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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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Transference Numbers of Dodecylammonium Chloride in Water–Organic Solvent Systems

BY A. W. RALSTON AND A. E. BRAKE

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).

After the completion of the electrolysis the stopcocks at the bottom of each U-tube were carefully opened, thus dividing the solution into three portions, namely, anode, cathode and middle.

Electrode Reactions.—The usual electrode reactions, the formation of silver chloride at the anode and the reduction of silver chloride to free silver at the cathode were observed.

The formation of a complex salt between silver chloride and dodecylammonium chloride at the anode resulted in a poorly adhering deposit which clouded the solution in this compartment. It is necessary to include the dodecylammonium chloride contained both in the electrode itself and in the detached material in the analytical results in order to obtain check results for the content of amine salt in the anode and cathode compartments. This procedure is much preferable to employing a correction such as that recently discussed by Hale and De Vries.[5] At the cathode the reduction of silver chloride to free silver in the presence of the colloidal electrolyte resulted in the production of a colloidal silver sol as evidenced by the development of a yellow color in these solutions. Both these effects were greatly reduced as the amount of organic solvent increased and they were not observed in those mixtures which were rich in organic solvent.

Analyses.—The concentration of dodecylammonium ion was determined by steam distillation of the amine and its titration with standard acid.[6] As stated previously, it was necessary to decompose the silver chloride–dodecylammonium chloride in order to obtain satisfactory analytical values. The chloride ion was determined gravimetrically as silver chloride after removal of the dodecylammonium ion. In the experiments with acetonitrile it was necessary to remove the acetonitrile by distillation of its azeotrope from the amine salt solution before satisfactory analytical results could be obtained.

Agreement between the analyses of the original solution and the middle portion was better than 1% for all results reported. The transference numbers in aqueous solution were reproducible within ±0.02 unit. In mixtures rich in organic solvent the analyses were in better agreement (±0.2%) and the transference numbers in methanol were reproducible within ±0.003 unit.

Results and Discussion

The cationic transference numbers at 30° of dodecylammonium chloride plotted against the mole percentage of methanol in the solvent are shown in Fig. 1. Two concentrations of dodecylammonium chloride were studied, 0.1 molar which is materially greater than the critical concentration and 0.01 molar which is less. At the concentration greater than the critical concentration increase in the percentage of methanol is attended by a very rapid decrease in T_c, the value reaching a minimum at approximately thirty mole per cent. of methanol and then slowing rising. The conductometric work, to which reference has previously been made,[2] showed that a maximum value in the equivalent conductivity of dodecylammonium chloride in methanol–water mixtures occurs at about thirty mole per cent. methanol. The rapid drop to a minimum in the transference number of the dodecylammonium ion and its subsequent rise presents further evidence of the transition of dodecylammonium chloride from a colloidal to an ordinary electrolyte as the composition of the solvent goes from pure water to pure methanol. This transition is apparently completed in the neighborhood of the minimum in the T_c curve. The rise in the transference numbers after the minimum can be attributed to the reduction in the viscosity of the solvent as its composition approaches pure methanol. Decrease in the viscosity of the solvent should have a greater relative effect upon the large dodecylammonium ion than upon the smaller chloride ion.

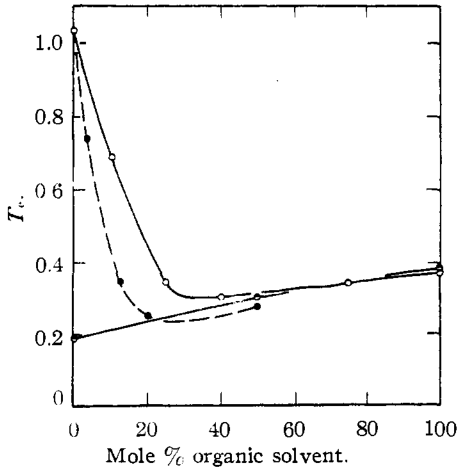

Fig. 1.—Transference numbers of dodecylammonium chloride in methanol–water and acetonitrile–water at 30°: ○, 0.1 M in methanol-water; ●, 0.1 M in acetonitrile-water; ◓, 0.01 M in methanol–water.

The transference numbers for the dodecylammonium ion in 0.01 molar dodecylammonium chloride show a gradual rise as the composition of the solvent goes from pure water to pure methanol. The values in the water-rich mixtures do not exhibit the abnormal behavior shown by the higher concentration of amine salt when the dodecylammonium chloride functions as a colloidal electrolyte. The increase in the value T_c is explainable on the basis of decreased solvation of the dodecylammonium ion coupled with viscosity changes in the solvent. It is of interest to note that in the methanol-rich solvents the values of T_c for 0.1 and 0.01 molar dodecylammonium chloride are similar and are in marked contrast with the rise to abnormally high values obtained in aqueous solutions in this concentration range.

