ration of the triester. Trimethylamine (6.5 g.) and tri-β-chloroethyl phosphate (10 g.) in 100 cc. of dry toluene, kept sealed at 25–30° for several days or at 78–80° for two days, gave a sirup. A solution of the sirup, prepared at 78–80°, in a mixture of isopropanol and ether yielded at 5° crystals (0.6 g.) which could be recrystallized from isopropanol (needles), but was not investigated further.

Chloroaurate.—The compound was precipitated by adding an aqueous solution (7 cc.) of 1 g. of pure triester to 10% excess of the calculated auric chloride in 10 cc. of water; yield, 2.7 g. It crystallizes from water (difficultly soluble) as clusters of short, yellow prismatic needles melting incompletely at 216° (uncorr.) and to a clear red liquid at 230°.

Anal. Calcd. for $C_{15}H_{39}O_4N_3PAu_3Cl_{12}$: C, 13.11; H, 2.86; N, 3.06; P, 2.26; Au, 43.07. Found (dried at 25° *in vacuo* over phosphorus pentoxide): C, 13.17; H, 2.88; N, 3.07; P, 2.28; Au, 43.20.

Summary

From the products of the phosphorylation of choline chloride with orthophosphoric acid and phosphorus pentoxide the amorphous calcium salt of the monocholine ester of phosphoric acid has been prepared free from choline but containing 3–4% of dicholine phosphate, a new chloroaurate of which is described. Monocholine phosphate chloroaurate prepared from the calcium salt was somewhat impure, but from it could be obtained the pure, crystalline chloroplatinate.

Trimethylamine condenses with tri-β-chloroethyl phosphate under appropriate conditions to give crystalline tri-(choline chloride) phosphate which yields a crystalline chloroaurate. An effect of heat on the pure triester is pointed out.

Improvements have been made in Plimmer and Burch's procedure for the preparation of tri-β-chloroethyl phosphate.

WASHINGTON, D. C. RECEIVED JULY 8, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Predominant Role of Association in the Dissociation of Simple Straight-Chain Sulfonic Acids in Water. I. Conductivity[1]

BY J. W. MCBAIN AND MARGARET D. BETZ

Among the simplest uni-univalent organic electrolytes are the straight-chain saturated alkyl sulfonic acids, RSO_3H, the higher members of which have been made for the first time and generously placed at our disposal by Prof. C. R. Noller and J. J. Gordon.[2] In a series of communications it will be shown that their behavior at great dilution is that of simple partially dissociated acids, but that in more concentrated solutions, such as from $N/20$ upward, a radical change takes place in their physical chemical properties, such as conductivity, freezing point and electromotive force.

This change is the opposite of that which the interionic attraction theory was set up to explain. It would appear to be due to association in the sense in which this term has so long been used in chemical science, as for example in describing the occurrence of double molecules in the vapor of acetic acid or in solutions of acetic and other acids in benzene. This association is not caused by Coulomb attraction of opposite charges, but it is due to van der Waals cohesive forces. It occurs even in spite of electrostatic repulsion, for it is very marked in the association of ions of like charge.

Since in all the more concentrated solutions the effect of association is so dominant as to submerge the ordinary behavior of interionic attraction, it must surely be a force of universal occurrence and a factor which is seldom negligible. This association must affect not merely ions but also the molecules from which they are derived. Since one of the authors introduced the conceptions of colloidal electrolytes and of neutral and ionic micelles more than twenty years ago,[3] it has been known that the group of colloidal electrolytes embraces more substances than the acids and bases put together.[4] However, it is not sufficiently recognized that colloidal electrolytes appear to be the rule rather than the exception in non-aqueous solutions and that even fairly simple substances in aqueous solution, such as

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[1] Experiments by Miss Betz.

[2] C. R. Noller and J. J. Gordon, THIS JOURNAL, **55**, 1090 (1933); for cetyl sulfonic acid see J. W. McBain and R. C. Williams, *ibid.*, **55**, 2250 (1933); B. Flaschenträger and G. Wannschaff, *Ber.*, **67**, 1121 (1934); R. C. Murray, *J. Chem. Soc.*, 739 (1933).

