

ler aggregates would be less stable because of their higher "degree of ionization" and would rapidly build up to the final form.

It is probable that both the mass and volume of the micelle will become greater with increase in the length of the aggregating anion. Undoubtedly, this would result in both a greater decrease in free energy and a lower "degree of ionization," the two effects contributing to enhanced stability. A marked lowering of the critical concentration is thus to be expected in going from a lower to a higher member in the paraffin-chain salt series.^{2,12}

The equilibrium between the micelles and the simple ions with increasing concentration of sulfonate can be treated most easily for a condition of constant temperature. The concentration of the sulfonate anion remains always just sufficient to satisfy the requirements for the stability of the micelle, since any excess over this minimum results in the formation of additional micelles. As the solution becomes more concentrated the sodium ion concentration steadily increases with a resulting decrease in the "degree of ionization" of the micelle; the stability is thereby enhanced and the sulfonate ion concentration becomes less. The critical concentration must, therefore, represent the maximum for the sulfonate ion. Figure 6 depicts a general idea of the components at different concentrations of an aqueous solution of a sodium alkyl sulfonate. No pretense is made of representing quantitative relationships.

Summary

1. A densimeter has been described for meas-

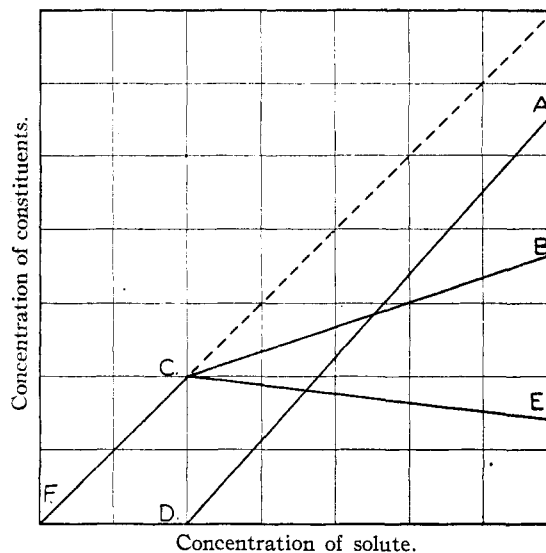


Fig. 6.—Generalized constitution diagram for aqueous solutions of the sodium salts of higher alkyl sulfonates. AD represents the concentration of solute in micelle form; FCB and FCE, the concentrations of sodium ion and alkyl sulfonate ion, respectively.

uring densities over a series of temperatures with only one filling and weighing required.

2. The densities and viscosities for dilute solutions of sodium dodecyl sulfonate have been determined at 40, 50, 60, and 70°. Breaks appear in the curves where ionic micelles are supposed to form.

3. The equilibrium between the ionic micelle and the sodium and alkyl sulfonate ions has been discussed in a qualitative manner.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

Studies of Sulfonates. V. Electrical Conductance of Sodium Decyl, Dodecyl, and Hexadecyl Sulfonate Solutions at 40, 60 and 80°—Micelle Formation

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Previous studies^{2,3} on solutions of these sulfonates definitely established the existence of critical concentrations at which certain property curves change abruptly, supposedly due to the formation of ionic micelles. The conductances have been determined by Reed and Tartar⁴ at 25 and 60° but unfortunately their data are too

limited to determine the critical concentrations with certainty. The object of the present study was to investigate the conductance-concentration curve more carefully over this range and to determine the effect of temperature.

Experimental

The Leeds and Northrup Dike conductivity bridge⁵ was calibrated with standard resistances. A Leeds and Northrup A. C. vacuum tube oscillator and amplifier were

(1) Standard Oil Company of California Fellow, 1937-38.

(2) Tartar and Wright, *THIS JOURNAL*, **61**, 539 (1939).

(3) Wright and Tartar, *ibid.*, **61**, 544 (1939).

(4) Reed and Tartar, *ibid.*, **58**, 322 (1936).

