PHYSICAL CHEMISTRY

S. V. NATANSON, N. S. SPASSOKUKOTSKII, E. S. KOZLOVA

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

S. V. NATANSON, N. S. SPASSOKUKOTSKII, E. S. KOZLOVA

ON THE FORMATION OF THE *J*-STATE IN AQUEOUS SOLUTIONS OF CYANINE DYES

(Presented by Academician A. N. Terenin, 21 IV 1964)

Many cyanine dyes form, in aqueous and water-gelatin solutions or in solutions of other high-molecular compounds, and also upon adsorption on various solid surfaces, polymolecular states that give rise in the absorption spectra to bands shifted into the short-wavelength region of the spectrum (*H*-bands) or into the longer-wavelength region (*J*-bands) relative to the principal molecular *M*-band ([1,2]). The study of changes in the absorption spectra of aqueous solutions of cyanine dyes as a function of the concentration and temperature of the solution ([1,2,7,8,10,11,19]) led many investigators to the conclusion that the appearance of the *J*-band in absorption spectra is connected with the formation of the corresponding polymolecular states of the dye in the solutions themselves.

In investigating the sensitizing action and physicochemical properties of cyanine dyes, we encountered a number of facts that made us doubt the correctness of such a view. These include, for example, the slight shift of the absorption maximum of the *J*-band in dyes adsorbed on silver bromide or on glass ([9]) in comparison with aqueous solutions; the change in the color of the dye solution depending on the thickness of the layer (for example, dyes I and II are red in a flask, violet-blue in a thin layer); and the fact that in some cases the absorption intensity of thin layers of one and the same solution in the region of the *J*-band proved higher than that observed in a thicker layer (see curves 1 and 2, Figs. 1 and 3).

All the facts cited are well explained if one assumes that *J*-states are formed exclusively upon adsorption on some surfaces, in particular on the glass walls of the vessel ([23]).

To verify the correctness of this assumption, measurements were made of the absorption spectra of one and the same aqueous dye solution in cuvettes with a larger layer thickness relative to the same solution with a smaller measured layer thickness (for example, 0.5 mm relative to 0.2 mm—Figs. 1 and 2, curve 3), and also, as usual, relative to analogous cuvettes filled with water (Figs. 1, 2, 3, curves 1 and 2). This method of measurement was undertaken in order, as far as possible, to eliminate the absorption of dye adsorbed on the walls of the cuvettes.

chemical structures I-III

Figure 1: chemical structures I-III

Fig. 1

Figure 2: Fig. 1

Thus a series of carbo- and monomethinecyanine dyes known for their tendency to form J-states in water was studied. As an example, this article gives the results of investigation of three dyes of the following structure:

I II III

The aqueous solutions used of these dyes were close to saturation—I and II, $5 \cdot 10^{-4}$ mol/liter; III, $1 \cdot 10^{-2}$ mol/liter.

The results of measuring the absorption spectra of aqueous dye solutions relative to water show that, in layers of different thickness, the intensity of the J-band is approximately the same (Figs. 1-3, curves 1 and 2), whereas when the absorption of these solutions is measured in layers of greater thickness relative to layers of lesser thickness it disappears altogether, even to the point of the appearance of a negative absorption value (Fig. 1, curve 3), or its intensity drops sharply (Fig. 2, curve 3). In this case the presence of weak or negative absorption in the region of the J-band, i.e., insufficient reproducibility of its intensity, is in such cases due to accidental causes (the quality of the glass and the polishing of its surfaces, the duration of the interval between filling the cuvettes, temperature, etc.). At the same time the intensity of the H-bands, as well as of the principal molecular band (M), in the thin layer is always correspondingly less than in the thick one, as should be the case in the presence of absorbing particles in the solution itself (Figs. 1-3, curves 1, 2).

Fig. 1. Absorption curves of a $1 \cdot 10^{-4}$ M aqueous solution of dye I, obtained when measuring in glass cuvettes: 1 —0.5 mm relative to 0.5 mm of water; 2 — 0.2 mm relative to 0.2 mm of water; 3 —0.5 mm relative to 0.2 mm of the same dye solution.

For final proof we tried to find materials that do not adsorb the dye. Coating the glass with fat, vaseline, and wax was investigated, as was the use of cuvettes made of polyethylene and methyl methacrylate. On all the listed substances adsorption of dyes with formation of J-states takes place, although it proceeds more slowly than on glass. The most favorable material in this respect proved to be methyl methacrylate. It is seen from Fig. 2 that in the absorption spectra of dye II solution in a methyl methacrylate cuvette, with the usual method of measurement (relative to water), the J-band is completely absent (curve 4). However, as the solution stood in the methyl methacrylate cuvette, in such a thin layer, after 15-20 min the appearance of the J-state was observed; the intensity of its absorption band gradually increased with time, similarly to what

Fig. 2

Figure 3: Fig. 2

Fig. 3

Figure 4: Fig. 3

takes place in Fig. 3 (curve 3).

Fig. 2. Absorption curves of a $5 \cdot 10^{-4}$ M aqueous solution of dye II, obtained when measuring: 1 –0.5 mm relative to 0.5 mm of water, 2 –0.2 mm relative to 0.2 mm of water, 3 –0.5 mm relative to 0.2 mm of the same dye solution, 4 –0.5 mm relative to 0.5 mm of water. 1-3 –in glass cuvettes, 4 –in a methyl methacrylate cuvette.

