

# On the Ionic Association Reactions of Dyes in Water-Dioxane Mixtures

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Dyes dissolve in water as anions and some dyes, as cations. They are not monomeric, but present as dimers or higher aggregates in water. The formation of these aggregates is considered by many chemists to be ascribed to the structural properties of water. The addition of organic solvents, such as dioxane or alcohol, to a highly aggregated aqueous solution may lead to disaggregation, and further to formation of ionic associates\*<sup>1</sup> of dye ions with counter ions, since the dielectric constant of solvent lowers with increasing organic solvents. The behaviors of dyes described above are known to be able to be examined apparently by means of conductance measurements of dye solutions.

In the previous papers of the author's,<sup>1-4</sup> the ionic association reactions in water-organic solvent mixtures of the sodium salt of Alizarine Saphirol SE (1,5-dihydroxy-4,8-diamino-anthraquinone-2-sulfonic acid), one of the anthraquinone type dyes, were studied.

The dyes containing azo groups are supposed to have conductance behaviors different from those of anthraquinone type dyes. However, their conductance behaviors in the solvents with low dielectric constant have not been known, so it seems valuable to examine the behaviors of azo dyes in it.

The ionic association reactions of dyes must be influenced by the nature of the counter ions of the dye ions. Little investigation, however, has been undertaken to examine the effects of the nature of the counter ions upon the ionic association of dyes in water-dioxane mixtures.

Therefore in this paper the ionic association reactions of azo dyes (Orange II and Methyl Orange), and the effects of the nature of the counter ions (lithium, sodium and potassium ions) of Alizarine Saphirol SE anion upon the ionic association reactions of the dyes in water-dioxane mixtures are examined by means of conductance measurements.

## Experimental

### Materials

1. Orange II (1-*p*-sulfobenzeneazo-2-naphthol sodium salt) : Orange II (O. II) was prepared by coupling diazotized sulfonic acid with  $\beta$ -naphthol in alkaline solution, and by recrystallizing from aqueous ethanol.
2. Methyl Orange (*p*-sulfobenzeneazo-4-dimethylaniline sodium salt):

\*<sup>1</sup> Ionic associates are sometimes termed "ion pair", and the theory of the ionic association was developed by Bjerrum in 1926<sup>2</sup>.

Methyl Orange (M.O.) was prepared by coupling diazotized sulfonic acid with N, N-dimethylaniline in a weakly acetic acid solution, and by recrystallizing from pure water.

3. Lithium and potassium salts of Alizarine Saphirol SE (1,5-dihydroxy-4,8-diaminoanthraquinone-2-sulfonic acid) : Lithium and potassium salts of Alizarine Saphirol SE(A. S.) were obtained by neutralizing the purified Alizarine Saphirol dye acid solution<sup>1)</sup> with lithium hydroxide and potassium hydroxide solution respectively, and by concentrating and then drying under reduced pressure.

4. Dioxane : Dioxane used in this experiment was purified as follows. Dioxane of a guaranteed reagent grade was boiled with potassium hydroxide under reflux for several hours. It was distilled through a 40 cm refluxing column after dehydration with metallic sodium.

#### Conductance measurements

The conductance measurements were made with a Yokogawa-Hewlett Packard Universal Bridge BV-Z-13B. A simple dilution cell with a cell constant of 0.06712 at 25°C was used. The measurements were made at 15, 25, 35 and 45±0.01°C. The specific conductance of the solvents was always less than 1.0×10<sup>-6</sup> mhos. The properties of the solvents used in this experiment are given in Table I.

