117. *Alkyl Sulphates. Part I. Critical Micelle Concentrations of the Sodium Salts.*

By H. C. Evans.

The variation in specific conductivity with change in concentration of aqueous solutions has been used in determining the critical micelle concentrations of a number of sodium alkyl sulphates in which the total hydrocarbon chain contains 8—19 carbon atoms and the position of the sulphate group ranges from the terminal to the medial position. Data are also presented for sodium 1-tetradecylpentadecyl sulphate. The slopes of the plots are used in estimating the number of gegenions in the micelles.

SODIUM alkyl sulphates, $CHRR'\cdot O\cdot SO_2\cdot ONa$, where R and R′ are unbranched, have very similar chemical properties. Except when the SO_4Na group occupies the ultimate or penultimate position, many of them are difficult or impossible to crystallize, and their identification by means of their chemical or the more usual physical properties is difficult. To assist in their identification the concentrations at which micelles first form in aqueous solution have been measured. This, it was thought, would suffice to identify isomers, and homologues could be distinguished by other methods.

Published information on the critical micelle concentrations of these compounds is scanty. Apart from the primary dodecyl sodium sulphate which has been used by many workers, almost the only alkyl sulphates which have been examined are the homologous 1-sulphates. These have been studied by Harkins and his co-workers [1] using the spectral (dye) method, by Lottermoser and Püschel [2] and by Flockhart and Ubbelohde [3] using a conductivity method, and by Powney and Addison [4] who measured the reduction in surface tension; these series of results are not in good agreement. Winsor [5] has reported the critical micelle concentrations of the isomeric sodium C_{14}-alkyl sulphates. Certain drawbacks and advantages are peculiar to each of the above methods of which the two most popular are the spectral (dye) method and the conductivity method. The former is technically simple, but the end point is not sharp and reliance must be placed on comparison with standard colours. Further, there are certain anomalies concerning the results obtained by this method which cast doubt on its theoretical significance.[6] In the present work the critical micelle concentrations have been determined by repeated measurement of conductivity as the solution is diluted. This method, in addition to giving a fairly precise value for this concentration, may also be interpreted so as to yield information on the actual mechanism of micelle formation.

EXPERIMENTAL

Materials.—Since many substances, *e.g.*, inorganic salts and long-chain alcohols, lower the critical micelle concentration of surface-active compounds, the compounds studied should be as pure as possible. Their preparation will be described in Part II of this series. Sodium *n*-alkyl and 1-methylalkyl sulphates were purified by recrystallization from ethyl methyl ketone and water. The other compounds (except one) were available only as solutions in water. In general these solutions contained <1% of impurity (see Part II), but they were further purified by foam-fractionation before use.

This was accomplished by blowing nitrogen through an approx. 1% solution of the alkyl sulphate contained at the base of a column 60 cm. in height. The rate of gas flow was adjusted so that the foam produced by the gas stream collapsed spontaneously at the top of the column; the resulting liquid was collected in the head of the apparatus and drained to a receiver.[7] This

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[1] Corrin and Harkins, *J. Amer. Chem. Soc.*, 1947, **69**, 679; Harkins, *ibid.*, p. 1428; Corrin, Klevens, and Harkins, *J. Chem. Phys.*, 1946, **14**, 480.

[2] Lottermoser and Püschel, *Kolloid Z.*, 1933, **63**, 175.

[3] Flockhart and Ubbelohde, *J. Colloid. Sci.*, 1953, **8**, 428.

[4] Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243.

[5] Winsor, *ibid.*, 1948, **44**, 463.

[6] Klevens, *J. Phys. Colloid Chem.* 1947, **51**, 1143; Mukerjee and Mysels, *J. Amer. Chem. Soc.*, 1955, **77**, 2937.

