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

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In the estimation of C. M. C. value by the electroconductivity method, the equivalent conductivity (Λ) *vs.* square root of concentration ($\sqrt{c}$) diagram or the specific conductivity (κ) *vs.* concentration (c) diagram plays an important role. In the former diagram the C. M. C. has been defined as an intersecting point of two curves; one is a straight line below C. M. C. and the other is a concave curve above it.

In many cases, however, the precise examination of experimental data shows that the plots of conductivity in highly diluted regions are not a straight line[1], but a slight maximum appears[2]. The deviation from a straight line is especially conspicuous when surfactant molecules contain a double long chain alkyl group[3] or highly hydrated counter ions[4]. The similar effects upon the conductivity result from the addition of a solvent[5], such as dioxane or alcohol, to surfactant solutions.

On the other hand, it is well known that the Kohlrausch's equation is not applicable exactly to the conductivity of a simple electrolyte. Therefore, it may be unsuitable to treat the plots of electroconductivity data below C. M. C. as a straight line, as if they obeyed the Kohlrausch's equation.

In a simple electrolyte solution, the electroconductivity usually obeys a corrected formula such as Onsager's[6] or Shedlovsky's[7] approximate equation:

Onsager's approx. eq.

$$\Lambda=\Lambda_0-A\sqrt{C}+BC, \qquad (1)$$

Shedlovsky's approx. eq.

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[1] P. F. Grieger and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 3803 (1948).

[2] M. E. L. McBain, W. B. Dye and S. A. Johnston, ibid., **61**, 3210 (1939).

[3] A. W. Ralston, D.N. Eggenberger and P.L. DuBrow, ibid., **70**, 977 (1948).

[4] G. L. Brown, P. F. Grieger and C. A. Kraus, ibid., **71**, 95 (1949).

[5] E. C. Evers and C. A. Kraus, ibid., **70**, 3049 (1948).

[6] L. Onsager, *Physik. Z.*, **27**, 388 (1926).

[7] T. Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1405 (1932).

TABLE I

COMPARISON OF THE CONDUCTIVITY AT THE MINIMUM OR THE MAXIMUM POINT WITH THE *C. M. C.* ESTIMATED BY THE USUAL METHODS

			C. M. C. (in mM./l.) estimated by								
Subst.	$C_{\min}$	$C_{\max}$	Elect. conductivity	Dye	Surface tension	Viscosity	Solubilization	Light scatt.	Transport number	Osmotic coeff.	Vapor press.
C_{10} SO_3Na	40° 40	40° 91.5	40° 40	38.7	40° 36.4						
C_{10} SO_4Na				room 26.2							
C_{10} K soap				25° 99.8			71.4				
C_{10} $N^+(CH_3)_3Br^-$	40° 51.0	40° 103.7	40° 70	63.6				70			
C_{12} SO_3Na	40° 10.5	40° 27.2	40° 11.0	23.5° 9.8	40° 10.0	40° 12	10				
C_{12} SO_4Na	30° 6.08	30° 20.2	40° 8.9	room 5.8	40∼75° 6∼9.6						30° 7.0
C_{12} K soap				25.8° 23.5			21.4			11.1	20.5
C_{12} Na soap	40° 22.5	40° 59	40° 28			96	50° 26				27
C_{12} $N^+(CH_3)_3Br^-$	40° 12.1	40° 34.2	40° 17.5					15			
C_{12} N^+  Br^-			30° 12.0	room 11.5							30° 20.6
C_{12} NH_3Cl	60° 12.1	60° 44.1	60° 13			15	14		30° 15		30° 16.5
C_{14} SO_3Na	40° 2.71	40° 8.51	40° 2.5		40° 2.6						
C_{14} NH_3Cl	60° 2.91	60° 16.1	60° 4.0						30° 4.0		

$$\Lambda_0=\frac{\Lambda-\beta\sqrt{C}}{1-\alpha\sqrt{C}}-BC, \qquad (2)$$

in which A, B, α and β are constants, and BC is a corrected term for the higher order interaction between ions.