Table I PROPERTIES OF THE SOLVENTS

Dioxane content	<i>t</i>	<i>D</i> *1	100 $\eta$ *2
60.0%	25° C	25.90	1.949
70.0	15	18.72	2.483
	25	17.69	1.918
	35	16.72	1.522
70.2	25	19.07	1.923
75.0	25	14.00	1.819
82.0	15	10.01	2.106
	25	9.53	1.671
	35	9.06	1.356
	45	8.62	1.117

\*1 dielectric constant of the solvent

\*2 viscosity coefficient of the solvent (*p*)

#### Analysis of Results

For singly charged ions an association may be represented by the reaction,



Here  $[C^+A^-]^0$  denotes an ionic associate being produced by the action of Coulombic force only, and it is different from an undissociated molecule produced by electronic linkage.

The data obtained in this experiment are analyzed by the Shedlovsky's method<sup>6)</sup> based on the Onsager's limiting equation (2)<sup>7)</sup>,

$$\Lambda = \Lambda_0 - (\alpha^* \Lambda_0 + \beta^*) c^{\frac{1}{2}} = \Lambda_0 - S_{(\Lambda)} c^{\frac{1}{2}}. \quad (2)$$

Here  $\Lambda$  ( $mho \cdot cm^2 \cdot eq^{-1}$ ) is the equivalent conductance at the dye concentration  $c$  ( $eq. liter^{-1}$ ),  $\Lambda_0$  is the equivalent conductance at infinite dilution. The term in the parenthesis  $(\alpha^* \Lambda_0 + \beta^*)$  in Eq. (2) denotes the Onsager's limiting slope, and both  $\alpha^*$  and  $\beta^*$  are the constants based upon the viscosity coefficient, the dielectric constant and the temperature of the solvents.

The ionic association constant  $K_A$  in the reaction (1) is given by Eq. (3),

$$K_A = \frac{1 - \alpha}{c \alpha^2 f_{\pm}^2}. \quad (3)$$

Here  $\alpha$  is the degree of dissociation of the associate  $[C^+ A^-]^0$ , and  $f_{\pm}^2$  is calculated by the Debye-Hückel equation (4),<sup>8)</sup>

$$-\log f_{\pm}^2 = A(c\alpha)^{\frac{1}{2}}. \quad (4)$$

Here  $A$  is the constant, and the  $A$  for uni-univalent electrolyte is given by

$$A = \frac{9.6494 \times 10^6}{DT^{\frac{3}{2}}}, \quad (5)$$

where  $D$  is the dielectric constant of solvents, and  $T$  is the absolute temperature of the solvents.

Shedlovsky defined  $\alpha$  by the following expression,

$$\Lambda = \alpha \Lambda_0 - \frac{\Lambda}{\Lambda_0} S_{(\Lambda)} (c\alpha)^{\frac{1}{2}}. \quad (6)$$

From Eq. (6) the quadratic function for  $\alpha^{\frac{1}{2}}$  is obtained as follows:

$$\alpha = \frac{\Lambda}{\Lambda_0} + \left( \frac{S_{(\Lambda)}}{\Lambda_0^{\frac{3}{2}}} \right) \Lambda (c\alpha)^{\frac{1}{2}}, \quad (7)$$

or

$$\alpha - \left( \frac{\Lambda}{\Lambda_0} \right)^{\frac{1}{2}} Z \alpha^{\frac{1}{2}} - \left( \frac{\Lambda}{\Lambda_0} \right) = 0, \quad (8)$$

where

$$Z \equiv \frac{S_{(\Lambda)} (\Lambda c)^{\frac{1}{2}}}{\Lambda_0^{\frac{3}{2}}}. \quad (9)$$

The solution of Eq. (8) for  $\alpha^{\frac{1}{2}}$  in terms of the variable  $Z$ , defined by Eq. (9), leads to

$$\alpha = \frac{\Lambda}{\Lambda_0} \left[ \frac{Z}{2} + \sqrt{1 + \left( \frac{Z}{2} \right)^2} \right]^2 = \frac{\Lambda}{\Lambda_0} S_{(Z)}. \quad (10)$$

