On the Absorption Spectra of Certain Dyes in Mixed Solvents

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Kh. L. Arvan and N. V. Ivanova

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As has already been reported earlier (1), for certain dyes in mixed solvents (water—organic solvent) a shift of the absorption band toward longer wavelengths is observed relative to its position in each of the pure solvents. It was not possible to connect this shift with changes in the physicochemical properties of the solvent (viscosity, refractive index,

Fig. 1. Dependence of the ratio of the magnitudes of the absorption maxima of certain dyes on the dye concentration in aqueous solutions: *a*—rose bengal, —eosin, —rhodamine B, —pyronine G, —methylene blue, —toluidine blue.

Fig. 2. Dependence of the position of the absorption-band maxima of certain dyes on the composition of the solvent (water—acetone). The numbers on the left indicate the magnitude of the band maxima of absorption in aqueous solutions: —tartrazine; the remaining designations of the curves are the same as in Fig. 1.

dipole moment, volume, etc.) upon change in its composition. In this connection, a hypothesis was put forward concerning mixed solvation of dyes in such solutions.

The magnitude of the relative shift of the band is determined both by the composition of the solvent and by the properties of the dissolved dye. In particular, the ability of the dye to associate in aqueous solutions proved to be significant.

The latter, as indicated, can be characterized, to a first approximation, by the quantity γ—the ratio of the maxima of the long-wavelength and short-wavelength absorption bands, attributed to monomers and dimers. The dependence of the value of this ratio on the concentration of the dye in aqueous solution determines the greater or lesser tendency of the dye to association. In this connection one should consider both the steepness of the slope of the γ curve and the dye concentration at which the deviation of the curve from the horizontal direction begins.

Figure 1 presents the dependence of the value of γ on concentration for some of the dyes studied in aqueous solutions, and Fig. 2 presents the dependence of the position of the maximum of the absorption band on the composition of the water-acetone mixture for these dyes. A comparison of the figures shows that the greatest dependence of the form of the absorption band on concentration,

Fig. 3

Figure 1: Fig. 3

characterized by the change in the value of γ, is observed for those dyes for which the greatest shift of the absorption band in mixtures occurs relative to its position in the pure solvents (methylene blue, rhodamine B, toluidine blue). Rhoduline orange, night blue, Nile blue, and Capri blue behave similarly. For those dyes whose absorption band in mixtures occupies a position intermediate between the positions in the pure solvents, the dependence of the value of γ on the dye concentration in aqueous solutions is much weaker (for example, eosin and Bengal rose).

Fig. 3. Dependence of the position of the maximum of the absorption band of rhoduline orange NO on the dielectric constant of the solvent (for pure solvents and mixtures): 1—water, 2—formamide, 3—methyl alcohol, 4—ethyl alcohol, 5—propyl alcohol, 6—butyl alcohol, 7—amyl alcohol, 8—acetone

In addition, a monotonic shift of the absorption band with a change in the composition of the solvent is observed for tartrazine, Congo red, and some other dyes, whose absorption spectra change almost not at all with a change in the dye concentration.

For nonassociating compounds, phthalimides, a nonmonotonic shift of the absorption bands analogous to that described above, with a change in the composition of the mixed solvent (water–dioxane), was observed by Klochkov[2]. The author explained this by the dependence of the position of the absorption bands on the dielectric constant of the solvent. Indeed, in this case the position of the absorption band is determined by the dielectric constant of the solvent both for pure solvents and for their mixtures.

For the associating dyes we investigated, the position of the absorption bands in mixtures, as is evident from Fig. 3, does not coincide with their position in pure solvents having the corresponding dielectric constants. Moreover, the shift of the spectrum with a change in the composition of the mixed solvent is opposite to that observed with an analogous change in the dielectric constant as a result of replacing one pure solvent by another. In view of this, taking into account the influence of the dielectric constant of the solvent further strengthens the relative shift of the spectra under mixed solvation.

From all these data it follows that the formation of mixed solvates, characterized by a shift of the absorption bands, is observed mainly for associating dyes. The question arises whether the presence of associates in solution is necessary for mixed solvation. However, a specially carried out investigation showed that rela-

the appreciable shift of the absorption band does not depend on the concentration of the dye, i.e., on its degree of dispersion.

What is significant in this respect is only the tendency of a given dye toward association, i.e., its structure. In view of the parallelism of the processes of association and mixed solvation, it may be assumed that they are caused by the presence of the same groups in the dye molecules and by the same intermolecular forces. The mobile equilibrium in solution is determined by the predominance of one process over the other. This, apparently, explains the cessation of dye association upon the formation of mixed solvates ([1]).

In conclusion, we express our gratitude to Prof. M. V. Savost' yanova for her constant interest in and attention to the work.

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REFERENCES

[1] Kh. L. Arvan, *Izv. AN SSSR, ser. fiz.*, **20**, 443 (1956). [2] V. P. Klochkov, *Optics and Spectroscopy*, **1**, 4, 546 (1956).

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