[7] Epton and Evans, Proc. 1st World Congr. on Surface Active Agents, in the press.

principle is not new [8] but it must be realized that (*a*) large quantities of unfractionated material are entrained unless the foam is allowed to drain thoroughly (this is achieved by allowing the foam to collapse spontaneously), and (*b*) inorganic salts are not removed in the foam, so that residual solution is richer therein than the original material. The procedure in the present experiments was to remove by foaming, and discard, the first third of the total surface-active material; this contained all the organic impurities. About half of the remainder was collected and used for conductivity measurements, while the inorganic salt remained behind.

The water used for dilution was treated as follows: Laboratory-distilled water was fractionally distilled in a glass apparatus and stored in closed bottles, freshly distilled water being used each day. Its specific conductivity varied between 5 and 1 × 10^{-6} ohm^{-1} cm.$^{-1}$.

Apparatus.—A conductivity bridge supplied with current at 1 kc. sec.$^{-1}$ from a Muirhead audio-frequency oscillator was used for part of this work. The balance point was detected by a headphone. This proved convenient for solutions the measured resistance of which did not rise above *ca.* 3000 ohms, but at higher resistances it became increasingly difficult to detect the balance point owing to the low sound level and to capacity effects. In later work a bridge was used in which the balance point was detected by a Cambridge galvanometer. It also operated at 1 kc. sec.$^{-1}$ with an accuracy of 0·1 ohm at 1000 ohms, and the capacity of the cell assembly could be balanced out by means of variable condensers. The electrodes, separable from the conductivity cell, comprised two parallel platinum plates about 0·8 cm. square and 0·8 cm. apart, spot welded to tungsten leads and protected by a glass sheath.[9] Before use the plates were coated with platinum black by Kohlrausch's method. The conductivity cell was so shaped that the volume of solution could be increased from 10 to 100 ml., and the electrode assembly was so inserted into the cell that a degree of movement could be obtained for stirring.

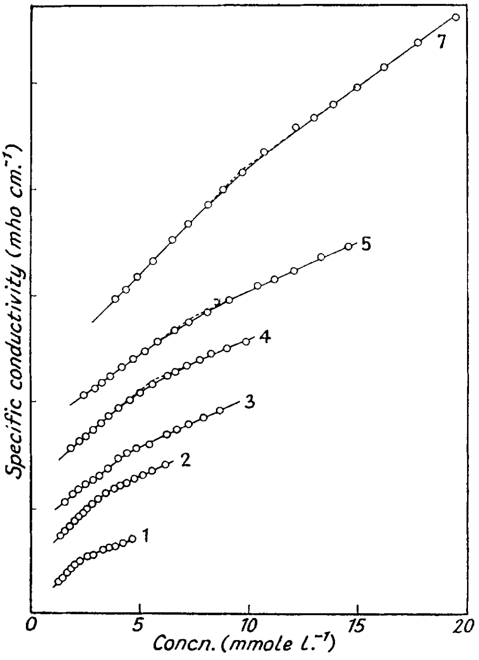

FIG. 1. *Specific conductivity of isomeric sodium C_{14}-alkyl sulphates.*
The conductivity ordinate has been shifted for each compound. The numerals for the individual curves denote the position (*P*) of the $NaO{\cdot}SO_2{\cdot}O$ in the chain R·CH·R′.

The cell constant was determined at 40° by measuring the resistance of 10^{-2}—10^{-4}N-potassium chloride and plotting the values against the published conductivity data. Where there were no published data at 40°, values were obtained by means of the equation quoted by Mellor.[10]

Technique.—Measurements were made in duplicate with the cells in a thermostat at 40·0° ± 0·05°, this temperature being chosen because many of the surface-active compounds in the region of the critical micelle concentration do not yield homogeneous solutions at room

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[8] Cf. Miles and Shedlovsky, *J. Phys. Chem.*, 1945, **49**, 71.
[9] Winsor, *Trans. Faraday Soc.*, 1950, **46**, 762.
[10] Mellor, " A Comprehensive Treatise on Inorganic and Physical Chemistry," Longmans Green & Co., London, Vol. II, p. 551.