The bracketed term may be used in the expanded form (11),

$$S(Z) = 1 + Z + \frac{Z^2}{2} + \frac{Z^3}{8} \dots \quad (11)$$

for small values of  $Z$ . Ordinarily it is not necessary to use terms higher than  $Z^2$  in evaluating  $S(Z)$ . A table of  $S(Z)$  is given by Daggett.<sup>9</sup>

The combination of Eq. (3) with (10) gives the Shedlovsky's expression (12),

$$\frac{1}{AS(Z)} = \frac{1}{A_0} + \frac{cAS(Z)f_{\pm}^2 K_A}{A_0^2} \quad (12)$$

According to Eq. (12), the plot of  $1/AS(Z)$  vs.  $cAS(Z)f_{\pm}^2$  should give a straight line, passing through  $1/A_0$  with a slope equal to  $(K_A/A_0^2)$ . Such a plot, based on the first approximate values of  $A_0$  given by extrapolation of plot of experimental  $A$  vs.  $c^{1/2}$ , yields a new value of  $A_0$ , from which more accurate values of  $1/AS(Z)$  and  $cAS(Z)f_{\pm}^2$  may be obtained and a new plot is constructed. This process is repeated until the final values of  $A_0$  and  $K_A$  are found.

### Results and Discussion

The equivalent conductances,  $A$ , of O. II in water-dioxane mixtures containing more than 50% dioxane are plotted against  $c^{1/2}$  in Fig. 1. The  $A$  vs.  $c^{1/2}$  plot of M. O. is shown in Fig. 2. These conductance behaviors are very

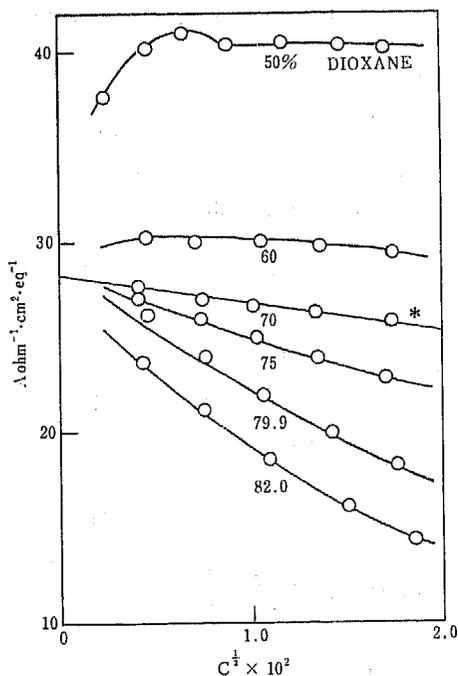


Fig. 1 Equivalent conductances of Orange II in water-dioxane mixtures at 25°C.

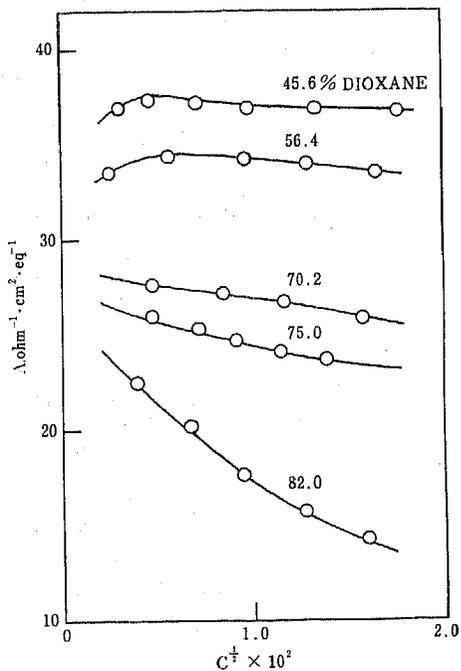


Fig. 2 Equivalent conductances of Methyl Orange in water-dioxane mixtures at 25°C.

