A New Analytical Method of Electroconductivity Data of Surfactant Solutions. II*

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In the previous paper[1], a new analytical method for the electroconductivity data of aqueous solution of surfactant was reported. In this paper we apply this method to arrange and analyse the effect of temperature and of the addition of organic solvents and inorganic salts on the properties of surfactant solution.

The Effect of Temperature

It has been reported that the dependence of critical micelle concentration (C. M. C.) of surfactant solution on temperature is not evident; but it will be expected that some parameter which is related to the critical phenomena of surfactant solution will change with temperature.

According to our analysis of the electroconductivity data for dodecyl ammonium chloride at various temperatures, taken from Ralston[2], it is pointed out that the concentration of the minimum and the maximum in $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve and the slope between them do not vary considerably, but $H_{\min}$ and $H_{\max}$,—the magnitude of $\Lambda_0-\Lambda/\sqrt{c}$ at the minimum and the maximum—, vary conspicuously with temperature. The results are shown in Fig. 1.

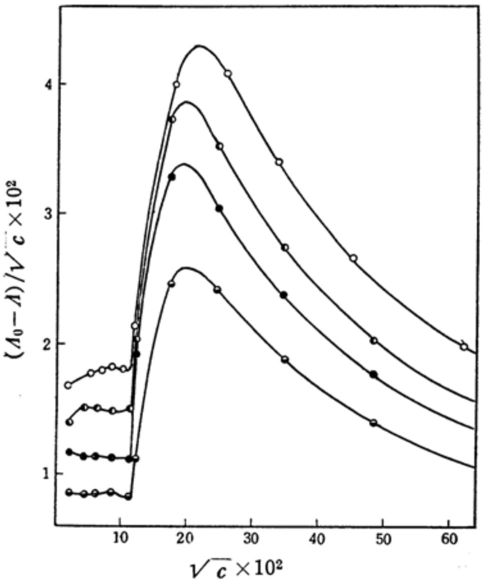

Fig. 1. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for the aqueous solution of dodecyl ammonium chloride at 20° ◒, 30° ●, 40° ◐ and 60°C ○.

The usual C. M. C. being remarkably invariant with temperature, H values might be of greater importance for the analysis of the effect of temperature on the critical phenomena of surfactant solution.

The Effect of Organic Solvent

From earlier data, it is noticed that the effects of addition of organic solvent upon the C. M. C. can be classified into those of lower fatty alcohols and of higher alcohols or hydrocarbons.

On the addition of a lower fatty alcohol, such as methyl or ethyl, the C. M. C. of surfactant shifts toward higher concentration with increasing alcohol content[3-5]. On the other hand, by the addition of a higher alcohol or a hydrocarbon, the C. M. C. is lowered[6-8], probably owing to solubilization. Such being the case, it is convenient to apply our analysis to each of two effects.

a) The Effect of Lower Fatty Alcohol: —Ward[3,4] and Kraus and his collaborators[5] measured the electroconductivity of sodium dodecyl sulfate and hexadecyl

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1) K. Meguro, T. Kondo, N. Ohba, et al., This Bulletin, **30**, 760 (1957).

2) A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *J. Am. Chem. Soc.*, **64**, 97 (1942).

3) A. F. Ward, *Proc. Roy. Soc.*, **A176**, 412 (1940).

4) A. F. Ward, *J. Chem. Soc.*, **1939**, 552.

5) E. C. Evers and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 3049 (1948).

6) G. L. Brown, R. F. Grieger and C. A. Kraus, ibid., **71**, 95 (1949).

7) S. H. Herzfeld, M. L. Corrin and W. D. Harkins, *J. Phys. Coll. Chem.*, **54**, 971 (1950).

8) A. W. Ralston and D. N. Eggenberger, *J. Am. Chem. Soc.*, **70**, 983 (1948).

pyridonium bromide in water alcohol mixtures.