temperature. A small known volume (usually 10 ml.) was placed in the cell and allowed to come to thermal equilibrium for *ca.* 20 min. Its resistance was determined, and a measured volume of water at 40° was added to the cell. After a short period the resistance was again measured and further water (total 90 ml.) was added; in all about 20 readings were taken. The specific conductivity of the solution was calculated and the values, after correction for the conductivity of water, were plotted against concentration. Straight lines were drawn through the upper and the lower part of the plot; the point of intersection showed the concentration at which micelles are formed.[11] The type of graph obtained is shown in Fig. 1 for the isomeric sodium C_{14}-alkyl sulphates. For compounds of lower molecular weight (*e.g.*, sodium octyl and 1-pentylhexyl sulphate) there is more pronounced curvature near the point of intersection, indicating probably that in this region the micellar size is indefinite. Since the existence of a curved portion is held to indicate a growth of micelles over the small concentration range involved, it follows that the point of intersection (see above) represents a concentration at which micelles are approximately half-developed.

RESULTS AND DISCUSSION

Table 1 gives the critical micelle concentrations of the sodium alkyl sulphates at 40°, each value being the average of duplicate determinations. Here and elsewhere, *L* denotes the number of carbon atoms in the "chain" R·CH·R′, and *P* denotes the position of the $NaO{\cdot}SO_2{\cdot}O$–group along that chain.

TABLE 1. *Critical micelle concentrations (cmc) of sodium alkyl sulphates at* 40°.

P	*L*	cmc (mM)	*P*	*L*	cmc (mM)	*P*	*L*	cmc (mM)
1	8	136	3	11	28·9	6	11	83
	12	8·65		14	4·30		16	2·35
	14	2·40		15	2·20		18	0·72
	16	0·58						
	18	$0{\cdot}16_5$	4	14	5·15	7	13	19·3
				16	1·72		14	9·70
2	8	180		18	0·45			
	10	49·5				8	15	6·65
	13	6·50	5	14	6·75		16	4·25
	14	3·30		15	3·40			
	15	1·71		19	0·33	9	17	2·35
	17	0·49						
	18	0·26				10	19	0·94
						15	29	0·08

Comparison with Other Data.—Wijga[12] has determined the critical micelle concentrations (cmc) of the isomeric sodium C_{14}-alkyl sulphates by conductivity measurements at 60°. His results are higher than those given in Table 1 by a factor which varies between 1·13 and 1·19 (average 1·17); the temperature coefficient (α) is therefore 0·0085 where $(\text{cmc})_t/(\text{cmc})_{40} = 1 + \alpha(t - 40)$. Winsor's results for the same compounds by the spectral (dye) method at room temperature[5] differ considerably, the values given by the two methods varying systematically with the position of the sulphate group. For sodium *n*-tetradecyl sulphate the dye method gives the lower value and for sodium 1-hexyloctyl sulphate the higher value, whereas the values are about equal for the 1-propylundecyl compound. Thus the spectral (dye) method needs to be used with care. For example the critical micelle concentration of a commercial mixture of sodium alkyl sulphates free from inorganic salt, determined by the dye method, is approximately that of the component having the lowest value. This appears to indicate that with such mixtures the dye tends to remain associated with the micellar form of the alkyl sulphate until the last micelles disappear with increasing dilution. The conductivity–concentration curves for these mixtures of alkyl sulphates show no definite break, indicating that micelles are formed over a relatively wide concentration range.

Apart from the isomeric C_{14} compounds and sodium 1-ethylnonyl sulphate[13] (by the spectral method), only the primary alkyl sulphates have been examined previously. Some

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[11] Wright, Abbott, Sivertz, and Tartar, *J. Amer. Chem. Soc.*, 1939, **61**, 549.

[12] Wijga, personal communication.

[13] Winsor, "Solvent Properties of Amphiphilic Compounds," Butterworths, London, 1954.

