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

RECEIVED JUNE 18, 1935

[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.

ohm. Temperature readings were standardized against a Bureau of Standards calibrated mercury thermometer and analyses were made by means of a Zeiss dipping refractometer. The sulfonic acids froth freely at 0°. Fifty-four solutions were measured; all results are given in the graphs, but only those for rounded concentrations are given in Tables I and II. The values for the activity coefficient γ were obtained following the procedure of Randall,(3) neglecting heat of dilution.

Table I

Molal Lowering of Freezing Point (Θ/m) and Activity Coefficients (γ) of Undecyl Sulfonic Acid in Aqueous Solution: $g = i/2 = \Theta/2\lambda m = 1 - j$

m	Θ/m	g	γ
0.01	3.452	0.929	0.838
.02	2.775	.747	.575
.04	1.850	.498	.358
.05	1.590	.428	.298
.09	1.005	.270	.175
.16	0.689	.186	.102
.25	.537	.145	.0680
.36	.539	.145	.0493
.49	.576	.155	.0383
.64	.608	.164	.0308
.81	.641	.173	.0252

Table II

Molal Lowering of Freezing Point (Θ/m) and Activity Coefficients (γ) of Lauryl Sulfonic Acid in Aqueous Solution; $g = i/2 = \Theta/2\lambda m = 1 - j$[a]

m	Θ/m	g	γ
0.001	3.6	0.99	0.957
.002	3.6	.99	.933
.005	3.46	.959	.874
.01	3.34	.897	.789
.02	2.65	.712	.604
.05	1.524	.410	.290
.09	0.669	.180	.151
.10	.604	.163	.136
.16	.576	.155	.091
.20	.554	.149	.074
.25	.550	.148	.062
.36	.539	.145	.045
.50	.544	.146	.034
.64	.576	.155	.028
.81	.591	.159	.023

[a] Experiments by M. E. L. McBain.

The Osmotic Coefficient, *g*.—Activity coefficients have been so commonly employed, especially in this country, that there appears to be a tendency to forget that the osmotic coefficient of Bjerrum, g, and the i value of van't Hoff have exactly equal thermodynamic validity and significance. Bjerrum's g is identical with van't Hoff's i/v where v is the total number of ions producible at infinite dilution from one formula weight. g is $\Theta/v\lambda m$ and is also equal to the $1-j$ of Lewis and Randall. Following Guggenheim's notation(4)

$$\ln 1/N_0f_0 \equiv g \ln 1/N_0 = L_F^\circ\Theta/RT^{\circ 2} = gm$$

and for freezing points of aqueous solutions within the experimental error even of the best determinations, $g = \Theta/\lambda m$. N_0 d log $f_0 = -N_S$ d log F_S.

For ideal solutions, g, like the activity coefficient of the solvent, f_0, and that of the solute, f_S, becomes unity. However, as we have just seen, g varies directly with the actual lowering of freezing point just as directly as m, while the change in the activity coefficients is far more indirect.

The relation between osmotic coefficient g and activity coefficient f is very similar to that between concentration of the hydrogen ion and pH in that the first varies directly when the second is changing as the inverse logarithm.

So intent have workers in this field been during the last dozen years upon discussing the interionic attraction explanation of the deviation of electrolytes from the behavior of ideal solutions, that it seems to have been commonly forgotten that the actual freezing point lowering of hydrochloric acid never deviates from that of a truly ideal solution by more than 6% over the whole range of concentration from infinite dilution to 1 molar. Indeed, according to the "International Critical Tables," the greatest deficit is that for 0.1 N solution, amounting to only 5.2%. Thereafter, it approaches more closely to the lowering of an ideal solution, equaling it below 0.6 M and surpassing it by 6% in 1 M solution. Similarly, in 1 M solution, the lowering for sucrose is 10.9% above that of an ideal solution and that of potassium chloride only 12.5% below the ideal value.

Nevertheless, the numerical scale in which activity coefficients are expressed exaggerates these deviations, making the activity coefficients for these three solutes in 1 M solution 0.8404,(5) 1.221 and 0.601,(6) respectively. It is interesting that the activity coefficient of hydrochloric acid should be so much less than unity when its actual freezing point lowering exceeds that of an ideal solution. Activity is a partial quantity and possesses no more *direct* significance than does any other partial quantity such as partial specific

---

(3) M. Randall, This Journal, **48**, 2512 (1926).

(4) E. A. Guggenheim, "Modern Thermodynamics by the Methods of Willard Gibbs," Methuen and Company, Ltd., London, 1933.

(5) M. Randall and L. E. Young, This Journal, **50**, 995 (1928).

(6) M. Randall and A. M. White, *ibid.*, **48**, 2514 (1926).

volume. For example, as shown by Lewis and Randall, the partial specific volume of magnesium sulfate is negative, which has very indirect connection with its real positive volume.