Our results by a new method are shown in Figs. 2 and 3. With increasing alcohol content of the solvent, the minimum and

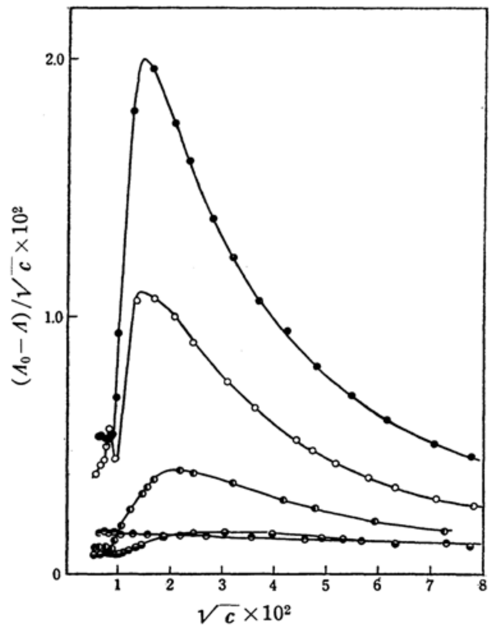

Fig. 2. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagrams for sodium dodecyl sulfate in water-ethanol mixture: ● 0.0%, ○ 9.91%, ◐ 20.02%, ◒ 29.78%, and ◓ 39.60% of ethanol.

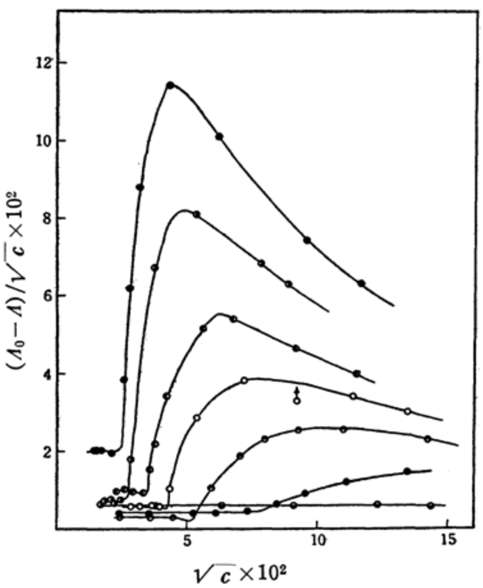

Fig. 3. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagrams for hexadecyl pyridonium bromide in water-methanol mixture: ● 0.0%, ◑ 6.36%, ◐ 14.70%, ○ 19.91%, ◓ 26.02%, ● 35.20% and ◒ 54.14% of methanol.

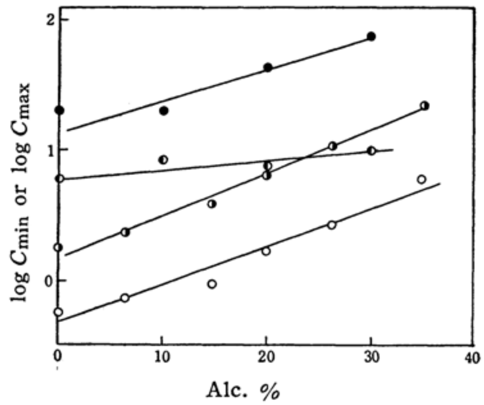

Fig. 4. The relations between alcohol content and $C_{\min}$ or $C_{\max}$: for sodium dodecyl sulfate, ◐ $C_{\min}$ and ● $C_{\max}$: for hexadecyl pyridonium bromide, ○ $C_{\min}$ and ◑ $C_{\max}$.

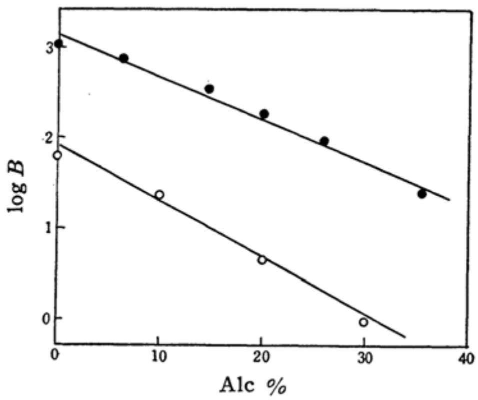

Fig. 5. The relations between alcohol content and log B; ○ sodium dodecyl sulfate and ● hexadecyl pyridonium bromide.

