

initial slope is about 40% less than the Onsager slope. The same phenomenon was observed by Wright, Abbott, Sivertz and Tartar,<sup>3</sup> and perhaps more emphasis has been given to it than it deserves. One should merely assume that, with such non-ideal electrolytes, higher dilutions than usual would have to be reached before the theoretical slope were attained. This idea is borne out by the high dilution data on the *n*-dodecylbenzenesulfonate.

The densities show breaks corresponding to the critical concentrations found by conductance methods. The lower reliability and sensitivity will be apparent on inspection.

**Acknowledgments.**—Grateful acknowledgment is made for a fellowship grant from the Standard Oil Company of California, which made this investigation possible. Thanks are also due to Mr. Stanley Pelan for assistance during the preparation of materials.

### Summary

1. The following new compounds have been prepared and described: sodium *n*-octylbenzene-*p*-sulfonate, *n*-dodecylbenzene, sodium *n*-dodecylbenzene-*p*-sulfonate, aniline *p*-sulfobenzoate. *n*-Caprylyl chloride and *n*-heptyl phenyl ketone

have been prepared, and melting points for these two compounds quoted in the literature have been found to be greatly in error. A method of determining the position of the sulfonate group in the alkylbenzenesulfonates is outlined.

2. Electrical conductances and densities of solutions of ethyl-, *n*-butyl, *n*-octyl- and *n*-dodecylbenzene-*p*-sulfonates have been determined, at 25, 40 and 60° for the first three, and at 60° and in high dilutions for the last. Some data are also presented for a purified mixture of ortho and para octylbenzenesulfonates.

3. Sharp breaks in the conductance and density curves for *n*-octyl- and dodecylbenzenesulfonates have been observed, and these have been interpreted in terms of Hartley's theory of colloidal electrolytes. It is shown that the benzene ring is equivalent to about three and one-half straight-chain carbon atoms in its effect on the critical concentration for micelle formation, but that this fact cannot be interpreted in terms of either the length of the benzene ring or the number of carbon atoms contained therein, but must be considered as an unanalyzed property of the benzene nucleus.

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## Electrolytic Properties of Solutions of Paraffin-chain Quaternary Ammonium Salts

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The explanation of the behavior of colloidal electrolytes on the basis of micelle formation is generally accepted, but there is disagreement among investigators regarding the nature of the micelle and the concentration at which its formation occurs.

Hartley<sup>1</sup> holds that, in general, the colloidal electrolytes below the critical concentration are ordinary, completely dissociated electrolytes, and that micelle formation takes place abruptly at the critical concentration. Because of adhering gegenions, the equivalent conductance falls rapidly at this point. The increase in equivalent conductance which frequently occurs at much greater concentrations is fairly satisfactorily accounted for on the basis either of a "retrograde dissociation," *i. e.*, liberation of adhering gegen-

ions, or of Debye-Hückel-Onsager effects upon the mobility of the free gegenions.

On the other hand, J. W. McBain<sup>2</sup> is of the opinion that the ions of a colloidal electrolyte progressively associate to form ionic micelles, even in very dilute solutions. At the critical concentration, lamellar micelles, "arise from ion pairs and higher aggregates..., increasing in size and amount until their development is sufficient to produce an X-ray pattern in solution." The increase in equivalent conductance at medium concentrations has been recently explained by E. L. McBain, Dye and Johnston<sup>3</sup> on the basis of the mass law as being due to the increase in the number of highly charged ionic micelles, which at this point become a dominating factor.

(2) J. W. McBain, *Nature*, **145**, 702 (1940).

(3) E. L. McBain, Dye and Johnston, *THIS JOURNAL*, **61**, 3210 (1939).

(1) Hartley, *Kolloid Z.*, **88**, 22 (1939).

With a view to clarifying certain concepts concerning micelle formation and the electrolytic properties of colloidal electrolytes, a study has been made of a series of normal paraffin-chain trimethylammonium salts ranging from *n*-butyl to *n*-hexadecyltrimethylammonium bromide. Previously, the alkyl positive ions have received comparatively little attention as colloidal electrolytes.<sup>4,5,6,7,8,9</sup> Emphasis has here been placed upon the behavior below the critical concentration because of the conflicting opinions concerning the formation of ion pairs and ionic micelles in this region and because of the lack of trustworthy data covering this point.

