermediate (subcolloidal) particles manifests itself somewhat differently in dry dye layers, which were prepared by pouring true solutions onto a glass substrate followed by drying. For this type of layer, a method was also developed for separating subcolloidal particles from ordinary colloidal particles. The dry layer on glass (after measurement of the absorption spectrum) was immersed in the solvent that had been used for the prepa-

formation of a true solution; then the specimen was removed and dried; after this, measurements were made of the specimen and of the solvent. It turned out that the absorption of the layer washed in this way is already devoid of the colloidal band and is characterized by a clearly expressed structure, whereas in the solvent the usual band of the true solution is observed (Fig. 4). Thus, in dry layers of dyes as well, subcolloidal particles are formed on the glass substrate.

The experimental material presented gives grounds to consider that the particles responsible for the complex structure in the absorption spectra of colloidal solutions and dry layers of dyes exist independently of the colloidal ones and can be separated from the overall system; moreover, they are formed only upon adsorption on glass.

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