[3] J. W. McBain and C. S. Salmon, THIS JOURNAL, **42**, 426 (1920); *Proc. Roy. Soc.* (London), **A97**, 44 (1920); J. W. McBain and H. E. Martin, *J. Chem. Soc.*, **105**, 957 (1914); J. W. McBain, *Trans. Faraday Soc.*, **9**, 99 (1913); *Kolloid-Z.*, **12**, 256 (1913); J. W. McBain, M. E. Laing and A. F. Titley, *J. Chem. Soc.*, **115**, 1279 (1919).

[4] Compare the extensive international symposium on colloidal electrolytes of September, 1934, *Trans. Faraday Soc.*, **31**, 1 (1935).

butyric acid[5] or potassium iodate,[6] partake of this behavior in measurable degree.

These sulfonic acids offer exceptionally favorable material for study on account of their ready solubility and complete freedom from hydrolysis. These hydrogen soaps are more colloidal than the ordinary alkali soaps of similar length of carbon chain.

Experimental

Macroscopic Observations on the Hydrogen Soaps.—The hydrogen soaps undecyl (C_{11}), lauryl (C_{12}) and myristyl (C_{14}), sulfonic acids, were in the form of very hygroscopic powders containing one molecule of water of crystallization. When added to water, the soaps form concentrated liquid crystal solutions which, when preparing the higher concentrations of isotropic solution, require several hours of heating at temperatures above 25° to redissolve completely in additional water. The highest concentrations of the sulfonic acids prepared in this manner were 1.13 N_w undecyl, 0.85 N_w lauryl, and 0.53 N_w myristyl. The more concentrated solutions of the undecyl and lauryl sulfonic acids were still stable at 0°. Myristyl sulfonic acid is less soluble and therefore above the freezing point of water has separated as an opaque white gel. As the temperature is raised, the myristyl sulfonic acid progressively dissolves, the curd becoming clearer and "melting" to a transparent solution at 15–16°. The sodium and potassium salts are so much less soluble that they require heating to 25 or 30°. All of the isotropic soap solutions froth freely, and undecyl and lauryl sulfonic acids yield a generous lather even at 0°.

Purest available potassium chloride and water (0.5×10^{-6} mhos) were used. Solutions were made up by weight and concentrations were determined by titration after being checked by refractive index with the Zeiss dipping refractometer with prism No. 1 and auxiliary prism. The readings in scale divisions were as follows.

Sulfonic acid		
Undecyl	$C_{11}H_{23}SO_3H$	15 + 80 *m* at 19.0°
Lauryl	$C_{12}H_{25}SO_3H$	15 + 80 *m* at 19.4°
Myristyl	$C_{14}H_{29}SO_3H$	15 + 99 *m* at 19.0°

As is well known, association does not much affect the value of molar refraction in solution.

The solubilities in grams per 100 g. of water of the calcium sulfonates were very approximately determined as follows.[7]

	Undecyl	Lauryl	Myristyl
Calcium	0.2	0.02	0.02

The densities at 25.00/4° were measured by Dr. M. E. L. McBain as follows, where molality, $m = N_w$ or weight normality.

Undecyl		Lauryl		Myristyl	
Concn., N_w	Density	Concn., N_w	Density	Concn., N_w	Density
0.3688	1.00171	0.375	0.99933	0.098738	0.99749
.4641	1.00301	.635	1.00063	.2369	.99829
.7823	1.00686	.820	1.00123	.4504	.99964

Conductivity measurements were made with the Grinnell Jones–Dykes type of bridge, supplied by Leeds and Northrup, with an oil thermostat at 25 ± 0.01° and the H-shaped cell of McBain and Titley with cell constant 13.239. The conductivity of lauryl sulfonic acid solutions at 25° was unaltered by lapse of time or by previous heating and quick cooling.