### Experimental Part

**Preparation of Materials.**—The *n*-alkyl trimethylammonium bromides were prepared by the reaction of trimethylamine with the alkyl bromides in alcoholic solution. Butyl and hexyl bromides were obtained from the Eastman Kodak Company. Octyl, decyl, dodecyl and hexadecyl bromides were prepared from the corresponding alcohols by the method of Kamm and Marvel.<sup>10</sup> The alcohols were obtained in a fairly pure state through the courtesy of The Procter and Gamble Company, and further purified by fractional distillation.

Trimethylamine was distilled from a concentrated aqueous solution, and passed over calcium oxide into alcohol until the concentration of amine was approximately 10%. Sufficient quantity of this alcoholic solution to ensure a 30% excess of the amine was refluxed with the alkyl bromide for an hour using a brine-cooled condenser. The salts were recrystallized from acetone and then from benzene. The butyl, hexyl and octyl compounds were quite hygroscopic.

The salts were analyzed for bromide ion by precipitation as silver bromide. The bromide content of butyltrimethylammonium bromide was found to be 40.83%; theoretical, 40.75%. The deviation in all other cases was smaller.

The sodium ethylbenzene-*p*-sulfonate and the potassium chloride were prepared in this Laboratory by R. G. Paquette. The water used had a specific conductance of  $1.0 \times 10^{-6}$  mho or less at 25°.

**Apparatus and Procedure.**—Conductance measurements were made by means of a Leeds and Northrup-Dike<sup>11</sup> bridge. A Leeds and Northrup vacuum-tube oscillator and amplifier were used.

Most of the measurements were made in the same series of cells used by Cadle<sup>12</sup> and by Wright, Abbott, Sivertz and Tartar.<sup>13</sup> The constants were redetermined at

- (4) Hartley and Samis, *Trans. Faraday Soc.*, **34**, 1288 (1938).
- (5) Hartley, Collie and Samis, *ibid.*, **32**, 795 (1936).
- (6) Malsch and Hartley, *Z. physik. Chem.*, **A170**, 321 (1934).
- (7) Hartley and Runnicles, *Proc. Roy. Soc. (London)*, **A168**, 420 (1938).
- (8) Hartley, *J. Chem. Soc.*, 1968 (1938).
- (9) Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).
- (10) Kamm and Marvel, *THIS JOURNAL*, **42**, 299 (1920).
- (11) Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).
- (12) R. D. Cadle, Thesis, University of Washington, 1940.
- (13) Wright, Abbott, Sivertz and Tartar, *THIS JOURNAL*, **61**, 549 (1939).

25° according to the specifications of Jones and Bradshaw<sup>14</sup> and calculated at 40 and 60°. They were found to have changed somewhat with time.

The measurement of the three most dilute hexadecyltrimethylammonium bromide solutions was carried out in a cell similar to that described by Shedlovsky.<sup>16</sup> A weighed quantity of water was added to the cell, and nitrogen passed through until the conductance of the water became constant, after which time small additions of a stock solution were made from a weight buret, yielding successively larger concentrations. Nitrogen was passed continuously except while measurements were actually being taken. It was not possible to use concentrations greater than 0.001 *N* with this cell, because of the low cell constant, 0.26229, at 25°. In other respects it was found satisfactory and gave results of a high degree of accuracy.

Therefore for making accurate measurements on dilute solutions of hexyltrimethylammonium bromide and sodium ethylbenzene-*p*-sulfonate, another cell, Fig. 1, was constructed which offered several advantages not possessed by the Shedlovsky cell and afforded measurements of the same degree of accuracy.

