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Fig. 1

Figure 1: Fig. 1

Abstract

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SPECTRAL STUDY OF THE INTERACTION OF TWO DYES IN SOLUTION

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It is known that in solutions of many dyes there occurs a process of aggregation, in particular dimerization. It consists in the association of two or several ions with one another. One of the most sensitive methods for recording this process is the spectroscopic method, based on the fact that a change in the state of a dye in solution is accompanied by a change in its absorption spectrum.

The study of the absorption spectra of solutions containing two azo dyes enabled Lemin and Vickerstaff (^{1}), as well as Derbyshire and Peters (^{2}), to establish the possibility that bimolecular compounds consisting of both dyes arise in them.

A similar phenomenon was observed by us in aqueous solutions containing a mixture of dyes of the thiazine and acridine series. Among the thiazines, the following were considered: thionine, methylene blue, and toluidine blue. Among the acridines—trypaflavine, acridine yellow, rhoduline orange, and also unsubstituted acridine (its hydrochloride salt). Measurements were made on an SF-4 spectrophotometer.

Fig. 1. Absorption of a mixture of methylene blue ($C = 2.8 \cdot 10^{-4}$ mol/l) and acridine yellow ($C = 2.8 \cdot 10^{-4}$ mol/l) in aqueous solution. **1**—calculated curve obtained from the condition of additivity of the absorption of both dyes; **2**—measured absorption of the mixture.

Figure 1 presents the absorption spectra of a mixture of two dyes (methylene blue and acridine yellow) in aqueous solution. Curve 1 is the calculated curve corresponding to the condition of additivity of absorption of both dyes; curve 2 is the experimentally obtained absorption of the mixture. As can be seen from the figure, the interaction of the dyes causes a change in the shape and a shift of the absorption band of each dye toward longer wavelengths. This is due to a change in the absorption spectrum of a dye when it binds with another, and also to a change in the state of the dyes' own aggregation in the mixture. To exclude the latter circumstance, the effect of various amounts of acridine yellow

Fig. 2

Figure 2: Fig. 2

was studied on such a dilute solution of methylene blue that the concentration of identical dimers in it was small (see Fig. 2).

The presence of a common point of intersection of several curves indicates that absorption in this region of the spectrum is determined by only two kinds of absorbing centers—free methylene blue and methylene blue bound with acridine yellow.

On the basis of the law of mass action, we calculated the fraction of methylene blue bound to acridine and its derivatives (α) at different contents of the latter in solution, as well as the absorption curves of methylene blue completely bound to these dyes (the dashed curve in Fig. 2)*. The same data were obtained for thionine and toluidine blue bound to acridine yellow.

For these complexes, the constants of their dissociation were calculated by the formula

$$K = \frac{[(1-\alpha)C_{\text{syn}}][\alpha_{\text{acr}}C_{\text{acr}} - \alpha C_{\text{syn}}]}{[\alpha C_{\text{syn}}]},$$

where C_{syn} is the concentration of the thiazine dye, C_{acr} is the concentration of the acridine dye, $1-\alpha$ is the fraction of free thiazine dye, and α_{acr} is the fraction of monomeric acridine dye (this factor is introduced to take into account the self-aggregation of the acridine dye). The results of the calculations are given in Table 1**.

Fig. 2. Effect of different amounts of acridine yellow on the absorption of methylene blue ($C = 1.41 \cdot 10^{-5}$ mol/l) in aqueous solution. 1 –methylene blue without acridine yellow; 2 –addition of acridine yellow ($C = 1.78 \cdot 10^{-5}$ mol/l); 3 –addition of acridine yellow ($C = 3.55 \cdot 10^{-5}$ mol/l); 4 –addition of acridine yellow ($C = 7.1 \cdot 10^{-5}$ mol/l); 5 –addition of acridine yellow ($C = 1.42 \cdot 10^{-4}$ mol/l); 6 –addition of acridine yellow ($C = 2.84 \cdot 10^{-4}$ mol/l); 7 –methylene blue completely bound to acridine yellow.