The conductivity data are recorded in Tables I, II and III. In column 4 is given the Arrhenius ratio μ_v/μ_∞ where however μ_∞ is taken as 378 for the most dilute solutions below and including

Table I

Conductivity of Undecyl Sulfonic Acid at 25°

N_w	K	μ_v	$100\ \mu_v/\mu_\infty$	$100\ \mu_v/\mu_\epsilon$
0.000950	0.000349	368.5	97.51	98.5
.00950	.00308	325.8	86.21	89.3
.04330	.008903	208.20	49.12	58.72
.06134	.010693	177.23	41.81	50.30
.0800	.013846	176.69	41.69	50.69
.1049	.017452	170.70	40.28	49.53
.3688	.062810	184.64	43.56	(59.0)
.4641	.08050	191.87	45.30	
.7761	.13196	199.81	47.14	
1.1375	.18337	202.25	47.72	

Table II

Conductivity of Lauryl Sulfonic Acid at 25°

N_w	K	μ_v	$100\ \mu_v/\mu_\infty$	$100\ \mu_v/\mu_\epsilon$
0.001	0.000347	348.1	92.11	93.04
.0061	.001987	327.2	86.58	89.08
.010	.003212	322.9	85.44	88.64
.0525	.00783	151.5	35.72	42.50
.075	.00954	129.9	30.63	36.71
.1025	.01479	148.3	34.97	(42.69)
.2550	.03860	161.3	38.03	
.35	.05238	162.9	38.41	
.511	.0796	175.7	41.43	
.75	.1112	175.9	41.48	
.814	.1196	176.6	41.64	

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(5) C. R. Bury and D. G. Davies, *J. Chem. Soc.*, 2413 (1932); Jones and Bury, *Phil. Mag.*, **4**, 841 (1927); Bury, *ibid.*, p. 980; Grindley and Bury, *J. Chem. Soc.*, 679 (1929); 1665 (1930); E. A. Goode, N. S. Bayliss and A. C. D. Rivett, *ibid.*, 1950 (1928).

(6) J. W. McBain, S. S. Kistler and W. McClatchie, *J. Phys. Chem.*, **35**, 130 (1931).

(7) Compare the values found for the corresponding sulfates by S. Lenher [*Am. Dye Reporter*, 6/11/33, 663–667].

TABLE III

CONDUCTIVITY OF MYRISTYL SULFONIC ACID AT 25°

N_w	K	μ_v	$100\ \mu_v/\mu_\infty$	$100\ \mu_v/\mu_\epsilon$
0.00122	0.000422	347.0	91.82	93.0
.010	.001696	170.6	40.23	46.35
.015	.001874	125.8	29.66	33.73
.031	.003536	115.4	27.21	31.73
.0514	.0605	119.7	28.23	33.62
.09873	.0114	118.9	28.04	(33.90)
.2369	.0281	126.7	29.88	
.4504	.06694	167.3	39.45	
.543	.0762	161.5	38.08	
.543	.07551	160.0	37.76	

0.01 N_w. For all the more concentrated solutions, as will be explained later, μ_∞ was taken as 426; probably (see later) this should have been increased to 546 in the most concentrated solutions, which would have decreased the final values of the ratio by about one-fourth.

During the past few years, it has become customary to calculate the degree of dissociation of uni-univalent electrolytes, $\alpha = \mu_v/\mu_\epsilon$, following the method of Sherrill and Noyes and MacInnes as developed by Shedlovsky, Davies, and others, upon the basis of the Debye–Hückel–Onsager and other equations. Incidentally, several authors have thus found that certain electrolytes, such as potassium nitrate or the potassium iodate already referred to, are not as fully dissociated as potassium chloride.

From the meager data available for large organic ions, we have taken the value for μ_∞ as $350 + 28 = 378$, where hydrogen ion accounts for 96.2% of the total. The initial Onsager slope for complete dissociation is therefore $\mu_\epsilon = 378 - 145.7\sqrt{N_v}$.

