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Conductivities of the Methyl Orange-Dodecyltrimethylammonium Complex in Dioxane-Water Mixtures

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The ionic-association reaction of the complex between the Methyl Organic anion and the dodecyltrimethylammonium cation in dioxane–water mixtures has been studied by analyzing the conductivity data. The equivalent conductivities at an infinite dilution and the ionic association constants (K_A) have been determined by means of Shedlovsky's treatment, and they have been compared with those of Methyl Orange (sodium salt). The K_A values have been seen to increase with a rise in the temperature and with an increase in the dioxane content. The Walden products have been essentially constant, and they have been found to be comparable to those of Methyl Orange (sodium salt). The data have been analyzed further by the use of the Denison-Ramsey equation, and the ion-ion distance in an associate has been obtained. The ionic-association reaction have been found to increase the heat content and also the entropy.

In a previous paper,[1] we have concluded, on the basis of the conductivity data, that the sodium salt of an anionic dye such as the sodium salt of 1,5-dihydroxy-4,8-diaminoanthraquinone-2-sulfonic acid exists in the form of an ionic associate in dioxane–water mixtures.

Recently, the formation of a complex between large organic ions of opposite charges in water has been found to be explainable in terms of a twofold interaction mechanism, *i.e.*, Coulombic and hydrophobic interactions.[2,3]

Since there have been few reports on the ionic-association reaction of large organic anions with large organic cations in organic solvent–water mixtures with low dielectric constants, it seems that it would be valuable to examine the conductivity behavior of complexes between large organic ions of opposite charges, such as the Methyl Orange–dodecyltrimethylammonium complex in dioxane–water mixtures, and to compare the ionic-association reaction of the complex with that of Methyl Orange (sodium salt).

In this paper, the conductivity data on this kind of ionic complex were used to determine the equivalent conductivity at an infinite dilution and the ionic association constant by means of Shedlovsky's treatment[4] based on Onsager's theory,[5] and the behavior of the complex in the mixtures was considered.

Experimental

Materials. The Methyl Orange (sodium salt) was prepared by coupling diazotized sulfanilic acid with *N*,*N*-dimethylaniline in a weakly acetic acid solution, after which the product was recrystallized three times from water.

The dodecyltrimethylammonium bromide was prepared by boiling a mixture of trimethylamine and dodecyl bromide in ethanol for several hours. The product was recrystallized from acetone and benzene after the ethanol has been removed by distillation.

The Methyl Orange–dodecyltrimethylammonium complex (M–D complex) was prepared as follows: 1 dm^3 of 10^{-3} mol/dm^3 Methyl Orange (sodium salt) was added to the same volume of a 10^{-3} mol/dm^3 dodecyltrimethylammonium bromide aqueous solution. The finely dispersed M–D complex was then separated by centrifugation from the solution. The M–D complex was purified by recrystallizing from ethanol. Microelemental analysis gave the following results. Found: C, 64.87; H, 8.93; N, 10.61%. Calcd for $C_{29}H_{48}N_4SO_3$ (1:1 M–D complex): C, 65.41; H, 9.02; N, 10.53%.

The dioxane used in this experiment was purified by the method described in a previous work.[1]

Conductivity Measurements. These measurements were carried out at 15, 25, 35, and 45±0.01 °C using the same apparatus and the same procedures as those described in a previous work.[1]

Results and Discussion

The equivalent conductivities, Λ, of the M–D complex in dioxane–water mixtures at 25 °C are plotted against the square root of the concentration, $C^{1/2}$, as shown in Fig. 1.[6] The Λ values in 45 and 70% dioxane are seen to become larger almost linearly with an increase in the dilution. In 82% dioxane, the Λ value decreases monotonically with an increase in the complex concentration. The dotted lines in Fig. 1 give the limiting slopes of the Onsager equation.[5] The slopes of the experimental curves of the Λ-$C^{1/2}$ plot are seen to be larger than those of the corresponding theoretical