The main chamber of the cell consisted of a 500-ml. seasoned Pyrex reagent bottle, to the bottom of which was sealed a chamber of 2.5-cm. diameter and a depth of 3.0 cm. The upper chamber contained electrodes of area 0.25 sq. cm. at a distance of approximately 5 cm. and in the lower chamber were electrodes of area 2.0 sq. cm. at a distance of approximately 1 cm. The shortest distance between parallel leads of opposite charge was 9.5 cm., effectively eliminating capacitance between leads. No filling tubes were necessary. Tank nitrogen, purified and saturated with water vapor at 25° by passing through a train of several bottles each of sulfuric acid, sodium hydroxide, and finally conductivity water, was admitted through the perforated orifice, C, and released through the fine tip, D. The upper electrodes were heavily platinized and the lower ones very lightly.<sup>17</sup>

The cell constants of the two pairs of electrodes were determined by comparison with one of the other cells at frequencies of 1000 and 2000 cycles. The difference at the two frequencies for both pairs of electrodes was less than 0.03% with resistances above 4000 ohms, but was 0.08% for the lower electrodes with a resistance of 800 ohms. This was to be expected with the light platinization. This pair was never used with resistances much below 4000 ohms.

The ratio between the two pairs of electrodes was determined with four widely different resistances, and the average deviation was less than 0.02%. The cell constant for the upper pair was 0.82356; for the lower pair, 0.14740.

- (14) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).
- (15) Washburn, *ibid.*, **38**, 2431 (1916).
- (16) Shedlovsky, *ibid.*, **54**, 1411 (1932).
- (17) Jones and Bollinger, *ibid.*, **55**, 1780 (1933).

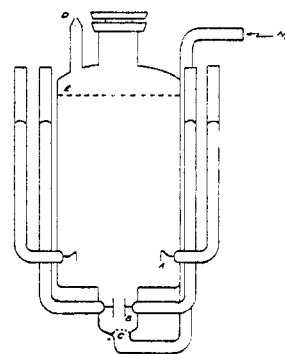


Fig. 1.—Conductance cell.

TABLE I  
DENSITIES AND EQUIVALENT CONDUCTANCES OF SOLUTIONS OF DECYL, DODECYL AND HEXADECYL TRIMETHYLAMMONIUM BROMIDES

Weight normality	Density, g./cc.			Equivalent conductance, mho		
	25°	40°	60°	25°	40°	60°
Decyl						
0.001000	(0.9971) <sup>a</sup>	(0.9923)	(0.9833)	100.0	132.6	179.7
.003000	(.9971)	(.9923)	(.9833)	97.8	129.4	176.0
.006000	(.9972)	(.9924)	(.9833)	96.1	127.3	172.6
.010000	.9973	.9924	(.9834)	94.2	124.9	169.1
.027492	.9977	.9928	.9836	89.2	118.5	161.0
.050000	.9982	.9932	.9840	84.1	111.6	152.0
.065000	.9986	.9935	.9843	80.6	108.0	148.3
.080000	.9989	.9938	.9846	78.1	99.8	142.1
.10000	.9993	.9940	.9847	64.2	88.8	130.5
.20000	1.0010	.9957	.9862	46.88	66.9	101.5
.40000	1.0043	.9986	.9888	36.92	53.73	82.1
.60000	1.0074	1.0013	.9911	34.07	50.00	76.5
Dodecyl						
0.000400	(0.9971) <sup>a</sup>	(0.9923)	(0.9832)	100.2	132.9	181.2
.000600	(.9971)	(.9923)	(.9832)	100.3	132.6	180.7
.002000	(.9971)	(.9923)	(.9833)	98.1	130.1	176.5
.005000	.9972	.9923	(.9833)	95.3	126.2	170.7
.006500	(.9972)	(.9923)	(.9833)	94.4	125.1	169.5
.010000	.9973	.9924	.9833	92.8	123.1	167.4
.013652	(.9973)	(.9925)	(.9834)	91.1	121.0	164.4
.015000		.9925	.9834	89.4	119.8	162.3
.017500	(.9974)	(.9926)	(.9834)	83.1	114.2	160.5
.020000	.9974	.9926	.9835	76.3	105.9	157.3
.050000	.9979	.9929	.9837	43.76	63.6	98.1
.10000	.9985	.9935	.9842	35.21	51.03	78.6
.20000	(.9997)	(.9945)	.9850	31.41	46.03	70.8
.35000	1.0017	.9961	.9863	30.18	44.57	68.6
.50000	1.0034	.9975	.9875	29.61	43.92	67.7
Hexadecyl						
0.000203	(0.9971) <sup>a</sup>	(0.9922)	(0.9832)	96.4		
.000409	(.9971)	(.9922)	(.9832)	96.2		
.000681	(.9971)	(.9922)	(.9832)	95.7		
.001000	(.9971)	(.9922)	(.9832)	93.0		
.003000	.9971	(.9922)	(.9832)	48.6		
.007000	.9971	.9923	.9832	35.41		
.010000	.9971	.9923	.9832	31.79		
.030000	.9972	.9923	.9832	25.70		
.050000	.9973	.9923	.9832	24.93		
.070000	.9974	.9924	.9832	23.95		
.10000	.9975	.9925	.9832	23.68		
.20000	.9980	.9927	.9832	23.97		
.30480	.9984	.9928	.9831	21.90		
.40000	.9989	.9930	.9831	21.22		