The fact of micelle formation of surfactant ions suggests that the interaction of those ions can not be neglected even in an appreciably dilute region below *C. M. C.* Accordingly, it is more reasonable to adopt the Onsager's equation (1) etc. than the Kohlrausch's equation, because we must consider the contribution of the interaction between surfactant ions to the conductivity in solution of the concentration below *C. M. C.* The deviation from the Onsager's equation (1) must be considered as "real deviation from the simple electrolyte".

The order of approximation of Shedlovsky's equation is higher than that of Onsager's equation, but we use the Onsager's equation (1) in this report to simplify the calculation and the analysis.

Now we defined the quantity;

$$(\Lambda_0-\Lambda)/\sqrt{C}, \qquad (3)$$

which is denoted by H and can be expressed as follows;

$$H=(\Lambda_0-\Lambda)/\sqrt{C}=A-B\sqrt{C}. \qquad (4)$$

If the quantity H is plotted against $\sqrt{C}$, the H *vs.* $\sqrt{C}$ diagram becomes a straight line in the case of the simple electrolyte, and the intercept on the axis of H is equal to A, while the slope of the plots gives B, the coefficient of corrected term.

In the case of surfactant solution, the deviation, from the linearity is observed in diluted region, that is, the remarkable minimum or kink and maximum are found in the diagram. Therefore, we use merely the value B as a parameter to appraise the slope of curve and not to show the corrected term exactly.

This deviation can be considered as "real deviation from the simple electrolyte", and will be due to the micelle formation. In Fig. 1 the relation between the usual *C. M. C.* and the concentration at the minimum or the maximum point is shown by the arrow line.

It is noticed here that the value Λ_0 which is necessary to draw the above diagram was obtained by the extrapolation of the plots to infinite dilution in usual Λ *vs.* $\sqrt{C}$ diagram, because the data in very diluted concentration—more diluted than the concentration where the slight maximum appears—can be treated as being in accordance with the Kohlrausch's equation.

The concentration of minimum does not always coincide with the usual *C. M. C.*; rather it is situated in the lower concentration than the latter. The numerical values of the concentration corresponding to the minimum or the maximum in contrast with the usual *C. M. C.* determined by various methods are listed in Table I. From this table it is found that the usual *C. M. C.* values determined by various methods fall into the region between the minimum and the maximum. We adopt this minimum and this maximum as parameters to show the critical phenomenon in surfactant solution, instead of the *usual* *C. M. C.*, and will show by the actual example that this method is more reasonable than the usual one.

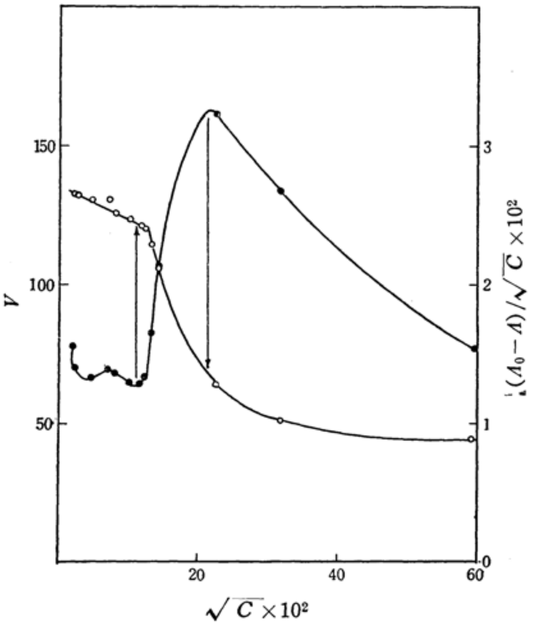

Fig. 1. Comparison of $(\Lambda_0-\Lambda)/\sqrt{C}$ *vs.* $\sqrt{C}$ diagram with the Λ *vs.* $\sqrt{C}$ diagram for dodecyl trimethyl ammonium bromide ;
○ Λ *vs.* $\sqrt{C}$, ● $(\Lambda_0-\Lambda)/\sqrt{C}$ *vs.* $\sqrt{C}$.

