On the Interaction of Sodium Alkyl Sulfate with Alkylpyridinium Chloride and with Alkyltrimethylammonium Bromide in a Solution

Masaru Mitsuishi and Mieko Hashizume
Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386

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The interaction between sodium alkyl sulfate and alkylpyridinium chloride or alkyltrimethylammonium bromide has been studied quantitatively by means of the conductometric method. The equilibrium constants of the reactions between them have been found to increase with an increase in the length of the alkyl chain. When the sum of the carbon atoms in an alkyl sulfate and of those of an alkylpyridinium chloride or of alkyltrimethylammonium bromide is less than twenty, no reaction has been found to take place. When it is larger than twenty-six, precipitates of the complex have been found. The interaction has been found to depend greately on the length of the alkyl chain. The interaction decreases the heat content and increases the entropy.

The interaction between the oppositely-charged organic ions in aqueous solution have been examined by means of UV-spectroscopic,[1-5] NMR-spectroscopic,[6] conductometric,[7] and polarographic procedures.[8] The experimental evidence suggests that the hydrophobic groups in the organic ions play an important role in the ion-pair formation between oppositely-charged organic ions. However, very few quantitative investigations of the ion-pair formation between oppositely-charged organic ions, and of the factors involved in the determination of the interactions between them, have been carried out. Therefore, it seems valuable to make a quantitative examination of the role of the hydrophobic groups in the ion-pair formation between oppositely-charged organic ions by means of conductometric measurements of the solution.

Experimental

Materials. The alkyltrimethylammonium bromides (ATB) and alkylpyridinium chlorides (APC) used were as follows: hexyltrimethylammonium bromide (C_6TB), octyltrimethylammonium bromide (C_8TB), decyltrimethylammonium bromide (C_{10}TB), dodecyltrimethylammonium bromide (C_{12}TB), tetradecyltrimethylammonium bromide (C_{14}TB), hexadecyltrimethylammonium bromide (C_{16}TB), dodecylpyridinium chloride (C_{12}PC), and hexadecylpyridinium chloride (C_{16}PC).

The ATB was obtained by boiling a mixture of trimethylamine and the corresponding alkyl bromide in ethanol, by removing the ethanol, and by then recrystallizing it from acetone and/or benzene.

The APC was obtained by recrystallizing commercial agents from acetone and benzene.

The sodium alkyl sulfates (SAS) used were as follows: sodium amyl sulfate (SC_5S), octyl sulfate (SC_8S), sodium decyl sulfate ($SC_{10}S$), sodium dodecyl sulfate ($SC_{12}S$), sodium tetradecyl sulfate ($SC_{14}S$), sodium hexadecyl sulfate ($SC_{16}S$), and sodium octadecyl sulfate ($SC_{18}S$). They were prepared by adding an excess of sulfuric acid to a solution of the corresponding alkyl alcohol, by neutralizing alkyl sulfate with sodium hydroxide, and by then recrystallizing the sodium alkyl sulfate from ethanol.

Conductance Measurements of a Solution. A solution of alkyl sulfate and one of alkylpyridinium chloride or alkyltrimethylammonium bromide were mixed in varied proportions; the conductance measurements on the mixtures were made with a Yokogawa-Hewlett Packard Universal Bridge BV-Z-13B at 15, 25, 35 and 45±0.01 °C. A simple dilution cell with a cell constant of 0.0514 at 25 °C was used.

Results and Discussion

The interaction of SAS with APC or ATB may be represented by Eq. (1), since all the examinations of the reactions between them have been carried out on a solution below the CMC of each electrolyte;

$$C^+ + nA^- \rightleftarrows CA_n \qquad (1)$$

Here, C^+ is an organic cations, like the alkylpyridinium ion (AP^+) or the alkyltrimethylammonium ion (AT^+), and A^- is an organic anion, like the alkyl sulfate ion (AS^-). The counter ion of AP^+ or AT^+, like Cl^- or Br^-, and the counter ion of AS^-, like Na^+, are assumed not to take part in the reaction at all, because the concentrations of the electrolytes are very low and the electrolytes are supposed to dissociate completely. In order to determine the n in Eq. (1) by the conductometric continuous-variation method,[9] a solution of C and one of A with the same molar concentration are mixed in various proportions and the conductances of the mixtures are measured.

