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Abstract

Full Text

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PHOTOREDUCTION AND DEMETHYLATION OF THIAZINE DYES ON SILICA SOL

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In our laboratory, experiments had previously been carried out to determine the reducing ability of water bound to the surface of a silicic-acid gel—microporous glass—with respect to methylene blue ([1]). In vacuum, photobleaching of the adsorbed dye was observed, and the color reappeared when oxygen was admitted. This result was interpreted as photoreduction of the dye by water molecules or by surface hydroxyl (silanol) groups, the presence and properties of which had previously been established in the laboratory from infrared absorption spectra ([2]).

Fig. 1. Effect of sol on dye dimerization.
1—absorption spectrum of an aqueous solution of methylene blue ($5 \cdot 10^{-5}$ M/l), 2—the same in the presence of sol (1.8 g/l).

The present work repeats these experiments under different conditions in order to obtain more reliable data on the photoreduction process. In our investigations, methylene blue and other thiazine dyes were adsorbed on weakly scattering aqueous sols of silicic acid, which made it possible to obtain absorption spectra of the adsorbate not only in the visible but also in the ultraviolet region.

The sols were prepared by two methods: 1) by hydrolysis of tetraethyl orthosilicate and 2) by reaction of sodium silicate with hydrochloric acid followed by electrodialysis of the solution ([3]). To determine the concentration of silica in the sol solution, a known volume of the solution was evaporated, calcined at 500°C, and the dry residue was weighed. We used solutions with concentrations from 8 to 0.5 g/l. The reaction of the solutions was neutral in all cases.

Fig. 2. Effect of illumination on the absorption spectra of aqueous dye solutions in the presence of sol. a—methylene blue, b—azure I, and c—thionine. Curves 1, 2, 3 correspond to absorption spectra recorded, respectively, before illumination, after illumination, and one hour after admitting air into the cuvette. Curve 4 is the absorption spectrum of methylene blue after four cycles of illumination in vacuum and admission of air in the dark.

Figure 2: Fig. 2. Effect of illumination on the absorption spectra of aqueous dye solutions in the presence of sol. a—methylene blue, b—azure I, and c—thionine. Curves 1, 2, 3 correspond to absorption spectra recorded, respectively, before illumination, after illumination, and one hour after admitting air into the cuvette. Curve 4 is the absorption spectrum of methylene blue after four cycles of illumination in vacuum and admission of air in the dark.

The sol solution was mixed in a definite ratio with an aqueous solution of a thiazine dye of known concentration. The coincidence of the positions of the maxima of both the monomeric (665 mμ) and dimeric ($\sim$ 610 mμ) forms in the absorption spectrum of the dye adsorbed on the sol with the positions of the maxima in the spectrum of the aqueous dye solution indicates the absence of strong perturbations in the molecule of the latter upon adsorption. Dimerization of methylene blue increases markedly when sol is introduced, as is seen from Fig. 1 (increase of the maximum corresponding to absorption by dimers, with a relative decrease of the monomer maximum). Coagulation of the sol, occurring as a result of cooling of the solution or its aging, intensifies aggregation of the dye. The absorption spectra of aqueous

solutions of azure I and thionine upon introduction of the sol change much less.

To carry out the photochemical reaction, a flat-walled evacuable cuvette made of uviol glass was used. Beforehand, in order to pump out the air, the colored sol solution was poured into a spherical side

Fig. 2. Effect of illumination on the absorption spectra of aqueous dye solutions in the presence of sol. *a*—methylene blue, *b*—azure I, and *c*—thionine. Curves 1, 2, 3 correspond to absorption spectra recorded, respectively, before illumination, after illumination, and one hour after admitting air into the cuvette. Curve 4 is the absorption spectrum of methylene blue after four cycles of illumination in vacuum and admission of air in the dark.

arm. Pumping was carried out without freezing, since the sol coagulates on cooling. It was established that the rate of photobleaching changed little when changing from pumping with a diffusion pump to pumping with a water-jet pump. The air-free solution was poured in vacuum into the cuvette in which the absorption spectra were measured. For measurements in the visible region, an SF-4 spectrophotometer and an SF-2M recording spectrophotometer were used; in the ultraviolet region, an SF-4 spectrophotometer was used. Illumination was carried out with focused light from a 500 W cinema lamp through a water filter

and light filters that excluded wavelengths

shorter than 600 mμ (for methylene blue and azure I) and 550 mμ (for thionine). The energy absorbed by the solution when the cuvette was placed at the focus of the lamp was 0.36 W for methylene blue and 0.21 W for thionine, at the dye concentration usually used, $5 \cdot 10^{-5}$ M/l.