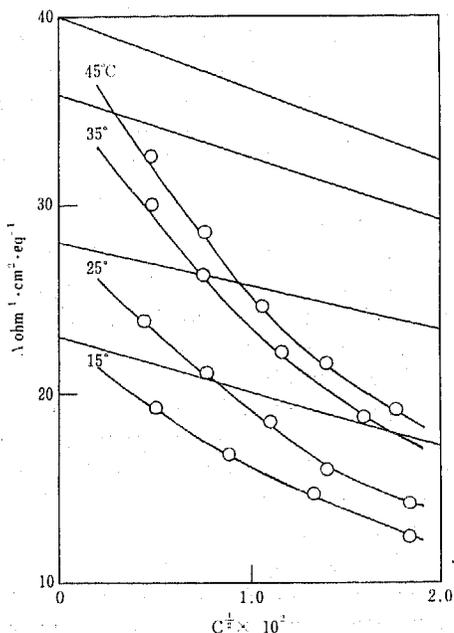


Fig. 3 Equivalent conductances of Orange II in the 82% dioxane.

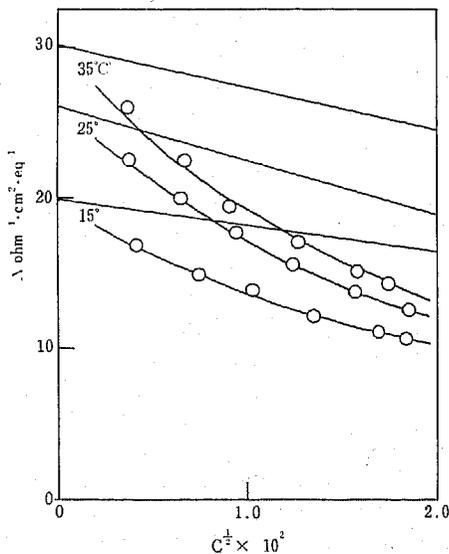


Fig. 4 Equivalent conductances of Methyl Orange in the 82% dioxane.

different from those of the ordinary electrolytes.<sup>10)</sup>

The  $\Lambda$  vs.  $c^{1/2}$  curves in the mixtures containing less than 60% dioxane, reach the maxima and decrease with increasing dilution. These behaviors are called "McBain effect" and suggest the presence of the ionic aggregates in the solutions.<sup>11)</sup>

In the 70% dioxane, the conductances are seen to become larger linearly with increasing dilution in Fig. 1. The dyes are supposed to be monomeric, since the McBain effect is not found at all. The sodium salt of A. S. was found to be monomeric in the mixtures of 60% dioxane in a previous paper of the author's.<sup>2)</sup> Therefore O. II seems to produce the ionic aggregates more easily than the sodium salt of A. S. did in water-dioxane mixtures. The straight line with an asterisk in Fig. 1 indicates the theoretical limiting slope calculated from Eq. (2). In the mixture containing 70% dioxane, all the experimental conductances are fairly well represented by the theoretical limiting slope; thus this evidence suggests that the dye is dissociated completely.

In the solutions containing more than 75% dioxane, O. II is considered to be present as the ionic associates, judging from the shapes of  $\Lambda$  vs.  $c^{1/2}$  curves.

The conductance behaviors of M. O. (Fig. 2) is fairly similar to those of O. II in water-dioxane mixtures.

The conductances of O. II and M. O. at various temperatures in the 82

% dioxane are shown in Figs. 3 and 4 respectively. The straight lines in these Figs. indicate the theoretical limiting slopes determined by Eq. (2). In Figs. 3 and 4, all the experimental conductances are found to be less than the conductances expected for the completely dissociated electrolytes represented by the straight lines. These evidences suggest that the two dyes are present as the ionic associates in the 82% dioxane. The conductances are seen to increase steeper as the temperatures are raised. These evidences indicate apparently that the ionic association constants of the reaction (1) at higher temperatures are larger than those at lower temperatures.

