A Study on the Micellar Solutions of Sodium Oleate and Elaidate

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Oleic and elaidic acid, which are known as geometrical isomers, have a certain difference in their physical and chemical properties such as their melting points. It is expected that the soaps of these isomers will behave themselves differently as regards the formation of micelles in solution. The examination of this probable difference will supply useful knowledge regarding the structure of micelles. There are already a good many data for the aqueous solutions of oleic acid salts but scarcely any for those of elaidic acid salts. The object of this work is to examine the effect of the geometrical isomerism on the formation and the structure of micelles by measuring the electrical conductivity, the interaction with a dye, the degree of hydrolysis, and the solubilizing power of aqueous solutions of sodium oleate (*cis* form) and elaidate (*trans* form). The dielectric polarization of *n*-heptane solutions of oleic and elaidic acid will also be determined in order to get information on the molecular association of these isomers.

Experimental

Procedure—The electrical conductivity was measured with the audio-frequency bridge of

Yokogawa & Co. using a frequency of 1000 cycles/sec., and the absorption spectrum with the spectrophotometer of Hitachi & Co.

For the measurement of pH of the solutions a glass electrode pH-meter was used.

The measurement of the dielectric constant was carried out by the method described in our previous paper[1].

Materials—Oleic acid was purified from the sample supplied by Armour & Co., U.S.A. by vacuum distillation. b.p. 202∼203°C/5 mmHg. Elaidic acid was prepared by isomerization of oleic acid using nitrogen oxides as catalyst[2], and then extracted with petroleum ether. The product was recrystallized several times from ethanol.

Sodium oleate and elaidate were prepared by adding these acids to the ethanol solution of sodium hydroxide; the amount of the acids was taken slightly less than the amount calculated, the adjustment to neutrality being made with phenolphthalein as an external indicator. The neutral solutions obtained were evaporated under reduced pressure and the products were recrystallized from ethanol and dried in a vacuum desiccator.

Pinacyanol iodide was a pure sample supplied by Nezu Chemical Laboratory.

Benzene was washed with concentrated sulfuric acid, water, dilute sodium hydroxide solution and again with water. After distilling over calcium chloride, it was dried over metallic sodium, and then redistilled. *n*-Heptane was purified in the same way as benzene.

Results and Discussion

1) Electrical conductivity—In Table I and Fig. 1 are given the values of equivalent conductivity (Λ) as a function of the square root of molarity for sodium oleate and elaidate in water. The curves for these two salts are similar to each other as shown in Fig. 1. The result for sodium oleate is in good agreement with that obtained by Flockhart et al.[3] As seen in this figure, Λ increases steadily with decreasing concentration in a very low concentration range. Such a behavior has not been found with other paraffin-chain salts such as salts of higher alkyl sulfonic acids. The position of the breaking point is not clear, which may owe to the hydrolysis as found by Ekwall[4] and Preston[5]. But if we observe carefully the $\Lambda-\sqrt{C}$ curve in Fig. 1, we can detect a slight breaking point. Regarding this point as the critical point, the critical micelle concentration of sodium oleate and elaidate are 2.7×10^{-3} and 2.5×10^{-3} mole/l., respectively. Beyond such a critical point, the equivalent conductivity decreases with increasing concentration just as in the case of other paraffin-chain salts.

In Table I are shown the values of equivalent conductivity in aqueous ethanol of 2 mole/l. and 4 mole/l. For aqueous ethanol of 2 mole/l. the equivalent conductivity decreases slowly and the critical

