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The Spectra and the Conductances of Alizarine Saphirol SE in Water-Ethanol Mixtures

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In order to explore the behavior of Alizarine Saphirol SE in water-ethanol mixtures, the absorption spectrum and the conductance of the dye solution were obtained. A characteristic spectrum of the dye aggregate in water is found to change gradually into a monomer spectrum with an increase in the proportion of an added ethanol. Moreover, the dye is found to show marked McBain effect in water, while showing a conductance curve typical of a weak electrolyte in 58.7% (v/v) ethanol.

A characteristic spectrum for an aggregate has been found in some solutions of such aromatic compounds as dyes.[1-4] In the spectrum of the solution of such compounds, with an increase in the proportion of an added organic solvent, the monomer peak is found to be intensified at the expense of the dimer and the higher multimers. This reduction of the aggregation has generally been ascribed to the reduced polarity of the medium.

Further, the so-called McBain effect has been found in equivalent conductances of such compounds in aqueous solutions, in which ionic micells are formed.[5-7] The McBain effect is, however, supposed to diminish as a result of the reduction of the aggregation of such compound in water-ethanol mixtures.

Some of these compounds, which behave as strong electrolytes in water, are supposed to behave as weak electrolytes in water - organic solvent mixtures with low dielectric constants as a result of the increase in the Coulombic attraction between ions of opposite charges.

Very little comparative investigation of the spectrum and the above-described conductance has been made. Alizarine Saphirol SE (sodium salt of 1, 5-dihydroxy-4, 8-diamino anthraquinone-2-sulfonic acid) may be considered, judging from its structure, to aggregate strongly in an aqueous solution. Therefore, it seemed valuable to explore the behavior of the dye in water-ethanol mixtures.

Experimental

Materials.—Alizarine Saphirol SE (C. I. Acid Blue 43, sodium salt of 1, 5-dihydroxy-4, 8-diaminoanthraquinone-2-sulfonic acid) was supplied by the Mitsui Chemical Industries Co., Ltd., and was purified as follows. The benzene-soluble impurities in the dye were removed by extraction with purified benzene. After the salting-out with sodium chloride from an aqueous solution had been repeated, sodium ions and chloride ions were removed completely through cation exchange

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[1] E. Rabinowitch and L. F. Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941).

[2] L. Michaelis and S. Granick, ibid., **67**, 1212 (1944).

[3] D. R. Lemin and T. Vickerstaff, *Trans. Faraday Soc.*, **43**, 491 (1947).

[4] P. Mukerjee and A. K. Ghosh, *J. Phys. Chem.*, **67**, 193 (1963).

[5] C. Robinson, *Trans. Faraday Soc.*, **31**, 245 (1935).

[6] C. Robinson and H. E. Garret, ibid., **35**, 771 (1935).

[7] N. Ando, *J. Chem. Soc., Japan* (*Nippon Kwagaku Kwaisi*), **64**, 1305, 1431 (1943).

resin (Amberlite IR-120) and also anion exchange resin (Amberlite IRA-410). Finally, the solution was neutralized with sodium hydroxide, concentrated under reduced pressure, and dried at 105°C.

Ethanol and urea of a guaranteed reagent grade were used.

Spectrophotometric Measurements.—The spectrophotometric measurements were carried out in a Shimadzu Spectrophotometer, QV50, using a 10 mm. cell.

Conductance Measurements.—The circuit of the conductance bridge is shown in Fig. 1, in which R is a General Radio variable resistance (10 kΩ—0.1 Ω) with an error of 0.05%, C is an air-variable condenser, and T is a pulse-transformer. An oscilloscope was used as an indicator of the bridge balance. Conductances were measured at 25±0.1°C in a Komatsu-Yamato Coolnics CTR-1 thermostat. The specific conductances of the solvents were always less than 1.0×10^{-6} mhos. Two conductance cells with different cell constants, 0.05336 and 0.26706, were used.

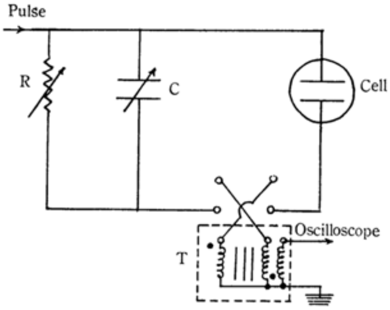

Fig. 1. Circuit of bridge.

Results and Discussion

The absorption spectra of Alizarine Saphirol in water are shown in Fig. 2, in which the spectrum is characterized by a prominent peak at about 590 mμ, or an α band, and a small shoulder at about 620 mμ, or a β band. With an increase in the concentration of the dye, Beer's law does not hold; the extinction coefficients at about 590 mμ and 620 mμ diminish, and also the shoulder falls progressively. This may be ascribed to the formation of aggregates of the dye in water.