The Graphs of $j/\sqrt{m}$ Against $\sqrt{m}$.—The $j/\sqrt{m}$ graphs of Lewis and Randall here assume a characteristic form, decidedly different from that either of weak or of strong electrolytes (see Fig. 1). All crystalloidal electrolytes, from the strongest, like potassium chloride, through progressively weaker ones, like acetic acid, to the weakest, such as sucrose, must lie between the graph marked KCl and $K = 0$, as Randall and Allen[7] also have shown. For $K = 1$, the graph is a straight line. For weaker electrolytes, the height of the "hump" is a measure of the weakness and it rises to a value of 46 for acetic acid at $m = 10^{-5}$, all curves approaching the same limit as KCl for infinite dilution.

In very dilute solutions, the sulfonic acids exhibit this normal behavior of weak electrolytes and they are drawn with the slopes corresponding with the conductivity results.. However, the heights of the maxima, 2.6 and 2.8 for the sulfonic acids, are those of a still weaker electrolyte for which $K = 0.005$; but this maximum does not lie at the position for such a weak electrolyte, namely, $m = 0.01$, but in the much stronger solution $m = 0.05$. Most striking and significant however is the disregard shown for the theoretical limiting curve $K = 0$. The graphs before reaching their maximum cut sharply across this boundary into the region forbidden for crystalloids whether electrolytes or not. Hence colloid is present in large quantity.

It is not enough to assume that the undissociated acid associates to form a colloid because of the very high conductivity which forces us to recognize the anions also as colloid. On the other hand, as will be shown in the next paper of this series dealing with electromotive force, it is not enough to assume that only the anions are colloid. Both molecules and anions must be colloidal for the total freezing point lowering is far less than that corresponding to the hydrogen ion indicated by the usual method of calculating e. m. f.

Cetyl sulfonic acid exhibits at 90° a similar high value of $j/\sqrt{m}$, apparently rising to a maximum of 2.5 at $m = 0.01$,[8] although this is in a dilution where the vapor pressure method becomes inaccurate. On the other hand, not even the highest soaps of sodium or potassium yield at 90° a value exceeding 1.2. For the laurates, it is only 0.64 and 0.67 at 90°, but at 0° the curve rises to a maximum of 1.65 for potassium laurate at $m = 0.1$ with the sudden nearly vertical dip in more dilute solutions which we have here found for the sulfonic acids.

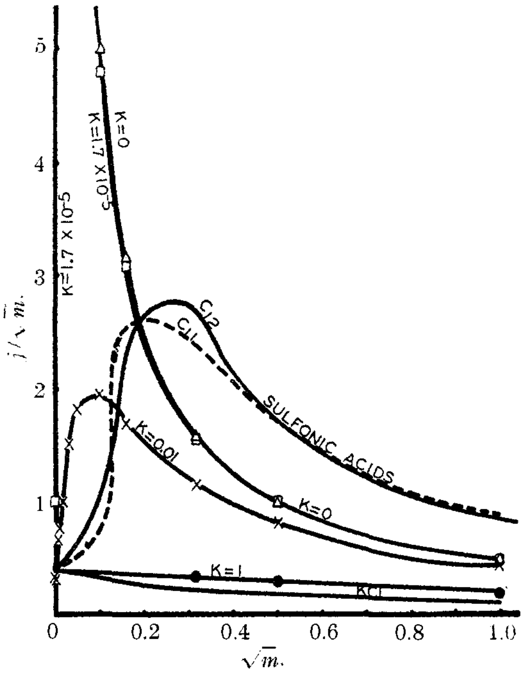

Fig. 1.—$j/\sqrt{m}$ graphs for sulfonic acids, showing their very different dehavior from that characteristic of either strong or weak electrolytes except in very dilute solution.

Discussion

Figure 2 exhibits the value of g of the sulfonic acids in comparison with hydrochloric acid. It will be noted that they too pass through a minimum and rise again with increase of concentration to the extent of 25 and 26%, respectively.

Figure 3 compares the activity coefficients[9] of lauryl, which is very similar to that of undecyl, with those of hydrochloric acid and of potassium laurate. The latter would appear to refute the suggestion of Linderstrøm-Lang[10] that soaps might be regarded as simple electrolytes 100% dissociated provided that the cations become lost as far as osmotic effects are concerned, upon

---

[7] M. Randall and C. Allen, THIS JOURNAL, **52**, 1818 (1930). Dissociation constants deduced by their rule from freezing point data would not be legitimate or free from ambiguity for these substances.

[8] J. W. McBain and R. C. Williams, *ibid.*, **55**, 2254 (1933).

[9] Compare the discussion of J. W. McBain and M. M. Barker, *Trans. Faraday Soc.*, **31**, 149 (1935).

