BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1667—1670 (1970)

The Visible Spectra of Alizarine Saphirol SE in Water-Dioxane Mixtures

Masaru MITSUISHI, Mieko HASHIZUME, Akira KATAYAMA[*1] and Nobuhiko KUROKI[*1]

Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano

(Received December 2, 1969)

The visible absorption spectra of Alizarine Saphirol SE in water-dioxane mixtures were obtained, and the spectral changes were considered on the basis of the results of the conductance measurements of the dye. In the spectra of the dye in the mixtures containing less than 60% dioxane, the absorption was found to increase with an increase in the dioxane content. This spectral change was attributed to the decrease in the tendency of the dye to aggregate. In the spectra of the dye in the mixtures containing more than 70% dioxane, however, the absorption found to decrease with an increase in the dioxane content, *i.e.*, with a reduction in the dielectric constant of the solvent. This spectral change was considered to be characteristic of the increase in the electrostatic interaction between the dye ion and the counter ion.

In a previous paper,[1] the ion-association constants were determined by means of Shedlovsky's treatment from the conductance behavior of Alizarine Saphirol SE in water-dioxane mixtures, and they were found to become enormously larger with an increase in the dioxane content of the mixtures, *i.e.*, with a lowering of the dielectric constant. In a solvent with a low dielectric constant, a spectrum characteristic of the ion association between the dye ion and the counter ion can be expected.

In water-organic solvent mixtures having a medium (*ca.* 20) or a low dielectric constant (*ca.* 5), however, no spectrum characteristic of the ion association of the aromatic sulfonate ion with the sodium ion has yet been reported. Therefore, it seems that it would be valuable to examine whether a characteristic spectrum of the interaction between the dye ion and the counter ion is found in the spectrum of Alizarine Saphirol in water-dioxane mixtures.

Experimental

The Alizarine Saphirol SE (sodium salt of 1,5-dihydroxy-4,8-diaminoanthraquinone-2-sulfonic acid) was

---

[*1] College of Engineering, University of Osaka Prefecture, Sakai, Osaka.

1) M. Mitsuishi, Y. Funatsu and N. Kuroki, This Bulletin, **42**, 2384 (1969).

a laboratory stock used in a previous work.[2]

The dioxane was purified by the method described in the previous work.[1]

The visible absorption spectra of the dye were measured by the procedures described in another previous work.[2]

Results and Discussion

The spectra of Alizarine Saphirol in water-dioxane mixtures are shown in Figs. 1 and 2. The spectra of the dye in water and in water-dioxane mixtures containing less than 60% dioxane in Fig. 1 are quite similar to those in water-ethanol mixtures.[2]

The spectrum of Alizarine Saphirol in water is characterized by a prominent peak at about 590 mμ (α-band) and a shoulder at about 620 mμ (β-band). Both the α- and β- bands are intensified by increasing the dioxane content, the β -band is more intensified than the α-band in the solvents containing more than 10% dioxane, and the β-band becomes a prominent peak. The wavelengths of maximal absorption are found to shift towards longer wavelengths. This spectral behaviour is similar to that found in the spectra of the dye in water-ethanol mixtures.[2] The curves from III to VI in Fig. 1 and all of the curves in Fig. 2 have doublet peaks at about 590 and 630 mμ.

These doublet peaks in the main band are known to be characteristic of a monomeric dye with two electron-donating groups, such as hydroxyl or amino groups, in the 1- and 4- positions of an anthraquinone nucleus.[3,4] From the conductance data reported in a previous paper,[1] Alizarine Saphirol was supposed to be monomeric in mixtures containing more than 60% dioxane. Therefore, the spectral changes produced by increasing the dioxane in the mixtures containing less than 60% dioxane (in Fig. 1) may be supposed to come from the decrease in the tendency of the dye to aggregate.

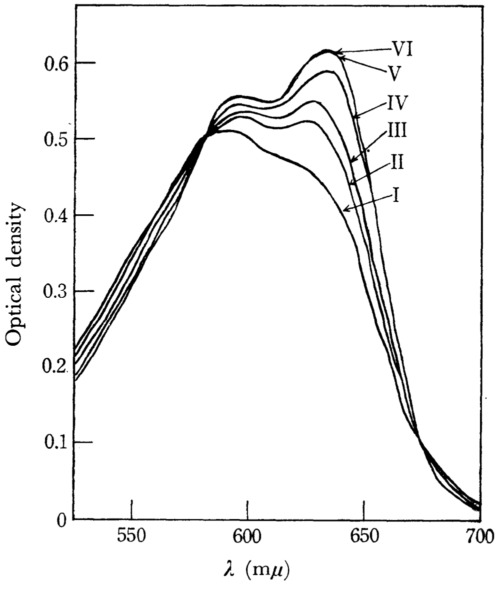

Fig. 1. Spectra of Alizarine Saphirol SE in water-dioxane mixtures at 25°C (3.79×10^{-5} mol/l, 10 mm cell), dioxane concentration; I, 0; II, 10%; III, 20%, IV, 45%; V, 60%; VI, 70%.