(5) Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

used. The measurements were made at a frequency of 2000 cycles; occasional checking at other frequencies, 500 and 1000, revealed no variations in conductance values. The construction,⁶ platinization,⁷ and standardization⁸ of the cells were in accordance with the specifications of Jones and co-workers. The cells were made of Pyrex glass with ground-glass connections for filling. The metal-glass seal was effected with tungsten wire to which was spot-welded the platinum rod support of the electrode. Six cells gave constants varying from 0.13368 to 2.8792. The two cells with the greatest constants were standardized at 25° with 0.01 *D* potassium chloride solution⁸ and the others by intercomparison. The variation of cell constant with temperature was calculated⁹ from the dimensions of the cells and the thermal expansion coefficients for platinum and Pyrex glass. The constants for the different cells decreased by 0.1 to 0.3% for the interval 25 to 80°.

The cells were filled and successively immersed in three oil thermostats at 40, 60 and 80°. With constant room temperature, control of the thermostats to 0.001° was attained by efficient stirring and by the use of very sensitive mercury-toluene regulators in connection with Thyatron tube relays. The temperatures were measured to 0.005° by checking against a thermometer calibrated by the United States Bureau of Standards.

Materials.—The salts were of the same lot and purity as used in an earlier study.² The solutions were made to weight normalities, the weights being corrected to vacuum.

Conductivity water for the solutions had a specific conductance of the order 1×10^{-8} ohm⁻¹ at 40°, 1.5×10^{-8} ohm⁻¹ at 60° and 2×10^{-8} ohm⁻¹ at 80°. The observed conductance of the solutions was corrected for the conductance of water.¹⁰

Technique.—Because of the low solubilities of these salts at room temperature,² it was necessary, with the exception of sodium decyl sulfonate, to heat the solutions to *ca.* 50° before transferring to the conductivity cell. This introduces unavoidable errors (evaporation, solution of glass, etc.) so that the conductance values for the most dilute solutions of sodium dodecyl and tetradecyl sulfonates have a greater experimental error than those for sodium decyl sulfonate. Sodium hexadecyl and octadecyl sulfonate solutions were not studied because the experimental error at the critical concentration (*ca.* 0.001 *N*) would be very great at the higher temperatures.

The solutions, prepared in steam-seasoned Pyrex bottles, were heated to 50°, and while in a thermostat (to prevent condensation of water vapor from the solution while transferring) were forced over into the conductivity cells by application of nitrogen gas pressure. The cells were then placed in the 40° bath, allowed to come to temperature equilibrium (twenty-five minutes), and then readings taken. The cells were next transferred to the 60° and finally the 80° baths. Two cells were filled with the same solution to afford duplicate determinations.

A slight downward drift in resistance was noticeable in the most dilute solutions, being hardly noticeable at 40° but decidedly so at 80°. This phenomenon was not

peculiar to solutions of sulfonates since the same drift was noticed for dilute solutions of potassium chloride and consequently was attributed to the slow solution of glass.¹¹ Drift corrections were applied to the readings and usually amounted to a small fraction of the water correction. No change with time was noted for the more concentrated solutions.⁴

To eliminate adsorption effects at the electrodes, the cells were filled with preliminary solutions and allowed to stand, preferably at the higher temperature.

Nitrogen was used in all cases in which there was a possibility of the solution or conductivity water coming in contact with air.

Data and Discussion

With the exception of the more dilute solutions at 80°, the data given in Table I are believed to be