[10] K. Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **16**, No. 6, 1-47 (1926); for other incompatible evidence see J. W. McBain, THIS JOURNAL, **50**, 1636 (1928).

finding themselves among the comparatively long anions (at most only 17 Å. long, but probably far less[11] or even spherical). It would further be necessary to assume that the anions are lost among each other and that ordinary ions added are not lost since, as is well known, they exert in soap solutions the full osmotic effects that they do in water. Since this is true for added potassium, sodium or hydrogen ions, it must be equally true of the same ions already present in the soap itself. In Fig. 3 for $m = 0.048$, $m = 0.22$, the activity coefficient of potassium laurate is almost that of the highly dissociated hydrochloric acid, whereas that of lauryl sulfonic acid with identical length of hydrocarbon chain is much less than half as great. According to his suggestion, the results should have been identical if only simple ions are present in both cases instead of differing by 2.5-fold.

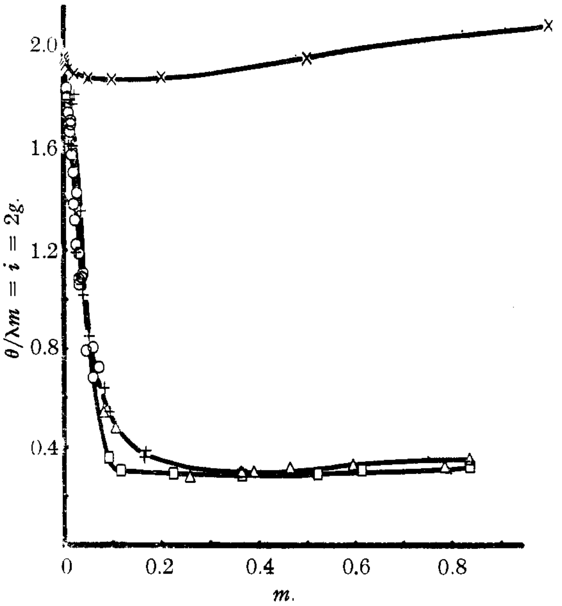

Fig. 2.—Osmotic coefficients of hydrochloric acid (×) and of undecyl (△) and lauryl (□) sulfonic acids.

It is obvious from the figures that the ionic micelle does not behave like a polyvalent ion whose charges are coincident. McBain,[12] in accordance with the suggestion of Bjerrum in 1923 and later corroborated by Scatchard and Kirkwood, explained this as being due to the distance apart of like charges on a single ionic micellar particle being greater than the average distance between ordinary ions in ordinary solutions such as potassium chloride. Simms,[13] whose work has not been accorded the attention it deserves for its fundamental importance in colloid phenomena and in the application of interionic attraction theory as the basis of electro-kinetics, has discussed the theory of widely spaced charges. He, in agreement with *ad hoc* calculations of Debye, formulated the influence of ionic strength for the two extreme cases; first where polyvalent charges coincide as in the Debye–Hückel theory of ordinary ions, and second where molecules or particles are polyvalent but with widely separated charges of like sign and behave effectively as univalent ions.

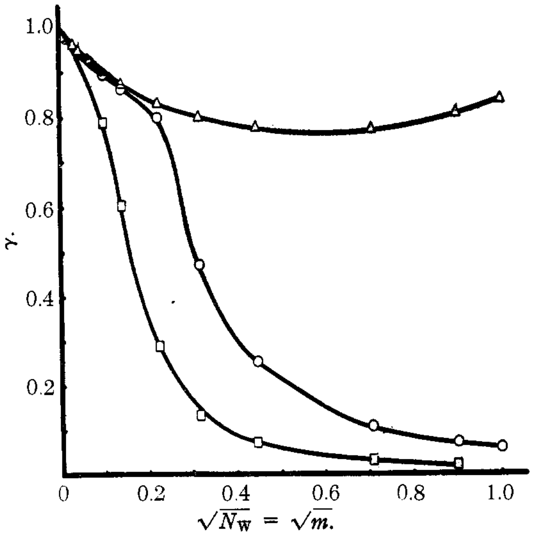

Fig. 3.—Activity coefficients of lauryl sulfonic acid (□), potassium laurate (○) and hydrochloric acid (△).

Summary

The osmotic coefficients of undecyl and lauryl sulfonic acids pass through a minimum in dilute solution, rising again with concentration by about 25%.

The graphs of $j/\sqrt{m}$ against $\sqrt{m}$ exhibit a highly characteristic form which departs strikingly from that of strong electrolytes or that for any simple weak electrolyte or non-electrolyte.

The only consistent interpretation of all the data is that whereas in dilute solutions they are simple moderately weak electrolytes, with increased concentration molecules and ions associate into neutral and ionic micelle, respectively, but that ionic micelles, owing to the wide spacing of their charges, have the ionic strength similar to uni-univalent electrolytes.

Stanford University, California

Received June 18, 1935

---

[11] I. Langmuir, Chap. 29, Vol. I of Jerome Alexander's "Colloid Chemistry," 1926, p. 838.

[12] J. W. McBain, This Journal, **50**, 1636 (1928); G. Scatchard and J. G. Kirkwood, *Physik. Z.*, **33**, 297 (1932).

[13] H. S. Simms, This Journal, **48**, 1239, 1251 (1926); *J. Phys. Chem.*, **32**, 1121 (1928); and *J. Gen. Physiol.*, **11**, 613 (1928).