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

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In previous papers[1,2] we have described that $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram is better than Λ vs. $\sqrt{c}$ diagram to analyze the critical phenomena of a surfactant solution. In $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram we were able to define two concentrations, $C_{\min}$ and $C_{\max}$, which characterize the critical phenomena. We also discussed various effects—such as the effect of alkyl chain length,—on them. On the other hand, we found that the values of $(\Lambda_0-\Lambda)/\sqrt{c}$ at $C_{\min}$, $C_{\max}$ and the gradient of $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve between $C_{\min}$ and $C_{\max}$, were very useful for analysis. These values were denoted by $H_{\min}$, $H_{\max}$ and B.

In this paper we consider the meaning of these constants.

The meaning of $C_{\min}$ and $C_{\max}$

Hartley and his associates[3] found the occurrence of a maximum equivalent conductivity in the aqueous solution of cetyl pyridonium chloride in a very high electric field. The $C_{\max}$ determined by our method in the case of cetyl pyridonium bromide corresponds to the concentration

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[1] K. Meguro et al., This Bulletin **30**, 760 (1957).

[2] K. Meguro et al., ibid., **30**, 905 (1957).

[3] J. Malsh and G.S. Hartley, *Z. physik. Chem.*, **A140**, 321 (1934).

TABLE I

COMPARISON OF $C_{\min}$ AND $C_{\max}$ WITH THE TRANSPORT NUMBER DATA

Substance	$C_{\min}$	Breaking pt. in Transport number vs. $\sqrt{c}$ curve	$C_{\max}$	Level off pt. in Transport number vs. $\sqrt{c}$ curve
$C_8H_{17}NH_3Cl$	—	423	—	525
$C_{10}H_{21}NH_3Cl$	15.4	22.5	108	96
$C_{12}H_{25}NH_3Cl$	12.1	12.7	44.1	40.0
$C_{14}H_{20}NH_3Cl$	3.6	5.0	15.8	15.6
$C_{16}H_{33}NH_3Cl$	0.62	1.4	4.9	5.6
$C_{18}H_{37}NH_3Cl$	0.40	0.35	1.7	1.4

of the maximum found by Hartley, as shown in Fig. 1.

Hartley made the following explanation for the occurrence of the maximum. At the concentration of surfactant near usual *C.M.C.*, the gegenions fixed on micelles are dissociated by applying high electric field; therefore, the gegenions and multicharged micelles come to contribute to the electroconductivity, and this contribution increases anomalously. At a more concentrated region, the fixed gegenions can not dissociate even in such a strong field; then the conductivity begins to fall again.

The $C_{\max}$ may be considered to show the concentration at which the fixation of gegenions on micellar surface is completed.

Furthermore, the data of transport number support this consideration. Ralston[4] found that the curve of transport number against the square root of normality shows a breaking point at a low concentration corresponding to the *C.M.C.*, and rises sharply to an anomalously high value with the increase of concentration, and then levels off. The concentration at which the value of transport number attains this anomalously high value is in good agreement with $C_{\max}$, as shown in Fig. 2. After attaining this value, the transport number keeps a constant level in ordinary concentration, which means that the electrical charge of micelle becomes constant if the equal size of micelle is assumed. That is, the fixation of gegenions on micellar surface may be considered to be completed at this point.

Table I shows the correspondence between this concentration and $C_{\max}$ of some alkyl amine hydrochlorides.

On the other hand, it may be supposed that $C_{\min}$ indicates the concentration at which the fixation of gegenions begins.

