crete "hexane effect" upon the orientation of addition of hydrogen bromide obtains with 3-butenoic, 4-pentenoic or 5-hexenoic acid.

BETHESDA, MARYLAND RECEIVED NOVEMBER 25, 1942

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

Studies of Sulfonates. VII. Conductances and Densities of Sodium Ethyl-, *n*-Butyl-, *n*-Octyl-, and *n*-Dodecylbenzene-*p*-sulfonate Solutions

BY R. G. PAQUETTE,[1] E. C. LINGAFELTER AND H. V. TARTAR

Previous work in this Laboratory has been devoted to various studies of straight-chain aliphatic sulfonates and discussions of their properties as colloidal electrolytes.[2,3] This paper presents the results of similar work on the sodium salts of the straight-chain alkylbenzenesulfonates, endeavoring to show the effect of the benzene nucleus on micelle formation and thereby to throw new light on the latter process. Compounds of this type have previously received little study, although commercial detergents containing them in impure mixtures have been marketed for some years. The pure *n*-octyl- and *n*-dodecylbenzene-*p*-sulfonates have not previously been described. Two shorter chain compounds ethylbenzene-*p*-sulfonate and butylbenzene-*p*-sulfonate have been included in this study.

Experimental

Sodium Ethylbenzene-*p*-sulfonate.—Ethylbenzene, b. p. 134–136°, (Eastman Kodak Company) was sulfonated according to Sempotowski's[4] directions and isolated as the barium salt which crystallizes well from aqueous solution. In contrast to his claim that only the para isomer is formed, about 30% of the product was found in the mother liquor in a much more soluble form which could be quite completely separated from the para isomer. The para barium salt yielded well-formed, long, flat plates, probably orthorhombic, which were further purified by recrystallization; the other salt separated in clumps of very fine needles (compare with the butyl compound), and was evidently the *o*-ethylbenzenesulfonate.

The barium para-sulfonate, after purification by recrystallization, was converted to the sodium salt with a slight excess of sodium carbonate, and then purified by several crystallizations from alcohol in the form of colorless leaflets.

Sodium *n*-Butylbenzene-*p*-sulfonate.—*n*-Butylbenzene, b. p. 181–183°, (Eastman Kodak Company) was sulfonated. Balbiano[5] used fuming sulfuric acid but is vague in his directions. One hundred grams of butylbenzene was treated first with 7 cc. of concentrated sulfuric acid and then with 100 g. of fuming sulfuric acid. The sulfonic acid was isolated as the barium salt, which was difficult to separate from the barium sulfate.

Two isomers were found; the first, less soluble, in the form of small leaflets and in much greater quantity; the second, quite soluble and crystallizing in small spherulites; they have been designated as α and β, respectively, by Balbiano.[5]

The barium salt of the α isomer was purified by recrystallization from water and then converted to the sodium salt which was purified by recrystallization from alcohol, using purified animal charcoal to aid in removing impurities. The salt was finally obtained in small plates of rhombic outline; the yield was 23%.

The structure of the α salt was determined by the method outlined below.

Caprylyl Chloride.—To prepare the long-chain alkylbenzenes it was necessary to proceed by way of the alkylphenyl ketones, since direct alkylation results in isomerization of the alkyl chain. Caprylyl chloride was prepared in 82% yield by the method of Krafft and Koenig[6] from *n*-caprylic acid, m. p. 15–16°, (Eastman Kodak Company). The product, after two fractionations *in vacuo* through a 17-cm. Vigreux column, was colorless and boiled at 81.5–84.5° (cor., 15 mm.), the bulk coming over at 83°, in agreement with Krafft and Koenig. The melting point, taken on a large sample, was −63 to −62.5° (cor.). Deffet[7] gives the melting point as −61.0°.

***n*-Heptylphenyl Ketone.**—This compound was prepared from the caprylyl chloride and purified benzene by the Friedel–Crafts reaction. The yield was 91% of colorless product, nearly all boiling at 164–165.5° (cor., 15 mm.). Meyer and Scharvin[8] give the boiling point as 165° (15 mm.).

***n*-Octylbenzene.**—The above ketone (160 g.) was reduced at boiling temperature with amalgamated zinc foil squares and strong hydrochloric acid, the method of Clemmensen.[9] After twenty-two hours, 42 g. of crude octylbenzene was obtained. The residue was treated for

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[2] Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

[3] Wright, Abbott, Sivertz and Tartar, THIS JOURNAL, **61**, 549 (1939).