TABLE I

EQUIVALENT CONDUCTIVITY

concn.	in water		in aq. ethanol of 2 mole/l.	in aq. ethanol of 4 mole/l.
	40°C	60°C	40°C	40°C
		sodium oleate		
0.0001	164	205	108.8	73.0
0.0002	150	194	102.0	71.2
0.0004	135	180	97.6	69.0
0.0007	123	167	93.6	68.0
0.001	113	157	92.3	68.0
0.0012	108	151	—	—
0.0015	104	149	90.0	68.5
0.0017	102	146	—	—
0.002	98.4	142	85.6	69.0
0.0025	95.6	137	80.0	69.5
0.003	91.7	132	76.4	69.2
0.004	—	—	72.4	67.4
0.005	75.4	112	—	—
0.006	—	—	65.6	65.2
0.008	—	—	59.5	63.0
0.01	61.9	89.6	56.0	61.6
0.02	53.6	73.6	48.0	54.8
0.05	46.3	67.4	41.8	45.6
0.1	43.2	63.6	—	—
		sodium elaidate		
0.0001	144	188	102.0	71.0
0.0002	132	180	99.0	68.7
0.0004	120	168	94.0	66.2
0.0007	113	159	91.4	66.8
0.001	110	155	89.5	67.5
0.0012	108	151	—	—
0.0015	106	148	84.1	68.0
0.0017	105	146	—	—
0.002	102	144	79.9	69.0
0.0025	97.2	142	76.0	69.5
0.003	89.3	131	72.5	68.6
0.004	—	—	69.0	67.0
0.005	71.0	102	65.9	—
0.006	—	—	62.5	63.3
0.008	—	—	57.4	60.6
0.01	54.7	80.4	53.9	58.3
0.02	46.4	67.6	45.8	49.5
0.05	39.9	55.8	35.4	42.3
0.1	38.0	53.9	—	—

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[1] M. Shirai and B. Tamamushi, This Bulletin, **30**, 542 (1957).

[2] K. Fuse and B. Tamamushi, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zassi*), **64**, 338 (1953).

[3] B. D. Flockhart and H. Graham, *J. Colloid Sci.*, **8**, 105 (1953).

[4] P. Ekwall, *Z. physik. Chem.*, **A161**, 198 (1932).

[5] W. C. Preston, *J. Phys. & Colloid Chem.*, **52**, 84 (1948).

point is slightly shifted towards lower concentrations than in water, as shown in Fig. 2. For aqueous ethanol of 4 mole/l. the critical point becomes indistinct, the micelle formation being probably inhibited on account of the affinity of the solvent medium for the hydrocarbon chains of the soap molecules.

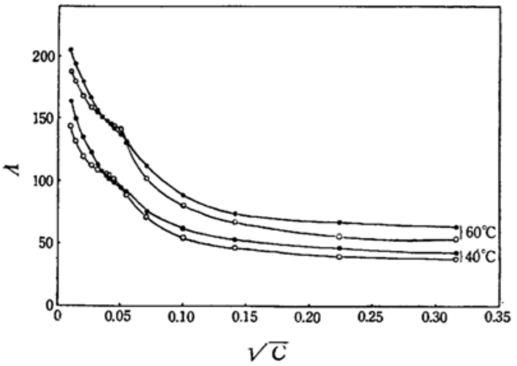

Fig. 1. Electrical conductivity in water. ●, sodium oleate; ○, sodium elaidate.

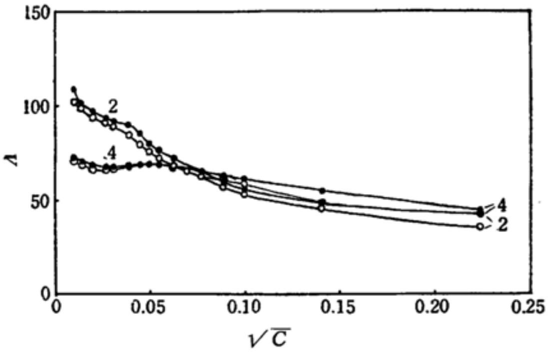

Fig. 2. Electrical conductivity in aqueous ethanol. Numbers on curves refer to the molarity of ethanol. ●, sodium oleate; ○, sodium elaidate.

In pure water the equivalent conductivity of sodium oleate is slightly greater than that of sodium elaidate at concentrations both below and beyond the critical micelle concentration except near that concentration, while in aqueous ethanol of 4 mole/l., where hydrolysis is reduced and the micelle formation is greatly inhibited, the equivalent conductivities of the two salts almost agree with each other. Therefore, it is conceivable that the smaller value of the equivalent conductivity of sodium elaidate is due to its greater power of micelle formation.