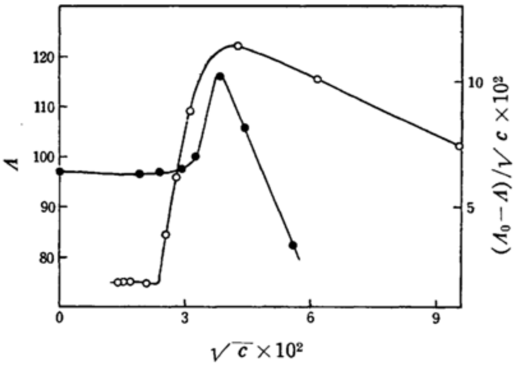

Fig. 1. Comparison of Λ vs. $\sqrt{c}$ curve for cetyl pyridonium chloride solution in high electric field (200 kV) with $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve for cetyl pyridonium bromide solution:

● Λ vs. $\sqrt{c}$ curve and ○ $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curve.

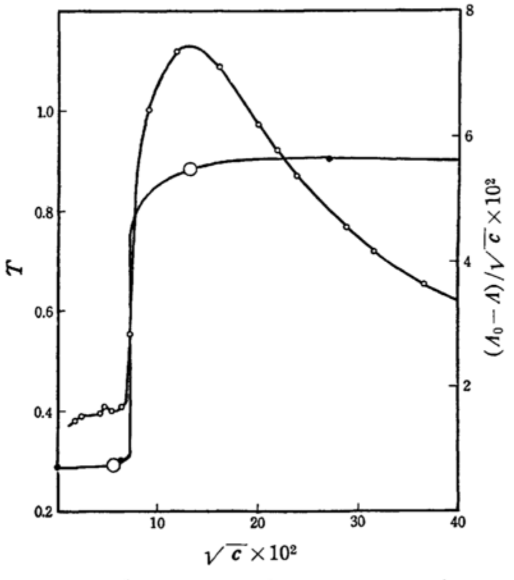

Fig. 2. Comparison of transport number diagram with $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram for tetradecyl ammonium chloride:

• and ○ transport number, and

∘ $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram.

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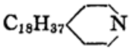
[4] A. W. Ralston, C. W. Hoerr and E. J. Hoffman, *J. Am. Chem. Soc.*, **64**, 97 (1942).

TABLE II

C_{min}, C_{max}, H_{min}, H_{max} AND B VALUES OF OCTADECYL PYRIDONIUM SALTS WITH REFERENCE TO THEIR GEGENIONS

Substance		C_{min}	C_{max}	H_{min}	H_{max}	B
	NO_3	(1.14)	0.42	(1.20)	19.6	4300
	Cl	0.24	1.09	0.30	11.0	1530
	IO_3	0.48	4.90	−3.85	2.80	374

The steepest region between C_{min} and C_{max} will be considered the region in which the gegenions are fixed. By this assumption, it is reasonable to suppose that the great change in electroconductivity takes place at the region between C_{min} and C_{max}.

The meaning of H_{max}

To consider the meaning of H_{max}, the effect of gegenions on the maximum point is very suggestive. It was recognized by Hartley$^{3)}$ and others$^{5-7)}$ that the gegenions of ionic surfactant play an important role in the formation of micelles and that the *C.M.C.* of surfactant depends on the degree of hydration of gegenions.

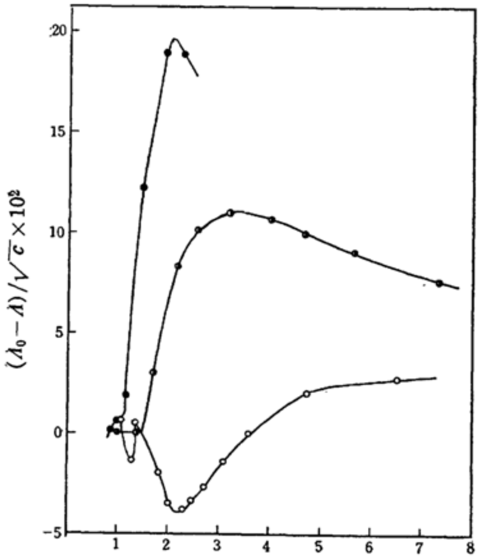


Fig. 3. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for the aqueous solutions of octadecyl pyridonium ● nitrate, ◑ chloride and ○ iodate at 25°C.

