[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Studies of Sulfonates. X.[1] Sodium Triisopropylbenzenesulfonate as a Colloidal Electrolyte[2,3]

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The colloidal electrolyte behavior of several sodium *n*-alkylbenzene-*p*-sulfonates has been previously reported.[6] It seemed of interest to compare the behavior of a polyalkylbenzene sulfonate, since the effective length of the molecule could be considerably decreased while maintaining a hydrocarbon residue of considerable molecular weight. The compounds which we have prepared and studied are triisopropylbenzenesulfonic acid and its sodium salt. These may be compared with the sodium *n*-octylbenzene-*p*-sulfonate,[6] which differs in molecular weight by that of one methylene group only.

The critical concentration for micelle formation has been determined from solubility and electrical conductance measurements and by the use of the dye, pinacyanol chloride.[7]

Experimental

Preparation of Compounds.—Triisopropylbenzene and tetraisopropylbenzene were prepared by the repeated alkylation of cumene (Eastman Kodak Co. white label) with isopropyl alcohol and sulfuric acid under reflux conditions. The alkylation procedure consisted of the slow addition of the sulfuric acid to a boiling solution of hydrocarbon and isopropyl alcohol. Using this method, the mole ratio and acid concentration found to give the greatest yield of alkylated product with minimum loss due to sulfonation was 1 mole hydrocarbon:1 mole isopropyl alcohol:1.2 moles 98% sulfuric acid. After each alkylation, the hydrocarbons were separated from the acid in a separatory funnel, washed with water and finally with 10% aqueous sodium hydroxide to remove sulfonic acids, and dried with calcium chloride. The final alkylated product was fractionated in an 18-inch helices-packed column at about 15 mm. pressure to separate the mono-, di- and triisopropylbenzenes, and the tetraisopropylbenzene was distilled from the residue in a special distillation apparatus. The tetraisopropylbenzene was further purified by three recrystallizations from isopropyl alcohol. From 1 liter of cumene there was obtained 650 ml. of triisopropylbenzene (boiling range 230–240° at 760 mm.) and 260 g. of tetraisopropylbenzene (m. p. 117.5°). Francis[8] gives the following data: 1,2,4-triisopropylbenzene, b. p. 244°; 1,3,5-triisopropylbenzene, b. p. 238°; 1,2,4,5-tetraisopropylbenzene, m. p. 118.4° Newton[9] reports that the triisopropylbenzene prepared by sulfuric acid alkylation consists of 84% 1,2,4-triisopropylbenzene and 16% 1,3,5-triisopropylbenzene. No serious attempt was made to separate these isomers, although our triisopropylbenzene fraction was fractionated at a slow rate several times, the first portion being discarded each time. Therefore our final product was probably quite largely 1,2,4-triisopropylbenzene, but almost certainly contained some 1,3,5-triisopropylbenzene.

100 ml. of triisopropylbenzene was dissolved in 300 ml. of carbon tetrachloride and agitated with 100 ml. of fuming sulfuric acid (15% free SO_3) for fifteen minutes. The layers were then separated, the carbon tetrachloride was evaporated off and the residue taken up in water. The aqueous solution was neutralized with sodium hydroxide and upon cooling yielded crystals of sodium triisopropylbenzenesulfonate.

Tetraisopropylbenzene was also sulfonated by the same method, yielding a product identical with that obtained from the triisopropylbenzene. The identity of the two substances is shown by a comparison of powder patterns of the sodium salts (see Table I). The product of the sulfonation of tetraisopropylbenzene was further shown to be triisopropylbenzenesulfonic acid by three additional experiments: (1) hydrolysis of the compound in boiling dilute sulfuric acid yielded a hydrocarbon boiling at 235–240°; (2) the equivalent weight of the solid hydrate, determined by titration with 0.1 *N* NaOH, was found to be 299.5 (calculated for triisopropylbenzenesulfonic acid monohydrate, 302.5); (3) the barium salt was prepared and analyzed for barium by precipitation of barium sulfate (found 19.50% Ba, calculated for barium triisopropylbenzenesulfonate 19.51% Ba). Newton[10] also found that the sulfonic acids formed from 1,2,4-triisopropylbenzene and 1,2,4,5-tetraisopropylbenzene by the action of chlorosulfonic acid were identical. Thus our product consists of a mixture of the isomeric triisopropylbenzenesulfonic acids.