Figure 1 also shows the transference numbers of the dodecylammonium ion in several acetonitrile–water mixtures. The decrease in the values of T_c is somewhat more abrupt than in the methanol–water solvents and the minimum occurs at a lower value of T_c and at a somewhat lower concentration of organic addend. It has been previously observed[2] that the addition of acetonitrile brings about a more rapid transition of this amine salt from a colloidal to an ordinary electrolyte than does the addition of methanol. A maximum in the equivalent conductivity curve was observed in the neighborhood of fifteen per cent. acetonitrile a value in approximate agreement with the minimum in the T_c values.

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[5] Hale and De Vries, This Journal, **70**, 2473 (1948).

[6] Ralston and Hoerr, *Ind. Eng. Chem., Anal. Ed.*, **16**, 459 (1944).

The values of Λ_c plotted against the solvent composition are shown in Fig. 2. It is significant that the values for 0.1 molar dodecylammonium chloride in those solvent compositions in which it functions as a colloidal electrolyte are identical for similar molar concentrations of methanol and acetonitrile. This suggests that the results described in this paper for methanol–water and acetonitrile–water systems may constitute examples of a general effect which may be encountered with other organic solvent–water systems. The values of Λ_c, unlike those of T_c, are of course greater for the lower concentration of amine salt in methanol–water mixtures under those conditions where the amine salt functions as an ordinary electrolyte.

The numerical values of T_c, Λ_c, T_a and Λ_a at 30° are shown in Table I.

TABLE I

Mole % CH₃OH	T_c	Λ_c[a]	T_a	Λ_a[a]
	$C_{12}H_{25}NH_3Cl$, 0.10 *M*			
0	1.033	40.3	−0.027	. .
10.0	0.689	27.6	+0.325	13.0
25.0	.343	15.1	.663	29.2
40.0	.302	13.0	.723	28.9
75.0	.345	15.2	.673	29.6
100.0	.369	18.5	.665	30.9
	$C_{12}H_{25}NH_3Cl$, 0.01 *M*			
0	0.189	19.3	0.814	83.0
.50	.301	15.9	.725	38.4
100	.378	27.6	.658	48.0
	$C_{12}H_{25}NH_3Cl$, 0.10 *M*			
CH_3CN				
3.66	0.738	36.9	0.316	15.8
12.5	.346	25.3	.656	47.8
20.0	.250	17.5	.719	50.3
50.0	.275	15.1	.725	39.8

[a] The ionic conductances were computed from data of reference.[2]

The negative value of T_a for dodecylammonium chloride in pure water is noteworthy. A value of 0.13 for T_a at 30° has previously been reported.[4] The low value is explainable on the basis of solubilization of the undissociated amine salt by the micelles.

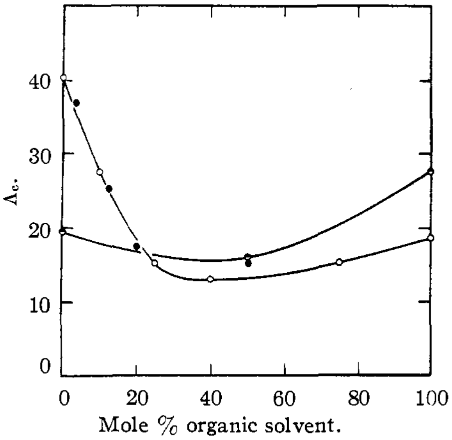

Fig. 2.—Cationic conductances of dodecylammonium chloride in methanol–water and acetonitrile–water at 30°: ○, 0.1 *M* in methanol–water; ●, 0.1 *M* in acetonitrile–water; ◒, 0.01 *M* in methanol–water.

Above forty mole per cent. methanol the values of Λ_a for 0.1 molar dodecylammonium chloride are in close agreement with those of Longsworth and MacInnes[7] for 0.05 molar lithium chloride and sodium chloride in similar methanol–water mixtures. This is further evidence of the normal behavior of dodecylammonium chloride in methanol-rich solvents. Below forty mole per cent. methanol the values are widely divergent owing to association of the colloidal electrolyte.

Summary

The values of T_c, T_a, Λ_c and Λ_a for dodecylammonium chloride in methanol–water and acetonitrile–water mixtures at 30° have been determined or derived.

At 0.10 *M* the transference numbers indicate a transition of dodecylammonium chloride from a colloidal to an ordinary electrolyte as the percentage of organic addend is increased.

CHICAGO, ILLINOIS

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(7) Longsworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).