TABLE 2. *Comparison of critical micelle concentrations (cmc) (10^{-3}M) of sodium primary alkyl sulphates.*

Method	Temp.	No. of carbon atoms (L) 8	12	14	16	18	Ref.
Spectral (Dye)	26—35°	—	6·1, 6·5	—	0·40	—	1
Surface tension	60	—	8	2·0	0·43	0·17	4
Conductivity	60	—	7·6	2·6	1·0	0·4	2
,, ...	25	130	8·1	—	—	—	14
,, ...	25—40	—	9·0	2·5	—	—	3
Present work	40	135	8·65	2·40	0·58	0·17	—
Temp. coeff. (%)	—	—	1·3	2·2	1·0	0·35	4

comparisons are given in Table 2 : after allowance for the effect of temperature, the previous results are all in general lower than the present values. Since the probable impurities in the system in general lower the critical micelle concentration, the present higher results may be due to the more rigorous purification.

Variation of Critical Micelle Concentration within Homologous and Isomeric Series.—Fig. 2, where the number (L) of carbon atoms is plotted against the logarithm of the critical micelle concentrations (cf. Table 1), shows that lines drawn through the points representing homologous series are straight except at their lower ends. The full lines represent the statistical equations derived from the numerical data. The broken lines for the series where the sulphate group is at position 7—10 along the chain were obtained by reading from the full lines the values of L at critical micelle concentrations of 1 and 10 mmoles l.$^{-1}$ and plotting them against P (the numerical position of the sulphate group along the chain). Values of L for $P = 7$—10 were then obtained by extrapolation, the critical micelle concentration of sodium 1-nonyldecyl sulphate being used as reference point. All the straight lines can be represented by equations

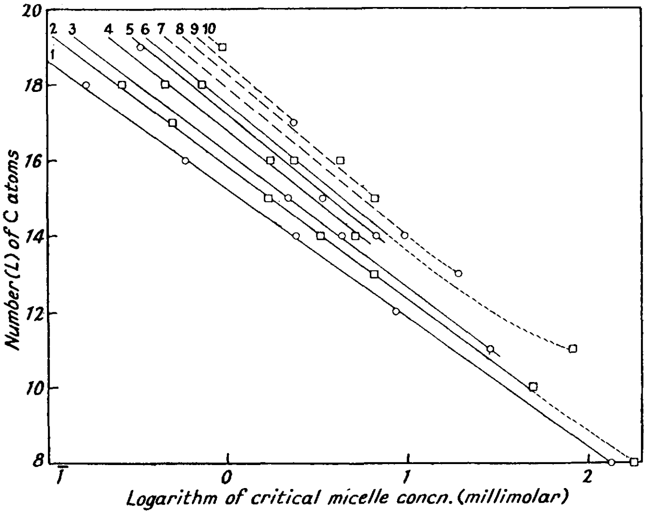

FIG. 2. *Logarithms of critical micelle concentrations of sodium alkyl sulphates, arranged in homologous series.*

———, Derived statistically.
— —, Obtained by extrapolation.
- - -, Non-linear relation.

The numbers attached to the individual curves denote P (cf. Fig. 1).

$$\log_{10} (\text{cmc}) = a - bL \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Values of the constants for the separate homologous series are given in Table 3. It will be noted from Fig. 2 that the slope $1/b$ of the lines increases somewhat as the sulphate group is shifted towards the middle of the chain, indicating a spread in critical micelle values with increase in chain length. The values of a show no systematic trend, and the results are probably best represented by considering a as approximately constant for all values of P. When the alkyl sulphates are arranged in isomeric series, for a given value of L, log cmc can be approximately represented by $a' - b'P$.

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[14] Haffner, Piccione, and Rosenblum, *J. Phys. Chem.*, 1942, **46**, 662.

TABLE 3. *Constants b (slope) and a (intercept) in eqn.* 1 (*empirical values*).