These conductivity data are plotted in Fig. 1. The curves are of the same form as those which have become familiar for ordinary soaps such as potassium laurate. The initial parts of the curves show that dissociation is definitely not complete and that the observed values for $\alpha = \mu_v/\mu_\epsilon$ correspond to approximate dissociation constants of the order of $K = 0.01$, 0.05 and 0.07. This compares with the value 0.3 for potassium laurate at 18°, that of hydrochloric acid and potassium chloride being taken as infinity. The values are only approximate on account of the associative factors which are beginning to assert themselves with increase in concentration. Figure 1 also includes for comparison the conductivity curves which are exhibited by fully dissociated uni-univalent and uni-decivalent electrolytes for 100% dissociation. In the latter case, according to Mukherjee,[8] the numerical factor in the final term of the Onsager equation is increased to 2925 (instead of our 145.7), and for a uni-centivalent electrolyte to 40,572. (That is, there would be no observable μ_v in all solutions accessible to measurement.) It is quite obvious that although the actual data lie below the limit for uni-univalent electrolytes, they all very greatly exceed the values possible for an ionic micelle regarded as a polyvalent ion in the ordinary sense. They show that the treatment of the ionic micelle as an ordinary polyvalent ion is wholly insufficient.[9]

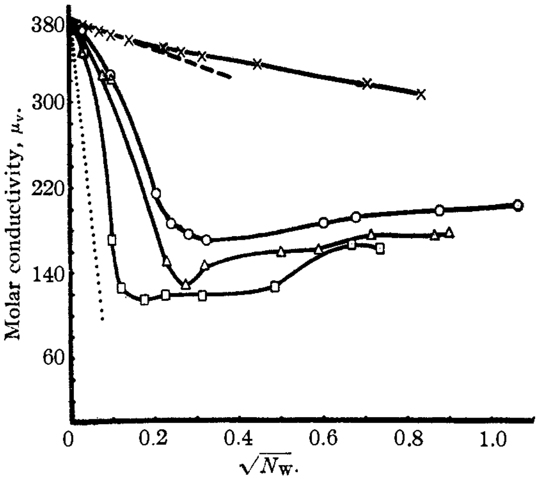

Fig. 1.—Molar conductivity: ×, hydrochloric acid "International Critical Tables"; ○, undecyl sulfonic acid; △, lauryl sulfonic acid; □, myristyl sulfonic acid. Dashed line indicates the slope for 100% for a uni-univalent electrolyte; dotted line indicates the slope for a uni-decivalent electrolyte.

The Behavior of these Acids at Ordinary Concentrations.—The most striking and remarkable feature exhibited by the conductivity of our sulfonic acids is the minimum at 0.1, 0.075, and 0.031 N_w solutions of undecyl lauryl, and myristyl, respectively. After passing through a minimum in these moderately dilute solutions, the conductivity rises markedly with increase of concentration. Such behavior in aqueous solution is unparalleled except by the higher sodium

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(8) I. Mukherjee, *Kolloid-Z.*, **62**, 264 (1933); **65**, 72 (1933).

(9) Thus, this suggestion thrown out by Van Rysselberghe and others is inappropriate since it is not in accordance with experiment [P. J. Van Rysselberghe, *J. Phys. Chem.*, **38**, 645 (1934)]. Similarly, the discussion of J. L. Moilliet, B. Collie, C. Robinson and G. S. Hartley [*Trans. Faraday Soc.*, **31**, 120 (1935)] is crippled by the same invalid assumption and also by the failure to recognize the existence of undissociated molecules and of their association products, the neutral micelles. Again, the conductivity, freezing point and electromotive force curves for soaps and for these sulfonic acids are not in accord with the simple mass action equation [compare R. C. Murray and G. S. Hartley, *ibid.*, p. 186].

and potassium soaps studied by McBain and collaborators[10] and the alkyl sulfates (salts and free acid) recently studied by Lottermoser and Püschel which closely parallel our findings.[11]

Figure 1 emphasizes by comparison with the initial Onsager slope the increasingly excellent conductivity of these acids in concentrated solution. It is enormously greater than that consonant with the behavior of a weak electrolyte as exhibited in the very dilute solutions, and still more so with the increasing weakness indicated in the slightly less dilute solutions before the minimum in conductivity is attained.

