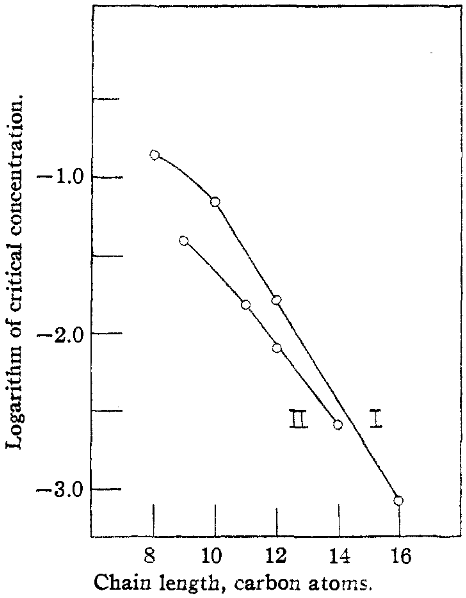

Fig. 6.—Critical concentration as a function of chain length: I, alkyl trimethylammonium bromides; II, sulfonic acids.

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[20] 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).

SEATTLE, WASHINGTON RECEIVED SEPTEMBER 8, 1942

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

Electrolytic Properties of Aqueous Solutions of Octyltrimethylammonium Octanesulfonate and Decyltrimethylammonium Decanesulfonate

BY ALLEN B. SCOTT, H. V. TARTAR AND E. C. LINGAFELTER

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 previous 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 first time, and the conductances of their aqueous solutions, at 25 and 40°, respectively, were determined.

Experimental Part

Preparation of Materials.—These salts were prepared from the corresponding alkyltrimethylammonium bromides and the sodium sulfonates, of the same lot and purity as that used by Wright, Abbott, Sivertz and Tartar[1] and by Cadle.[2] Silver decanesulfonate was precipitated from an aqueous solution of the sodium salt, washed repeatedly with water at 0°, and dissolved in hot alcohol. This solution was titrated with an alcoholic solution of decyltrimethylammonium bromide, with the dichromate ion as the external indicator. The precipitate of silver bromide was removed and the decyltrimethylammonium decanesulfonate was obtained by evaporation of the alcohol and purified by two recrystallizations from water. The yield of purified salt was 90%.

Octyltrimethylammonium octanesulfonate was prepared in the same manner except that the recrystallization was from acetone. Silver octanesulfonate has a considerable solubility in water even at 0° and consequently with this precipitation, the final yield of purified salt was only 31%.

Both double long-chain salts are white, crystalline solids. The octyl-octane salt is very soluble in water at room temperature; the decyl-decane salt is practically insoluble below 35° (the Krafft point), but above was very soluble, yielding opalescent solutions.

Apparatus and Procedure.—The conductance apparatus and thermostats have been described previously.[3] The cell designed for low concentrations was used with octyltrimethylammonium octanesulfonate solutions below 0.015 *N*. It was not suitable for use with the decyltrimethylammonium decanesulfonate solutions because of excessive foaming upon the passage of the nitrogen; this use of separate cells and solutions decreased the accuracy in dilute solutions.

By means of a modified Sprengel pycnometer the densities were determined at one of the higher concentrations for each salt, and at other concentrations were calculated by assuming a linear relation between density and concentration, as the rate of change was very small. These values were used to convert weight to volume normalities.

Discussion

The conductance data are given in Table I and presented graphically in Figs. 1 and 2. The breaks in both specific and equivalent conductance curves are very sharp. The Onsager slope is followed exactly at low concentrations by octyltrimethylammonium octanesulfonate; below the critical concentration it behaves in all respects as an ordinary strong electrolyte. These results do not indicate any gradual change from ionic to micellar species. The data for the decyl–decane salt below the critical concentration are insufficient to allow any conclusions to be drawn.

TABLE I

CONDUCTANCE OF SOLUTIONS OF OCTYLTRIMETHYLAMMONIUM OCTANESULFONATE AND DECYLTRIMETHYLAMMONIUM DECANESULFONATE

Normality	Equivalent conductance, mho	Normality	Equivalent conductance, mho
C_8-C_8 salt at 25°		C_{10}-C_{10} salt at 40°	
0.00002263	51.08	0.00032528	65.5
.00010005	50.88	.00057060	65.5
.00020623	50.60	.0011745	64.8
.00038061	50.21	.0015672	58.5
.00075220	49.64	.0025142	37.14
.0014138	48.94	.0053627	18.40
.0021019	48.28	.0097615	10.94
.0029091	47.75	.022394	5.87
.0036988	47.30	.040003	4.085
.0053777	46.50	.063860	3.194
.0097442	44.90	.088103	2.780
.012651	44.09		
.015618	43.35		
.025527	35.25		
.039874	23.95		
.067642	15.47		
.12511	9.83		