Determined statistically :			Obtained by extrapolation :		
P	b	a	P	b	a
1	0·294	4·49	7	0·256	4·59
2	0·286	4·53	8	0·251	4·58
3	0·280	4·55	9	0·245	4·55
4	0·266	4·47	10	0·240	4·52
5	0·258	4·44			
6	0·270	4·72			

It may be noted that the equation of the type (1) in which L is replaced by the overall length of the surface-active ion, found by Klevens[15] to hold for simple uni-univalent amphiphilic salts in general irrespective of the nature of the hydrophilic group, must apply only to those homologous series comprising compounds in which the hydrophilic group is in the terminal position. If Klevens's relation were applicable to all homologous series then, for example, sodium *n*-tetradecyl, 1-methyltetradecyl, and 1-ethyltetradecyl sulphate would have approximately the same critical micelle concentration since the effective length $(L - P)$ of each of these amphiphilic ions is the same. Reference to Fig. 2 shows that in fact sodium *n*-tetradecyl, 1-ethyltridecyl, 1-pentylundecyl, and 1-octylnonyl sulphate have approximately the same critical micelle concentrations.

Although the relation between members of a homologous series appears to be linear for compounds containing more than 10 carbon atoms, the possibility exists that with more than 19 carbon atoms the lines of Fig. 2 may again become convex. Thus, although the critical micelle concentration of sodium 1-tetradecylpentadecyl sulphate, calculated from equation (1) with values of a and b extrapolated from the data of Table 3, is *ca.* $0{\cdot}5 \times 10^{-4}$M, and thus in reasonable agreement with the experimental value $(0{\cdot}8 \times 10^{-4}\text{M})$, the latter is probably not within the range covered by the linear equation.

Structure of Micelles.—According to McBain,[16] when long-chain ions form clusters, the equivalent conductivity of the solution should be increased. If n single long-chain ions form a homoionic micelle, it can be deduced that the equivalent conductivity of the micellar ion should be $n^{2/3}$ times that of the single ions. The fact that the equivalent conductivity of amphiphilic salt solutions usually decreases above the critical micelle concentration has been explained as due to the inclusion within the micelle of ions of opposite charge (gegenions) to that of the long-chain ions. The number of these gegenions in relation to the number of long-chain ions must therefore be a determining factor for the equivalent conductivity of amphiphilic salts above the critical micelle concentration. The relations to be expected may be considered by using Hartley's model for the micelle, which is probably a fairly accurate representation of micellar form at concentrations not greatly above the critical micelle concentration.

If the micellar ion is composed of n long-chain ions and m gegenions :

$$n\text{NaX} \rightleftharpoons n\text{Na} + n\text{X} \rightleftharpoons (\text{X}_n\text{Na}_m)^{n-m} + (n - m)\text{Na}$$

the specific conductivity of a solution of amphiphilic salt NaX at concentration c above the critical micelle concentration c_0 may then be regarded as divisible into three components : that due to the single ions at the critical micelle concentration, that due to the micellar ions, and that due to the sodium ions in excess.

The specific conductivity κ at concentration c may be written in the form

$$1000\kappa = c_0(\Lambda_{\text{Na}} + \Lambda_{\text{X}}) + \frac{c - c_0}{n}\Lambda_{\text{mic}} + (c - c_0)\frac{(n - m)}{n}\Lambda_{\text{Na}}$$

where Λ_{Na}, Λ_{X}, and Λ_{mic} are the equivalent conductivities of the Na, X, and micellar ions. If the specific conductivity at the critical micelle concentration is denoted by κ_0, this equation becomes equation (2) :

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[15] Klevens, *J. Amer. Oil Chemists' Soc.*, 1953, **30**, 74.