Figure 1 shows the results obtained by the conductometric continuous-variation method for the interaction of C_{16}TB with SC_8S. The mixture is made by the addition of x_1 liter ($x_1 \leq 1$) of SC_8S of 1.0×10^{-4} mol/l to x_2 liter ($x_2 = 1 - x_1$) of C_{16}TB of 1.0×10^{-4} mol/l, the conductance measurement is carried out, and then specific conductance of the mixture is plotted against the composition. The straight lines, AB and CD, indicate the specific conductances of the SC_8S and C_{16}TB solution respectively. When no reaction between SC_8S and C_{16}TB takes place, the specific conductance of the mixture must be on the straight line BD. Since the

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Table 1. Equilibrium constants of the interactions between sodium alkyl sulfates and alkylpyridinium chlorides

Alkyl-pyridinium chlorides	Sodium alkyl sulfates	Temperature (°C) 15	25	35	45
$C_{12}PC$	$SC_{10}S$	1.19×10^5	9.06×10^4	7.22×10^4	
	$SC_{12}S$		1.11×10^6	8.11×10^5	6.28×10^5
$C_{16}PC$	SC_8S	1.43×10^6	1.07×10^6	7.22×10^5	

specific conductance is found to be the smallest in the equimolar mixture, the n in Eq. (1) is 1, *i.e.*, an equimolecular complex with no charge is formed in the mixture.

Figure 2 shows the specific conductance *vs.* composition plot of a mixture of SC_5S and $C_{12}PC$ at 25 °C. The specific conductance of the mixture is equal to the sum of the specific conductances of SC_5S and $C_{12}PC$ with the corresponding concentrations. The results indicate that no reaction between SC_5S and $C_{12}PC$ takes place in the mixture.

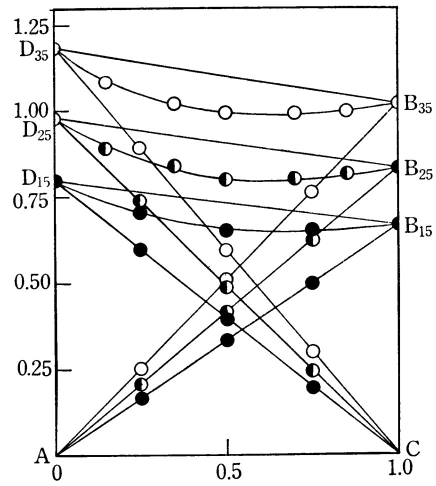

Fig. 1. The specific conductances of the mixture of x_1 liters of sodium octyl sulfate of 1.0×10^{-4} mol/l and $(1-x_1)$ liters of hexadecyltrimethylammonium bromide of 1.0×10^{-4} mol/l at 15 (●), 25 (◐), and 35 °C (○).

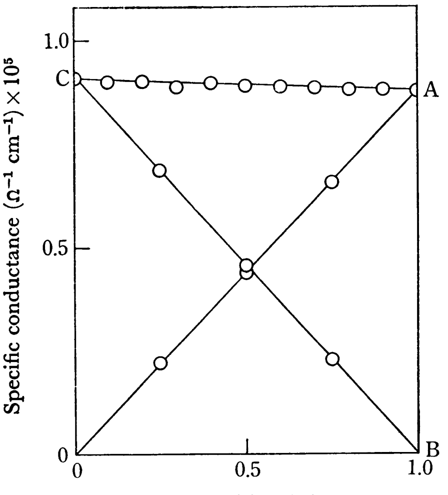

Fig. 2. The specific conductances of the mixture of x_1 liters of sodium amyl sulfate of 1.0×10^{-4} mol/l and $(1-x_1)$ liters of dodecylpyridinium chloride of 1.0×10^{-4} mol/l at 25 °C.

The specific conductance *vs.* composition plots for the mixtures of the other substances, SAS and APC or ATB, are to be similar to either Figs. 1 or 2.

When the reaction between SAS and APC or ATB takes place, only the equimolecular complex is formed in the solution. The equilibrium constant, K, of Eq. (1) is given by Eq. (2);

$$K = \frac{X_{CA}}{X_{C^+}X_{A^-}} \tag{2}$$

Here, the X denotes the mole fraction of each component.

When the reaction takes place in a mixture of x_1 liter of C of c mol and x_2 liter of A of c mol, the specific conductance, κ, of the mixture is given by Eq. (3);

$$\kappa = (cx_1-z)\frac{\alpha}{10^3} + (cx_2-z)\frac{\beta}{10^3} + \frac{z(\gamma_- + \delta_+)}{10^3} \tag{3}$$

Here, z is the concentration of the product, CA, in the reaction. The α and β symbols are the equivalent conductances of the C electrolyte and the A electrolyte respectively. The γ_- and δ_+ symbols are the equivalent ionic conductance of the counter ion of C^+ and that of A^- respectively.

The concentration of the product, z, is obtained by means of Eq. (4);

$$z = \frac{c(x_1\alpha + x_2\beta) - 10^3\kappa}{(\alpha+\beta) - (\gamma_- + \delta_+)} \tag{4}$$

The equilibrium constants shown in Tables 1 and 2 were calculated from Eqs. (4) and (2). It may be seen that the equibrium constants increase with the number of carbon atoms in the alkyl chain.