[4] Sempotowski, *Ber.*, **22**, 2663 (1889).

[5] Balbiano, *Gazz. chim. ital.*, **7**, 345 (1877).

[6] Krafft and Koenig, *Ber.*, **23**, 2384 (1890).

[7] Deffet, *Bull. soc. chim. Belg.*, **40**, 385 (1931). In the original article the second digit of the number has failed to print well; the freezing point has consequently been misquoted by the abstract journals as −6.0. The second digit should be either a "4" or a "1," quite probably the latter. (Courtesy of M. L. Raney, Director of Libraries, University of Chicago.)

[8] Meyer and Scharvin, *Ber.*, **30**, 1943 (1897).

[9] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., **20**, 57 (1940).

twenty-seven hours more to obtain 41 g. of product; further treatment of the residue for fourteen hours gave only a few milliliters. The crude octylbenzene was purified by fractional distillation through a 17-cm. Vigreux column under reduced pressure. The final product (64 g., 46%) boiled at 127–129° (cor., 11 mm.) with the main portion at 127.5°. The m. p. of a large sample was −45.7 to −45.5° (cor.). Ahrens[10] gives −7° for the m. p., but he is undoubtedly in error, since a plot of melting point *versus* number of carbon atoms for the known *n*-alkylbenzenes roughly follows a straight line passing close to −47° for 14 carbon atoms.

Sodium *n*-Octylbenzene-*p*-sulfonate.—The *n*-octylbenzene was added to a small amount of concentrated sulfuric acid and sulfonation was effected by the slow addition of 25% fuming sulfuric acid at about 70° under constant agitation. The amount of sulfuric acid was kept as small as possible and the temperature was the lowest consistent with a reasonable rate of sulfonation. The reaction mixture was neutralized with sodium hydroxide, and evaporated to dryness, and the sulfonates extracted with alcohol.

Two isomers were obtained. The one occurring in larger quantity (about $^{2}/_{3}$) was separated and purified by several further crystallizations from alcohol. Fortunately, the crystal habits of the two isomers were quite different under the conditions used, and the separation could be followed and controlled by microscopic examination. The first isomer appeared as thin plates which were elongated hexagons in outline. The other appeared as clusters of very thin feather-like forms. The second isomer, always mixed with the first, remained in the mother liquors. It was purified, but the two were not separated by crystallizations from alcohol. A few conductance and density measurements were made on the mixture. The first isomer was shown to be the *n*-octylbenzene-*p*-sulfonate by a method to be outlined presently. The other was doubtless the ortho isomer. Both were white and crystalline and moderately soluble (about 10 g./liter at room temperature). The barium salts were soluble to the extent of about 0.1 g./liter at room temperature.

***n*-Undecyl Phenyl Ketone.**—Lauroyl chloride, b. p. 134–137° (11 mm.), was obtained from the Eastman Kodak Co. The ketone was prepared, as before, by the Friedel–Crafts reaction. The product, after three fractionations under reduced pressure through a 7-cm. Vigreux column, was pale yellow and boiled at 214–215° (cor., 16 mm.). The m. p., taken on a large sample, was 43° and was essentially constant over a wide range of fraction frozen. Melting points of 46 and 47° were found by v. Auwers[11] and Sabatier and Mailhe,[12] respectively. The yield was 63%.

***n*-Dodecylbenzene.**—Eighty grams of the *n*-undecyl phenyl ketone was reduced as described above. Boiling was continued for forty-four hours to obtain 45 g. of product, then twenty hours more to obtain an additional 5 g. of crude dodecylbenzene. Forty hours of further boiling yielded no more. The residue was very high boiling material. The crude substance was purified by fractionation through a 7-cm. Vigreux column. It was a colorless slightly viscous liquid boiling at 185–188° (cor., 15 mm.), the bulk coming over at 185°. The yield was 43 g., or 57%. This compound has not previously been described.