To see the relation between the degree of hydration of gegenions and C_{max}, H_{max}, etc., our method was applied to octadecyl pyridonium nitrate, chloride and iodate, and the results obtained are illustrated in Fig. 3 and Table II, in which it must be noted that there is good correspondence between C_{max} or H_{max} and lyotropic series of gegenions as below:

(a) The lyotropic number increases in the order:

$IO_3 < Cl < NO_3$
6.2 10.0 11.6

(b) The value of C_{max} decreases in the order:

$IO_3 > Cl > NO_3$
4.9 1.09 0.42

(c) The value of H_{max} increases in the order:

$IO_3 < Cl < NO_3$
2.8 11.0 19.6

The adsorption (fixation) of gegenions on the surface of micelles is important for the explanation of the above relations. Considering the work of Wo. Ostwald$^{8)}$ and Y. Osaka$^{9)}$ on the adsorption of salts on charcoal, we have reached the following conclusion.

(a) The larger the degree of hydration of ion, the higher the concentration, at which the adsorption attains saturation.

(b) The higher the degree of hydration, the larger the quantity of adsorbed ions at saturation.

It may be considered from the relation (a) that the adsorption of gegenions on the micelle surface is saturated as in the above order.

On the other hand, it may be assumed that H_{max} depends on the quantity of ions adsorbed at saturation. If the quantity of gegenions adsorbed on micelle at saturation is large, the variation of electroconductivity also becomes large; then, H_{max} becomes large.

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5) P. F. Grieger and C. A. Kraus, ibid., **70**, 3803 (1948).
6) G. L. Brown, P. F. Grieger and C. A. Kraus, ibid., **71**, 95 (1949).
7) K. Meguro, T. Kondo et al., *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1236 (1956).
8) Wo. Ostwald, *Kolloid-Z.*, **87**, 128 (1939).
9) Y. Osaka, *J. Tokyo. Chem. Soc.*, **37**, 241 (1916).
10) Wo. Pauli and L. Sternbach, *Kolloid-Z.*, **84**, 291 (1938).

A new concept for the mechanism of micelle formation

In the above considerations, some doubts still remain as to whether the micelle formation precedes the fixation of gegenions or fixation of gegenions and micelle formation occur simultaneouly; that is, the fixation causes the micelle formation.

Some suggestion on this problem can be obtained in the correspondence between surfactant solution and polyelectrolyte solution.

Pauli,⁽¹⁰⁾ Seiyama⁽¹¹⁾ and Takahashi⁽¹²⁾ found the following Λ vs. $\sqrt{c}$ diagram for sodium alginate solution (Fig. 4.), which is very similar to the one of surfactant solution.

Furthermore, Koizumi and Mataga⁽¹³⁾ found the disappearance of fluorescence of Rhodamine 6G by addition of a small amount of potassium polyvinyl sulfate: they also found the recovering of fluorescence in concentrated solution of this polyelectrolyte. The same phenomenon can be found in the case of sodium dodecyl sulfate and Rhodamine 6G system; that is, when the concentration of surfactant is lower than its *C.M.C.*, the fluorescence disappears, while it recovers when the concentration is over the *C.M.C.*

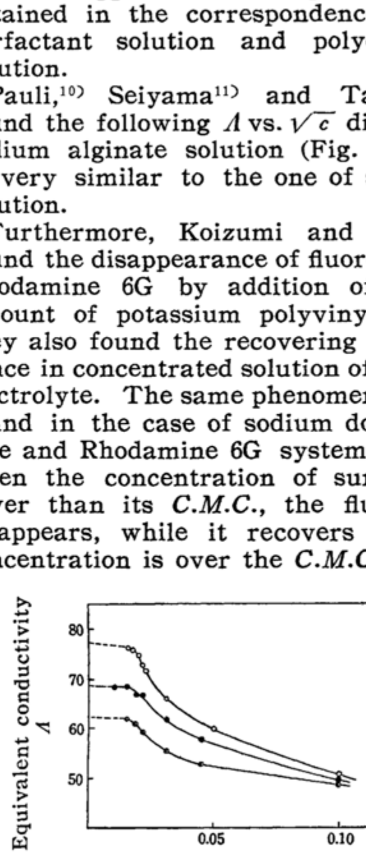

Fig. 4. Λ vs. $\sqrt{c}$ diagram for sodium alginate solution. (taken from Takahashi).