Figure 2 shows changes in the absorption spectra of solutions of methylene blue, azure I, and thionine in the presence of sol after illumination. As little as five minutes' illumination of a methylene-blue solution causes a substantial weakening of the dye absorption bands both in the visible and in the ultraviolet regions. The bleaching process is accompanied by the appearance of an absorption band with a maximum at 255 mμ, corresponding to the leuco compound of methylene blue, which confirms that it is indeed photoreduction of the dye ([4]). After air is admitted into the cuvette with the bleached solution, the color regenerates, but the absorption band is found to be shifted toward shorter wavelengths, as in experiments with microporous glass ([1]). The new position of the maximum coincides with the absorption maximum of the dye azure I, shown in Fig. 2b. A solution of azure in the presence of sol is considerably less photosensitive than a solution of methylene blue, and only after 30–40 min of illumination do changes in the spectrum become noticeable. In this case incomplete bleaching is observed, with a shift of the maximum toward the short-wave side and the appearance of the leuco-compound absorption band in the ultraviolet. The regeneration product after admission of air has a spectrum coinciding with the absorption spectrum of thionine (Fig. 2c). A solution of thionine in the presence of sol is insensitive to illumination. The slight bleaching observed as a result of many hours' illumination is irreversible and is not accompanied by a shift of the band.

Upon repeated cycles of illuminating solutions of methylene blue with sol in vacuum to complete bleaching and admitting air until regeneration, a further shift of the band is observed, with a decrease in the optical density at the maximum. The final product of such treatment has an absorption spectrum lying between the spectrum of azure I and that of thionine (Fig. 2a, curve 4).

The addition of a small amount of acid to the sol solution containing the dye does not change the latter' s spectrum, but greatly lowers its sensitivity to light. Already at pH 5, complete bleaching requires approximately 1.5–2 hours instead of 10–15 min for a neutral solution. At lower pH values the solution is practically insensitive to illumination.

The leuco form of methylene blue formed as a result of photoreduction in the presence of sol has the same reducing action toward inorganic oxidants (for example, Fe^{3+} ions) as the leuco form obtained under homogeneous conditions ([5]). When, in vacuum, several drops of an aqueous solution of ferric chloride with *o*-phenanthroline are added to a solution with sol that has been bleached by illumination, a violet coloration appears, owing to regeneration of methylene blue, with the simultaneous appearance of the red coloration of the $Fe(\text{Phen})_3^{2+}$

ion. Just as in the case of oxidation of the leuco form by oxygen, the dye maximum after restoration of the color shifts toward the short-wave side.

It should be noted that the reduction reaction of Fe^{3+} ions by the leuco form of the dye takes place entirely on the surface of the sol, and not in the bulk. A similar reaction carried out on powdered silica gel showed that the amount of Fe^{2+} ions present in the solution (after separation of the powder by centrifugation) is negligibly small compared with that adsorbed on the silica-gel surface.

The accidental coincidence of the absorption maximum of the photoproduct of methylene blue with the dimer maximum of the latter was attributed in the preceding work ([1]) to the process of dimerization of the dye occurring under the influence of heating of the adsorbate by light. However, an increase in temperature should, on the contrary, hinder dimerization of the dye ([6,7]). In our

under the conditions, heating the solution with regenerated methylene blue on the sol up to 70° caused no change whatever in the absorption spectrum. The change in the spectrum observed upon regeneration is completely irreversible and therefore cannot be attributed to dimerization of the dye.

This is also confirmed by the spectra presented. Curve 2 in Fig. 2a has a well-pronounced inflection on the short-wavelength slope, which is characteristic of absorption spectra of dye monomers. In addition, the absorption spectra of dimers of both methylene blue and other dyes have a more or less pronounced subsidiary maximum on the long-wavelength slope ([7], [8]). The shift of the ultraviolet absorption band of the regenerated dye relative to the original one is also noteworthy. In the case of dimerization, no shift of the absorption band of methylene blue in the ultraviolet region occurs ([9]).

Thus, as a result of oxidation of the leuco form of thiazine dyes adsorbed on aqueous sols and microporous glass, a new dye is formed, and not a dimerization of the original one. The coincidence of the absorption spectra of the photoproduct of methylene blue with the spectrum of azure I and, correspondingly, of the absorption spectrum of the photoproduct of azure I with the spectrum of thionine makes it possible to suppose that a process of demethylation of thiazine dyes takes place simultaneously with the formation of the leuco form. Indeed, azure I and thionine differ from methylene blue only by the successive replacement of one and two groups $N(CH_3)_2$ by NH_2.

An analogous phenomenon was observed earlier by Wotherspoon and Oster ([10]) for the same thiazine dyes adsorbed on polyacrylic and polymethacrylic acids, although without formation of the leuco form. In our case the formation of the leuco form is closely connected with the demethylation process. One may suppose the formation of an adsorption bond of the dye with surface OH groups of silica, occurring both through the central nitrogen atom and through the nitrogen of the auxochromic groups $N(CH_3)$. Evidently, photoreduction of the dye molecule of methylene blue and azure at the expense of hydrogen atoms of the OH groups of silica must be accompanied by replacement of the methyl

groups of the dye by hydrogen atoms and must cause methylation of the surface groups—a process well studied for solid silica gel under other conditions ([11]). The thionine molecule, having no methyl groups and being unable to carry out such an exchange, does not form a leuco form.

The photoreduction reaction of methylene blue and azure proceeding to completion gives grounds for assuming that under our conditions all dye molecules are in the adsorbed state. The suppression of the photoreduction reaction by acid that we observed is possibly due to disruption of this adsorption interaction.

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Note: Figure translations are in progress. See original paper for figures.