[16] McBain, *Trans. Faraday. Soc.*, 1913, **9**, 99; Alexander, "Colloid Chemistry," Reinhold Publ. Corp., New York, 1944, Vol. V, p. 102.

$$1000\,\frac{\kappa - \kappa_0}{c - c_0} = \frac{1}{n}\,\Lambda_{\text{mic}} + \frac{n - m}{n}\,\Lambda_{\text{Na}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

An approximate value of n can be calculated as follows :[17]

Volume of hydrocarbon interior of micelle $= (4/3)\pi l^3$ where l is the length (Å) of the longer portion of the hydrocarbon chain attached to the sulphate group. The volume of 1 molecule of hydrocarbon of molecular weight M and density $d = 10^{24}M/Nd$, where $\boldsymbol{N}$ is Avogadro's number. Hence the number of long-chain ions in the micelle

$$n = \frac{4}{3}\pi l^3\, Nd/10^{24}M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Λ_{mic} can be obtained as follows :

It can be deduced in conjunction with Stokes's law that the conductance of an ion in unit electrical field is proportional to the (charge) ^{2} divided by the radius of the ion (assumed spherical). Hence when n long-chain ions form a micelle of charge $(n - m)$ the conductivity is given by

$$\Lambda_{\text{mic}}/\Lambda_{\text{X}} = (n - m)^2/n^{\frac{1}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now $\Lambda_{\text{Na}} + \Lambda_{\text{X}} = 1000\kappa_0/c_0$, which is the slope S_1 of the specific conductivity–concentration curve below the critical micelle concentration, and the left-hand side of eqn. 2 is the slope S_2 above this concentration. It follows therefore from eqns. 2 and 4 that

$$1000S_2 = \frac{(n - m)^2}{n^{4/3}}(1000S_1 - \Lambda_{\text{Na}}) + \frac{n - m}{n}\,\Lambda_{\text{Na}} \quad . \quad . \quad . \quad . \quad (5)$$

At the low concentrations employed, Λ_{Na} may be taken as the value at infinite dilution; at 40° this is 66 (Glasstone[18]). Hence m can be evaluated from the quadratic eqn. 5. Table 4 gives the values of n calculated from eqn. 3 and those of m, the positive values only being considered.

TABLE 4. *Number of long-chain ions* (n) *and of gegenions* (m) *forming micelles, calculated from the slopes of the conductivity–concentration graphs below and above the critical micelle concentration* (S_1 *and* S_2 *respectively*).

P	L	$1000S_1$	$1000S_2$	n	m/n	m	P	L	$1000S_1$	$1000S_2$	n	m/n	m
1	8	86	50	17	0·685	12	5	14	77	49	21	0·532	11
	12	96	40	40	0·744	30		15	89	63	25	0·579	15
	14	97	40	55	0·766	42		19	92	65	51	0·657	34
	16	106	45	74	0·791	59							
	18	75	43	94	0·664	63	6	11	88	76	5	0·312	2
								16	88	67	24	0·556	13
2	8	87	53	11	0·536	6		18	101	77	36	0·629	23
	10	86	54	20	0·580	12							
	13	88	46	37	0·682	25	7	13	88	64	7	0·434	3
	14	103	46	45	0·750	34		14	107	73	11	0·544	6
	15	106	51	52	0·752	39							
	17	103	43	69	0·779	54	8	15	89	68	10	0·455	5
	18	103	42	79	0·796	63		16	84	71	13	0·427	6
3	11	93	57	18	0·596	11	9	17	97	76	12	0·491	6
	14	79	46	35	0·667	23							
	15	106	56	42	0·720	30	10	19	146	73	16	0·523	9
4	14	81	50	27	0·588	16	15	29	126	59	34	0·789	24
	16	81	54	40	0·604	24							
	18	82	57	54	0·626	34							

The values of the ratio m/n are of the magnitude to be expected from general considerations, and their variation with increase in L (for constant P) and with increase in P (for constant L) is in accord with the properties of the model adopted. Fig. 3, a plot of n against m, shows that all the alkyl sulphates examined fall on a curve passing through the origin and nearly linear. This is the more remarkable at the lower end of the curve, for it is difficult to envisage a spherical micelle containing only 5 long-chain ions and

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[17] Ward, *Proc. Roy. Soc.*, 1940, *A*, **174**, 412.

[18] Glasstone, "Electrochemistry of Solutions," Methuen, 1930, p. 69.

