BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2384—2386 (1969)

# On the Ionic Association of Alizarine Saphirol SE in Water-dioxane Mixtures

Masaru MITSUISHI, Yasuko FUNATSU and Nobuhiko KUROKI*[1]

*Faculty of Fiber Science and Technology, Shinshu University, Ueda, Nagano*

(Received December 19, 1968)

In the previous paper, we have concluded from spectroscopic and conductance measurements that Alizarine Saphirol SE (sodium salt of 1,5-dihydroxy-4,8-diaminoanthraquinone-2-sulfonic acid) exists in the form of ionic associates in water-ethanol mixtures with a low dielectric constant.[1] This association was ascribed to the increase of Coulombic attraction between the dye ion and the counter ion. It may be reasonable to expect that Alizarine Saphirol also exists in the ionic associate in water-dioxane mixtures having lower dielectric constants than those of water-ethanol mixtures. Such interactions between the dye ion and the counter ion in the mixtures is supposed to be expressed quantitatively in terms of ion association constant of the dye ion with the counter ion in the solution.

Since literatures on the association constant of a dye in water-organic solvent mixtures can hardly be found, it seems valuable to examine the dissociation constant of Alizarine Saphirol in water-dioxane mixtures in order to obtain some suggestive information not only on the dispersed state of the dye but also on the effect of dioxane on the ultraviolet and visible spectra of the dye in the mixtures.

In this paper, the conductance data were used to determine the equivalent conductance at infinite dilution and ion association constant by means of Shedlovsky's treatment[2] based on Onsager's limiting theory.

## Experimental

**Materials.** The Alizarine Saphirol SE (sodium salt of 1,5-dihydroxy-4,8-diaminoanthraquinone-2-sulfonic acid) was taken from the laboratory stock used in the previous work[1]. The dioxane was purified as follows. Dioxane of a guaranteed reagent grade was boiled with potassium hydroxide under reflux for several hours. It was distilled after dehydration with metallic sodium through a 40 cm refluxing column.

**Conductance Measurements.** The conductance measurements were made with a Yokogawa-Hewlett Packard Universal Bridge BV-2-13 B. A simple dilution cell with cell constant 0.0688 was used. All the measurements were made at 25±0.01°C. The specific conductance of the solvents was always less than $1.0\times 10^{-6}$ mhos.

**Dielectric Constant Measurements.** Dielectric constant measurements were made by means of heterodynebeat method at 500 Kc/sec. The heterodyne circuit was prepared in our laboratory, and an oscilloscope was used as a detector. The electric capacity was determined with a precision condenser of Ando Electric Co., Ltd. The sample cell was Yamato Kagaku's Dielectric cell EL-25. Benzene ($\varepsilon=2.273$) was used as a standard material.

**Viscosity Measurements.** The viscosity of the solvent was determined with an Ostwald type viscometer.

## Results and Discussion

Shedlovsky's equation to obtain the association constant $K_A$ and the equivalent conductance at infinite dilution $\Lambda_0$ of 1–1 electrolyte is based on Onsager limiting theory expressed as

$$\frac{1}{\Lambda S_{(z)}}=\frac{1}{\Lambda_0}+\frac{c\Lambda S_{(z)}f_{\pm}^2}{K\Lambda_0^2}, \qquad (1)$$

where $\Lambda$ is the equivalent conductance at concentration $c$, and $f_{\pm}^2$ is given by the Debye-Hückel limiting law. The values of $S_{(z)}$ have been tabulated by Daggett.[3] $K$ is the dissociation constant and equal to $1/K_A$.

According to Eq. (1), the plot of $1/(\Lambda S_{(z)})$ against $c\Lambda S_{(z)}f_{\pm}^2$ should give a straight line,

---

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

1) M. Mitsuishi and G. Aida, This Bulletin, **39**, 246 (1966).

2) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

3) H. M. Daggett, *J. Am. Chem. Soc.*, **71**, 1497 (1949).

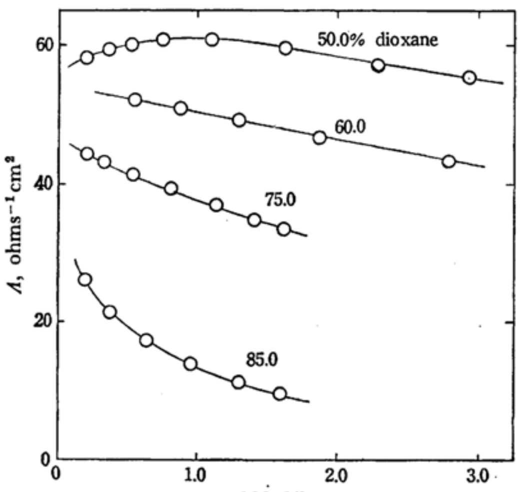

Fig. 1. Conductance of Alizarine Saphirol SE in water-dioxane mixtures.

passing through $1/\Lambda_0$ with a slope equal to $1/(K\Lambda_0)^2$; thus the association constant $K_A$ and the equivalent conductance at infinite dilution $\Lambda_0$ can be determined.