2) **Interaction with dye**—Sheppard and Geddes[6] found that, when pinacyanol salt is added to the solutions of surface active agents, its absorption spectrum changes at the critical micelle concentration. This experimental fact serves as a method of measurement of the critical micelle concentration[7]. Fig. 3 shows the optical density of solutions of pinacyanol iodide in sodium oleate and elaidate solution at an absorption maximum near 615 mμ as a function of the concentration of the salts. The critical rise of the optical density has been considered to be due to micelle formation, but the appearance of a minimum below the rise is yet unknown. From this figure we obtain 1×10^{-3} mole/l. as the critical micelle concentration for sodium oleate as well as for elaidate. However, as the concentration of the added dye appropriate for spectroscopic measurement is the same order of magnitude as those of the fatty acid salts, a considerable salt effect on the critical micelle concentration should be expected. Thus, the above obtained values of the critical micelle concentration must be considerably smaller than the true ones.

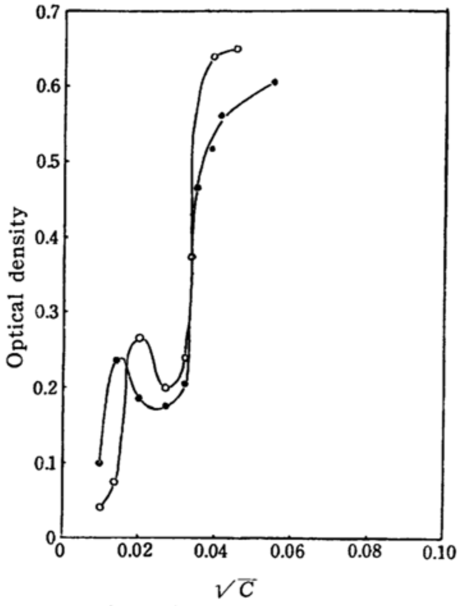

Fig. 3. Optical density of γ band of soap-pinacyanol iodide. ●, sodium oleate; ○, sodium elaidate.

3) **Hydrolysis**—The degree of hydrolysis (β), which is defined as the ratio of the concentration of hydroxyl ion generated by hydrolysis to that of total soap concentration, can be calculated from pH values. In Table II and Fig. 4 is indicated

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[6] S. E. Sheppard and A. L Geddes, *J. Chem. Phys.*, **13**, 63 (1945).

[7] M. L. Corrin, H. B. Klevens and W. D. Harkins, ibid., **14**, 216 (1946).

TABLE II
DEGREE OF HYDROLYSIS

concn.	in water		in aq. ethanol of 2 mole/l.		in aq. ethanol of 4 mole/l.	
	pH	β (%)	pH	β (%)	pH	β (%)
			sodium oleate			
0.0001	7.56	1.10	7.30	0.60	7.25	0.54
0.0002	7.83	1.02	7.65	0.63	7.49	0.47
0.0004	8.10	0.95	8.08	0.91	7.65	0.34
0.0006	8.31	1.03	—	—	—	—
0.0007	—	—	8.43	1.15	7.80	0.27
0.0008	8.60	1.28	—	—	—	—
0.001	8.85	2.14	8.62	1.26	7.99	0.30
0·0015	—	—	8.85	1·43	8.12	0.27
0.002	9.40	3.80	8.97	1.42	8.32	0.32
0.0025	—	—	9.07	1.42	8.48	0.36
0.003	—	—	9.13	1.36	8.52	0.33
0.004	9.60	3.02	9.17	1.12	8.67	0.35
0.006	6.71	2.58	9.32	1.05	8.92	0.42
0.008	9.81	2.44	9.39	0.93	9.02	0.40
0.01	9.85	2.15	9.47	0.89	9.12	0.40
0.02	10.00	1.51	9.52	0.50	9.35	0.34
0.05	10.03	0.65	9.65	0.23	9.48	0.18
			sodium elaidate			
0.0001	7.80	1.90	—	—	7.65	1.14
0.0002	8.08	1.82	7.82	1.00	7.70	1.28
0.0004	8.42	1.99	8.35	1.21	7.75	0.91
0.0006	8.69	2.47	—	—	—	—
0.0007	—	—	8.52	1.43	7.80	0.64
0.0008	8.89	2.90	—	—	—	—
0.001	9.06	3.47	8.86	2.19	7.97	0.65
0.0015	—	—	9.08	2.40	8.27	0.58
0.002	9.67	7.05	9.21	2.45	8.40	0.47
0.0025	—	—	9.30	2.41	8.60	0.48
0.003	—	—	9.38	2.40	8.67	0.47
0.004	9.95	6.75	9.49	2.35	8.75	0.43
0.006	10.00	5.03	9.62	2.10	9.02	0.53
0.008	9.06	4.35	9.68	1.81	9.02	0.40
0.01	10.10	3.80	9.70	1.51	9.05	0.40
0.02	10.02	1.58	9.82	1.00	9.18	0.23
0.05	10.10	0.76	9.88	0.46	9.42	0.16