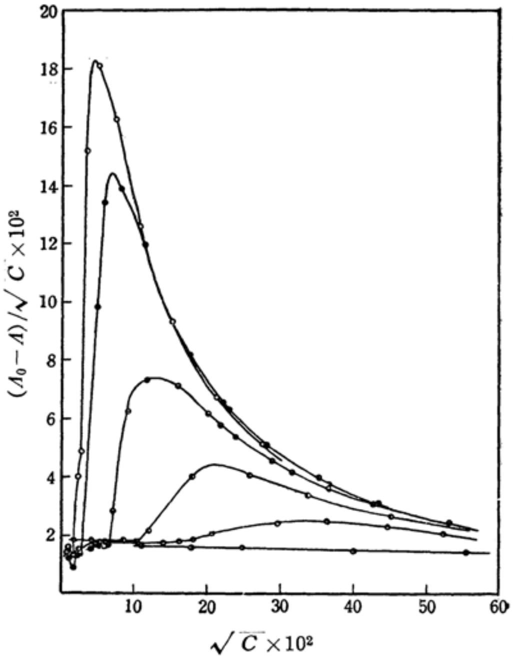

Fig. 2. $(\Lambda_0-\Lambda)\sqrt{C}$ *vs.* $\sqrt{C}$ curves for the aqueous solution of ○ octadecyl-, ● hexadecyl-, ◒ tetradecyl-, ◐ dodecyl-, ◓ decyl-, and ◑ octyl ammonium chlorides at 60°C.

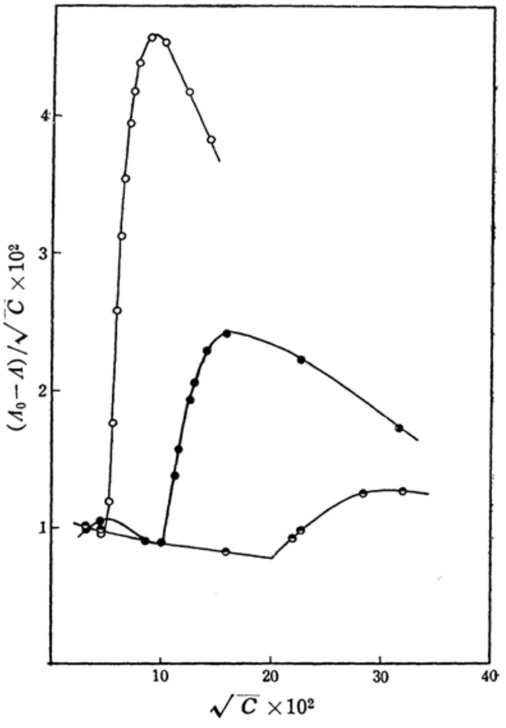

Fig. 3. $(\Lambda_0-\Lambda)/\sqrt{C}$ *vs.* $\sqrt{C}$ curves for the aqueous solution of ○ sodium tetradecyl-, ● sodium dodecyl- and ◓ sodium decyl-sulfonate at 40°C.

Effect of Alkyl Chain Length

The effect of alkyl chain length on the *C. M. C.* has been investigated by some authors and they have concluded that the longer the chain length, the lower the *C. M. C.*

Applying our method to the data of alkyl ammonium chlorides[8,9] and sodium alkyl sulfonates[10], we obtained the following results as shown in Figs. 2 and 3.

(a) Each curve shows a remarkable minimum and a maximum.

(b) The position of the minimum or the maximum shifts toward lower concentration with increasing alkyl chain length.

(c) The value of H at the maximum position increases with the length of alkyl chain.

(d) The slope between the minimum and the maxium becomes steep with the increase in the length of alkyl chain.

Harkins[11] found the following relation between the *C. M. C.* and alkyl chain length.

$$\log C.M.C. = a + bN, \qquad (5)$$

in which a and b are constants and N is the number of carbon atoms in an alkyl radical. A similar relation can be obtained by plotting the logarithm of the position of the minimum or the maximum against the number of carbon atoms in an alkyl radical. Fig. 4 shows the relation between $\log C_{\min}$ or $\log C_{\max}$ and N.