TABLE I
SPECIFIC CONDUCTANCE OF SODIUM ALKYL SULFONATE SOLUTIONS

Molality	Mhos $\times 10^4$		
	40°	60°	80°
Sodium Decyl Sulfonate			
0.001000	0.963	1.328	1.712
.002000	1.906	2.627	3.387
.010000	9.081	12.529	16.178
.025000	21.713	29.939	38.600
.048000	38.188	54.424	70.932
.051000	39.540	56.842	74.98
.080000	51.460	75.233	104.27
.1020	60.608	88.544	122.56
.2000	104.49	150.82	204.04
Sodium Dodecyl Sulfonate			
0.001000	0.944	1.301	1.681
.002000	1.855	2.558	3.301
.007500	6.725	9.277	11.960
.010000	8.863	12.236	15.808
.012600	10.361	15.194	19.753
.013500	10.686	15.902	21.046
.015500	11.398	17.159	23.930
.016700	11.839	17.861	25.526
.019700	12.856	19.431	28.113
.024881	14.673	22.137	32.23
.051000	24.055	35.803	50.68
.1000	42.52	62.86	86.74
Sodium Tetradecyl Sulfonate			
0.0020	1.824	2.521	3.240
.0028	2.4997	3.491	4.508
.0031	2.6565	3.865	5.0053
.0035	2.806	4.271	5.6300
.0039	2.9609	4.5877	6.260
.0042	3.049	4.7717	6.7120
.0048	3.276	5.1083	7.5585
.0053	3.4458	5.3774	8.0936
.0060	3.6876	5.7373	8.6783
.0075	4.1876	6.4849	9.780
.0010	5.0115	7.7088	11.444
.0150	6.654	10.113	14.690
.0200	8.261	12.469	17.868

(6) Jones and Bollinger, *This Journal*, **53**, 411 (1931).

(7) Jones and Bollinger, *ibid.*, **57**, 280 (1935).

(8) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(9) Washburn, *ibid.*, **38**, 2431 (1916).

(10) Kendall, *ibid.*, **39**, 7 (1917).

(11) Taylor, *J. Phys. Chem.*, **37**, 765 (1933).

reliable to 0.1%; and to a lesser value for the more concentrated solutions.

The data of Reed and Tartar⁴ are in fair agreement, with the exception of sodium dodecyl sulfonate.

Behavior in Dilute Solutions.—The conductances for these sulfonates in dilute solutions indicate that they behave as strong electrolytes up to a critical concentration. A plot of the equivalent conductance against the square root of normality shows a linear relationship within experimental error. In Fig. 1 the curves have been extrapolated to zero concentration to obtain the limiting equivalent conductance for the salts. These together with those for the corresponding alkyl sulfonate ions, obtained by subtracting that for the sodium ion, are given in Table II. The data are in close agreement to those of Lottermoser and Puschel.¹²

Compound	Reciprocal ohms		
	40°	60°	80°
Sodium Alkyl Sulfonates			
Decyl	99.7	138.5	180.5
Dodecyl	97.5	135	177
Tetradecyl	95.5	133	174
Alkyl Sulfonate Ions			
Decyl	30.7	43.0	56.5
Dodecyl	28.5	39.5	53
Tetradecyl	26.5	37.5	50

The curve for sodium decyl sulfonate has a slope of 80 at 40°, 109 at 60° and 140 at 80°. The theoretical slope calculated from Onsager's equation is 106 at 40°, 151 at 60°, and 203 at 80°. The comparison of the experimental with theoretical slopes shows that the conductances of these sulfonate solutions do not diminish as rapidly with concentration. In Fig. 1, the curve for sodium chloride is plotted from data of this investigation (presented later). The equivalent conductances were decreased by 64 to bring the curve within comparable range. It will be seen that it falls off more rapidly than for sodium decyl sulfonate.

Howell and Robinson¹³ made the opposite observation for solutions of sodium dodecyl sulfate, for which they found a slope at 20° of 90, the theoretical being 70. They did not, however, present evidence to show that there was no hydrolysis in the most dilute solutions; a very small

(12) Lottermoser and Puschel, *Kolloid-Z.*, **63**, 175 (1933).
 (13) Howell and Robinson, *Proc. Roy. Soc. (London)*, **155A**, 388 (1936).

amount of hydrolytic change easily could cause a decided increase in the experimentally determined slope. Their values for the limiting equivalent conductances are considerably higher than those obtained by Lottermoser and Puschel.¹²