The absorption spectra of Alizarine Saphirol in water-ethanol mixtures are shown in Fig. 3, in which both the α and β band are intensified and shift slightly towards longer wavelengths, with an increase in the proportion of an added ethanol, and in which the β band is more intensified than the α band in 30%, 40% (v/v) and richer ethanol solvents. This effect of ethanol on the spectrum of the dye is supposed to be the reduction of the aggregation due to the reduced polarity of the medium. A similar effect of ethanol was found by Rabinowitch and Epstein on Methylene Blue.1)

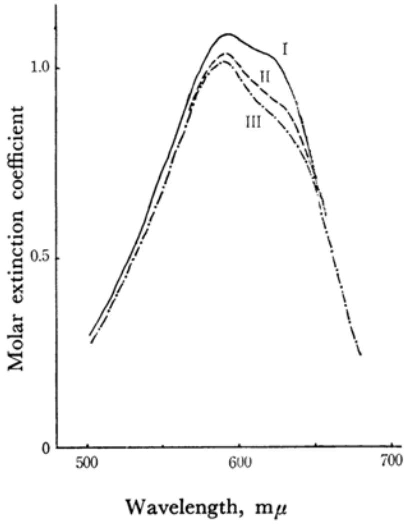

Fig. 2. Spectrum of Alizarine Saphirol SE in water at room temperature.
Concentration of the dye:
Curve I, 1.274×10^{-5} M; II, 6.370×10^{-5} M; III, 12.74×10^{-5} M

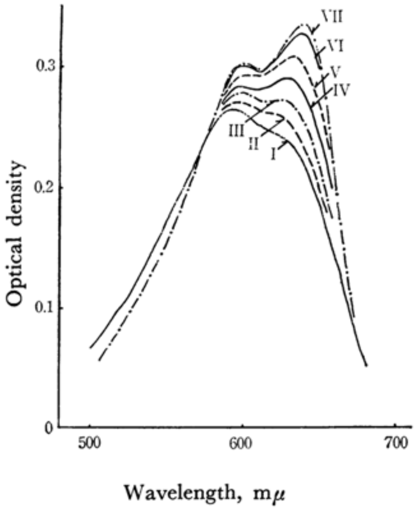

Fig. 3. Spectrum of Alizarine Saphirol SE in water-ethanol mixtures at room temperature. Optical densities determined in 10 mm. cells. Concentration of ethanol by volume: curve I, 0%; II, 10%; III, 20%; IV, 30%; V, 40%; VI, 60%; VII, 90% (v/v)

In order to compare the effect of ethanol with that of urea on the spectrum of the dye, the spectrum of Alizarine Saphirol in the presence of urea is shown in Fig. 4, in which, with an increase in the proportion of an added urea, both the α and the β band shift towards longer wavelengths. The optical density of the β band is larger than that of the α band in 7.2 M urea aqueous solution. The effect of the addition of urea is very similar qualitatively to that of ethanol, as is shown in Fig. 3. Thus urea is considered to reduce the aggregation of the dye in water.

The effects of the temperature on the spectra of Alizarine Saphirol in water-ethanol mixtures are shown in Fig. 5. In Fig. 5, both the α and β bands of the dye in water and 30% (v/v) ethanol are intensified with raising the temperature, although β band appears to be intensified more than the α band. The rise in the temperature seems to reduce the aggregation due to the change in structural properties of water. No marked temperature effect on the spectrum of Alizarine Saphirol is, however, found in either 60 or 90% (v/v) ethanol. From these findings in the spectra, it may be considered that the shift of the spectra with an increase in the concentration of Alizarine Saphirol in an aqueous solution in Fig. 2 is due to the increase in number of aggregates, while the shift of the spectra with an increase in the proportion of an added ethanol (in Fig. 3) or urea (in Fig. 4) is due to the inhibition of the aggregation. These findings in the spectra, however, give no suggestion whether ethanol and urea prevent aggregation by interacting with water molecules related with the aggregation mechanism, or by interacting with Alizarine Saphirol directly.

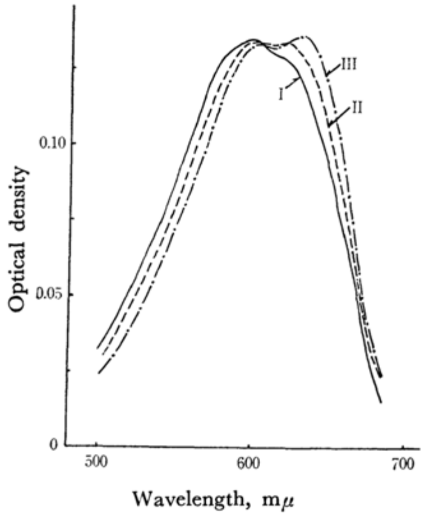

Fig. 4. Effect of urea on the spectrum of Alizarine Saphirol SE in aqueous solution. Optical densities determined in 10 mm. cells. Concentration of urea: curve I, 0 M; II, 1.6 M; III, 7.2 M