the result of the pH measurement, together with the degree of hydrolysis calculated therefrom. As shown in Fig. 4 the value of β decreases with increasing concentration and shows a minimum at some concentration below the critical micelle concentration. Then, it rises and reaches the maximum near the critical micelle concentration. Beyond that concentration it decreases gradually. The fact that a minimum and a maximum appear in $\beta-\sqrt{C}$ curve, has been explained by Stainsby and Alexander[8], and Cook[9] in relation to the micelle formation. They supposed that even below the critical micelle concentration submicelles could be formed. By submicelles are meant particles smaller than the well-recognized micelles but containing at least two molecules or ions per particle. The free acid molecules produced by hydrolysis will condense to submicelles, and accordingly, hydrolysis will go on further. With further increase in concentration of salts the counter ion association will take place and the micelle will be formed. At such concentrations the unhydrolyzed ions will condense to micelles too, and consequently, hydrolysis goes on no longer.

As is seen in Fig. 4 the concentrations

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[8] G. Stainsby and A. E. Alexander, *Trans. Faraday Soc.*, **45**, 585 (1949).

[9] M. A. Cook, *J. Phys. & Colloid Chem.*, **55**, 383 (1951).

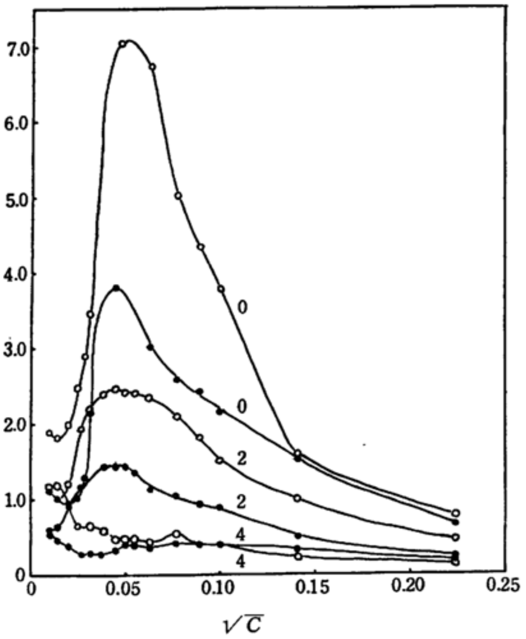

Fig. 4. Degree of hydrolysis in water and aqueous ethanol. Numbers on curves refer to the molarity of ethanol. ●, sodium oleate; ○, sodium elaidate.

where minimum and maximum of β appear for sodium oleate are nearly the same as for elaidate, while the value of β is much greater for sodium elaidate than for sodium oleate except at very large concentrations. This result is presumably due to the fact that sodium elaidate has a greater micelle forming power as well as a greater solubilization power for free acid than sodium oleate. Beyond the critical micelle concentration, β for each salt falls on nearly the same value.

In aqueous ethanol the maximum of β which is caused by hydrolysis and promoted by the submicelle formation becomes smaller. In aqueous ethanol of 4 mole/l., where the critical micelle concentration is not recognized by $\Lambda-\sqrt{C}$ curve, the maximum of β is almost diminished and β decreases monotonously with increasing concentration as in the case of ordinary electrolytes. These results obtained for the aqueous solutions and aqueous ethanol solutions correspond to the conductivity behavior of the salts, and support the view that the hydrolysis of the salts has a close relation with the micelle formation.