<sup>a</sup> Interpolated.

It might be expected that there would be a great variation in the cell constant as the height of solution in this cell was varied, due to the volume of the conducting medium. However, when the cell was filled to, or above, E, the change in resistance upon adding or removing 25 ml. was less than 0.01%. The change toward higher resistance became progressively more rapid as solution was removed, indicating that below a certain height the cell constant varies greatly with height of solution. Consequently, the surface of the solution was always kept at or above E.

Measurements were made in the same manner as with the Shedlovsky cell. The upper concentration limit, *i. e.*, that concentration above which the resistance between the upper electrodes decreased below 1000 ohms, for these electrolytes was from 0.02 to 0.03 *N*. Three concentrations could be prepared and measured in an hour.

The conductance cells were thermostated in oil-baths, held to within 0.001° at 25, 40 and 60°. Regulation was by means of a thyatron tube relay and mercury-toluene

regulators. The absolute value of the temperature, based upon an accurately calibrated platinum resistance thermometer, was correct within 0.005°.

Solutions were prepared by weight in seasoned Pyrex bottles, except for those measured in the Shedlovsky cell and the one shown in Fig. 1. As the density of all salts used was very nearly that of water, no buoyancy correction was made. The solutions were prepared and measured as rapidly as possible to avoid absorption of carbon dioxide, and the cells were filled from the bottles by nitrogen pressure. The specific conductance of the water used for each solution was measured in a special cell of low constant, and subtracted from that of the solution. The most concentrated solution of each series was prepared first from the dried salt, and the others prepared by dilution.

Adsorption caused troublesome drifts with the hexadecyltrimethylammonium bromide solutions, but was eliminated as a factor either by allowing the cells to stand filled with preliminary solutions, or by extrapolating the drifts to zero time.

**Density Measurements.**—Relative densities were determined to demonstrate the effect of micelle formation, and also to convert weight to volume normalities. A modified Sprengel pycnometer was used having a volume of about 25 ml. The volume was accurately adjusted by overflow of the solution from the two tips as the pycnometer came from a lower temperature to that of the bath. The pycnometer was calibrated with boiled distilled water; successive determinations checked to better than 1 part in 250,000. However, the calibration varied from time to time, so that the error in solution densities, even with frequent calibration, was about 2 parts in 100,000. The oil thermostats were used, and the pycnometer was cleaned prior to weighing by wiping several times with benzene and finally with a slightly dampened cloth.

Densities of butyl, hexyl and octyltrimethylammonium bromides were used only for calculating volume concentrations; they were determined at three concentrations, and at intermediate points were found by graphical interpolation.

### Results and Discussion

Conductance and density data for the six alkyl trimethylammonium bromides are given in Tables I and II, and in Figs. 2, 3 and 4. The four highest members of the series give evidence of micelle formation, as indicated by the downward breaks in the equivalent conductance curves. As in the case of sodium octane sulfonate,<sup>12,18</sup> the data indicate that the octyl salt either forms but few micelles, or possibly micelles having about the same conductance as the dissociated electrolyte.

E. L. McBain, Dye and Johnston<sup>3</sup> contend that the breaks in specific and equivalent conductance curves are not sharp and suggest a gradual formation of micelles and complexes. In the same paper are given curves for the specific

(18) Reed and Tartar, *This Journal*, **58**, 322 (1936).