Sodium *n*-Dodecylbenzene-*p*-sulfonate.—The *n*-dodecylbenzene was sulfonated as described above. Unwisely, isolation was attempted by way of the barium salt. The latter was so insoluble as to require tedious processing of the sulfonate–sulfate mixture with sodium carbonate solution before the sodium salt could be obtained. Neutralization of the sulfonation mixture with sodium hydroxide is to be preferred. The product was crystallized once from water and twice from alcohol. Nearly all the material isolated was the pure para isomer; a small residue of another isomer was separated in the purification process. A considerable amount of sulfonate was retained by the barium sulfate and could not be removed; consequently, the amount of each isomer formed is unknown. The yield of para compound was 23 g., or 38%.

The para isomer crystallized well from water or alcohol, forming small elongated hexagonal plates from the former solvent and small sheaves of fine curving needles from the latter. The solubility in water was about 2 g./1000 g. of water at room temperature, about 35 g./1000 g. at 60°, and much higher at boiling temperature. The solubility in alcohol was considerably less.

The other isomer crystallized from alcohol in small leaflets of rhombic outline. Attempts to separate it from admixed para-sulfonate were unsuccessful.

Determination of Structures.—The positions of the sulfonate groups in the butyl-, octyl- and the dodecylbenzenesulfonate were determined as follows. One gram samples of the sulfonates (due to paucity of material) were oxidized to sulfobenzoic acid by a slight excess of acidified dichromate, and the sulfobenzoic acid was isolated as the slightly soluble barium salt. From this the acid was prepared by careful titration with sulfuric acid. Identification of the acids by m. p. is difficult because of their hygroscopic nature. The aniline salts were therefore prepared according to the suggestion of van Duin,[13] by adding strong aniline hydrochloride solution. The aniline salts are difficultly soluble (more so in the case of the para compound) and separate as needles. The products were washed, dried, and the melting points were taken. The melting points were then compared with those of the isomeric aniline sulfobenzoates made by unambiguous methods. The aniline *o*-sulfobenzoate melted at 183° (cor.); van Duin gives 180° (uncor.?). The para derivative melted quite sharply at 258.5° (cor.) with some decomposition. It has not previously been described. The large difference in melting points makes differentiation easy.

The three sulfonates isolated in pure form were subjected to this determination. They gave aniline sulfobenzoates melting at the same temperature, 256° (cor.), with some decomposition. This would seem to be very strong evidence that all were the *p*-sulfonates. However, a mixed melting point determination was performed, using the authentic specimen of aniline *p*-sulfobenzoate and the derivative obtained from the dodecylbenzenesulfonate. The mixture melted at 257.5° (cor.).

Conductances.—The electrical conductances were determined at 25, 40 and 60° by the usual methods for the

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[10] Ahrens, *Ber.*, **45**, 2772 (1912).

[11] v. Auwers, *ibid.*, **45**, 2772 (1912).

[12] Sabatier and Mailhe, *Compt. rend.*, **158**, 834 (1914).

[13] van Duin, *Rec. trav. chim.*, **40**, 724 (1921).

ethyl-, butyl- and octylbenzenesulfonates; and at 60° only and at high dilutions for the dodecylbenzenesulfonate. The latter measurements were made using the modified Shedlovsky cell described by Sivertz, Reitmeier and Tartar.[14] The last-mentioned conditions were necessary because of the low solubility and low "critical concentration" of the dodecylbenzenesulfonate.

The Leeds and Northrup Jones–Dike bridge, conductance cells, and oil thermostats regulated to 0.001° have been previously described.[3] Temperature determinations were checked by a platinum resistance thermometer previously calibrated by the Bureau of Standards and again carefully checked in these laboratories against the ice point and the hydrated sodium sulfate transition temperature. The values reported are believed to be accurate to less than ±0.005°. Resistances were measured by means of a Leeds and Northrup Mueller bridge.

It was found sufficient to dry the salts in air at 65°. They underwent no further loss in weight *in vacuo* over phosphorus pentoxide, and actually increased in weight by about 0.01% when subjected to the heated desiccator treatment found necessary by Wright, Abbott, Sivertz and Tartar[3] with the *n*-alkanesulfonates. This marked difference in hygroscopicity is noteworthy.

In determining the conductances of the octylbenzenesulfonate solutions, the usual techniques[3] were used. Owing to the limited supply of material, duplicate determinations were not made, except in doubtful cases. Adsorption effects were found to be insignificant, except at very low concentrations.