The conductivity rises above the minimum by 18, 36, and for myristyl no less than 45%. The old hypothesis of McBain and Salmon, which appears still valid, is that simple anions of low mobility associate to form ionic micelles of high mobility in accordance with Stokes' law, since they have retained their electrical charges. However, it is here necessary to assume an extraordinarily high mobility for the ionic micelle, rising to that of the hydroxyl ion for each charge on the ionic micelle. If the equivalent conductivity of the charges of the ionic micelle had been raised only to that of the chlorine ion, the maximum increase of conductivity would be the inadequate value 424/378 = 1.125 fold. That found by McBain and Williams[2] for acetyl sulfonic acid at 90° was likewise larger, namely, 1.25 fold. The existence of this remarkable enhancement of conductivity is therefore beyond dispute.

The alternative hypothesis adopted by Franklin and Kraus for solutions in liquid ammonia, to the effect that a large portion of the current may be borne by free electrons and be semi-metallic in nature, seems unnecessarily bold for these aqueous solutions. Also, the recent hypothesis of Fuoss and Kraus[12] applies only to minima in solvents of low dielectric constant and of very low dissociating power.

The Debye–Hückel theory was set up to explain why ions show less conductivity than that which corresponds to their intrinsic mobility. We have here the opposite phenomenon, a great and increasing conductivity in spite of inter-ionic attraction.

The intrinsic mobilities of ions in strong aqueous solutions are, however, really high. For example, in the diffusion of potassium chloride where the effects of interionic attraction almost completely eliminate themselves, the potassium and chloride ions actually move much faster than at infinite dilution.[13] The differential or "instantaneous" diffusion coefficients are far larger in concentrated solutions of potassium chloride than they are in pure water.

Equally relevant is the demonstration by McBain and Van Rysselberghe[14] by means of migration data that in all concentrated solutions containing even one ion that is more than univalent, complex anions are formed in large amount. Similarly, by means of ultra-filtration, McBain, Kistler and McClatchie[6] have shown that moderate concentrations of such salts as cadmium iodide or potassium or sodium iodates contain appreciable proportions of constituents so large that they are held back by an ultrafilter that is permeable to all simple ions and molecules.

A high conductivity per electrical charge must always occur where the linear velocity in cm./sec./volt/cm. is exceptionally high, as is the case with air bubbles and suspended hydrocarbons.[15] When further, the number of charges is equal to the number of chemical equivalents in the particle, we observe a very high total conductivity as in the present case.

Freezing point experiments to be described do not allow of any alternative hypothesis of increased relative concentration of hydrogen ion in stronger solutions, nor do they admit of measurable amounts of simple free molecules; nor is it apparent how a Grotthuss mechanism can be invoked in explanation of our data.

The enhanced mobility of the ionic micelle is not due merely to close packing as compared with the original ions, it is also due to the stripping off of the water of hydration from those ions in order that they may come into contact and be close packed and anhydrous in the interior of the particle.

Finally, the association here irresistibly dem-

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[10] However, in 0.0025 *N* potassium, sodium, lithium and calcium (but not strontium nor strychnine) salts of gum arabic, D. R. Briggs observed a minimum [*J. Phys. Chem.*, **38**, 872 (1934)].

[11] A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933). See also the maximum obtained in moderately dilute solutions of methylene blue by C. Robinson and H. E. Garrett, *Trans. Faraday Soc.*, **31**, 253 (1935).

[12] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387 (1933).

[13] B. W. Clack, *Proc. Phys. Soc.* (London), **37**, 116 (1925); **36**, 313 (1924); *Phil. Mag.*, **15**, 1061 (1933); J. W. McBain and C. R. Dawson, *Proc. Roy. Soc.* (London), **A148**, 32 (1935); see also M. E. L. McBain, This Journal, **55**, 545 (1933), and private communication regarding Sky Blue F.F. by Dr. L. M. Neale, Manchester, England.