TABLE I

POWDER PATTERN DATA FOR SODIUM TRIISOPROPYLBENZENESULFONATE

Compound prepared from triisopropylbenzene		Compound prepared from tetraisopropylbenzene	
Intensity[b]	Ring diameter, mm.[a]	Intensity[b]	Ring diameter, mm.[a]
w	6.5	w	6.7
m	8.0	m	8.1
s	8.9	s	9.0
m	12.2	m	12.1
w	13.5	w	13.6
w	15.8	w	16.0
m	17.9	m	17.9
w(b)	20.0	w(b)	20.0
w	24.1	w	24.2
w+	26.9	m−	27.0
		w−	28.5
w	29.7	w	29.8
m	32.2	m	32.3
m−	34.3	m−	34.4
w+	35.6	mw	35.6
about 5 weak unmeasurable rings		about 5 weak unmeasurable rings	
m	47.7	m	47.6

[a] Diffraction patterns taken with unfiltered CuKα radiation in a cylindrical camera with radius = 5.00 cm. [b] S = strong, m = medium, w = weak, (b) = broad.

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[1] Paper IX of this series, Neff, Wheeler, Tartar and Lingafelter, THIS JOURNAL, **70**, 1989 (1948).

[2] Taken from a thesis submitted by Gordon R. Shuck in partial fulfillment of the requirements for the Ph.D. degree at the University of Washington.

[3] Presented at the Research Conference of the Puget Sound Section of the American Chemical Society, November, 1947.

[4] Standard Oil Company Research Fellow, 1946–1947.

[5] Present address: Procter and Gamble Co., Ivorydale, Ohio.

[6] Paquette, Lingafelter and Tartar, THIS JOURNAL, **65**, 686 (1943).

[7] Corrin, Klevens and Harkins, *J. Chem. Phys.*, **14**, 480 (1946).

[8] Francis, *Chem. Rev.*, **42**, 144 (1948).

[9] Newton, THIS JOURNAL, **65**, 320 (1943).

[10] Newton, THIS JOURNAL, **65**, 2439 (1943).

The solubility of sodium triisopropylbenzenesulfonate in water was determined at intervals over the range 10 to 49°. Two large test-tubes, each containing 30 ml. of water and excess solid were placed in a water thermostat regulated to ±0.05° and stirred mechanically for two hours. One of the solutions had been heated above the bath temperature to obtain complete solution, while the other had been made up below the bath temperature. Thus, agreement between the results from the two solutions indicated that equilibrium had been established. After the excess solid had settled, samples were pipetted from the solutions by means of a pipet whose tip was covered with filter paper. The samples were discharged into weighing bottles, evaporated to dryness, and weighed again. The results of the solubility determination are given in Fig. 1.

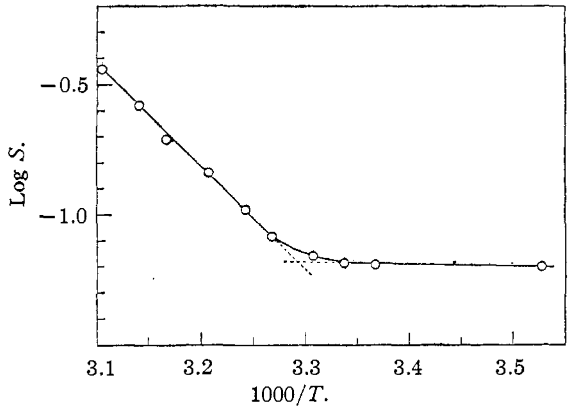

Fig. 1.—Solubility of sodium triisopropylbenzene-sulfonate in water (moles per 1000 g. of water).

The electrolytic conductance of aqueous solutions of sodium triisopropylbenzenesulfonate and of triisopropylbenzenesulfonic acid were measured using the bridge and cells previously described.[11] The cells were replatinized and their constants redetermined before use. The results are given in Figs. 2 and 3.