Degree of polymerization of Na alginate ○ 11 ● 35 ◐ 97

If we assume that a molecule of polyelectrolyte corresponds to a micelle of surfactant it will be reasonable to assume the fall of Λ in Λ vs. $\sqrt{c}$ diagram and of the recovering of fluorescence of dye would not be caused by the formation of micelles but by the fact that the number of micelles reaches some definite amount.

According to the theory of Osawa and Kagawa⁽¹⁴⁾, many phenomena for polyelectrolyte solution will be explained by the fixation of gegenions on polyelectrolyte ion; then the dropping of Λ and the recovering of fluorescence in surfactant solution will also be explained as follows;

(1) Owing to the amphipathic properties of surfactant, loose micelles exist in more dilute solution than usual *C.M.C.*.

(2) When the concentration of these loose micelles reaches a definite value, the gegenions are fixed on them; then the charges on micellar surface decrease, decreasing the repulsion among surfactant ions which form micelles, and the micelles become compact. That is to say, the usual *C.M.C.* indicates the concentration at which the compact micelles begin to form.

It should be considered that the micelles of non-ionic surfactants are formed on account of their amphipathic properties; therefore, in this case only the loose micelles can be produced. This fact will be ascertained by the obscurity of critical phenomena in nonionic surfactant solution.

If we consider two types (loose and compact) of micelle, it is necessary to take into account the following facts regarding the discussion of effects on critical phenomena of surfactant solution.

(I) The effects which alter the concentration where the compact micelles appear.

(II) The effects which alter the ability of forming micelles.

The solvent effect and the salt effect on critical phenomena will be ascribed mainly to the effect mentioned in I, but the effect mentioned in II is not well known.

We found the effect which will be regarded as the one mentioned in II in the system of non-ionic and ionic surfactant mixture.

The effect of the addition of polyoxyethylene dodecyl ether on the conductivity of sodium dodecyl sulfate solution was measured.⁽¹⁵⁾ As a result, the following Λ vs. $\sqrt{c}$ diagram was obtained (Fig. 5), which is charaterized by the facts that the breaking point of sodium dodecyl sulfate corresponding to its *C.M.C.* in the usual sense becomes less pronounced with

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11) T. Seiyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **53**, 122 (1950).

12) T. Takahashi, K. Kimoto and Y. Takano, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **72**, 292 (1951).

13) M. Koizumi and N. Mataga, ibid., **75**, 273 (1954).

14) F. Osawa, N. Imai and I. Kagawa, *J. Polymer Sci.*, **13**. 93 (1954).

15) O. Yoda, K. Meguro, T. Kondo and T. Ino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 905 (1956).

increasing concentration of the non-ionic surfactant and almost disappears at 10^{-2} M of non-ionic surfactant without a shift of the breaking point toward either side of concentration. This phenomenon is really new, and usually the additions of salt, solvent and solubilizate are accompanied by shifts of the breaking point.

The $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ diagram based on the same data is shown in Fig. 6, in which it is noticed that the $C_{\min}$ gradually disappears without a shift as the amount of added non-ionic surfactant increases, and that the $H_{\max}$ becomes lower and the slope turns less steep with increasing concentration of non-ionic surfactant. Because $H_{\max}$ is proportional to the amount of gegenions adsorbed on micelle surface, and because $C_{\min}$ shows the concentration at which the compact micelle begins to form by the fixation of gegenions, we can consider that the addition of non-ionic surfactant prevents the formation of compact micelles. This consideration will be supported by the following experiment.