The modified Shedlovsky cell was used with the dodecylbenzenesulfonate at concentrations below about 0.0017 *M*. The technique was very similar to that described by Sivertz, Reitmeier and Tartar,[14] except that it was found desirable to dry the cell without the use of organic solvents. The water used had its conductance reduced to about 1 × 10^{-6} ohm^{-1} at 60° before use by washing with tank nitrogen. Water was weighed into the dry cell, and solutions were made up by successive additions of stock solution from a weight buret. Purified nitrogen was used for stirring and for operation of the cell. Considerable difficulty was introduced by the necessity of working at 60°. The Shedlovsky cell was designed to operate near room temperature, and had a number of exposed parts which caused condensation. Heated wrappings only partially alleviated the difficulty. Also, due to the limited solubility of the salt, the stock solution had to be heated to near 60° before each addition, with consequent possibilities for error. Between 0.0001 and 0.0015 *N* the error averages at about 0.3%; at higher concentrations, it is smaller.

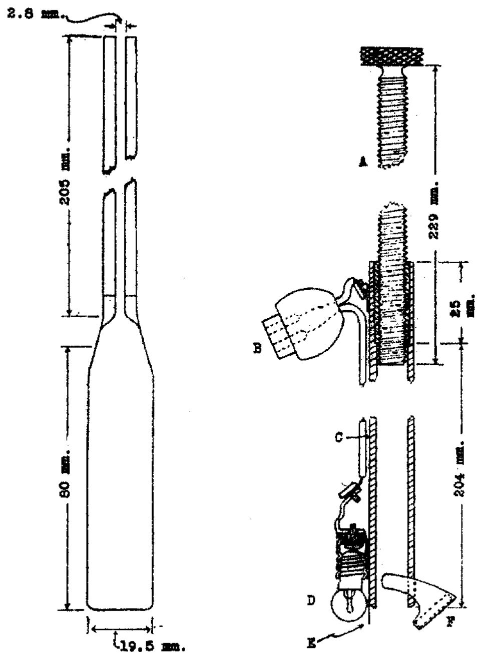

Fig. 1.—Pycnometer and cathetometer: A, $^{5}/_{16}''$ S. A. E. thread; B, connection plug; C, 0.25″ brass pipe; D, flashlight bulb; E, diffusing screen; F, mirror with 45° angle.

The estimated error in the conductances of the octylbenzenesulfonate is about 0.1% at concentrations above 0.01 *M*, and it increases to several tenths of one per cent. at the lowest concentration.

Densities.—An attempt was made to increase the accuracy of the density measurements necessary for converting from weight to volume units of concentration to the point where the data could serve as independent criteria of micelle formation.[15] The measurements were made by means of a dilatometer type of pycnometer requiring only one weighing for measurements at a series of temperatures (Fig. 1). The pycnometers were constructed of Pyrex glass with volumes of about 23 cc. The capillaries were calibrated throughout their lengths by the addition of small weighed quantities of mercury, followed by measurement with a cathetometer.

The pycnometers were filled and emptied by means of small capillaries. They were treated with cleaning solution, rinsed thoroughly with conductivity water and dried at about 60° by evacuation. Oil was removed from the exteriors with absorbent paper followed by washing with strong soap solution, rinsing with hot water and drying with a clean cloth. The weighings were made to 0.1 mg. with the usual precautions, including the use of a similar counterpoise; vacuum corrections were applied.

The bulbs were calibrated with conductivity water. Noticeable distillation of water into the stems occurred at the higher temperatures, especially 60°, but errors were reduced by careful standardization of conditions. The formation of air bubbles was obviated by heating the solutions, before filling the pycnometers, to near 100° for about ten minutes.

The pycnometers were immersed in the oil thermostats, the construction of which prevented the use of an ordinary cathetometer. A special cathetometer was therefore designed to measure the height of liquid in the capillary, see Fig. 1. In operation, the instrument is lowered over the capillary tube of the pycnometer and the screw is adjusted until observation from above by means of the mirror shows that the meniscus is in the plane of the lower end of the tube. Measurements could be made within 2 cm. of the bath level, thus eliminating errors due to cooling of the

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(14) Sivertz, Reitmeier and Tartar, This Journal, **62**, 1379 (1940).

(15) See, *e. g.*, Wright and Tartar, *ibid.*, **61**, 544 (1939).