4) **Solubilization**—In Table III is given the experimental result of solubilization of benzene in terms of moles of solubilized benzene per mole of soap. It is shown that sodium elaidate has a greater solubilization power for benzene than sodium oleate, which is consistent with the result of pH measurement.

TABLE III

SOLUBILIZATION

substance	concn. of salt (mole/l.)	moles of benzene / mole of salt
sodium oleate	0.02	7.5
sodium elaidate	0.02	9.0
sodium oleate	0.1	12.5
sodium elaidate	0.1	15.0

5) **Dielectric polarization in nonpolar solvent.**—The experimental result of the measurement of dielectric polarization in *n*-heptane is shown in Table IV and Fig. 5, where x is the mole fraction, ε the dielectric constant, d the density, P_2 the molecular polarization of the solute, and μ the dipole moment. The electronic polarization P_E is computed from the atomic refraction and the atomic polarization P_A is assumed to be 5% of the electronic polarization. The molecular polarization decreases considerably with increasing concentration both for oleic and elaidic acid, but this decrease is slightly greater for elaidic acid than for oleic acid. This experimental fact shows that elaidic acid has a greater tendency towards association than oleic acid in a non-polar solvent. On the other hand, the molecular polarization at infinite dilution is nearly the same for both acids, and consequently, the dipole moment calculated

TABLE IV

DIELECTRIC POLARIZATION

n-heptane solution temp. 40°C

oleic acid

x	ε	d	P_2(cc.)
0.000000	1.9213	0.6709	(144.0)
0.003509	1.9272	0.6719	133.1
0.005808	1.9300	0.6726	126.2
0.009164	1.9325	0.6736	118.8
0.013354	1.9350	0.6750	112.7
0.018383	1.9377	0.6763	109.3

$P_E+P_A=90.7$ cc. $\mu=1.65$

elaidic acid

x	ε	d	P_2(cc.)
0.000000	1.9213	0.6709	(143.0)
0.002772	1.9262	0.6722	131.1
0.006295	1.9308	0.6736	120.5
0.009259	1.9335	0.6749	114.4
0.011743	1.9350	0.6757	111.4
0.016467	1.9386	0.6784	105.6

$P_E+P_A=90.7$ cc. $\mu=1.64$

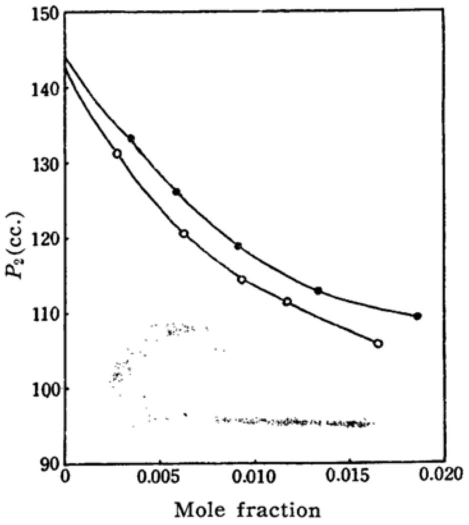

Fig. 5. Molecular polarization in *n*-heptane. ●, oleic acid; ○, elaidic acid.

from them is also nearly the same for both acids.

From these experimental results it is concluded that sodium elaidate has a slightly greater tendency towards association into micelles and a greater solubilization power for hydrocarbons, and accordingly has a greater degree of hydrolysis than sodium oleate.

Summary

The electrical conductivity, the interaction with pinacyanol iodide, the degree of hydrolysis, and solubilization power for benzene have been measured for sodium oleate and elaidate.

The conductivity behavior of these salts is consistent with the experimental result for hydrolysis and the latter result is also consistent with that of solubilization measurement. The result of dielectric polarization is also compatible with other results.

All these experimental results show that sodium elaidate has a slightly greater tendency towards micelle formation than sodium oleate.

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