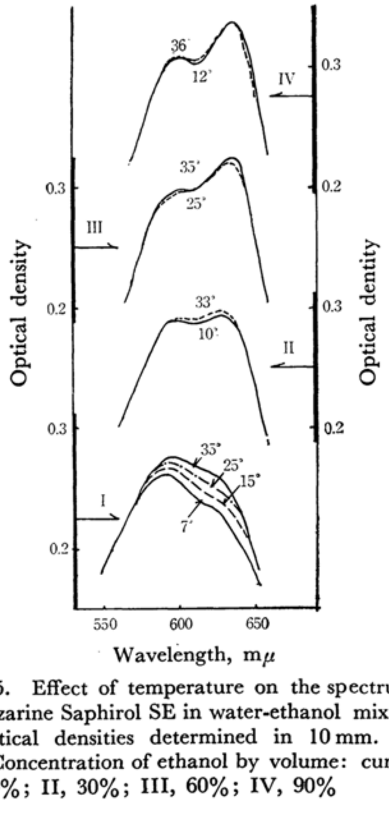

Fig. 5. Effect of temperature on the spectrum of Alizarine Saphirol SE in water-ethanol mixtures. Optical densities determined in 10 mm. cells. Concentration of ethanol by volume: curve I, 0%; II, 30%; III, 60%; IV, 90%

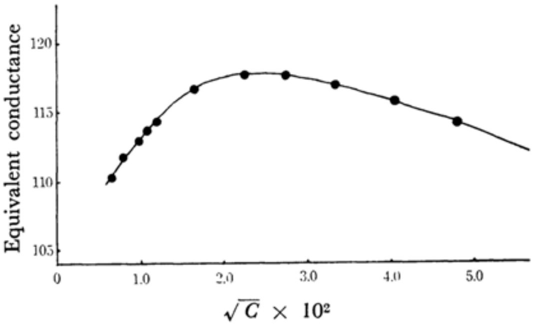

Fig. 6. Equivalent conductance of Alizarine Saphirol SE in water at 25±0.1°C.

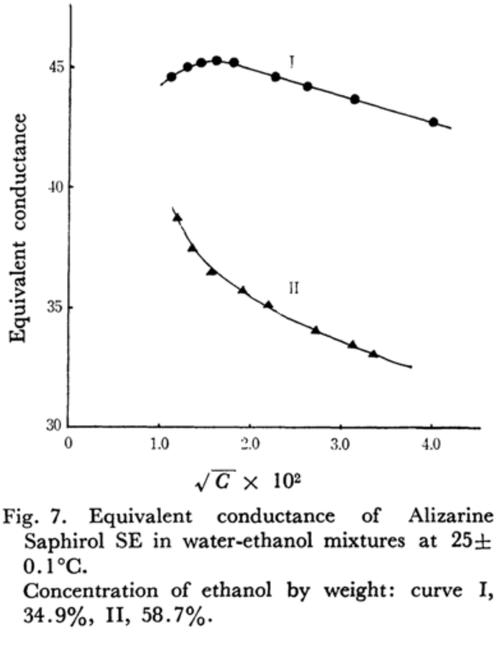

Fig. 7. Equivalent conductance of Alizarine Saphirol SE in water-ethanol mixtures at 25±0.1°C.
Concentration of ethanol by weight: curve I, 34.9%, II, 58.7%.

The equivalent conductances (Λ) of Alizarine Saphirol in water are plotted against the square root of the molar concentration, $\sqrt{C}$, in Fig. 6. The Λ-$\sqrt{C}$ curve reaches a maximum, and the so-called McBain effect is found in the curve which suggests the presence of ionic micells. The curves I and II in Fig. 7 show the equivalent conductances in 34.9 and 58.7% (v/v) ethanol respectively. Also the McBain effect is found in 34.9% ethanol (curve I), the conductances decrease gradually with an increase in the concentration of the dye in 58.7% ethanol (curve II). This conductance behavior of curve II is similar to that of a weak electrolyte. Thus, in 58.7% ethanol, Alizarine Saphirol is supposed not to form aggregates, but to exist as a monomer. These conductance findings are in agreement with the considerations made from the spectrophotometric evidence.

Since Alizarine Saphirol is the sodium salt of a sulfonic acid, it will behave as a strong electrolyte in an aqueous solution. However, it is natural for Alizarine Saphirol to behave as a weak electrolyte in water-ethanol mixtures of a low dielectric constant due to the increase in Coulombic attraction between ions of opposite charges.

Summary

The absorption spectra and the conductances of Alizarine Saphirol SE (sodium salt of 1, 5-dihydroxy-4, 8-diaminoanthraquinone-2-sulfonic acid) in water-ethanol mixtures have been obtained, and the dispersed states of the dye have been examined qualitatively.

1) A characteristic spectrum of the dye aggregate in water has been obtained; a prominent peak at about 590 mμ and a small shoulder at about 620 mμ were found in the spectrum, and Beer's law did not hold. Alizarine Saphirol showed a marked McBain effect in an equivalent conductance in water.

2) The small shoulder of the spectrum at about 620 mμ changed to a prominent peak with an increase in the proportion of ethanol added, and the absorptions at both about 590 and about 620 mμ shifted towards longer wavelengths. The dye did not show any McBain effect, and the typical conductance curve of a weak electrolyte was obtained in 58.7% (v/v) ethanol.

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