TABLE I

CONDUCTANCES AND DENSITIES OF SODIUM ALKYLBENZENE SULFONATE SOLUTIONS

Weight normality	Temp., 40°		Temp., 60°		Wt. normality $\times 10^4$	Temp., 60°	
	Density, g./cc.	Equivalent cond., ohm^{-1}	Density, g./cc.	Equivalent cond., ohm^{-1}		Density, g./cc.	Equivalent cond., ohm^{-1}
	Sodium Ethylbenzene-*p*-sulfonate				Sodium *n*-Dodecylbenzene-*p*-sulfonate		
0.0007362	....	104.6	....	145.5	2.346	(0.9833)[a]	129.5
.0010000	0.9923	103.7	0.9834	143.8	3.9831	(.9833)	129.0
.002032	....	104.0	....	144.5	6.6972	(.9833)	128.1
.003000	.9923	102.7	.9833	142.4	10.056	(.9834)	126.5
.003626	....	103.0	....	142.8	0.9430	(.9832)	132.8
.005000	.9925	101.3	.9833	140.5	1.858	(.9832)	136.4
.008000	.9924	100.8	.9834	139.3	11.037	(.9834)	126.6
.010000	.9929	99.8	.9839	138.3	14.066	(.9834)	121.6
.020000	.9937	96.6	.9845	133.8	17.508	(.9834)	111.5
.030000	.9943	94.8	.9853	131.2	1.125	(.9832)	130.4
.050000	.9957	91.6	.9866	126.8	3.308	(.9833)	128.5
.081218	.9979	88.2	.9887	122.1	6.707	(.9833)	127.3
.081402	....	88.2	....	122.0	9.458	(.9834)	126.6
.090000	.9985	87.3	.9893	120.8	16.808	(.9834)	113.4
.10022	.9991	86.5	.9899	119.7	1.373	(.9832)	130.0
.12212	1.0007	85.0	.9915	117.6	2.163	(.9833)	128.9
.15000	1.0026	83.2	.9932	115.2	5.280	(.9833)	128.5
.30000	1.0126	76.3	1.0029	105.8	8.021	(.9834)	128.4
					0.5787	(.9832)	132.9
					4.124	(.9833)	129.6
					0.2648	(.9832)	141.7
					9.188	.9834	128.9
					22.07	.9834	102.5
					60.00	.9836	73.6
					100.00	.9837	63.4
					200.00	.9841	54.5

[a] Interpolated.

Weight normality	Temp., 25°		Temp., 40°		Temp., 60°	
	Density, g./cc.	Equivalent cond., ohm^{-1}	Density, g./cc.	Equivalent cond., ohm^{-1}	Density, g./cc.	Equivalent cond., ohm^{-1}
			Sodium *n*-Butylbenzene-*p*-sulfonate			
0.080000	1.0027	62.5	0.9976	84.8	0.9884	117.8
.10000	1.0038	61.3	.9986	83.3	.9892	115.7
.15000	1.0073	58.7	1.0020	79.9	.9925	110.8
.30000	1.0168	52.8	1.0111	72.5	1.0012	101.7
.50000	1.0282	48.2	1.0221	66.3	1.0119	93.1
			Sodium *n*-Octylbenzene-*p*-sulfonate			
0.0010000	0.9971	71.0	0.9923	96.5	0.9833	134.2
.0020000	.9972	70.5	.9924	95.8	.9834	133.6
.005000	.9974	68.7	.9925	93.3	.9835	129.9
.010000	.9977	67.2	.9928	91.3	.9837	127.1
.012500	.9979	65.2	.9930	89.7	.9839	125.6
.015000	.9980	60.7	.9931	85.5	.9840	124.9
.017000	.9982	56.8	.9933	80.5	.9842	121.3
.020000	.9984	52.6	.9934	74.9	.9843	114.4
.030000	.9989	44.5	.9939	63.5	.9848	97.0
.050000	(1.0000)[a]	38.9	(.9950)[a]	55.5	(.9858)[a]	83.5
.10000	1.0026	34.9	.9975	49.7	.9882	73.5
			Mixed Sodium *n*-Octylbenzenesulfonates			
0.0006526	(0.9971)[a]	73.1	(0.9923)	99.2	(0.9833)	138.3
.001386	.9971	72.4	.9923	98.4	.9833	137.1
.005474	.9974	70.2	.9926	95.3	.9835	132.8
.010000	(.9977)[a]	68.8	(.9928)	93.5	(.9838)	130.3
.020000	.9983	53.7	.9934	76.3	.9843	116.0
.040000	.9994	42.4	.9945	60.3	.9853	90.9

[a] Interpolated.