As the concentration at the minimum is nearly equal to the *C. M. C.* determined by Harkins. it is natural to obtain such a linear relation between the position of minimum and the number of carbon atoms. However, no attention has been paid to the concentration of the maximum position, the magnitude of which is several times that of the usual *C. M. C.* We found that a similar relation also exists between the position of the maximum and the number of carbon atoms. This fact is very interesting and could not be found at all by any of the earlier methods.

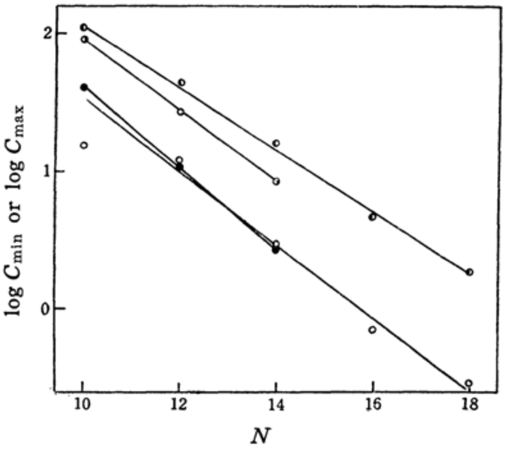

Fig. 4. The relation between logarithm of $C_{\min}$ or $C_{\max}$ and the number of carbon atoms, N, in an alkyl radical : for alkyl ammonium chlorides, ○ $C_{\min}$ and ◐ $C_{\max}$; for sodium sulfonates, ● $C_{\min}$ and ◑ $C_{\max}$.

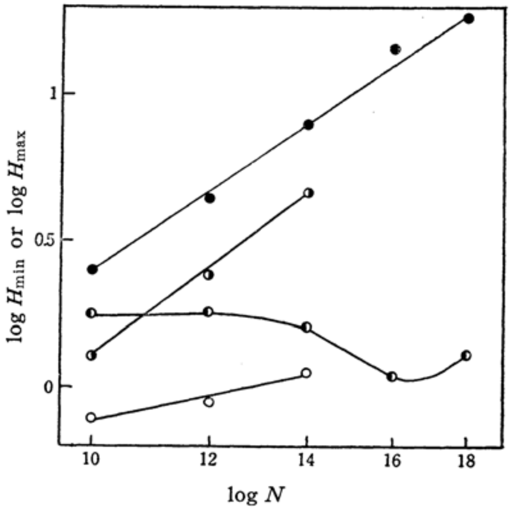

Fig. 5. log H *vs.* log N diagram for alkyl ammonium chlorides, ◐ $H_{\min}$, ● $H_{\max}$; for sodium alkyl sulfonates, ○ $H_{\min}$ and ◑ $H_{\max}$.

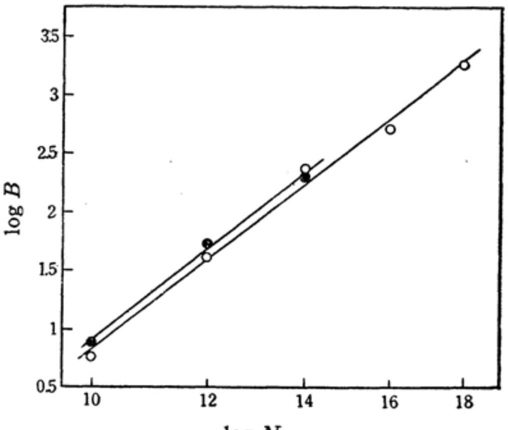

Fig. 6. log B *vs.* log N diagrams, ○ alkyl ammonium chlorides and ● sodium alkyl sulfonates.

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

[9] A. W. Ralston and C. W. Hoerr, ibid., **64**, 773 (1942).

[10] K. A. Wright, A. D. Abott, V. Sivertz and H. V. Tartar, ibid., **61**, 549 (1939).

[11] M. L. Corrin and W. D. Harkins, ibid., **65**, 692 (1943).

On the other hand, when we plot both logarithms of H and B against the logarithm of N, we can also find a linear relation between them. These results are shown in Figs. 5 and 6.