The equivalent conductances at the infinite dilution,  $\Lambda_0$ , and the ionic association constants,  $K_A$ , of O. II and M. O. are determined by means of the Shedlovsky's method, and they are shown in Tables 2 and 3 respectively. From Tables 2 and 3, the ionic association constants are seen to become larger progressively as the proportion of dioxane in the mixtures is raised at 25°C; thus the  $K_A$  values become larger progressively as dielectric constants of the solvents lower. The  $K_A$  values are seen to become larger progressively as the temperature is raised in the 82% dioxane. The ionic association constants of O. II and M. O. are less than those of the sodium salt of A. S. in the 82% dioxane.

Walden products ( $\Lambda_0\eta$ ) are also shown in Tables 2 and 3, and they are seen to decrease slightly with the increase of dioxane content in the mixtures. The decrease of Walden products with increasing dioxane content seems to be less than that of the sodium salt of A. S.. These results found in

Table 2 CONSTANTS FOR ORANGE II

Dioxane	$t$	$\Lambda_0$	$\Lambda_0\eta$	$K_A$
70.0%	25° C	27.60	0.529	0.0
75.0	25	27.47	0.500	$6.21 \times 10^3$
79.9	25	28.15	0.485	$3.16 \times 10^3$
82.0	15	22.78	0.480	$7.40 \times 10^3$
	25	27.82	0.485	$7.82 \times 10^3$
	35	35.60	0.483	$9.59 \times 10^3$
	45	39.90	0.446	$1.10 \times 10^4$

Table 3 CONSTANTS FOR METHYL ORANGE

Dioxane	$t$	$\Lambda_0$	$\Lambda_0\eta$	$K_A$
60.0%	25° C	28.40	0.563	0.0
70.2	25	28.40	0.546	$2.07 \times 10^3$
75.0	25	27.02	4.492	$5.20 \times 10^3$
82.0	15	19.97	0.420	$6.98 \times 10^3$
	25	25.92	0.433	$8.94 \times 10^3$
	35	30.13	0.409	$1.05 \times 10^4$

Walden products have been explained in terms of the competition between water and dioxane molecules for the position in the first coordination sphere of the ions, and these interactions presumably affect the conductance behaviors of the dyes.

From Tables 2 and 3, the  $K_A$  values of the dyes in the 82% dioxane are seen to increase with the rise in the temperatures of the solvents. The Walden products are essentially constant in the solvents of the same composition, even if the temperatures are different.

In an attempt to analyze the data further, the relations of the  $K_A$  to the  $D$  and the  $T$  of the solvent must be examined by Denison-Ramsey equation (13)<sup>12</sup> as a first approximation,

$$K_A = \exp(e^2/aDkT). \quad (13)$$

Here  $e$  is the electron charge,  $a$  is the center-to-center distance of the ions in an associate and  $k$  is the Boltzmann constant.

According to Eq. (13), the plot of  $\log K_A$  vs.  $1/DT$  must be linear. The plots of  $\log K_A$  vs.  $1/DT$  of O. II and M. O. are shown in Figs. 5 and 6 respectively. The plots are seen to be linear as expected from Eq. (13). These evidences indicate apparently that the ionic associations of the dyes are due to the electrostatic interactions between the dye ions and the counter ions.

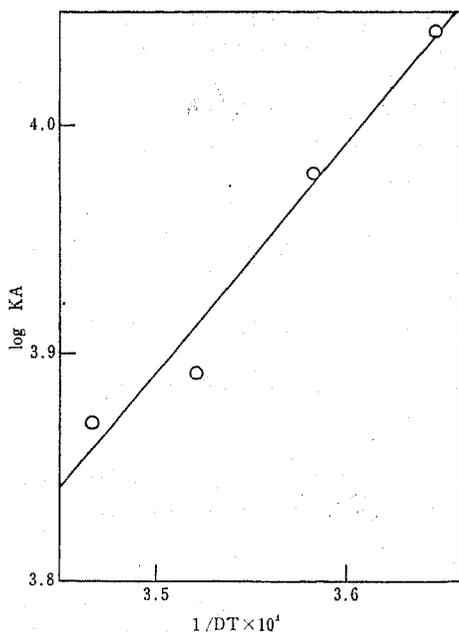


Fig. 5 The relation between  $\log K_A$  and  $1/DT$  for Orange II in the 82% dioxane.