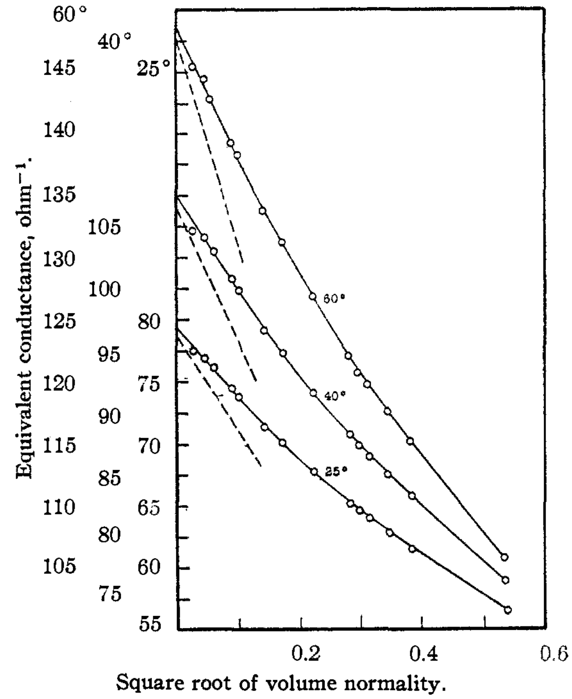

Fig. 2.—Equivalent conductance of sodium ethylbenzene-*p*-sulfonate solutions.

capillaries. The distance from the end of the tube to the screw was measured by means of a narrow steel depth gage (Lufkin gage head No. 511, scale No. 2311), graduated in hundredths of an inch and read by means of a low-power microscope. There was little difficulty in reproducing measurements within less than ±0.001 in., which corresponds to 6×10^{-6} density units. This accuracy is much greater than could be obtained with a graduated capillary, and perhaps somewhat greater than what would have been obtained with the average cathetometer, had the use of the latter been possible. The simple and inexpensive construction and the convenience and accuracy of this instrument suggest its use for other similar measurements upon straight tubes.

The accuracy of the density measurements was limited mainly by the errors due to bubble formation, which were not at first completely eliminated, and by gradual change in the volume of the bulbs. They were calibrated several times during about a year of use. In one the change during this time amounted to only 0.0004 cc., but in another the change was 0.0027 cc. The average error of the density measurements is about ±0.00003 density units. There is reason to believe that with elimination of the errors mentioned considerably greater accuracy could be expected. The data were, however, more accurate than necessary for converting from weight to volume units of concentration, but they were not sufficiently accurate to serve as well as conductances for the indication of colloidal properties.

Results

The conductances and densities are presented in Table I, and the conductances are shown graphically in Figs. 2–5. To conserve space, only the plots of equivalent conductance against the square root of the concentration are presented. The data on the conductance of sodium ethylbenzenesulfonate at 25° are presented only in graphical form; more comprehensive data, especially for dilute solutions, are given in the paper which immediately follows. Plots of specific conductance against concentration for the octyl and dodecyl compounds are very similar to those of Wright, Abbott, Sivertz and Tartar.[3] The dotted lines show the Onsager slopes.

The concentrations at the downward breaks in the equivalent conductance curves (critical concentration for micelles) are for the *n*-octylbenzene-*p*-sulfonate 0.011, 0.012, and 0.015 N_v at 25, 40 and 60°, respectively; for the *n*-dodecylbenzene-*p*-sulfonate, 0.0012 N_v at 60°.