The values of B are almost the same in the case of the samples containing the equal number of carbon atoms. For reference the B values obtained for many examples are shown in Table II. This fact may be used to estimate the alkyl chain length of an unknown surfactant.

TABLE II
B VALUES FOR OBTAINED VARIOUS SURFACTANTS

Substance		B
$C_{18}H_{37}NH_3Cl$	60°	1800
N^+  Cl^-	25°	1530
$N^+(CH_3)_3Br^-$	25°	1200
$C_{16}H_{33}NH_3Cl$	60°	517
N^+  Cl^-		1080
$N^+(CH_3)_3Br^-$	60°	375
$C_{14}H_{29}NH_3Cl$	60°	238
SO_3Na	40°	201
$C_{12}H_{25}NH_3Cl$	60°	41
SO_3Na	40°	56
OSO_3Na	25°	59
$N^+(CH_3)_3Br^-$	60°	35
$C_{10}H_{21}NH_3Cl$	60°	6
SO_3Na	40°	8
$N^+(CH_3)_3Br^-$	60°	6

Effect of the Number of Alkyl Chains

Ralston[12] found an anomalously high Λ value in a low concentration region of the surfactant containing two long alkyl chains, such as dialkyl ammonium salts, and he reported that it was difficult to determine the $C. M. C.$ exactly owing to this anomalous maximum.

According to our method, however, it is easy to determine the minimum and the maximum values even in such a case. The result obtained is shown in Fig. 7. The anomality does not appear in our analysis as in the case of compounds with a single long chain, except the fact that the minimum merely becomes more pronounced in this case.

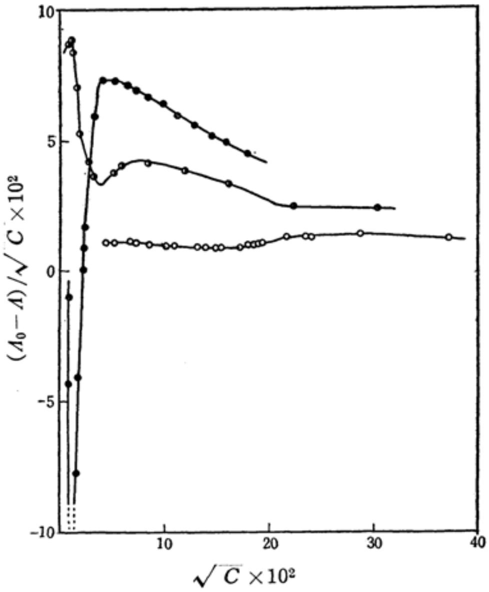
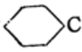


Fig. 7. $(\Lambda_0-\Lambda)/\sqrt{C}$ vs. $\sqrt{C}$ diagram, for the aqueous solutions of ○ dioctyl-, ◑ didecyl- and ● didodecyl- dimethyl-ammonium chlorides.

Effect of Ionic Head Group

Now we extend our analysis to the compounds with an alkyl chain of the same length but a different ionic head group.

TABLE III
VALUE OF $C_{\min}$, $C_{\max}$, $H_{\min}$, $H_{\max}$, B AND THE USUAL $C. M. C.$, SHOWING THE EFFECT OF IONIC HEAD GROUP

Substance		$C_{\min}$	$C_{\max}$	$H_{\min}$	$H_{\max}$	B	$C. M. C$
$C_{12}H_{25}SO_3Na$	40°	10.5	27.2	0.89	2.42	56	11.0
$C_{12}H_{25}OSO_3Na$	20°	6.08	20.2	0.50	2.20	58.8	8.6
$C_{11}H_{23}COONa$	40°	22.5	59.0	1.18	1.78	129	28
$C_{18}H_{37}NH_3Cl$	60°	0.78	1.85	4.50	18.3	1800	0.53
$C_{18}H_{37}N^+(CH_3)_3Cl^-$	25°	0.29	0.99	3.65	13.3	1200	0.34
$C_{18}H_{37}N^+$  Cl^-	25°	0.24	1.09	0.30	11.0	1530	0.25

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[12] A. W. Ralston, D.N. Eggenberger and P.L. DuBrow, J. Am. Chem. Soc., **70**, 977 (1948).

