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The Conductances of Alizarine Saphirol SE in Water-dioxane Mixtures at Various Temperatures

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It was reported, in our previous paper,[1)] that Alizarine Saphirol SE forms the ion-associates in water-dioxane mixtures with low dielectric constants.

In the present paper, the thermodynamic properties of the ion-association reactions of Alizarine Saphirol SE in 70 and 82% dioxane are examined.

Experimental

Materials. The Alizarine Saphirol SE (sodium salt of 1,5-dihydroxy-4,8-diaminoanthraquinone-2-sulfonic acid) was a laboratory stock used in a previous work.[1)]

The dioxane was purified by the same method as that described in the previous work.[1)]

Conductance Measurements. These measurements were carried out at 15, 25, and 35°C by the same procedures as those described in the previous work.[1)]

Results and Discussion

The conductances of Alizarine Saphirol in water-dioxane mixtures at 15, 25, and 35°C are shown in Fig. 1.

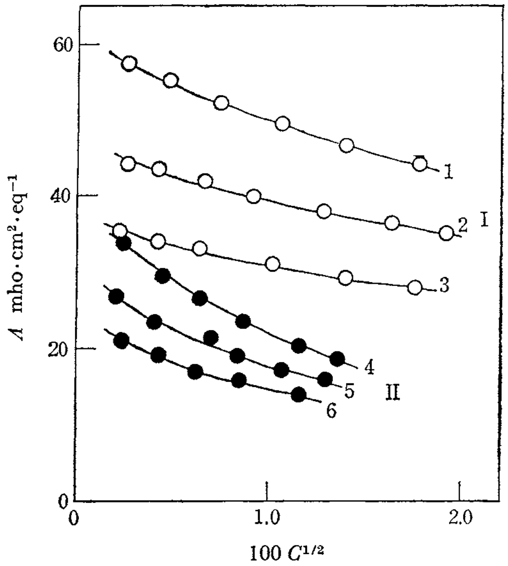

Fig. 1. Equivalent conductances of Alizarine Saphirol SE in 70 and 82 %dioxane. I, 70% dioxane (1 : 35, 2 : 25, 3 : 15°C), II 82% dioxane (4 : 35, 5 : 25, 6 : 15°C).

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

From the results of the conductance measurements indicated in Fig. 1, the equivalent conductances at an infinite dilution, Λ_0, and the ion-association constants, K_A, were calculated by means of Shedlovsky's treatment[2] based on the Onsager limiting equation in a manner similar to that described in the previous work;[1] the results are shown in Table 1.

Table 1. Calculated parameters

Dioxane	t °C	D	$100\,\eta$ poise	Λ_0	$\Lambda_0\eta$	K_A
70.0%	15	18.72	2.483	35.6	0.884	1.31×10^3
	25	17.69	1.918	45.3	0.869	1.39×10^3
	35	16.72	1.522	58.2	0.886	1.63×10^3
82.0%	15	10.01	2.106	23.0	0.484	8.67×10^3
	25	9.53	1.671	27.5	0.460	9.86×10^3
	35	9.06	1.356	36.5	0.495	1.30×10^4

D: Dielectric constant of the solvent.
η: Viscosity coefficient of the solvent.[3]

From Table 1, the K_A values of the dye in water-dioxane mixtures are found to increase with the rise in the temperature of the solvents. The Walden products, $\Lambda_0\eta$, are essentially constant in the solvents of a constant composition, even if the temperatures are different.

The relation among K_A, the dielectric constant, D, and the temperature, T, of the solvent is given by this equation:[4]

$$K_A = e^b, \tag{1}$$

where,

$$b = e^2/aDkT. \tag{2}$$

In Eq. (2), e is the electron charge, a is the center-to-center distance of the ions in an associate and $\boldsymbol{k}$ is the Boltzmann constant.

In accordance with Eq. (1), the plot of log K_A against DT must be linear. The plots of log K_A *vs.* the DT of Alizarine Saphirol in 70 and 82% dioxane are shown in Fig. 2; the plots are found to be linear. These evidences suggest that the ion associates of Alizarine Saphirol in 70 and 82% dioxane are due entirely to the electrostatic interactions between the dye ion and the counter ion.

The a values of Alizarine Saphirol in 70 and 82% dioxane can be obtained from the slopes of the plot of log K_A *vs.* DT; they are indicated in Table 2. As can be seen from Table 2, the a value in 70% dioxane is larger than that in 82% dioxane.

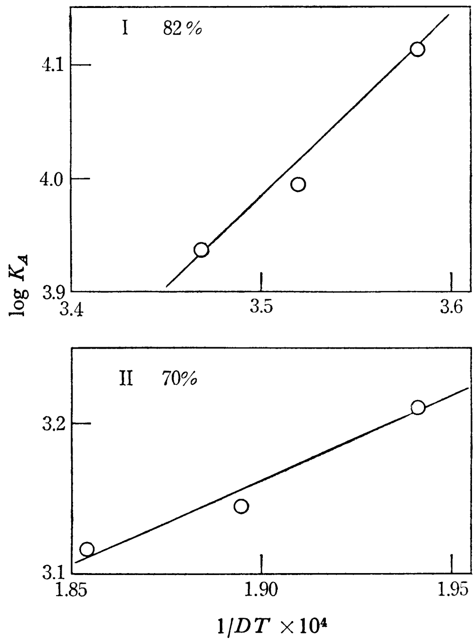

Fig. 2. The relation between log K_A and $1/DT$ in 82% (I) and 70% dioxane (II).

Table 2. Thermodynamic parameters of the ion association reaction of Alizarine Saphirol SE in water–dioxane mixtures at 25°C

Dioxane	$K_{A_{298}}$	ΔH (kcal/mol)	ΔG° (kcal/mol)	ΔS° (cal/deg·mol)	a (Å)
70.0%	1.39×10^3	1.93	−4.3	21.1	6.72
82.0%	9.86×10^3	3.57	−5.5	30.5	4.74

In the ion-association reaction of Alizarine Saphirol in water-dioxane mixtures, the enthalpy change (ΔH) and the entropy change (ΔS°) can be obtained from Eqs. (3) and (5) respectively:

$$\mathrm{d}\ln K_\mathrm{A}/\mathrm{d}(1/T) = -\frac{\Delta H}{\boldsymbol{R}}, \tag{3}$$

$$\Delta G^\circ = -\boldsymbol{R}T\ln K_\mathrm{A}, \tag{4}$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ, \tag{5}$$

where $\boldsymbol{R}$ is the gas constant.

From the best straight line given by the method of least squares for the log K_A *vs.* $1/T$ plot over the whole temperature range, the ΔH values are obtained, the ΔS° values are obtained from Eq. (5), and are as indicated in Table 2.

As is shown in Table 2, since the ΔH values are positive, the reaction is endothermic; these ΔH values are comparable to those of the ion-association reactions of several inorganic salts in water.[5,6]

The ΔS° values of the reactions are positive.

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These results are considered to reflect the evidence that the degree of freedom of the system increases, since the solvent molecules are removed from the solvation sphere of the ions when the dye ion forms an ion associte with the counter ion.

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