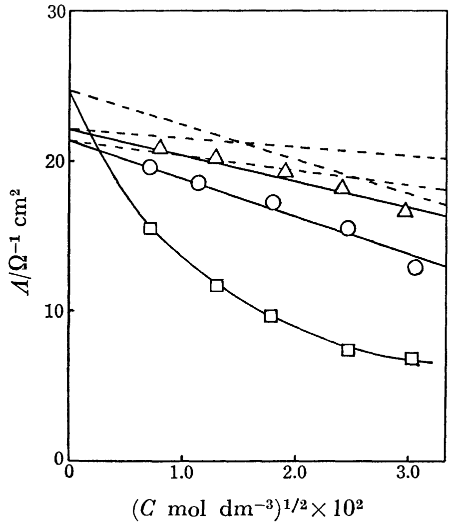

Fig. 1. Equivalent conductivities of Methyl Orange–dodecyltrimethylammonium complex in dioxane–water mixtures at 25 °C.
△: 45% dioxane, ○: 70% dioxane, □: 82% dioxane.

Table 1. Constants for sodium Methyl Orange and Methyl Orange–dodecyltrimethylammonium complexes in dioxane–water mixtures

Solutes	Solvents	t/°C	Λ_0	$\Lambda_0\eta$	K_A
Sodium Methyl Orange	82% dioxane	15	19.97	0.420	6.98×10^3
		25	25.92	0.433	8.97
		35	30.13	0.409	1.05×10^4
M–D Complex	45% dioxane	15	16.21	0.398	3.15×10^2
		25	22.10	0.406	3.64
		35	28.58	0.409	4.90
		45	37.18	0.425	6.31
	70% dioxane	15	15.84	0.393	8.32×10^2
		25	21.47	0.412	9.72
		35	27.30	0.416	1.05×10^3
		45	34.40	0.426	1.19
	82% dioxane	15	18.36	0.387	1.70×10^4
		25	24.72	0.413	1.91
		35	30.73	0.417	2.01
		45	36.14	0.404	2.51

lines. These results suggest that the ionic-association reaction between the Methyl Orange anion and the dodecyltrimethylammonium cation takes place in the mixtures. Similar plots were also obtained at 15, 35, and 45 °C.

From the results of the conductivity measurements, the equivalent conductivities at an infinite dilution, Λ_0, and the ionic-association constants, K_A, were obtained by means of Shedlovsky's treatment,[4] based on Onsager's limiting equation,[5] in a manner similar to that described in the previous work[1] and the results are shown in Table 1. From Table 1 the K_A values of Methyl Orange (sodium salt) and the M–D complex are seen to increase with a rise in the temperature of the solvents at a constant solvent composition, and they also increase with the dioxane content, *i.e.*, with a lowering in the dielectric constant of the solvents. The K_A values of the M–D complex are much larger than those of Methyl Orange (sodium salt) in 82% dioxane. This suggests that the dodecyltrimethylammonium ion contributes strongly to the formation of the ionic associate with the Methyl Orange.

The Walden products,[7] $\Lambda_0\eta$, of the Methyl Orange (sodium salt) and the M–D complex are also shown in Table 1. Their $\Lambda_0\eta$ values are essentially constant. This can be explained most simply by assuming that the ions in the mixtures are selectively hydrated over the entire solvent composition range studied, *i.e.*, the dioxane molecules are excluded from the first coordination sphere of the ions.[8,9] The evidence that the Walden products of the Methyl Orange (sodium salt) in 82% dioxane are almost equal to those of the M–D complex may suggest also that the Stokes's radii of the sodium and dodecyltrimethylammonium ions are equal to each other.

In an attempt to analyze the data further, the relation of K_A to $1/DT$[10] was examined by means of the Denison-Ramsey equation[11] as a first approximation,

$$K_A = \exp\,(e^2/aDkT). \tag{1}$$

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. 1, the plot of K_A *vs.* $1/DT$ must be linear. As an example, the plot of log K_A *vs.* $1/DT$ for the M–D complex in 82% dioxane is shown in Fig. 2. This plot gives a straight line. From the slope, the a value is obtained. The a values of Methyl Orange (sodium salt) and the M–D complex in the mixtures are shown in Table 2. All the a values are seen to be reasonable except for the one in 45% dioxane, and they are comparable to those of some of the organic and inorganic electrolytes in organic solvent–water mixtures.[1,12–15]