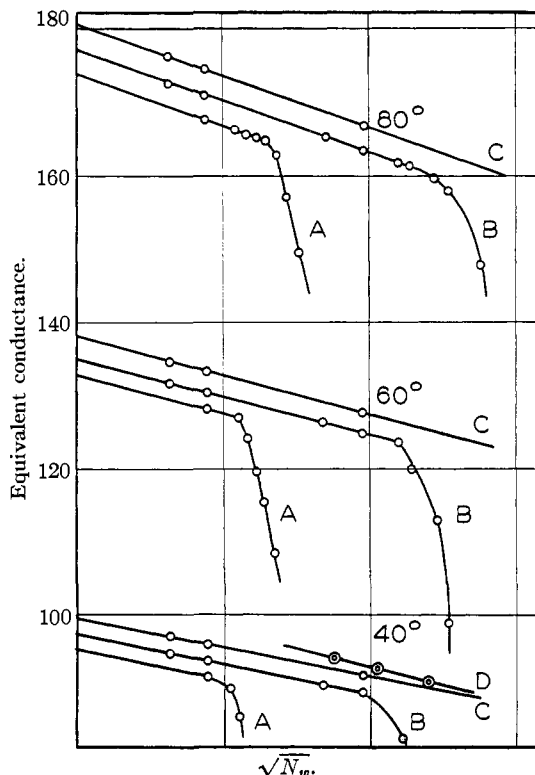


Fig. 1.—Equivalent conductance against $\sqrt{N_w}$ for dilute solutions below critical concentration. Curves A, B, and C are for sodium tetradecyl, dodecyl, and decyl sulfonates, respectively. Curve D is for sodium chloride at 40° (curve is for $\Delta -64$ to bring to comparable range).

Discussion of the Break in the Conductance Curve.—The treatment of conductance data for paraffin-chain colloidal electrolytes usually has been the graph of equivalent conductance against a root function of the concentration. The familiar curve so obtained has been the subject of numerous interpretations; McBain has stressed the importance of the minimum whereas Hartley has emphasized the break.² Lottermoser and Puschel¹² attempted to explain the sudden decrease of equivalent conductance as due to the formation of neutral colloid.

The use of the root function of concentration overemphasizes the rate of decrease of equivalent conductance beyond the break. Furthermore, if ionic micelles are present, the equivalent con-