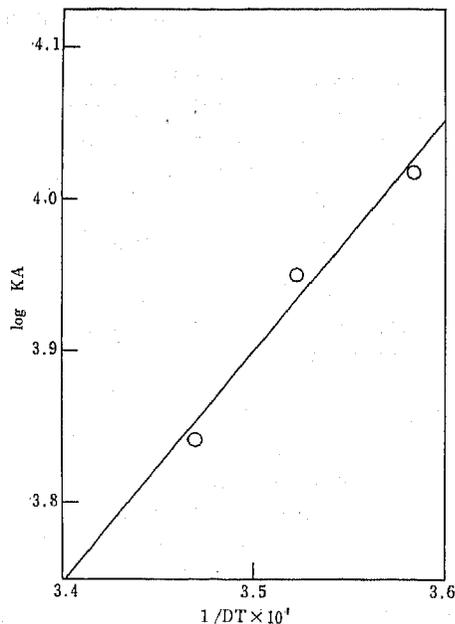


Fig. 6 The relation between  $\log K_A$  and  $1/DT$  for Methyl Orange in the 82% dioxane

Table 4 THERMODYNAMIC PARAMETERS OF THE IONIC ASSOCIATION REACTIONS OF ORANGE II AND METHYL ORANGE IN THE MIXTURES CONTAINING 70% DIOXANE AT 25°C

Dyes	Dioxane	$K_{A298}$	$\Delta H^\circ$ (Kcal/mol)	$\Delta G^\circ$ (Kcal/mol)	$\Delta S^\circ$ (cal/deg·mol)	$a$ (Å)
Orange II	82.0%	$7.82 \times 10^3$	0.11	-5.31	18.3	7.3
Methyl Orange	82.0	$8.94 \times 10^3$	0.17	-5.39	18.6	5.0

The  $a$  values of O. II and M. O. can be obtained from the slopes of the  $\log K_A$  vs.  $1/DT$ , and they are given in Table 4. They are considered to be reasonable.

The enthalpy change ( $\Delta H^\circ$ ) and the entropy change ( $\Delta S^\circ$ ) in the ionic association reaction may be obtained from Eqs. (14) and (15) respectively,

$$\frac{d \ln K_A}{d(1/T)} = -\frac{\Delta H^\circ}{R}, \quad (14)$$

$$\Delta G^\circ = RT \ln K_A,$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (15)$$

Here  $R$  is the gas constant.

From the slopes of the best straight lines given by the method of the least squares for the  $\log K_A$  vs.  $1/T$  plot over the whole temperature range, the  $\Delta H^\circ$  values are obtained, and the  $\Delta S^\circ$  values are obtained from Eq. (15), and they are shown in Table 4. Since the  $\Delta H^\circ$  values are positive, the reaction is endothermic. These  $\Delta H^\circ$  values are comparable to those of the ionic association reactions of some of inorganic electrolytes in water,<sup>13,14)</sup> and are less than that of the sodium salt of A. S.<sup>3)</sup> in the 82% dioxane.

The  $\Delta S^\circ$  values of the ionic association reactions of the two dyes are positive. These results are considered to reflect the evidence that the freedom of the system increases, since the solvent molecules are removed from the solvation sphere of the ions when the dye ions form the ionic associate with the counter ions.

Thus, the conductance behaviors of the two azo dyes in water-dioxane mixtures are considered to be slightly different from the anthraquinone type dyes, such as the sodium salt of A. S..