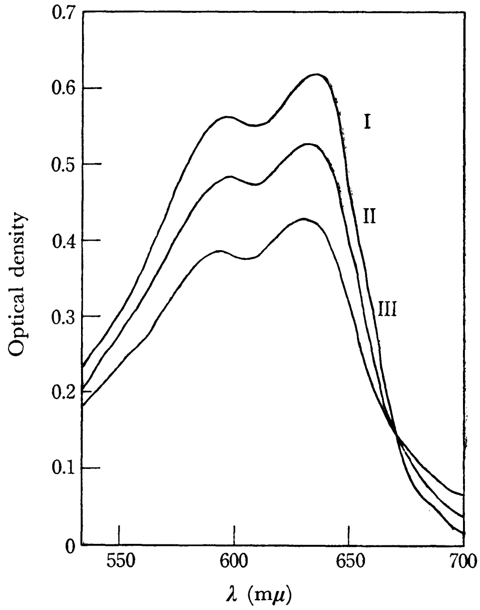

Fig. 2. Spectra of Alizarine Saphirol SE in water-dioxane mixtures at 25°C (3.79×10^{-5} mol/l, 10 mm cell), dioxane concentration; I, 70%; II, 82%; III, 85%.

In Fig. 2, the intensities of both the α- and β-bands are found to decrease progressively with an increase in the dioxane content in the mixtures containing more than 70% dioxane, and an isosbestic point is found at about 670 mμ. As no such spectral change in Alizarine Saphirol is found in water-ethanol mixtures, the spectral changes induced by an increase in the content may be supposed to be caused by the reduction of the dielectric constant of the mixtures to values lower than those of the water-ethanol mixtures.*2

The presence of an isosbestic point at about 670 mμ suggests that a certain equilibrium is set up in the mixtures.

Next, let us examine the cause of the spectral changes induced by increasing the dioxane content

---

[2] M. Mitsuishi and G. Aida, This Bulletin, **39**, 246 (1966).

[3] C. H. Allen, C. V. Wilson and C. F. Frame, *J. Org. Chem.*, **7**, 169 (1942).

[4] G. S. Egerton and A. G. Roach, *J. Soc. Dyers Colour.*, **74**, 401 (1958).

*2 The dielectric constants of ethanol and of 70, 82, and 85% dioxane are 24.3, 17.7, 9.5, and 8.2 respectively.

in the mixtures. In previous papers,[1,5)] the following equilibrium among the dye ion, the sodium ion, and the ionic associate of the dye was established in water-dioxane mixtures with a low dielectric constant;

$$D^- + Na^+ \rightleftarrows (D^-Na^+)^0 \qquad (1)$$

where, D^- and $(D^- \, Na^+)^0$ are the dye ion and the ionic associate respectively.

The ion-association constant, K_A, was obtained by the equation;

$$K_A = \frac{1-2}{c\alpha^2 f_\pm{}^2} \qquad (2)$$

where, α and $f_\pm$ are the degree of dissociation of the ionic associate and the mean activity coefficient of the ion at the dye concentration, C.

The electrostatic interaction between the dye ion and the counter ion was found to increase enormously with an increase in the dioxane content in the mixtures.[1),*3] Accordingly, the spectral changes seen in Fig. 2 may be produced when the ion-association constant of the dye increases enormously with an increase in the dioxane contents of the mixtures.

If the spectral changes in Alizarine Saphirol induced by an increase in the dioxane content are caused by the increase in the electrostatic interaction between the dye ion and the counter ion, *i.e.*, by the increase in the concentration of the ionic associate, spectral changes similar to those shown in Fig. 2 must be observed under any condition that cause the equilibrium constant, K_A, of Eq. (2) to vary.

The ion-association constants of the dye in water-dioxane mixtures with a low dielectric constant and a constant composition were found to increase with a rise in the temperature of the solution.[5),*4] In water-dioxane mixtures of a constant composition, the degree of dissociation of the ionic associate obviously decreases with an increase in the dye concentration; that is the concentration of the ionic associate increase with an increase in the dye concentration.[*5]

Therefore, if the spectral changes induced by an increase in the dioxane content (Fig. 2) are similar to those spectral changes induced by raising the temperature of the solution and by increasing the dye concentration in the mixtures with a constant composition, the spectral changes shown in Fig. 2 may be concluded to be induced by the increase in the interaction between the dye ion and the counter ion.