TABLE II  
EQUIVALENT CONDUCTANCES OF SOLUTIONS OF BUTYL, HEXYL AND OCTYL TRIMETHYLAMMONIUM BROMIDES

Weight normality	Equivalent conductance, mho		
	25°	40°	60°
	Butyl		
0.001000	109.6	144.9	195.9
.002000	108.2	143.0	193.4
.003000	107.7	142.4	192.9
.005000	106.1	140.4	190.1
.006800	105.1	139.1	188.1
.010000	103.6	137.2	185.7
.020000	99.7	(128.7)	178.8
.030000	97.2	128.9	174.5
.045000	94.2	125.2	169.4
.070000	90.4	120.3	163.4
.10000	86.8	115.7	157.5
.15000	82.2	109.9	149.8
.20000	78.7	105.4	144.0
.25000	75.7	101.7	139.2
.35000	70.9	95.6	131.5
.60000	62.4	84.8	117.8
	Hexyl		
0.002000	106.8	141.5	191.8
.005000	103.9	137.5	186.4
.007000	102.6	135.9	184.0
.010000	101.5	134.4	181.9
.020000	97.4	129.1	175.2
.030000	95.0	126.2	171.3
.050000	90.8	120.8	164.3
.081232	86.1	114.9	156.4
.10000	83.9	112.1	152.6
.15000	79.0	105.9	145.2
.20000	75.3	101.3	139.2
.25000	72.1	97.2	134.1
.35000	66.9	90.9	126.2
.60000	57.8	79.4	111.4
.80000	52.7	72.9	103.2
	Octyl		
0.002000	95.6	126.8	171.8
.005000	94.7	125.4	169.9
.020000	88.6	117.6	159.4
.040000	83.0	110.4	150.3
.070000	79.2	105.6	144.2
.10000	75.7	101.4	138.8
.14000	71.7	96.4	132.6
.20000	65.5	88.8	122.9
.40000	52.5	72.6	104.0
.60000	44.4	62.7	91.6
.80000	39.6	56.7	83.6

conductance of undecane, dodecane and tetradecanesulfonic acids which display breaks which cannot be described as other than sharp. The same is true of the alkyl trimethylammonium bromides. Grindley and Bury<sup>19</sup> have shown how the mass action principle can be applied to explain a sharp break if the change involved is from an ion to an aggregate of twenty or more ions.

(19) Grindley and Bury, *J. Chem. Soc.*, 679 (1929).

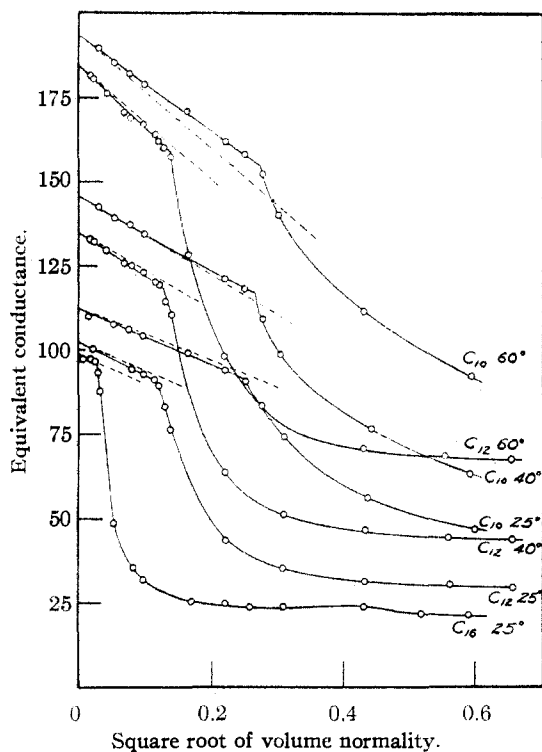


Fig. 2.—Equivalent conductance of decyl-, dodecyl- and hexadecyltrimethylammonium bromide solutions. Subtract 10 from ordinate for decyltrimethylammonium bromide.