TABLE II

EQUIVALENT CONDUCTANCE OF IONS

Ion	Limiting equivalent cond., ohm⁻¹ 25°	40°	60°
Ethylbenzene-*p*-sulfonate	29.3	38.5	53.3
n-Butylbenzene-*p*-sulfonate	25.6	34.3	48.0
n-Octylbenzene-*p*-sulfonate	23.1	29.9	41.9
n-Octylbenzene-*o*+*p*-sulfonate	24.4	31.9	45.8
n-Dodecylbenzene-*p*-sulfonate	....	....	36.5

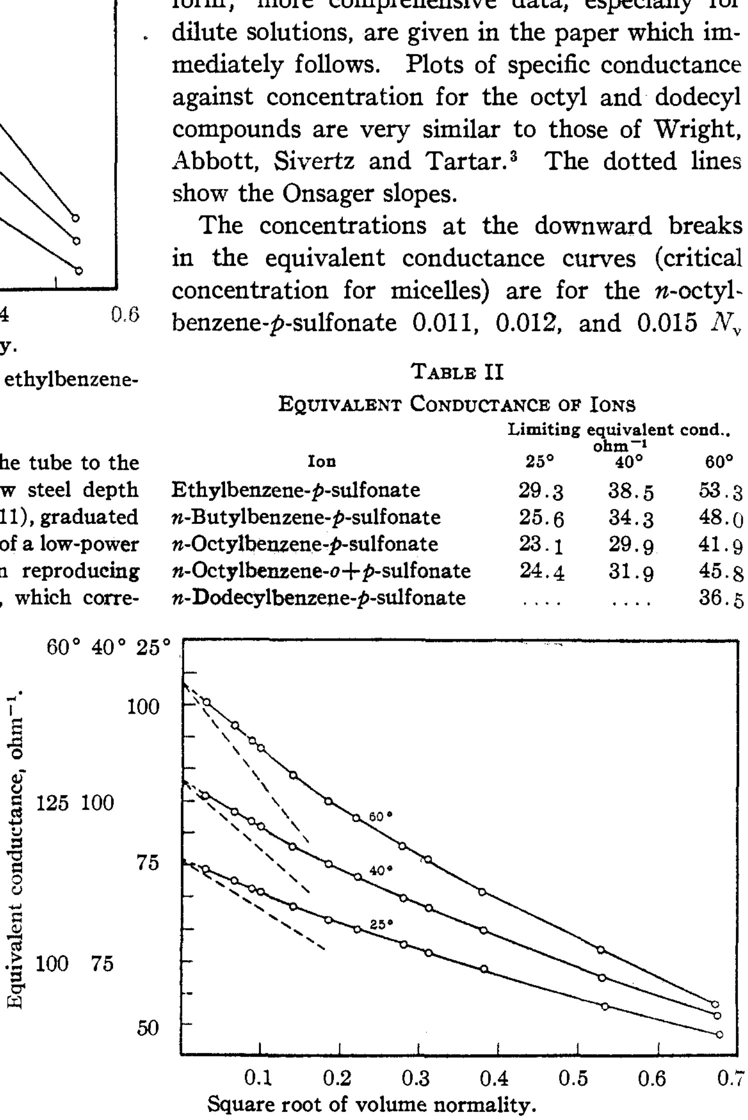

Fig. 3.—Equivalent conductance of sodium *n*-butylbenzene-*p*-sulfonate solutions.

The limiting conductances of the anions are listed in Table II. The ionic conductances of sodium ion were taken to be 50.1,[16] 69.0,[17] and 95.5 ohm^{-1} [17] at 25, 40 and 60°, respectively.

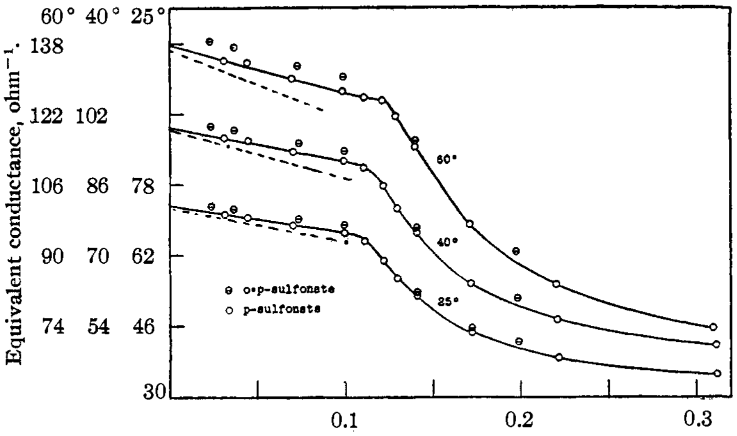

Fig. 4.—Equivalent conductance of sodium *n*-octylbenzene-*p*-sulfonate solutions.