Table 2. Equilibrium constants of the interactions between sodium alkyl sulfates and alkyltrimethyl ammonium bromides

Alkyl-trimethyl-ammonium-bromides	Sodium alkyl sulfates	Temperature (°C) 15	25	35
CT_6B	$SC_{16}S$	2.66×10^5	2.08×10^5	1.62×10^5
	$SC_{18}S$	1.58×10^6	9.83×10^5	6.89×10^5
CT_8B	$SC_{14}S$	5.43×10^5	4.23×10^5	3.36×10^5
	$SC_{16}S$	2.04×10^6	1.53×10^6	1.12×10^6
$CT_{10}B$	$SC_{12}S$	9.67×10^4	7.28×10^4	5.34×10^4
	$SC_{14}S$	1.01×10^6	8.28×10^5	6.78×10^5
$CT_{12}B$	$SC_{10}S$	7.44×10^4	5.78×10^4	4.42×10^4
	$SC_{12}S$	1.03×10^6	9.28×10^5	8.06×10^5
$CT_{14}B$	SC_8S	6.17×10^4	4.76×10^4	3.71×10^4
	$SC_{10}S$	1.47×10^6	1.17×10^6	8.72×10^6
$CT_{16}B$	SC_8S	1.17×10^6	8.89×10^5	6.72×10^5

Table 3. Thermodynamic parameters of the interactions between sodium alkyl sulfates and alkylpyridinium bromides at 25 °C

Alkyl-pyridinium chlorides	Sodium alkyl sulfates	K_{298}	$-\Delta H^\circ$ (kcal/mol)	$-\Delta G^\circ$ (kcal/mol)	ΔS° (cal/K mol)
$C_{12}PC$	$SC_{10}S$	9.06×10^4	2.4	6.8	15
	$SC_{12}S$	1.11×10^6	5.0	8.2	11
$C_{16}PC$	SC^3S	1.07×10^6	5.5	8.2	9

Let N_1 and N_2 be the carbon atoms of the alkyl groups of SAS and APC or ATB respectively. When the sum of the carbon atoms of N_1 and N_2 is less than twenty, as in the mixture of SC_5S and $C_{12}PC$, no reaction takes place between SAS and ATB in the solution. When the sum is twenty-two, the equilibrium constant is smaller than 6×10^5, whereas it is larger than 6×10^5 when the sum reaches twenty-four. At a value for the sum of more than twenty-six, the reaction is found to be heterogeneous, for precipitates appear.

It is obvious from Tables 1 and 2 that the interaction of SAS with APC or ATB is highly dependent on the length of the alkyl group, though the behavior of the hydrophobic group in the complex is not clear.

The enthalpy changes, ΔH°, in the reaction of SAS with APC or ATB were obtained from the slopes of the straight lines of the log K *vs.* $1/T$ plot over the whole temperature range; they are shown in Tables 3 and 4. The ΔH° values, which are always negative, are comparable with those of the interactions between the acid dye (C. I. Acid Blue 120) and some nonionic surface-active agents,[10] and with those of the interactions between the oppositely-charged organic ions, such as ionic dyes and ionic surface-active agents.[7]

Table 4. Thermodynamic parameters of the interactions between sodium alkyl sulfates and alkyltrimethylammonium bromides at 25 °C

Alkyl-trimethyl ammonium chlorides	Sodium alkyl sulfates	K_{298}	$-\Delta H^\circ$ (kcal/mol)	$-\Delta G^\circ$ (kcal/mol)	ΔS° (cal/K mol)
C_6TB	$SC_{16}S$	2.08×10^5	4.4	7.3	10
	$SC_{18}S$	9.83×10^5	7.3	8.2	3
C_8TB	$SC_{14}S$	4.23×10^5	4.3	7.7	12
	$SC_{16}S$	1.53×10^6	5.3	8.4	10
$C_{10}TB$	$SC_{12}S$	7.18×10^4	5.2	6.6	5
	$SC_{14}S$	8.28×10^5	3.5	8.1	15
$C_{12}TB$	$SC_{10}S$	5.78×10^4	4.6	6.5	6
	$SC_{12}S$	9.28×10^5	2.2	8.1	20
$C_{14}TB$	SC_8S	4.76×10^4	4.5	6.4	6
	$SC_{10}S$	1.17×10^6	4.6	8.3	12
$C_{16}TB$	SC_8S	8.89×10^5	4.9	8.1	11

The ΔS°'s of the interaction between SAS and APC or ATB are found to be positive, as are shown in Tables 3 and 4. It can be presumed that the iceberg structure of water around the hydrophobic groups in the organic ions weakens when alkyl chains in both the ions are held together.

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