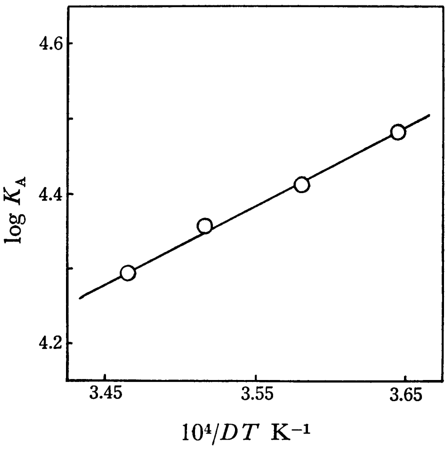

Fig. 2. The relation betweem log K_A and $1/DT$ in 82% dioxane.

The enthalpy changes ($\Delta H°$) and entropy changes ($\Delta S°$) in the ionic-association reactions can be obtained in the usual way; they are also shown in Table 2. Since the $\Delta H°$ values are positive, the reactions are endothermic. The $\Delta H°$ values are comparable to those for the ionic-association reactions of several organic

Table 2. Thermodynamic parameters of ionic-association reactions at 25 °C and center-to-center distance of ions in an associate

Solute	Solvents	K_A	$\Delta H°$/kcal[a] mol^{-1}	$\Delta G°$/kcal mol^{-1}	$\Delta S°$/cal K^{-1} mol	a/Å[b]
Sodium Methyl Orange	82% dioxane	8.94×10^3	0.17	−5.39	19	5.0
M–D Complex	45% dioxane	3.64×10^2	6.10	−3.50	32	1.4
	70% dioxane	9.72×10^2	2.05	−4.08	21	6.8
	82% dioxane	1.91×10^4	2.22	−5.84	27	8.2

a) 1 cal=4.814 J. b) 1 Å=1 nm.

salts in water and some of the anionic dyes in dioxane–water mixtures.[1)]

The $\Delta S°$ values for the reactions are also positive. The results can be considered to reflect the fact that the degree of freedom of the system increases, since the solvent molecules are removed from the solvation sphere of the ions when the ionic-association reaction takes place. The $\Delta S°$ values are comparable to those for the reaction of the sodium salt of an acid dye in dioxane–water mixtures, and those for some of the thallium and the calcium salts in water.[16),17)]

References

1) M. Mitsuishi, M. Hashizume, A. Katayama, and N. Kuroki, *Bull. Chem. Soc. Jpn.*, **43**, 955 (1970).

2) M. Mitsuishi and M. Hashizume, *Bull. Chem. Soc. Jpn.*, **46**, 1946 (1973).

3) G. I. Mukhayer and S. S. Davis, *J. Colloid Interface Sci.*, **56**, 350 (1976).

4) T. Shedlovsky, *J. Frankline Inst.*, **225**, 739 (1938).

5) L. Onsager, *Physik. Z.*, **27**, 388 (1926).

6) As the M–D complex was slightly soluble in water and 20% dioxane, no conductivity measurement was made.

7) The symbol "η" represents the solvent viscosity.

8) Some electrolytes, such as LiCl and LiF, are considered to be selectively hydrated in water–ethanol mixtures containing more than 25% ethanol.[9)]

9) G. Wada, *Nippon Kagaku Zasshi*, **77**, 391 (1956).

10) J. T. Denison and J. B. Ramsey, *J. Am. Chem. Soc.*, **77**, 2615 (1955).

11) "D" represents the dielectric constant of the solvent.

12) R. M. Fuoss and G. Atkinson, *J. Am. Chem. Soc.*, **55**, 1019 (1933).

13) C. J. Hallada and G. Atkinson, *J. Am. Chem. Soc.*, **83**, 3759 (1961).

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

15) R. W. Kunze and R. M. Fuoss, *J. Phys. Chem.*, **67**, 911 (1963).

16) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 617 (1953).

17) G. H. Noncolls, *Discuss. Faraday Soc.*, **24**, 108 (1957).