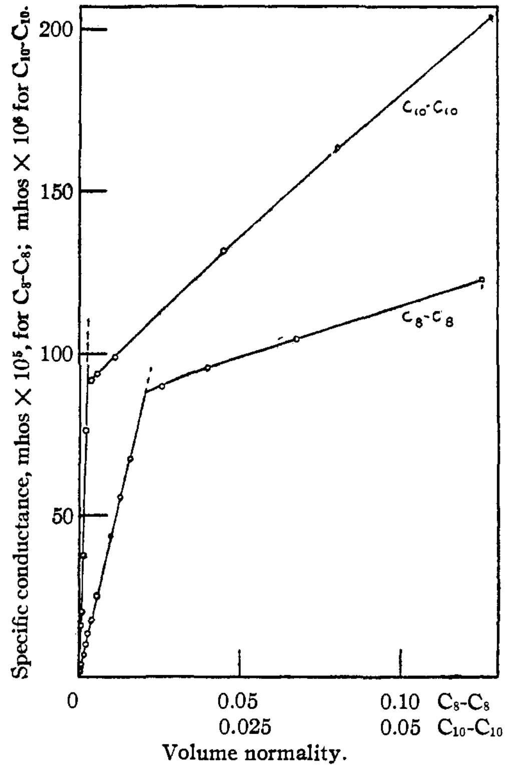

Fig. 1.—Specific conductance of solutions of octyltrimethylammonium octanesulfonate at 25° and of decyltrimethylammonium decanesulfonate at 40°.

Sodium octanesulfonate and octyltrimethylammonium bromide are transition compounds

---

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

[2] Cadle, doctorate thesis, University of Washington, 1941.

[3] See paper, by Scott and Tartar, THIS JOURNAL, **65**, 692 (1943).

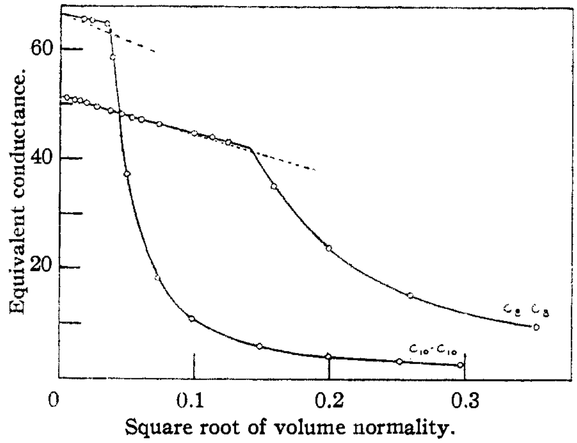

Fig. 2.—Equivalent conductance of solutions of octyltrimethylammonium octanesulfonate at 25° and of decyltrimethylammonium decanesulfonate at 40°.

from colloidal to non-colloidal electrolytes, *i. e.*, they show a slight evidence of micelle formation at high concentrations. However, the salt containing the octyltrimethylammonium cation and the octanesulfonate anion displays remarkable colloidal electrolytic properties. Similarly, decyl trimethylammonium decanesulfonate forms micelles at a much lower concentration than either of the corresponding single long-chain salts and the changes in specific conductance at the critical concentration are both marked and abrupt.

This is to be expected from a consideration of the forces involved in the formation of micelles. In the case of single long-chain salts, the forces tending to cause micelle formation, thus reducing the area of the water–hydrocarbon interface, are opposed by the coulombic forces between the ions. In the case of double long-chain salts, both cations and anions are present in the micelle, and the coulombic repulsions are thus greatly decreased. This results in a much lower critical concentration accompanied by a radical decrease in equivalent conductance at this point.

The rate of increase of specific conductance above the critical concentration indicates that the micelles cannot be exactly neutral, but must contain a small excess of one ion. Available data[4] indicate that the critical concentrations of the alkyltrimethylammonium salts are slightly higher than the critical concentrations of the corresponding alkane sulfonates. Therefore, the sulfonate ions have a somewhat greater tendency to form micelles than the ammonium ions, and the assumption appears justified that the excess in the micelles is of sulfonate ions. However, since the conductances of the two types of ions do not differ greatly, a calculation of the magnitude of the charge on the micelle is practically independent of this assumption.

We may first show that the micelles cannot be neutral. If the micelles are neutral, the reaction for their formation can be written

$$nA^+ + nS^- = M$$

where n represents the number of ions of each type in a micelle; A^+, the alkyltrimethylammonium ion; S^-, the alkanesulfonate ion; and M, the micelle. Hartley has assumed,[5] for micelles of this type, that the interior is a sphere of essentially "liquid" paraffin, with a radius equal to the length of one of the hydrocarbon chains. Radii of micelles determined from diffusion measurements[6] seem to be in satisfactory agreement with such an assumption. On this basis, the value of n was calculated using an average molar volume of 16.2 cc. per carbon atom plus 16.4 cc. per chain end calculated from density data of Egloff[7] and a chain length of 11.4 Å. for C_8 and 14.0 Å. for C_{10} calculated from the atomic radii given by Pauling.[8] The computation showed $2n$ to be approximately 26 and 39 for the 8-carbon and 10-carbon chains, respectively. Consequently, the formation of micelles from octyltrimethylammonium octanesulfonate may be represented by