Hexadecyltrimethylammonium bromide is the only member of this series whose equivalent conductance attains a minimum value at medium

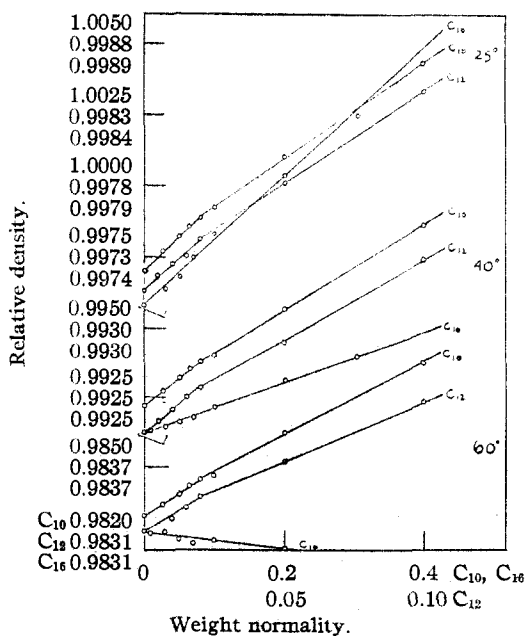


Fig. 3.—Densities of decyl-, dodecyl- and hexadecyltrimethylammonium bromide solutions.

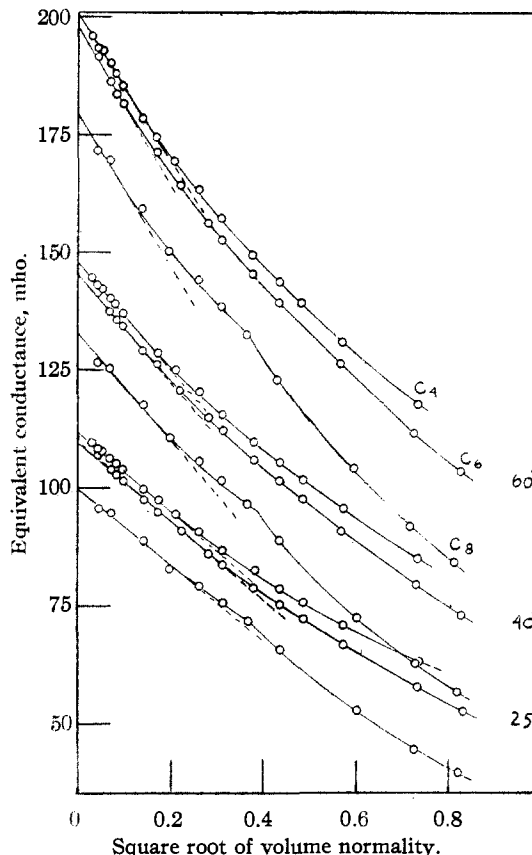


Fig. 4.—Equivalent conductances of butyl-, hexyl- and octyltrimethylammonium bromide solutions.

concentration; after rising slightly, it again falls. Similar increases in equivalent conductance with concentration occur with solutions of the soaps, sulfonic acids and alkyl sulfates, but are absent in the sulfonates. In the cases where this minimum occurs, there is not much shift in concentration with chain length, and it is not a reasonable expectation that with dodecyl and decyltrimethylammonium bromides there might be a minimum at concentrations above those studied.

It is evident, therefore, that the rise in equivalent conductance at higher concentrations is by no means a characteristic property of colloidal electrolytes.

Existing data on the behavior of colloidal electrolytes below the critical concentration have often been misinterpreted. The data of Shedlovsky<sup>16</sup> for potassium chloride at 25°, plotted in Fig. 5, show that the slope of the equivalent conductance curve deviates 20% from the theoretical Onsager slope at 0.01 *N*, and 5.4% at 0.001 *N*. The theoretical slope obtains only at concentrations below 0.0001 *N*. Unless conductance meas-

urements are made with cells designed for high dilutions, such as the Shedlovsky cell or that described in this paper, to concentrations well below 0.001 *N*, no conclusions are warranted (in the majority of cases) regarding the limiting slope or the limiting equivalent conductance.