The critical concentration of the sodium salt was determined to be 0.061 M at 50° by the use of the dye pinacyanol chloride.[7]

Discussion of Results

The solubility and pinacyanol chloride results with sodium triisopropylbenzenesulfonate and the conductance of the acid clearly indicate that these substances behave as colloidal electrolytes. The absence of any marked discontinuity in the conductance curve of the sodium salt illustrates the danger of basing conclusions on one property alone.

The values obtained for the critical concentration from the several properties seem to agree as well as corresponding results for other colloidal electrolytes. The values for the sodium salt are 0.065 M (from solubility) and 0.061 M (from the pinacyanol chloride method), while the value for the acid is 0.055 M (from the equivalent conductance). In particular, it may be pointed out that a comparison of the data of Wright, Abbott, Sivertz and Tartar[11] with those of McBain, Dye and Johnston[12] show the critical concentrations of the alkane-sulfonic acids to be slightly less than those of the sodium alkane-sulfonates.

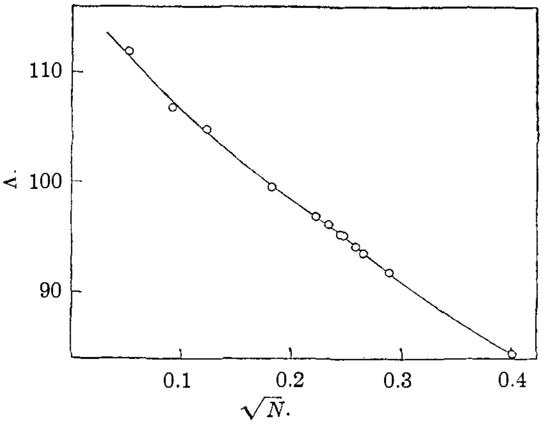

Fig. 2.—Equivalent conductance of aqueous solutions of sodium triisopropylbenzenesulfonate at 50°.

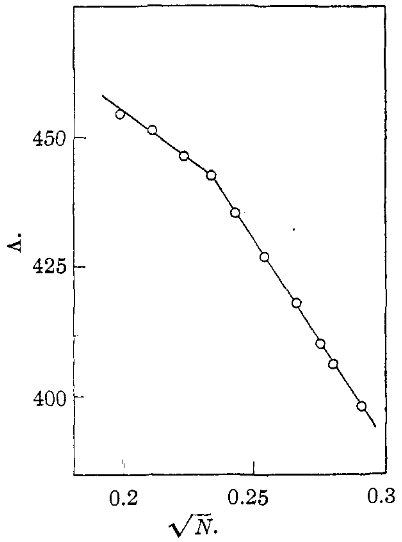

Fig. 3.—Equivalent conductance of aqueous solutions of triisopropylbenzenesulfonic acid at 50°.

The average value for the sodium salt, 0.063 M, may be compared with the value for sodium n-octylbenzene-p-sulfonate, 0.013 M.[6] Thus, although the triisopropylbenzenesulfonate ion contains one more carbon atom, it does not aggregate until a higher concentration is reached. This indicates the importance of the shape of the molecule in determining the tendency toward micelle formation, agreeing with the observation of Hartley[13] that branching of the hydrocarbon portion increases the critical concentration. It does not seem possible at present to decide whether this effect is a consequence of the efficiency of packing in the micelle, the size of the micelle, or the interfacial free energy of the unassociated ion.

Furthermore, the observation that the conductance of the sodium salt does not decrease at the critical concentration indicates that the fraction of gegenions attached to the micelles is smaller

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

[12] McBain, Dye and Johnston, *ibid.*, **61**, 3210 (1939).

[13] Hartley, *Trans. Far. Soc.*, **37**, 130 (1941).

than is the case for the long-chain compounds. This may be due to the greater distance between charges on the surface of the micelle, or to a smaller aggregation number.

Summary

1. Triisopropylbenzenesulfonic acid has been prepared by the sulfonation of triisopropylbenzene and of tetraisopropylbenzene.

2. Triisopropylbenzenesulfonic acid and its sodium salt have been shown to be colloidal electrolytes, with critical concentrations of 0.055 and 0.063 *M*, respectively.