The conductance of Alizarine Saphirol in water-dioxane mixtures is plotted against $\sqrt{c}$ in Fig. 1. In the solutions above 60% dioxane, the so-called McBain effects are not found on the $\Lambda$ - $\sqrt{c}$ curves, so that Alizarine Saphirol is supposed to be monomeric in the solution.

In the previous paper, Alizarine Saphirol has been considered to be in the form of ionic associate in water-ethanol mixtures with a low dielectric constant from the conductance data.¹⁾ It is reasonable to expect that Alizarine Saphirol exists in the form of ionic associate in the water-dioxane mixtures having dielectric constant lower than that of the water-ethanol mixtures. As shown in Fig. 1, the $\Lambda$ - $\sqrt{c}$ curve of alizarine Saphirol in 85% dioxane is similar to that of weak electrolyte; thus the association constant is supposed to be appreciable.

Shedlovsky's treatment was used to determine $\Lambda_0$ and $K_A$, and the parameters resulting from the data analysis are given in Table 1.

The dielectric constants of the solvents in Table 1 are a little lower than those of Kunze and Fuoss,⁴⁾ and the viscosities of the solvents are comparable to those of Kunze and Fuoss

From Table 1, the ionic association constant $K_A$ is seen to become larger with the increase of the proportion of dioxane in the mixtures; thus $K_A$ becomes larger with the lowering of the dielectric constant of the solvent. This indicates obviously that the interaction between the dye ion and the counter ion increases with the lowering of the dielectric constant of the solvent.

In an attempt to analyze the data further, $\log K_A$ was plotted against $1/\varepsilon$ for the dye, and the result is shown in Fig. 2. Since the resulting plot is quite linear, the ionic associate in water-dioxane mixtures is considered to be formed entirely by the electrostatic interaction between the dye ion and the counter ion.

The Walden products ($\Lambda_0\eta$) are given in Table 1. It is found that $\Lambda_0\eta$ decreases steeply with the lowering of the dielectric constant of the solvent. The Walden products of some inorganic electrolytes in water-organic solvent mixtures have been found to become smaller than those in pure water by Atkinson *et al.*⁵⁾ who reported on the behavior of $MnSO_4$ in the mixtures of dioxane, methanol or acetone with water. A similar result has been obtained by Yokoi *et al.*⁶⁾ on Cu-*m*-benzenedisul-

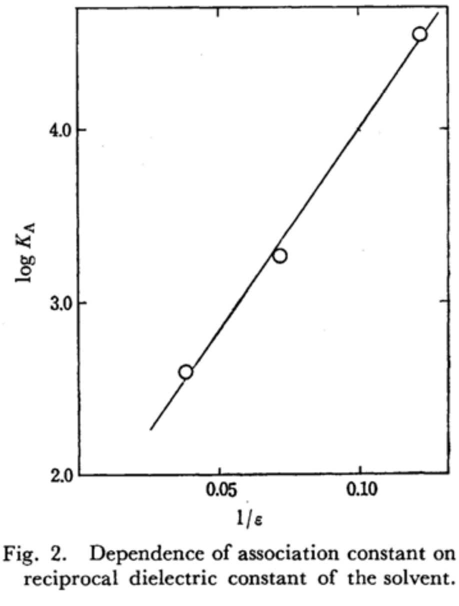

Fig. 2. Dependence of association constant on the reciprocal dielectric constant of the solvent.

TABLE 1. CALCULATED PARAMETERS

| Dioxane in mixtures | $\varepsilon$ | $\eta$ | $\Lambda_0$ | $\Lambda_0\eta$ | $K_A$ |
|---|---|---|---|---|---|
| 60.0 wt % | 25.9 | $1.949\times10^{-2}$ poise | 52.7 ohms$^{-1}$ cm$^2$ | 1.02 | $3.98\times10^2$ |
| 75.0 | 14.0 | 1.819 | 44.3 | 0.802 | $1.88\times10^3$ |
| 85.0 | 8.2 | 1.557 | 29.2 | 0.455 | $3.46\times10^4$ |

---

4) R. W. Kunze and R. M. Fuoss, *J. Phys. Chem.*, **67**, 914 (1963).

5) G. Atkinson and S. Petrucci, *J. Am. Chem. Soc.*, **86**, 7 (1964).

6) M. Yokoi and E. Kubota, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **86**, 894 (1965).

fonate in water-methanol mixtures. These results have been explained in terms of the competition between water and polar organic molecules for positions in the first coordination sphere of the ions. In addition to this effect, in the case of Alizarine Saphirol, the dye contains electron donating or electron accepting groups, such as $\rangle C=O$, $-NH_2$ and $-OH$, so that there would be strong and specific interactions between dioxane and these groups, and these interactions presumably affect the conductance behavior of the dye.

The conductance data alone, however, will not be sufficient to clarify the specific interactions between the dye ion and solvent molecule, so that it is necessary to investigate further by ultraviolet-visible, ESR and NMR spectroscopic measurements.

The authors wish to thank Professor Haruo Gotoh and Professor Masatoki Yokoi for their helpful discussions.