the maximum point shift toward higher concentrations, and the value of $H_{\max}$ decreases and at last the maximum disappears, while the slope between the minimum and the maximum becomes gradually gentle. From these data, we can find linear relations between log $C_{\min}$ or log $C_{\max}$ and alcohol content, between log $H_{\max}$ and alcohol content, and between log B and alcohol content as shown in Figs. 4 and 5 and Table I. (The meaning of the notations, $C_{\min}$, $C_{\max}$ and B is the same as in the previous paper.)

b) The Effect of Solubilization:— Previously it was noted that the effect of the addition of higher alcohols or hydrocarbons on the C. M. C. was due to the solubilization of these substances in the micelle of surfactant. It is well known that there are two types in solubilization phenomena. One is of "palisade type",

TABLE I

THE CHANGE OF C_{min}, C_{max}, H_{min}, H_{max} AND B VALUES WITH ALCOHOL CONTENT

Substance	Alc. content %	C_{min}	C_{max}	H_{min}	H_{max}	B
$C_{12}H_{25}OSO_3Na$—EtOH	0.00	6.08	20.2	0.50	2.34	58.8
	9.91	8.50	20.2	0.45	1.10	23.6
	20.02	7.35	44.1	0.10	0.40	4.63
	29.78	9.90	75.8	0.08	0.16	0.98
$C_{16}H_{33}N^+C_5H_5Br^-$—MeOH	0.00	0.45	1.76	1.93	11.4	1080
	6.36	0.50	2.30	0.66	8.2	650
	14.70	1.16	3.85	0.95	5.5	350
$C_{18}H_{37}N^+C_5H_5Cl^-$—MeOH	0.00	0.24	1.06	0.30	11.0	1530
	9.90	0.56	2.03	0.83	6.80	700
	14.86	0.39	3.70	−0.73	4.52	333

TABLE II

Type of Solubilization	Effect	H_{min}	H_{max}	C_{min}	C_{max}
Palisade type	Increase in the amount of solubilizate	0	+	−	−
	Increase in the alkyl chain length of solubilizate	0	+	−	−
Sandwich type	Increase in the alkyl chain length of solubilizate	?	−	0	0

0: no remarkable change; +, increase; −, decrease

and the other of "sandwich type". The solubilization of higher alcohols belongs to the former type, and the solubilizates are situated in the micelle like palisades. On the other hand, the solubilization of nonpolar hydrocarbons, such as alkane and benzene, belongs to the latter type, and the solubilizates are situated, like contents of a sandwich, between surfactant molecules which construct a micelle.

If the difference between these types of solubilization could be observed by a suitable plotting of electroconductivity data, it would be very interesting, but it is impossible to do so by the usual plotting such as Λ vs. $\sqrt{c}$. According to our method, however, we can clearly distinguish them. In Fig. 6 and 7 is shown our analysis of palisade type solubilization, and in Fig. 8 that of sandwich type.

Comparing the effect of increase in the amount and in the alkyl chain length in the palisade layer on H_{min}, H_{max}, C_{min} and C_{max}, with the effect of increase in the alkyl chain length of solubilizates in the sandwich layer on the same values, we can obtain the results shown in Table II. The effects on these values, especially on H_{max} and C_{max}, form a good contrast between the palisade and the sandwich type. The fact that the effects of increase in the amount and in the alkyl chain length of solubilizates in the palisade layer correspond to those of increase in alkyl chain length of a surfactant molecule is suggestive of the existence of an intimate relation between them.

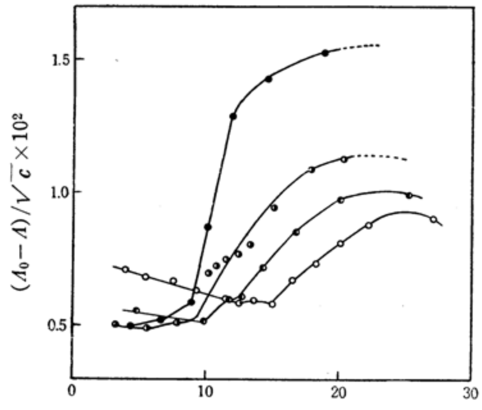

Fig. 6. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for dodecyl ammonium chloride in 24.65% methanol on addition of moles dodecanol per mole salt: ○ 0.0%, ◐ 0.110%, ◑ 0.261% and ● 0.651%.