2 gegenions, as is apparently the case for sodium 1-pentylhexyl sulphate ($P = 6$, $L = 11$). It must be remembered however that micelle formation is a dynamic process with constant interchange of ions between micellar and intermicellar states, the micelle itself being a statistical aggregate. The only serious anomaly is the value of m for the n-octadecyl compound, which is low owing to the abnormally low value found for the slope of the conductivity–concentration plot below the critical micelle concentration. Of particular interest is the value for sodium 1-tetradecylpentadecyl sulphate; despite its low critical micelle concentration and exceptional behaviour at very low concentrations (see below), at concentrations appreciably above the critical micelle concentration its micelles show similar behaviour to those of other alkyl sulphates. Also included in Fig. **3** are data

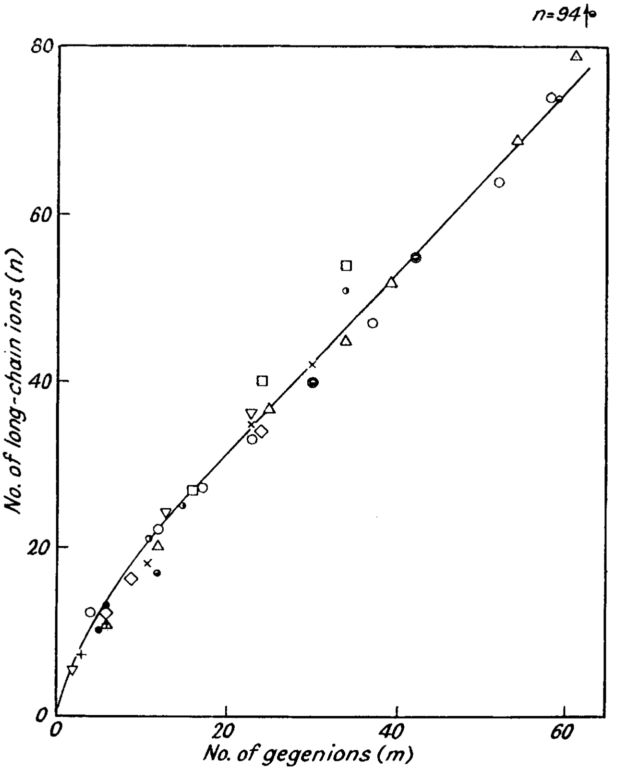

FIG. 3. *Micellar composition of sodium alkyl sulphates and sodium alkane*-1-*sulphonates.*

○, Sulphonates (Wijga[12]) ($P = 1$).
Sulphates : ◒, $P = 1$.
△, $P = 2$.
×, $P = 3$.
□, $P = 4$.
◑, $P = 5$.
▽, $P = 6$.
+, $P = 7$.
●, $P = 8$.
◇, $P = 9$, 10, 15.

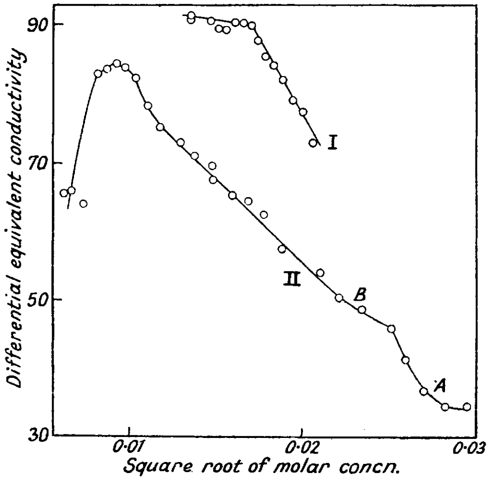

FIG. 4. *Equivalent conductivity of sodium* n-*octadecyl* (I) *and* 1-*tetradecylpentadecyl sulphate* (II).

calculated from the slopes of the conductivity–concentration curves for sodium alkanesulphonates determined by Wijga.[12] Despite the fact that his measurements were made at 60° (Λ_{Na} is here taken as 84) the points for the sulphonates lie very close to the curve for the sulphates.