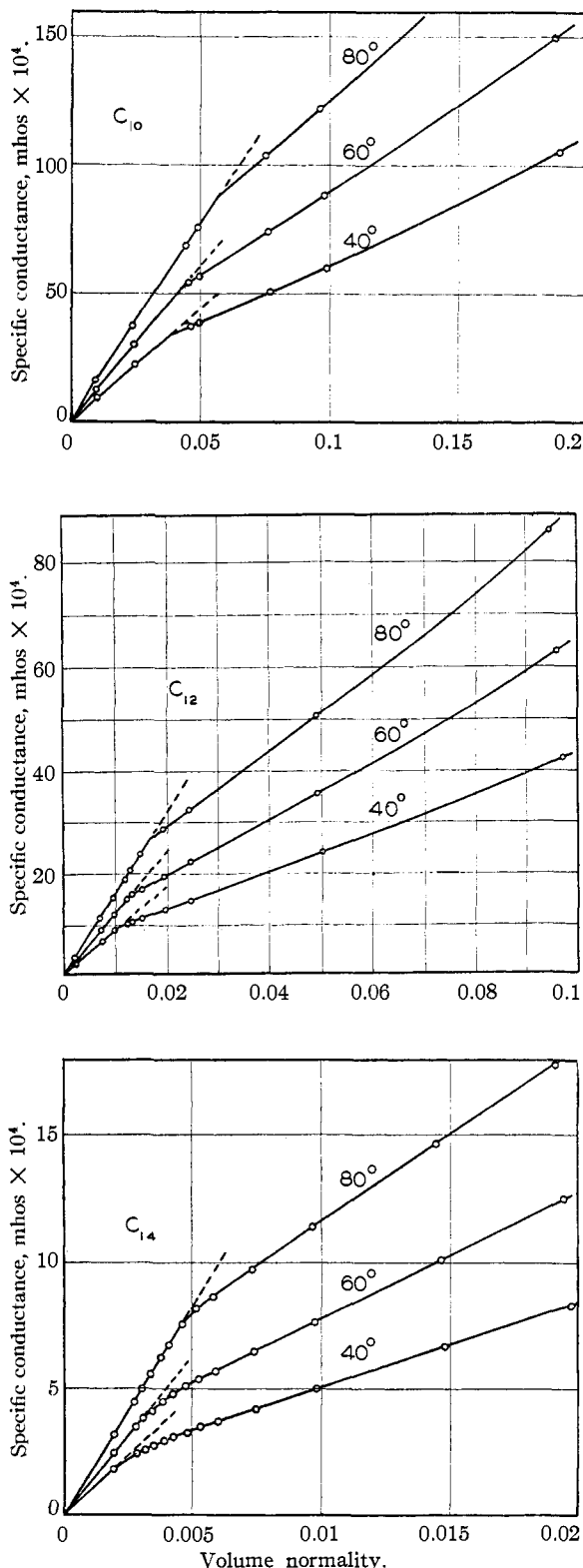


Fig. 2.—Specific conductance-concentration curves for sodium decyl (C_{10}), dodecyl (C_{12}), and tetradecyl (C_{14}) sulfonate solutions.

ductance function loses some of its usual significance because it involves the effect of both micelles and simple ions.

For the moment, suppose the concentration of ionized sulfonate to remain constant past the break and the excess of solute over this value to form ionic micelles of a definite size and ionization. Up to the break, increase in specific conductance will be due to the simple ions but beyond, further increase will be due to the ionic micelle and its ionized sodium ions. A graph of specific conductance against volume normality might then result in two essentially straight lines intersecting at the critical concentration.

The graph of the data of this study given in Fig. 2 shows that, except for a very slight curvature at the critical concentration (more pronounced with rise in temperature), the specific conductance curve is as described above. It is remarkably linear to fairly concentrated solutions where the specific conductance actually increases at a still greater rate.

In a previous discussion,³ it was suggested that the sulfonate ion concentration should not remain constant after the break but would decrease. Furthermore, the "degree of ionization" of the micelle should become less because of increasing sodium ion concentration. If the decrease in both instances is a linear function of the concentration, the linearity of the specific conductance curve would be preserved. However, the sulfonate ion concentration cannot decrease indefinitely but must make an asymptotic approach to zero concentration. The rate of decrease of "ionization" for the micelle may also become less at the higher concentrations. Because of this reduction in rate of decrease of sulfonate ion concentration and "degree of ionization" of the micelle, the specific conductance will increase more rapidly than in more dilute solutions, thus explaining at least part of the effect observed at the higher concentrations.

It will be noted, Fig. 2, that the critical concentration increases with rise in temperature, confirming earlier observations.³ From a large scale graph, the concentration at which the specific conductance curve just begins to bend has been recorded in Table III.

An examination of the published data for other types of paraffin-chain colloidal electrolytes shows that the behavior of the sulfonates is quite general. The specific conductance-concentration

TABLE III
CRITICAL CONCENTRATIONS FOR SODIUM ALKYL SULFONATES

Compound	Volume normality		
	40°	60°	80°
Decyl	0.040	0.043	0.058
Dodecyl	.0110	.0120	.0140
Tetradecyl	.0025	.0033	.0046

curves given in Figs. 3 and 4 for such different compounds as hexadecyl pyridinium bromide,¹⁴