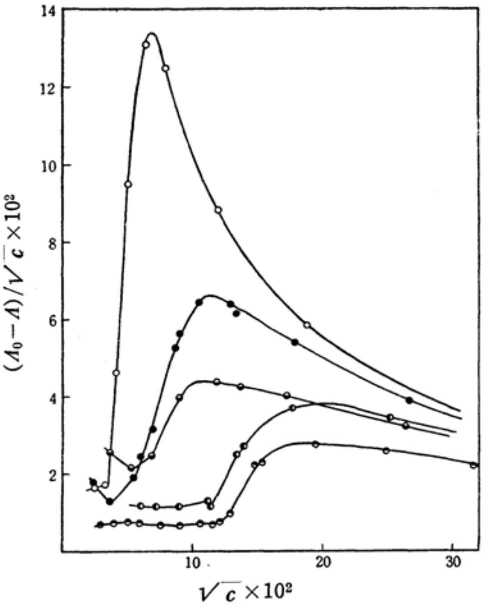

Fig. 7. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for dodecyl ammonium chloride solutions at 30°C in the presence of following substances; ◓ in water, ◒ hexanol, ● octanol, ○ dodecanol and ◐ octadecanol. (Adopted from Ref. 8)

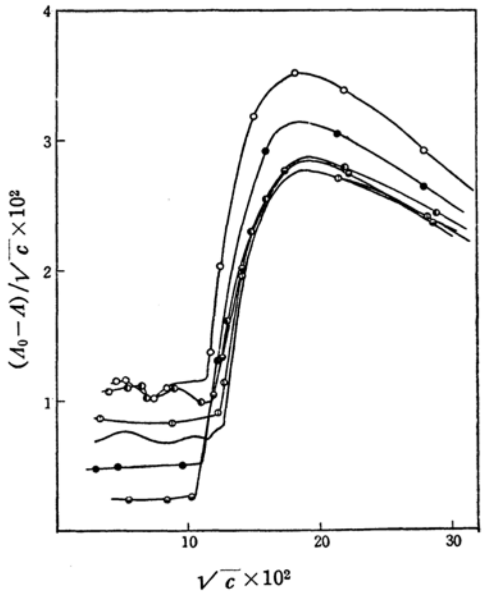

Fig. 8. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for dodecyl ammonium chloride solutions at 30°C in the presence of the following substances: (—) in water, ○ hexane, ● octane, ◒ dodecane, ⦶ heptadecane and ◑ octadecane. (Adopted from Ref. 8)

The Effect of Added Salt

It is well known that the presence of an electrolyte affects considerably the behavior of aqueous solution of surfactants[9,10]. In general, the added salt promotes the micelle formation of surfactants. In order to apply our method to this case, Ralston's data[9] on the electroconductivity of aqueous solution of dodecyl ammonium chloride in 0.005 N and 0.015 N sodium chloride were used. The results obtained are shown in Fig. 9.

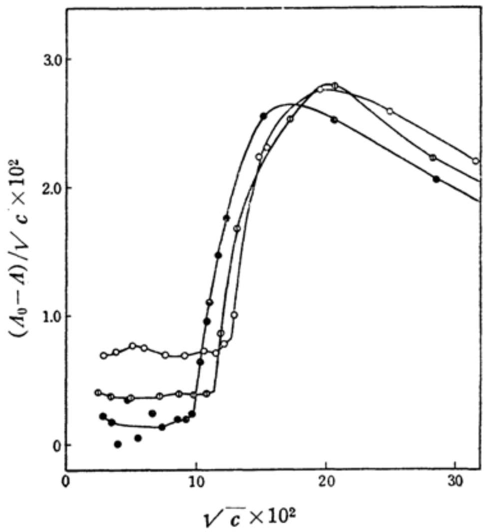

Fig. 9. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for dodecyl ammonium chloride in sodium chloride solutions: ○ 0.0 N, ⦶ 0.005 N and ● 0.015 N.

The most remarkable thing is the occurring of influence upon $H_{\min}$ and no remarkable effect on $H_{\max}$ by the addition of salt, while $C_{\min}$ and $C_{\max}$ shift toward lower concentration with increasing concentration of the salt.

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9) A. W. Ralston and D. N. Eggenberger, ibid., **70**, 980 (1948).
10) M. L. Corrin and W. D. Harkins, ibid., **69**, 683 (1947).