$$13A^+ + 13S^- = M$$

and the equilibrium constant is

$$K = \frac{(M)}{(A^+)^{13}(S^-)^{13}}$$

Since the micelles begin to form in appreciable amounts rather suddenly at the critical concentration, 0.02016 M, the value of K may be calculated by assuming that at a stoichiometrical concentration of 0.02026 M the concentration of the ions is 0.02016 M, while the rest of the compound is in micelles. This leads to a value of K of about 1×10^{39}. Using this value for K, at the highest stoichiometrical concentration employed, 0.12511 M, the estimated concentrations of the

---

(4) See preceding paper by Scott and Tartar to obtain correct reference.

(5) Hartley, "Aqueous Solutions of Paraffin Chain Salts," Hermann et Cie, Paris, 1936.

(6) Hartley and Runnicles, *Proc. Roy. Soc.* (London), **A168**, 420 (1938); A. D. Abbott, doctorate thesis, University of Washington, 1942.

(7) Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Co., New York, N. Y., 1939.

(8) Pauling, "Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, New York, 1940.

components are: $(A^+) = (S^-) = 0.02629\ M$; $(M) = 0.0076015\ M$. If the conductivity of this solution were due entirely to the completely ionized solute the specific conductance, on the basis of data below the critical concentration, should be 1090×10^{-6} mho. But the observed specific conductance is 1229×10^{-6} mho, which shows that the micelles contribute appreciably to the conductivity of the solution.

To obtain an estimate of the charge on the micelle, we may consider the micelle to be formed by the reaction

$$12A^+ + 13S^- = M$$

Calculating as above, we find K to be about 2×10^{37}. Then at a stoichiometrical concentration of $0.12511\ M$, we calculate $(A^+) = 0.03091\ M$, $(S^-) = 0.02306\ M$, $(M) = 0.00785\ M$. Using these data the calculated specific conductance is 1167×10^{-6} mho. The observed value is 1229×10^{-6} mho.

A similar treatment of the equilibrium $12\ A^+ + 14\ S^- = M$ yields a calculated specific conductance of 1320×10^{-6} mho.

Thus it appears that the charge on the micelle is between 1 and 2.

The conductances of the ions used in the calculations were estimated by extrapolating the data obtained below the critical concentration and assuming the transference number to be that at infinite dilution, $t_+ = 0.545$. The conductance of the charged micelle was estimated by the use of Stokes' law, assuming a spherical micelle of 17.5 Å. radius.

Similar considerations on the decyltrimethylammonium decanesulfonate indicate a charge of the same magnitude, although in this case there must be some larger aggregates formed, as evidenced by the opalescence of the solutions.

Using the equilibrium constant computed above for solutions of octyltrimethylammonium octanesulfonate containing singly charged micelles, the concentrations of the ions and of the micelles can be computed for any solution at 25°. Fig. 3 shows these concentrations plotted against the stoichiometrical concentration for a series of solutions. The sharpness of the breaks in the curves is in harmony with the experimental data on specific conductance.

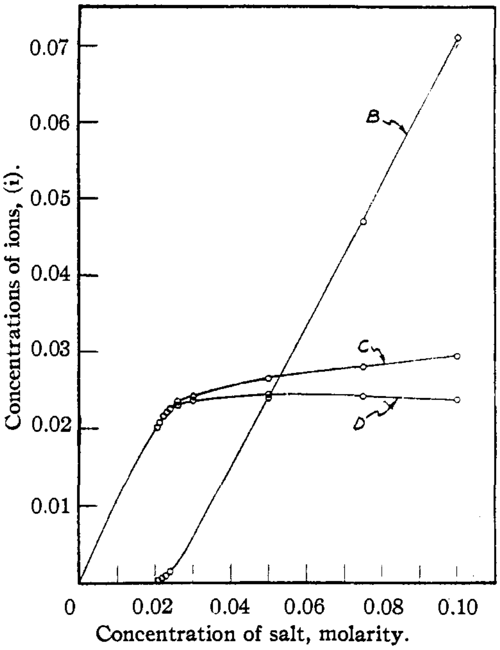

Fig. 3.—Composition of octyltrimethylammonium octanesulfonate solutions (estimated): B, 12 (M); C, (A^+); D, (S^-).

Summary

1. The preparation of octyltrimethylammonium octanesulfonate and decyltrimethylammonium decanesulfonate has been described.

2. Conductance measurements have been made which show that these salts form slightly conducting micelles at concentrations much below that for corresponding single long-chain salts.

3. Evidence has been presented to show that the micelles bear an electric charge of the order of unity.

SEATTLE, WASHINGTON RECEIVED SEPTEMBER 8, 1942