For this purpose the data for sodium dodecyl sulfate[13,14], sodium dodecyl sulfonate[15] and sodium dodecanoate[16] as anionic surfactants, and those for octadecyl ammonium chlorides[8], octadecyl pyridonium chloride[5] and octadecyl trimethyl ammonium chloride[1] as cationic surfactants, were analysed, in which sodium dodecanoate and octadecyl ammonium chloride were chosen especially as hydrolysable surfactants.

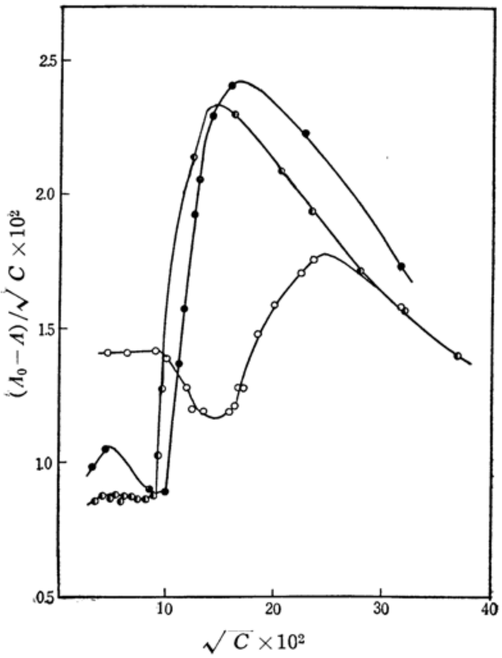

Fig. 8. $(\Lambda_0-\Lambda)/\sqrt{C}$ *vs.* $\sqrt{C}$ diagram for the aqueous solutions of ◐ sodium dodecyl sulfate, ● sodium dodecyl sulfonate and ○ sodium dodecanoate at 40°C.

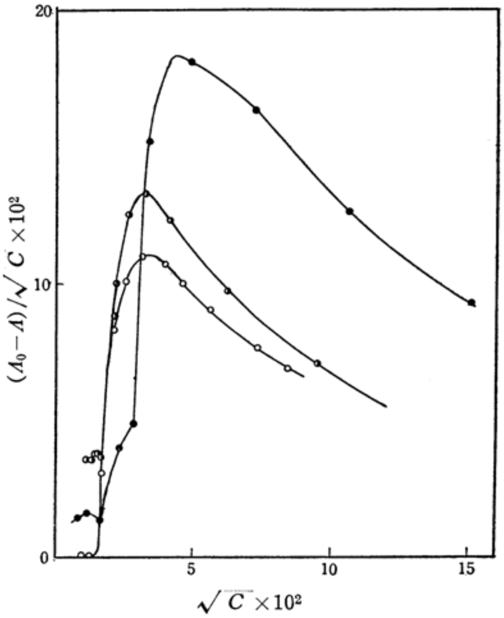

Fig. 9. $(\Lambda_0-\Lambda)/\sqrt{C}$ *vs.* $\sqrt{C}$ diagrams for the aqueous solutions of ● octadecyl ammonium chlorides at 60°C, ◑ octadecyl trimethyl ammonium chloride at 25°C and ○ octadecyl pyridonium chloride at 25°C.

The results are shown in Figs. 8 and 9. The obtained value of C_{min}, C_{max}, H_{min}, H_{max} and B are tabullated in Table III, in which the values of *C. M. C.* estimated by the usual method are given in the last column for reference.

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[13] A. F. Ward, *Proc. Roy. Soc.*, **A176**, 412 (1940).

[14] A. F. Ward, *J. Chem. Soc.*, **1939**, 522.

[15] K. A. Wright, A. D. Abott, V. Sivertz and H. V. Tartar, *J. Am. Chem. Soc.*, **61**, 599 (1948).

[16] P. Eckwall, *Kolloid Z.*, **101**, 135 (1942).