3. The comparison of these compounds with sodium *n*-octylbenzene-*p*-sulfonate illustrates the importance of molecular shape as well as size in determining the tendency toward aggregation.

4. The conductance of the sodium salt shows no discontinuity at the critical concentration, indicating a relatively small fraction of attached gegenions.

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Transference Numbers of Dodecylammonium Chloride in Water–Organic Solvent Systems

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Dodecylammonium chloride is a typical cationic colloidal electrolyte and the equivalent conductivity of its aqueous solutions shows an abrupt drop at 1.44×10^{-2} molar[1] at which concentration it undergoes a transition from an ordinary to a colloidal electrolyte. It has been shown recently[2] that the addition of organic solvents such as acetone, methyl or ethyl alcohol or acetonitrile to aqueous solutions of dodecylammonium chloride increases the concentration of colloidal electrolyte at the critical point. As the concentration of organic addend is increased the conductivity curves of dodecylammonium chloride are no longer characteristic of those of a colloidal electrolyte and resemble those of an ordinary electrolyte. This decreased tendency toward association has been attributed to the decreased ionizing powers and dielectric properties of the mixed solvent, the latter factor increasing the effectiveness of the repulsion of similarly charged ions. When the equivalent conductivities of various concentrations of dodecylammonium chloride are plotted against the mole per cent. of organic addend the effect of the organic addend is seen to vary greatly depending upon whether the concentration of colloidal electrolyte is more or less than the critical concentration. At concentrations lower than critical the conductivity falls to a minimum and then rises smoothly as the composition of the solvent approaches that of the pure organic addend. On the other hand, the conductivity curves for concentrations higher than the critical concentration rise quite sharply to a maximum and then gradually decrease as the mole percentage of organic addend is increased. It has been postulated that these maxima occur at those points which represent a transition of the dodecylammonium chloride from a colloidal to an ordinary electrolyte. Since it is well established that at concentrations beyond the critical point the transference number of the associated ion exhibits a characteristic, sharp rise, it is apparent that transference data would be of great assistance in the interpretation of the effect of organic addends upon the colloidal behavior of dodecylammonium chloride. This present paper presents transference data upon dodecylammonium chloride in two of the water–organic solvent systems studied; namely, water–methanol and water–acetonitrile, and correlates these data with the conductometric behavior of these systems.

Experimental

Apparatus.—The Washburn cell[3] employed in earlier transference experiments in these laboratories[4] was again employed for a portion of the work herein reported.

Comparable results were obtained in a smaller apparatus designed to economize amine salt and to avoid complications of changing solution density. This cell consisted of three U-tubes sealed together, having a uniform internal diameter of 15 mm. and a mean total length of 80 cm., and required only 150 ml. of solution. The cell was provided with glass stopcocks at the bottom of each U-tube and with vent tubes at the top. The electrodes were helices of 18 gage, pure silver wire (15 turns of 1 cm. diameter). A silver surface for the anode and a silver chloride surface for the cathode were produced electrolytically. Two silver coulometers of the Kohlrausch type were employed. Observations and initial adjustment of current were made with the usual resistances and meters. Constant temperature of 30° was obtained by the use of a large air bath having temperature control to ±0.05°.

Materials.—The dodecylammonium chloride employed in these studies has been previously described.[1] The solutions were made with freshly prepared conductivity water, dried and redistilled acetonitrile and C. P. absolute methanol.

Procedure.—Experiments in the Washburn cell were conducted in the manner previously described.[4]

In the smaller cell the silver anode was washed repeatedly in distilled water and dried by burning off methanol before use. The silver-chloride cathode, also washed, was suspended in the solution to be electrolyzed with occasional stirring for a day prior to its use. This permitted the establishment of the initial concentration of dodecylammonium chloride in the pores of the cathode surface.

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[1] Ralston and Eggenberger, THIS JOURNAL, **70**, 436 (1948).

[2] Ralston and Eggenberger, *J. Phys. and Colloid Chem.*, **52**, 1494 (1948).

[3] Washburn, THIS JOURNAL, **31**, 322 (1909).

[4] Hoerr and Ralston, *ibid.*, **65**, 976 (1943).