It is seen from Table 1 that the activity of interaction in the class of thiazines increases in the sequence: thionine –methylene blue –toluidine blue; in the class of acridines, unsubstituted acridine binds less than the others, while acridine yellow and rhoduline orange are more active in this respect.

According to our data, enhancement of self-aggregation in the class of acridines proceeds in the sequence: acridine –trypaflavine –acridine yellow –rhoduline orange; in the class of thiazines: thionine –methylene blue –toluidine blue. Thus, it turns out that the activity of binding of two dyes to each other is the greater, the greater the tendency of each of them toward homogeneous dimerization. The only exception is rhoduline orange, whose capacity for self-aggregation is considerably higher than that of all the other acridine dyes, while its capacity for binding methylene blue is approximately the same as that of acridine yellow.

Investigation of the influence of solvent, temperature, and storage time of the solutions showed that the properties of the complexes are analogous to the properties of ordinary dimers:

1) Both dimers and heterogeneous complexes arise mainly in aqueous solutions. In organic solvents, complex formation was observed by us only when the temperature was lowered.

* The calculation was carried out by a method analogous to that which we previously applied in the case of homogeneous dimerization of methylene blue (3).

** The results of the calculation of the quantities α, K, and the absorption curves are somewhat distorted by the fact that the initial methylene-blue solution nevertheless contains some amount of homogeneous dimers. Work with still more dilute solutions is made difficult by their rapid decolorization (4).

2) Both are destroyed when the temperature is raised. Heating diminishes the deviation of the absorption curves of the mixture from the curves calculated from the condition of additivity.
3) The formation of complexes, like the formation of homogeneous aggregates (when the concentration is increased or when an electrolyte is introduced into the solution), in some way stabilizes the magnitude of the absorption of dilute solutions prone to decolorization (^{4}).

As already mentioned above, the absorption curve of each of the interacting dyes, in addition to being shifted, undergoes a change in shape (Fig. 1). The presence of the second dye causes a decrease in the relative magnitude of the secondary short-wavelength maximum, which indicates a decrease in the fraction of dimers in the solution. This indicates that complex formation is accompanied by a weakening of the aggregation of each of the interacting dyes. The greatest disaggregation is observed, naturally, under the action of the second component that is most active in the sense of binding. Thus, the influence of acridine in this respect is considerably weaker than the influence of its derivatives.

Table 1

Dissociation constants of complexes of two dyes

Acridine dye	Thiazine dye: thionine	Thiazine dye: methylene blue	Thiazine dye: toluidine blue
Acridine	–	$11{,}8 \cdot 10^{-4}$	–
Trypaflavine	–	$1{,}4 \cdot 10^{-4}$	–

Acridine dye	Thiazine dye: thionine	Thiazine dye: methylene blue	Thiazine dye: toluidine blue
Acridine yellow	$1{,}2 \cdot 10^{-4}$	$0{,}8 \cdot 10^{-4}$	$0{,}4 \cdot 10^{-4}$
Rhoduline orange	–	$0{,}8 \cdot 10^{-4}$	–

On the basis of an investigation of the temperature dependence of the complex-formation process, we calculated the energy of complex formation. For the compound of methylene blue with acridine yellow it proved to be, approximately, 9 kcal/mole. This is one and a half times greater than the energy of homogeneous dimerization of methylene blue,* which is in full agreement with the fact of the destruction of homogeneous aggregation during complex formation.

A weakening of homogeneous aggregation was also observed in the interaction of other dyes that we studied (rhodamine B–acridine yellow and sulfonated phthalocyanine—tartrazine).

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* The dimerization energy of methylene blue is 6 kcal/mole. The difference of this value from that given by us earlier (3) is explained by a certain refinement of the calculation.

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

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