The micellar composition envisaged here cannot, without further proof, be applied to systems containing added inorganic salt. Tartar and his co-workers [11] show that the effect of sodium chloride on the specific conductivity of sodium dodecylbenzenesulphonate solutions is, *inter alia*, to decrease S_2 appreciably, although S_1 is almost unaltered. Eqn. 5 shows that, provided the rest of the terms remain unaltered, a decrease in S_2 will increase m. Hence the addition of inorganic cations to a solution of anionic amphiphilic salt appears to increase m, as would indeed be expected from general considerations.

Hutchinson and Melrose's light-scattering experiments [19] with sodium *n*-dodecyl sulphate indicate rather larger values of n than those obtained by calculation. Their solutions contained a large excess of inorganic cations which, they believed, decreased the charge on the micelle without affecting its size. It is probable however that their values are somewhat too high, particularly compared with other estimates quoted in their paper. In an earlier paper [20] Hutchinson applied the value $n = 80$ which he found for sodium *n*-dodecyl sulphate to the slope of Lottermoser and Püschel's conductivity curves,[2] and obtained $m/n = 0{\cdot}825$. Using the value $n = 80$ in eqn. 5 we obtain $m/n = 0{\cdot}786$, compared with 0·744 calculated on the basis of $n = 40$. It appears therefore that the values of m/n do not depend strongly upon n, which can be varied within wide limits without much alteration in the calculated ratio of gegenions to long-chain ions. The value of m/n obtained from Lottermoser and Püschel's data may possibly be high owing to the presence of inorganic salt in their solution, for the critical micelle concentration determined by them is somewhat low (Table 2).

Equivalent Conductivity of Sodium 1-*Tetradecylpentadecyl Sulphate.*—McBain has pointed out that, not only should homoionic aggregation lead to an increase in conductivity, but the latter will also be increased above the conductivity at infinite dilution even if gegenions are present in the micelle, provided that the excess charge $(n - m)$ is sufficiently high, *i.e.*, the relative number of gegenions is sufficiently small. The Λ–c curve should therefore contain a maximum in such cases. This effect has been observed for several cationic amphiphilic compounds,[21] and as the molecular weight of the compound, is increased the maximum occurs at a lower concentration and becomes more pronounced. This effect, hitherto unreported for anionic amphiphilic compounds, was found to occur for sodium 1-tetradecylpentadecyl sulphate. Fig. 4 shows the plot of Λ against the square root of the concentration for this salt and, for comparison, for the *n*-octadecyl compound, Λ having been corrected for the conductivity of the water. For the former salt there is a sharp rise in Λ at about $0{\cdot}6 \times 10^{-4}$M, passing through a maximum at about $0{\cdot}85 \times 10^{-4}$M, and thereafter falling continuously; the latter salt gives a normal type of curve. A further point of interest in this graph lies in the low-conductivity region. At the beginning of the experiment at the higher concentrations the solution of sodium 1-tetradecylpentadecyl sulphate in water was turbid and on dilution was still turbid at point *A*; at point *B* however it was visually clear. The existence of the break in the curve between *A* and *B* may therefore be held to mark a phase change; on Winsor's interpretation [13] the salt is present at the lower concentrations as an S_1 isotropic solution, whereas at concentrations above the break the S_1 solution is in equilibrium with a liquid-crystalline phase *G*, the two forming together a stable emulsion which shows visible turbidity.

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" SHELL " RESEARCH LIMITED, THORNTON RESEARCH CENTRE,
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[19] Hutchinson and Melrose, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 363.

[20] Hutchinson, *J. Colloid Sci.*, 1954, **9**, 191.

[21] McDowell and Kraus, *J. Amer. Chem. Soc.*, 1951, **73**, 2173; Ralston, Eggenberger, and DuBrow, *ibid.*, 1948, **70**, 977.