The conductances of the potassium and the lithium salt of A. S. at various temperatures in the mixtures containing 70% dioxane are shown in Figs. 7 and 8 respectively. The straight lines in the Figs. 7 and 8 indicate the Onsager's limiting slopes.

The data given in Figs. 7 and 8 were analyzed by means of the Shedlovsky's treatment and the results are shown in Table 5. The results for the sodium salt of A. S., which were presented in a previous paper of the author's,<sup>3)</sup> are also shown in the same Table.

From Table 5, it can be mentioned that the  $A_0$  of the potassium salt of A.

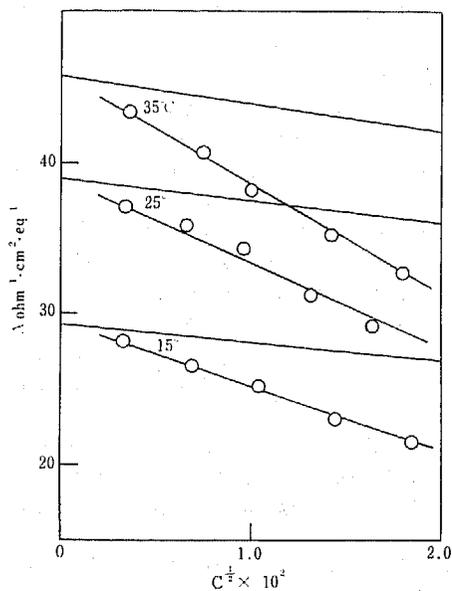


Fig. 7 Equivalent conductances of potassium salt of Alizarine Saphirol SE in the 70% dioxane.

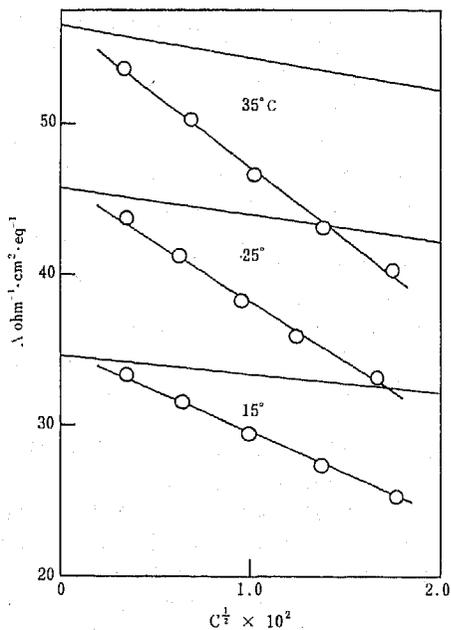


Fig. 8 Equivalent conductances of lithium salt of Alizarine Saphirol SE in the 70% dioxane.

Table 5 EQUIVALENT CONDUCTANCES AT INFINITE DILUTION AND IONIC ASSOCIATION CONSTANTS FOR THREE KINDS OF SALTS OF ALIZARINE SAPHIROL SE

Salts	$t$	$\Lambda_0$	$KA$
Potassium salt of Alizarine Saphirol SE	15° C	29.0	$1.56 \times 10^8$
	25	38.9	$1.72 \times 10^8$
	35	45.6	$1.87 \times 10^8$
Lithium salt of Alizarine Saphirol SE	15	34.4	$1.71 \times 10^8$
	25	45.1	$1.97 \times 10^8$
	35	56.3	$2.23 \times 10^8$
Sodium salt of Alizarine Saphirol SE	15	35.6	$1.31 \times 10^8$
	25	45.3	$1.39 \times 10^8$
	35	58.2	$1.63 \times 10^8$

S. is much smaller than those of the lithium and the sodium salt of A. S., and that the  $\Lambda_0$  of the lithium salt of A. S. is comparable to that of the sodium salt of A. S..