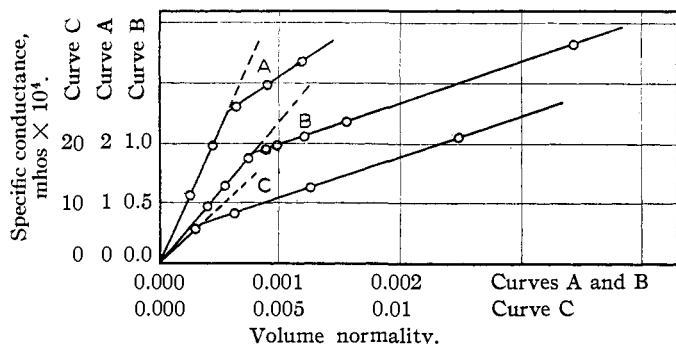


Fig. 3.—Specific conductance-concentration curves for hexadecyl sulfonic acid (16) at 40° (Curve A); hexadecyl pyridinium bromide (15) at 35° (curve B); and tetradecyl sulfuric acid (13) at 25° (curve C).

hexadecyl sulfonic acid,¹⁵ tetradecyl sulfuric acid¹² and sodium myristate¹⁶ show that they are of the same type as those for the sulfonates. The

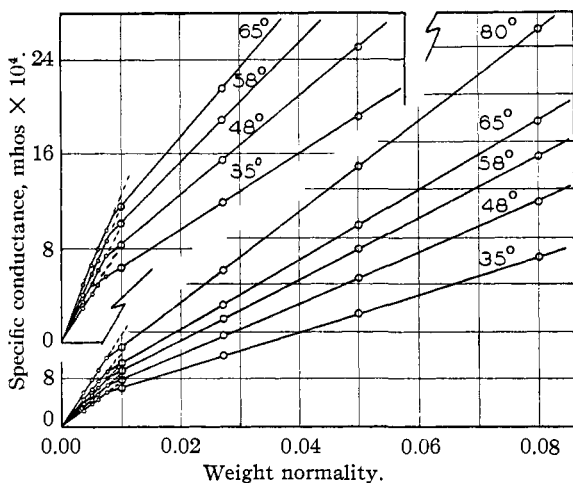


Fig. 4.—Ekwall's data¹⁶ for sodium myristate solutions. Upper inset, ordinate has been magnified to show the breaks in the curves.

curve for hexadecyl pyridinium bromide at 35° has a very sharp break at a concentration of 0.00075 N

(14) Hartley, Collie and Samis, *Trans. Faraday Soc.*, **32**, 799 (1936).

(15) Hartley, *THIS JOURNAL*, **58**, 2347 (1936).

(16) Ekwall, *Z. physik. Chem.*, **161A**, 195 (1932).

and shows no departure from linearity up to the last concentration given (0.11 N). The break for hexadecyl sulfonic acid at 40° occurs at 0.00060 N; at 60 and 80° there appear two breaks at each temperature, a behavior not observed for any of the other compounds investigated.

The meager data available for dilute solutions of the soaps indicate that they behave similarly. Hydrolysis¹⁶ is, apparently, significant only in very dilute solutions where micelles do not occur. The data for sodium myristate presented in Fig. 5 bring out the linear behavior of the specific conductance over the range where micelles are supposed to form. The breaks are not perfectly sharp but show a slight curvature similar to the sulfonates. These occur at concentrations of 0.0068 N (35°), 0.0072 N (48°), 0.0082 N (58°), 0.0086 N (65°) and 0.0092 N (80°). As sodium myristate has a paraffin-chain length equivalent to only thirteen carbon atoms,¹⁷ it is to be expected that its critical concentration might occur approximately half way between that for sodium dodecyl and tetradecyl sulfonates (*vide infra*).

The Effect of Added Electrolyte on the Critical Concentration.—Howell and Robinson¹³ studied