[14] J. W. McBain and P. J. Van Rysselberghe, This Journal, **52**, 2336 (1930).

[15] See for example R. DuBois and A. H. Roberts, *J. Phys. Chem.*, **35**, 3070 (1931).

onstrated is real association, not the electrostatic clustering of ions in Bjerrum's well-known modification of the interionic theory that currently passes under the name. It is association of like parts of the uncharged portions of the molecules and ions under the influence of van der Waals forces.

Since neutral molecules are admittedly present in large proportion in dilute solutions, it would be very strange if these too did not associate with each other to form neutral micelles. Indeed, if it occurs with the ions in spite of electrostatic repulsion, it must be far more complete with the similar neutral molecules. For ordinary soaps, McBain and collaborators have deduced the presence of practically uncharged neutral micelles, using several distinct lines of evidence, none of which can otherwise be even semiquantitatively explained—ultrafiltration, ultracentrifuge and electrolytic migration.

Surely, if association can play so predominant a role in these simple cases, it must be of practically universal occurrence and only seldom completely negligible.

Summary

In dilute solutions, the straight chain sulfonic acids are simple partially dissociated electrolytes.

A remarkable transformation sets in at about $N/20$ where the conductivity is at a minimum, increasing with concentration by 18, 36 and 45% for the three sulfonic acids here studied.

The only explanation so far found is association of *like* ions to form ionic micelle, whose *equivalent* conductivity in concentrated solutions attains to that of the hydroxyl ion.

Association is so dominant that it completely submerges the ordinary features of interionic attraction.

STANFORD UNIVERSITY, CALIFORNIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Association in the Dissociation of Simple Straight-Chain Sulfonic Acids in Water. II. Freezing Point[1]

BY J. W. MCBAIN AND MARGARET D. BETZ

Conductivity has shown that in dilute solution the sulfonic acids are simple and moderately weak, but that with increasing concentration a transformation takes place, due to formation of ionic micelles whose equivalent conductivity rivals that of the hydroxyl ion itself. Here we present freezing point data which likewise show this great influence of association. The molal freezing point lowerings fall rapidly in very dilute solution, pass through a minimum, and steadily increase with rising concentration—again the opposite effect from such factors as usually determine dissociation constant and interionic attraction. Association of like ions, overcoming Coulomb repulsion, produces ionic micelles. Neutral molecules associate even more readily to form neutral micelles.

Freezing point measurements of free sulfonic acids are untroubled by the hydrolysis whose effects are often disturbing with ordinary soaps.[2] Myristyl sulfonic acid, like most of the soaps, is too insoluble for study at 0°. The lowering observed with sulfonic acids, like that with octoates, decoate, laurate and oleates, is readily measurable, but except in concentrated solution, much less than that for an acetate or hydrochloric acid.

Experimental Data

More concentrated solutions were investigated by the Beckmann method, which of necessity gives too low a freezing point, since a solution cannot continue to freeze except below its freezing point; however, undercooling was confined to 0.10°. More dilute solutions were measured by the Richards method, in some cases using a 0° room and a Beckmann thermometer, in others using a platinum resistance thermometer with a Leeds and Northrup Mueller bridge and high sensitivity type H galvanometer of 17 ohms resistance, reading more closely than 1/10,000

(1) Experiments by Miss Betz, except where indicated.

(2) J. W. McBain, M. E. Laing and A. F. Titley, *J. Chem. Soc.*, (London,) **115**, 1289 (1919). Errata: On page 1289, twenty-third line, after "solutions" insert "due to separation of acid potassium laurate." Page 1289, Table VI, last column, the next to the last number should read 1.355* instead of 0.355; the next to the last number in each column should be marked with an asterisk. Page 1290, second line, delete "soap" and insert "acid potassium laurate"; Table VII, first number of fifth column should be 0.206 instead of 1.196; in the last column the first seven numbers should be marked with an asterisk.