McBain, Dye and Johnston cite the data of Wright, Abbott, Sivertz, and Tartar,<sup>13</sup> and data they presented on certain sulfonic acids to show that the equivalent conductance curves of colloidal electrolytes have slopes in dilute solutions less than that predicted by the Onsager equation. The failure of the equivalent conductance to decrease as rapidly as predicted by theory "could only be accounted for on the basis of small amounts of highly conducting ionic micelle," at concentrations below the critical concentration. They admit the possibility of systematic error in their data and methods essential to accurate work at low concentrations were not employed. The data of Wright, Abbott, Sivertz and Tartar extended only down to 0.001 *N*, and the best straight line was drawn through all points below 0.01 *N*, obviously producing a slope considerably less than the theoretical. Hence it cannot be shown by existing conductance data that ionic micelles are formed below the critical concentration; in fact, a deviation from the Onsager slope is to be expected in these cases.

A study of the conductance of sodium ethylbenzene-*p*-sulfonate in this Laboratory by ordinary methods showed its limiting slope to differ from the Onsager slope, whereas, using the cell of Fig. 1, it was found to follow the theory exactly at very low concentrations (Table III and Fig. 5), and it is reasonable to assume that other sodium sulfonates behave similarly.

The alkyl trimethylammonium bromides, on the other hand, all confirm the Onsager theory within the limits of experimental error, even though accurate, high-dilution techniques were used only with the hexadecyl and hexyl compounds at 25°. The reason is evident from a consideration of the data of Table III, obtained at low concentrations by the use of the cell of Fig. 1, plotted in Fig. 5. Hexyltrimethylammonium bromide follows the Onsager slope to much higher concentrations than does either potassium chloride or sodium ethylbenzene-*p*-sulfonate, and has, throughout the range studied, very little curva-

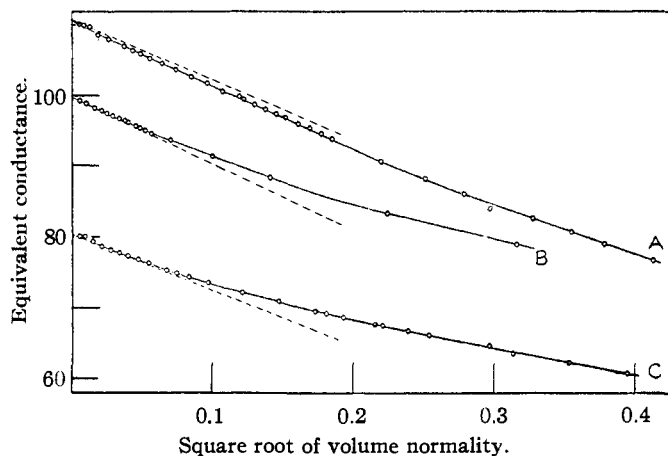


Fig. 5.—Equivalent conductance of solutions of A, hexyltrimethylammonium bromide; B, potassium chloride (Shedlovsky's data); C, sodium ethylbenzene-*p*-sulfonate.

TABLE III  
EQUIVALENT CONDUCTANCES OF SOLUTIONS OF HEXYL-  
TRIMETHYLAMMONIUM BROMIDE AND SODIUM ETHYLBEN-  
ZENE-*p*-SULFONATE AT 25°

Hexyltrimethylammonium bromide		Sodium ethylbenzene- <i>p</i> -sulfonate	
Volume normality	Equivalent conductance	Volume normality	Equivalent conductance
0.00002921	110.1	0.00003437	80.12
.00009674	110.14	.00009669	80.10
.00017360	109.69	.00022978	79.44
.00036736	108.75	.00045401	78.80
.00067349	108.06	.00074885	78.28
.0013243	107.04	.0011270	77.82
.0013909	107.04	.0015849	77.38
.0018277	106.60	.0021539	76.87
.0024159	106.04	.0029477	76.32
.0032781	105.34	.0045240	75.41
.0041413	104.72	.0055833	74.95
.0055942	103.76	.0069889	74.41
.0073825	102.76	.0094280	73.60
.0092997	101.79	.014726	72.15
.011828	100.67	.021544	70.85
.014370	98.90	.029636	69.58
.014935	99.47	.032888	69.11
.017151	98.67	.037159	68.64
.019067	98.04	.046520	67.61
.021179	97.38	.048822	67.43
.023142	96.81	.057014	66.67
.026195	95.98	.064278	66.02
.028786	95.34	.082473	64.66
.031648	94.63	.098436	63.67
.034471	93.94	.12510	62.22
.048523	90.47	.15635	60.74
.063454	88.11	.20871	58.62
.078153	85.93		
.088647	83.99		
.10723	82.55		
.12649	80.55		
.14394	78.91		
.17104	76.64		