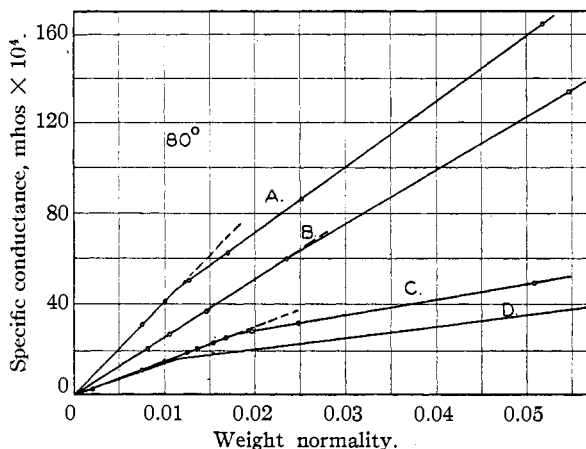


Fig. 5.—Effect of added electrolyte on critical concentration for sodium dodecyl sulfonate solutions at 80°. Curve A represents curve for solutions equimolar with respect to sodium chloride and sodium dodecyl sulfonate (total concentration is twice N_w); curve B, sodium chloride solutions; curve C, sodium dodecyl sulfonate solutions. Curve D represents the difference of curve B from A.

the effect of added electrolyte with common ion on the electrical conductance of sodium alkyl sul-

(17) See discussion for potassium laurate, Wright and Tartar, *THIS JOURNAL*, **61**, 544 (1939).

fate solutions. They presented no experimental data but stated that the "conductance by difference of the added electrolyte is practically unchanged" over the range of concentration immediately following the break.

In a previous discussion³ we have stated that the stability of the micelle should be enhanced by a lowering of the electrical charge through a decrease in "degree of ionization." As this is affected by the sodium ion concentration, addition of sodium chloride should result in a decrease of the critical concentration.

In the present work, solutions equimolar with respect to sodium chloride and sodium dodecyl sulfonate were prepared to weight normalities by careful addition of conductivity water to weighed quantities of a stock solution. Conductances were measured for a number of these solutions over the critical concentration range at 40, 60 and 80°. The conductances for sodium chloride solutions were also measured over the same concentration range and temperatures.

TABLE IV

EFFECT OF ADDED ELECTROLYTE ON SPECIFIC CONDUCTANCE OF SODIUM DODECYL SULFONATE SOLUTIONS

Molality	Mhos $\times 10^4$		
	40°	60°	80°
Sodium Chloride Solutions			
0.007740	12.145	16.308	20.635
.010503	16.324	21.916	27.710
.014454	22.217	29.829	37.696
.023604	35.594	47.744	60.286
.054858	79.210	105.77	133.98
.10000	139.49	186.45	234.64
EQUIMOLAL SOLUTIONS OF SODIUM CHLORIDE AND SODIUM DODECYL SULFONATE			
0.007627	18.232	24.721	31.493
.010169	22.993	32.157	41.400
.012814	27.477	38.429	51.171
.01698	34.501	47.985	63.751
.02530	48.511	66.957	87.815
.05188	92.97	127.20	164.25

TABLE V
EFFECT OF ADDED ELECTROLYTE

Temp., °C.	Critical concentration		Increase of sodium ion concn., %	Decrease of critical concn., %
	Before N_v	After N_v		
40.00	0.0110	0.0081	47	26
60.00	.0120	.0092	53	23
80.00	.0146	.0117	60	20

The data are given in Table IV and presented graphically in Fig. 5. A very decided decrease in critical concentration occurs in accordance with the theory. In Table V the change in critical concentration has been recorded together with the increase of sodium ion concentration and the corresponding percentage decrease of critical concentration. It will be noted that the effect of sodium ion on the critical concentration decreases considerably with rise in temperature.

Acknowledgment.—The work presented in this paper and also that in the two immediately preceding papers was made possible by a fellowship grant from the Standard Oil Company of California. Grateful acknowledgment is made for this assistance.

Summary

1. The specific conductances of dilute aqueous solutions of sodium decyl, dodecyl and hexadecyl sulfonates have been determined at 40, 60 and 80°. At a given temperature, the plot of specific conductance *versus* volume normality results in two straight lines intersecting at the critical concentration. The breaks and the linearity of the curves have been discussed in relation to the ionic micelle theory.

2. The addition of sodium chloride to solutions of sodium dodecyl sulfonate was observed to lower the critical concentration, the lowering becoming less marked with rise in temperature.

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