The difference in  $\Lambda_0$  for a set of electrolytes having a common anion is considered to be dependent on the difference in the equivalent ionic conduc-

tance at infinite dilution for cations,  $\lambda_0^+$ . The differences in  $\Lambda_0$  among three kinds of salts of A. S. in Table 5 must be dependent on the differences in  $\lambda_0^+$  values of  $K^+$ ,  $Li^+$  and  $Na^+$  in the 70% dioxane. Therefore the  $\lambda_0^+$  of  $K^+$  must be the smallest in the 70% dioxane, although the  $\lambda_0^+$  of  $K^+$  is the largest in water in the set of cations,  $K^+$ ,  $Li^+$  and  $Na^+$ .

Generally, ions in solution are undoubtedly solvated, so the conductances observed are actually those of solvated ions. The potassium ion having the lowest  $\lambda_0^+$  in the set of cations must be not only the largest ion, but also the solvated ion with the largest number of solvent molecules.

As stated above, dioxane is considered to compete with water for the positions in the first coordination sphere of the ion, especially of the cation. Since the coordination numbers of water for  $K^+$  are the smallest in the set of values for  $Li^+$ ,  $K^+$  and  $Na^+$  in water, dioxane molecules are considered to be held by  $K^+$  most easily. Consequently, the  $\Lambda_0$  values of the potassium salt of A. S. in the 70% dioxane are considered to be smaller than those of the lithium and the sodium salt of A. S..

The ionic association constants for the lithium salt of A. S. are seen to be the largest, and for the sodium salt of A. S. the smallest. These evidences are supposed to be difficult to be explained in terms of the nature of the counter ions,  $K^+$ ,  $Li^+$  and  $Na^+$ .

The center-to-center distances of the ions in an associate ( $a$ ) and the thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$ ) in the ionic association reaction of the three kinds of salts of A. S. are obtained by the same treatment described above. They are shown in Table 6.

The quantities  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  for the potassium and the lithium salt of A. S. are seen to be comparable to those of the ionic association reaction of the sodium salt of A. S., O. II and M. O. in water-dioxane mixtures.

From Table 6, it seems to be noteworthy that the center-to-center distances become larger as the radii of the ions become larger.

Thus, the equivalent conductances at infinite dilution and the center-to-center distance of ions in an ion associate are considered to be influenced by the nature of the counter ions of A. S. in water-dioxane mixtures.

Table 6 THERMODYNAMIC PARAMETERS FOR POTASSIUM, LITHIUM AND SODIUM SALT OF ALIZARINE SAPHIROL SE IN THE 70% DIOXANE AT 25°C

Salts	$K_{A_{2UH}}$	$\Delta H^\circ$ (Kcal/mol)	$\Delta G^\circ$ (Kcal/mol)	$\Delta S^\circ$ (cal/deg·mol)	$a$ (Å)
Potassium salt of Alizarine Saphirol SE	$1.72 \times 10^8$	0.08	-4.4	15.1	8.0
Lithium salt of Alizarine Saphirol SE	$1.97 \times 10^8$	0.11	-4.5	15.5	5.0
Sodium Salt of Alizarine Saphirol SE *1	$1.36 \times 10^8$	1.93	-4.3	21.1	6.7

\*1 Cf Reference 3

### Summary

The ionic association reactions of azo dyes (Orange II and Methyl Orange), and the effects of the nature of the counter ions (lithium, sodium and potassium ions) of Alizarine Saphirol SE (A. S.) anion upon the ionic association reaction of the dyes in water-dioxane mixtures were examined by means of the conductance measurements.

The ionic association constants of Orange II and Methyl Orange at 25°C in the 82% dioxane were found to be  $7.82 \times 10^8$  and  $8.94 \times 10^8$  respectively, and they were slightly smaller than that of the sodium salt of A. S.. In the 70% dioxane, the equivalent conductance at infinite dilution of the potassium salt of A. S. was found to be much smaller than those of the lithium and the sodium salt of A. S.. It was noteworthy that the center-to-center distances of the ions in an associate were found to become larger as the radii of the cations become larger.

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