Discussion

From Hartley's point of view,[18] the formation of micelles is determined by the water–hydrocarbon interfacial energy, the destruction of most of this interface in the formation of micelles from ions supplying the energy necessary to remove the ions from the unaggregated form. Thus, the longer the hydrocarbon chain, the greater the energy available, and the lower the critical concentration. But whether the length of the chain or the number of carbon atoms controls in micelle formation is not clear.

The critical concentrations observed with the octyl- and dodecyl-benzenesulfonates when compared with those for the *n*-alkanesulfonates found by Wright, Abbott, Sivertz and Tartar,[3] show that the benzene ring is equivalent to about three and one-half straight-chain carbon atoms in its effect. The actual length of the benzene ring is very nearly the same as that of three and one-half carbon atoms in a normal paraffin chain, if one takes into account the zigzag nature of the latter. This fact suggests strongly that the length of the hydrocarbon chain controls micelle formation.

The water–hydrocarbon interfacial tensions in the bulk for *n*-hexane and benzene are, respectively, 51.1 and 33.6.[19] Unless the length of the molecule determines the interfacial tension, it would seem that specific factors in the structure of the benzene nucleus cause the reduced surface tension, and hence the lowered straight-chain equivalent.

Bolam and Hope[20] have investigated several phenanthrenesulfonic acids, which show colloidal electrolyte behavior. The critical concentrations are somewhat more indefinite than those of the compounds reported in this paper or those of paraffin-chain compounds in general. The values obtained lie in the range corresponding to normal paraffin chains of about 11–13 carbon atoms. The length of the molecules is equivalent to that of a seven-carbon straight chain. From this it is apparent that, in the case of aromatic compounds, neither length nor number of carbon atoms can be said to control. Rather, the aromatic nucleus must be considered as a separate unit having a specific effect.

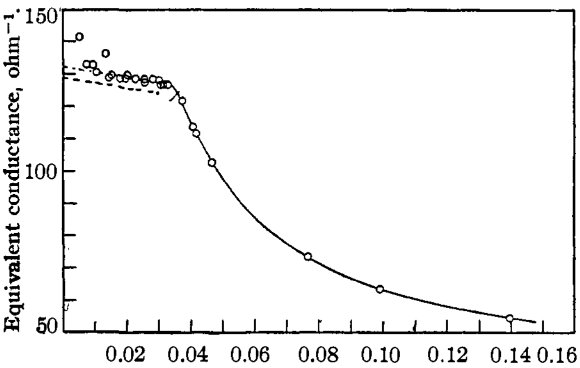

Fig. 5.—Equivalent conductance of sodium *n*-dodecylbenzene-*p*-sulfonate solutions.

The mixture of *n*-octylbenzenesulfonates was used to obtain a few points in Fig. 4. The points form a curve nearly parallel to that of the *p*-sulfonate, and the break would be at about the same concentration. The densities are the same, within experimental error. Thus it would seem that the position of the sulfonate group has little or no effect on the critical concentration. This would lead to the same conclusion as in the preceding paragraph.

The initial slope of the conductance curve for the dodecylbenzenesulfonate is quite close to the theoretical Onsager slope. This is not true in the case of the octylbenzenesulfonates, where the

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[16] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, 54, 2762 (1932).

[17] By graphical interpolation from Smithsonian Physical Tables.

[18] For a summary of Hartley's theory in its latest form see: Hartley, *Kolloid Z.*, 88, 22 (1939).

[19] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Erg. IIIa, p. 223.

[20] Bolam and Hope, *J. Chem. Soc.*, 843 (1941).

initial slope is about 40% less than the Onsager slope. The same phenomenon was observed by Wright, Abbott, Sivertz and Tartar,[3] 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.

SEATTLE, WASHINGTON RECEIVED SEPTEMBER 8, 1942

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

Electrolytic Properties of Solutions of Paraffin-chain Quaternary Ammonium Salts

BY ALLEN B. SCOTT AND H. V. TARTAR

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[1] 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 gegenions, or of Debye–Hückel–Onsager effects upon the mobility of the free gegenions.

On the other hand, J. W. McBain[2] 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[3] 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.

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

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

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