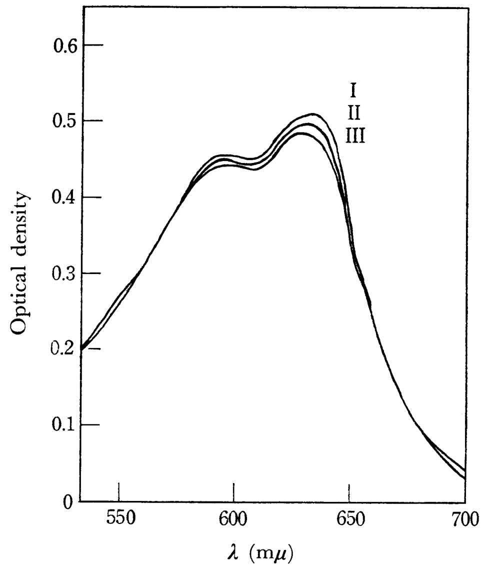

Fig. 3. Spectra of Alizarine Saphirol SE in 82% dioxane at various temperatures (3.79×10^{-5} mol/*l*, 10 mm cell); I at 16°C; II, 24°C; III, 35°C.

The effect of raising the temperature of the solution on the visible spectrum of Alizarine Saphirol in 82% dioxane is shown in Fig. 3. The intensities of both the α- and β-bands are found to decrease with a rise in the temperature of the solution, *i.e.*, with an increase in the ion-association constant, and an isosbestic point is found at about 670 mμ. The spectral change seen in Fig. 3 is found to be less than that seen in Fig. 2, but these spectral changes can be explained reasonably by taking into consideration the fact that the effect of the increase of dioxane content is larger than that of the elevation of the temperature of the solvent with a constant composition on the ion-association constant of the dye.[*6]

The visible spectrum of Alizarine Saphirol in 70% dioxane is shown in Fig. 4. The intensities of both the α and β-bands are found to decrease with an increase in the dye concentration, and an isosbestic point is found at about 670 mμ. The decrease in the intensities seen in Fig. 4 may be supposed to be induced by the decrease in the degree of dissociation of the ionic associate. The spectral change shown in Fig. 4 is less than that shown in Fig. 2, but these changes can be explained reasonably by taking into consideration the fact that the effect of the increase in the dioxane content is larger than that of the increase in the dye concentration in the solvent

---

5) M. Mitsuishi, M. Hashizume, A. Katayama and N. Kuroki, This Bulletin, **43**, 960 (1970).

[*3] The ion association constants of the dye in 70, 82, and 85% dioxane at 25°C are 1.88×10^3, 9.86×10^3, and 3.46×10^4 respectively.

[*4] For example, the ion association constants at 15, 25, and 35°C in 82% dioxane are 8.67×10^3, 9.86×10^3, and 1.30×10^4 respectively.

[*5] For example, the degrees of the dissociation of the ionic associate at dye concentration of 0.79, 2.34, and 5.64×10^{-5} mol/*l* in 70% dioxane are estimated to be about 0.990, 0.970, and 0.935 respectively.

[*6] *Cf.* footnotes *4 and *3.

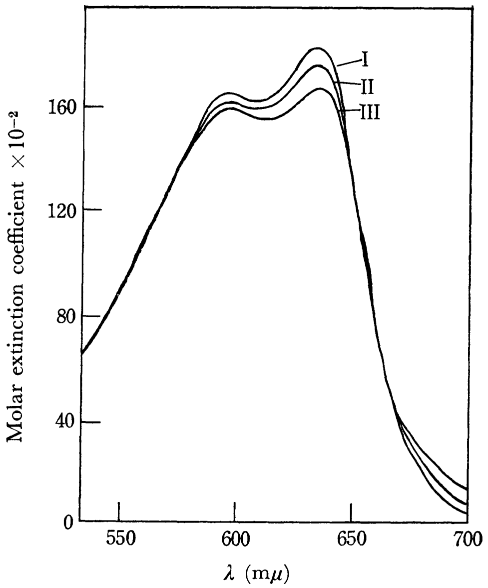

Fig. 4. Spectra of Alizarine Saphirol SE in 70% dioxane at 25°C, dye concentration; I, 0.179×10^{-5} mol/l; II, 2.34×10^{-5} mol/l; III, 5.64×10^{-5} mol/l.

of a constant composition on the degree of dissociation of the ion associate.[7]

From the results noted above, the spectral changes in Alizarine Saphirol induced by increasing the dioxane content in mixtures containing more than 70% dioxane (Fig. 2) has been found to be quite similar to those changes induced by raising the temperature of the solution (Fig. 3) and those induced by increasing the dye concentration in mixtures with a constant composition (Fig. 4). That is to say, the intensities of the main band of the visible spectra of Alizarine Saphirol in water-dioxane mixtures with low dielectric constants are invariably found to decrease under any conditions where the interaction between the dye ion and the counter ion increases in the mixtures.

As has been described above, we can conclude that the changes in the spectra of Alizarine Saphirol induced by increasing the dioxane content in mixtures containing more than 70% dioxane are to be attributed to the increase in the interaction between the dye ion and the counter ion, and that such spectral changes are characteristic of the increase in the electrostatic interaction between the two ions.

The authors wish to thank Professor Haruo Gotoh for his helpful discussions.

---

[7] The values of α at a concentration of 3.79×10^{-5} mol/l in 70, 82, and 85% dioxane are estimated to be about 0.945, 0.750, and 0.640 respectively.