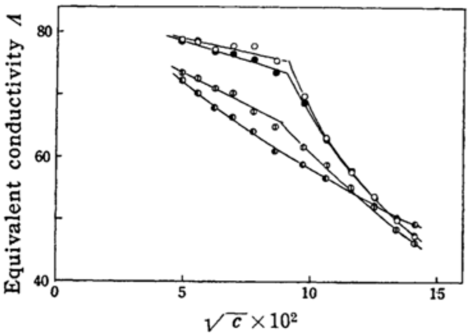

Fig. 5. Λ vs. $\sqrt{c}$ curves for sodium dodecyl sulfate in the aqueous solutions of polyoxyethylene dodecyl alcohol ether:
○ in water, ● 10^{-4}, ⦶ 10^{-3} and ◐ 10^{-2} mole/l.

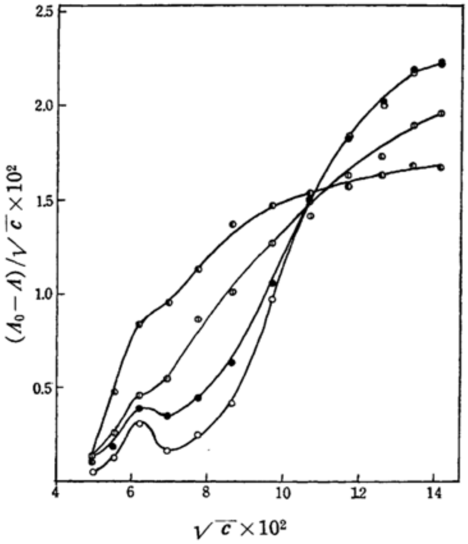

Fig. 6. $(\Lambda_0-\Lambda)/\sqrt{c}$ vs. $\sqrt{c}$ curves for sodium dodecyl sulfate in the aqueous solution of polyoxyethylene dodecyl alcohol ether:
○ in water, 10^{-4}, ⦶ 10^{-3} and ◐ 10^{-2} mole/l.

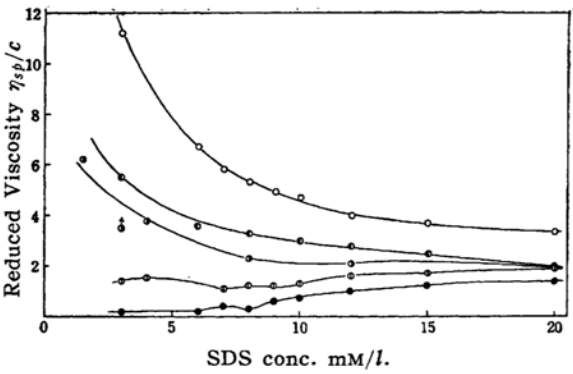

Fig. 7. η_{sp}/c vs. c diagram for sodium dodecyl sulfate in the aqueous solution of polyoxyethylene dodecyl alcohol ether:
● in water, ⦶ 1×10^{-3}, ◑ 2.5×10^{-3}, ◐ 5×10^{-3} and ○ 1×10^{-2} mole/l.

Sata and Tyuzyo[16] found the minimum of η_{sp}/c in the diagram of η_{sp}/c vs. c for the solution of ionic surfactant. We found that the small addition of non-ionic surfactant cancels this minimum, and the curve of η_{sp}/c vs. c approaches to that of polyelectrolyte solution rather than that of surfactant solution (Fig. 7). This fact can be considered that the non-ionic surfactant (molecular or loose micellar) adsorbs ionic surfactant on its lyophobic groups and therefore the micelle formation of ionic surfactant is prevented.

It seems necessary to discuss the various effects on critical phenomena from the two standpoints mentioned above, and these considerations are very useful to obtain the real feature of various effects.

In above explanation our discussion was mainly focused on the compact micelles. Now we should consider the formation of loose micelles, but it is impossible to consider its formation because of the lack of exact data of electroconductivity in very dilute surfactant solution.

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[16] N. Sata and K. Tyuzyo, This Bulletin, **26**, 177 (1953).