It seems quite probable that the J-state on the surface of glass (or of another adsorbent) is produced as a result of the adsorption of individual dye molecules, which, apparently, may be centers of ob-

of these polymolecular filamentary ([1,2]) particles. The principal axis of the latter may in this case be directed at some angle to the surface of the adsorbent ([22]). Owing to this, at relatively high concentrations of dye solutions, gels may form which, on the surface of glass upon evaporation of the solvent, give homogeneous film-like layers (cf. ([9])). The appearance of gels is probably connected, as usual, with the formation of comparatively weak bonds between the individual filaments of polymolecular particles. The possibility is not excluded of the formation of J-states on the walls of the vessel and in alcoholic solutions at a high dye concentration, especially at low temperatures, similar to that described by Scheibe ([24]). It should be noted that the width of the J-band, its intensity, and its position in the spectrum are apparently determined by the formation, in a given system, of one uniform J-state or of several, whose absorption maxima often differ by only 10-20 mμ, and therefore merge into one broader band ([19,22,25]). In the case of nonpolymerizing cyanines, for example thiazolinocarbocyanine, with gradual evaporation of the solvent a homogeneous layer analogous to that described above is not obtained. Instead, a layer is formed consisting of individual crystallites of the dye, readily visible under the microscope.

Fig. 3. Absorption curves of a $1 \cdot 10^{-2}$ M aqueous solution of dye III, obtained upon measurement in layers of different thickness relative to water: **1** and **2**–between glass plates, **3**–between plates of methyl methacrylate.

As a result of the work carried out it may be considered proven (at least for the dyes investigated) that in aqueous solutions polymolecular J-states are formed only as a result of adsorption of the dye on solid surfaces or on some other adsorbents.

All-Union Scientific Research
Kino-Photo Institute

Received
14 IV 1964

CITED LITERATURE

[1] E. E. **Jelley**, Nature, **138**, 1009 (1936); **139**, 631 (1937).
[2] G. **Scheibe**, Angew. Chem., **49**, 563 (1936); **50**, 51 (1937).
[3] G. **Scheibe**, Naturwiss., **25**, 495 (1937).
[4] J. A. **Leermakers**, B. H. **Carrol**, S. J. **Staud**, J. Chem. Phys., **5**, 873 (1937).
[5] G. **Scheibe**, A. **Marreis**, H. **Ecker**, Naturwiss., **25**, 474 (1937).
[6] G. **Scheibe**, Sci. et inds Photogr., **8**, 97 (1937).
[7] G. **Scheibe**, Koll. Zs., **82**, 1 (1938).
[8] H. **Ecker**, Koll. Zs., **92**, 35 (1940).
[9] A. **Schöntäg**, Zs. Wiss. Photogr., **99**, 18 (1940).
[10] S. E. **Sheppard**, Rev. Mod. Phys., **14**, 303 (1942).
[11] S. E. **Sheppard**, A. L. **Geddes**, J. Am. Chem. Soc., **66**, 2003 (1944).
[12] S. E. **Sheppard**, R. C. **Houk**, C. **Dittmar**, J. Phys. Chem., **46**, 158 (1942); Sci. inds photogr., **179**, 104 (1946).
[13] H. O. **Dickinson**, Trans. Farad. Soc., **43**, 486 (1947).
[14] G. **Scheibe**, Zs. Elektrochem., **52**, 283 (1948).
[15] R. **Merrill**, R. **Spenser**, J. Am. Chem. Soc., **72**, 2894 (1950).
[16] B. H. **Carroll**, W. **West**, Fundam. Mechan. Photogr. Sensit., London, 1951, p. 162.
[17] H. W. **Wood**, Sci. et inds Photogr., **23A**, 110 (1952).
[18] E. B. **Lifshits**, S. V. **Natanson**, I. I. **Levkoev**, ZhFKh, **28**, 1572 (1954).
[19] S. V. **Natanson**, DAN, **106**, 497 (1956).
[20] A. D. **Derkacheva**, Izv. AN SSSR, ser. fiz., **20**, 410 (1956).
[21] M. V. **Savostyanova**, Usp. khim., **32**, 1233 (1963).
[22] S. V. **Natanson**, Report at the International Colloquium on Scientific Photography in Liège, 1959; Congr. et Colloq. l' Université de Liège, **23**, Scient. photogr., 1962, p. 457; Kinotekhnika, **2**, 23 (1963).
[23] S. V. **Natanson**, N. I. **Sennikova**, Kinotekhnika, **2**, 56 (1963).
[24] G. **Scheibe**, Zs. Naturforsch., **9b**, 85 (1954).
[25] I. I. **Levkoev**, E. B. **Lifshits**, S. V. **Natanson**, N. N. **Sveshnikov**, Z. P. **Sytnik**, Report at the International Conference on Scientific Photography, Cologne, 1956; Trudy NIKFI, **10** (20), 55 (1957); Ergebn. Intern. Konf. Wiss. Phot., Köln, 1958, S. 109.

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