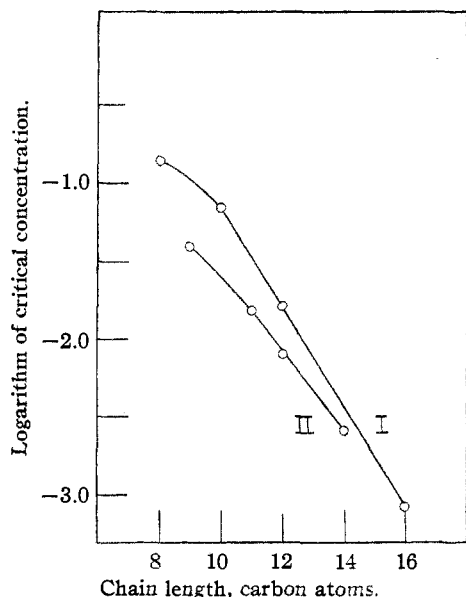


Fig. 6.—Critical concentration as a function of chain length: I, alkyl trimethylammonium bromides; II, sulfonic acids.

ture. The limiting slope is, in fact, slightly steeper than the theoretical, as Shedlovsky found for potassium nitrate and silver nitrate.

The alkyl trimethylammonium ions have somewhat higher critical concentrations than the corresponding sulfonate ions, indicating that the three methyl groups of the former exert no, or a negligible, influence toward micelle formation. In Fig. 6, the logarithm of the critical concentration is plotted against the chain length. The relationship is roughly linear, but the problems involved are too complex to allow a quantitative treatment of this relation on the basis of existing data.

A slight break in the density-concentration curve was observed at the critical concentration with decyl and dodecyltrimethylammonium bromides. The change in density with concentration was so slight with the hexadecyl compound that the experimental error was sufficient to mask this effect. The segment below the break was linear, as is to be expected for an electrolyte in this concentration range. Wright and Tartar<sup>20</sup> found an upward curvature in this portion with sodium dodecanesulfonate.

### Summary

1. A convenient conductance cell for accurate measurement of low concentrations has been described.

2. Conductance measurements have been made on aqueous solutions of butyl, hexyl, octyl, decyl and dodecyltrimethylammonium bromides at 25, 40 and 60°, and of hexadecyltrimethylammonium bromide and sodium ethylbenzene-*p*-sulfonate at 25°.

3. The four highest alkyl trimethylammonium bromides studied were shown to form micelles; the conductance data have been interpreted in terms of existing theories. Evidence has been given that ionic micelles do not form below the critical concentration.

4. Density measurements were made and micelle formation in solutions of decyl and dodecyltrimethylammonium bromides was indicated by this means.

(20) Wright and Tartar, *THIS JOURNAL*, **61**, 544 (1939).

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## Electrolytic Properties of Aqueous Solutions of Octyltrimethylammonium Octanesulfonate and Decyltrimethylammonium Decanesulfonate

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The ordinary paraffin-chain colloidal electrolytes contain one kind of ion which aggregates to form ionic micelles, while the other ion remains free or is bound to the micelle by electrostatic forces. It was considered a matter of interest to study the properties of salts composed of a long-chain anion as well as a long-chain cation. This type of electrolyte will be designated herein as a "double long-chain salt" as distinguished from the usual "single long-chain salt." Whereas pre-

vious studies of the properties of colloidal electrolytes in the neighborhood of the critical concentration have been complicated by the presence of the gegenion and uncertainty as to its exact role in micelle formation, in the present investigation the interpretation of the electrolytic behavior becomes more simple.

Two compounds of this type, octyltrimethylammonium octanesulfonate and decyltrimethylammonium decanesulfonate, were prepared for the