a 3.5 N potassium chloride bridge have been compared with values computed from diffusion potentials and the activity coefficients of hydrochloric acid on the assumption that $f_H = f_{Cl} = f_{HCl}$. Discrepancies are noted which become very large, rising to 10 millivolts for 1 N hydrochloric acid.

Hydrochloric acid added to these colloidal electrolyte solutions of sulfonic acids produces slightly more effect upon e. m. f. even than it does in water, showing that the ionic micelles cannot be regarded as equivalent to polyvalent ions in which the charges are concentrated in one point.

In very dilute solution, the sulfonic acids behave like weak electrolytes and the degree of dissociation rapidly falls, but in more concentrated solution remains almost constant or tends to rise again.(6)

(6) Still larger readings in the most concentrated solutions are robbed of significance because precipitate forms between the sulfonic acid and the salt bridge and they change rapidly with time.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Straight-Chain Sulfonic Acids in Water. IV. Comparison of Results, and So-called "Hammarsten Effects"

BY JAMES W. MCBAIN

Colloidal electrolytes were discovered through comparison of conductivity with osmotic coefficient. Preceding parts of this series have shown that undecyl, lauryl and myristyl sulfonic acids, although conforming in dilute solution to the behavior of a simple half weak electrolyte, form the ionic micelle and neutral micelle characteristic of colloidal electrolytes in all stronger solutions. Further significant results follow from the comparison of these three kinds of data for the solutions between 0.1 and 1.0 N where the graphs tend to rise with concentration. The data are collected in Figs. 1, 2 and 3.

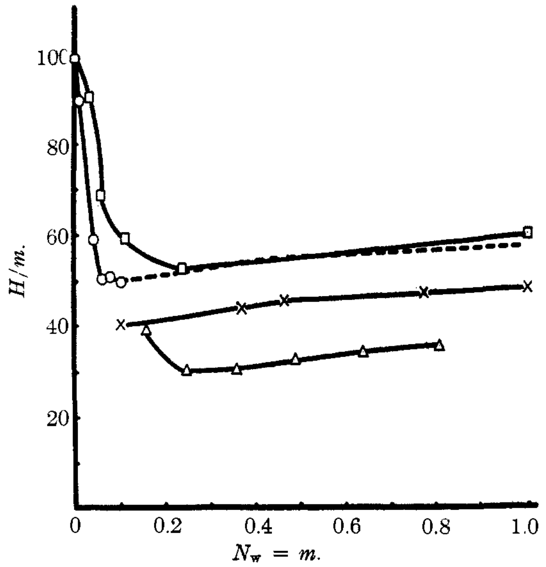

Fig. 1.—Hydrogen-ion concentration of undecyl sulfonic acid: □ is e. m. f.; ○ is conductivity, $100\mu\nu/\mu_\epsilon$; × is Arrhenius ratio, $100\mu/\mu_\infty$; △ is freezing point.

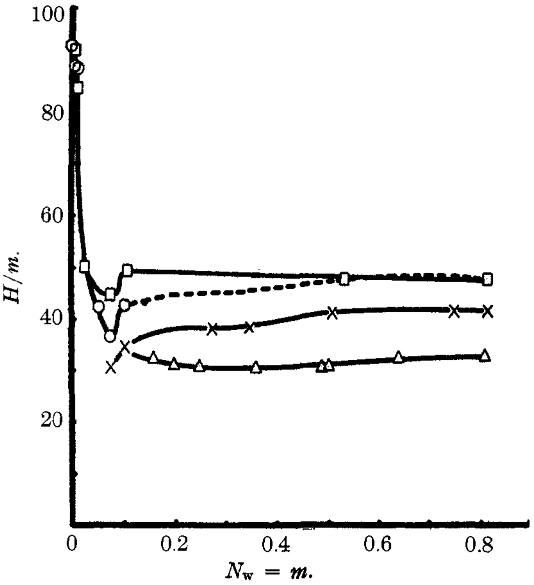

Fig. 2.—Hydrogen-ion concentration of lauryl sulfonic acid: □ is e. m. f.; ○ is conductivity, $100\mu\nu/\mu_\epsilon$; × is Arrhenius ratio, $100\mu T/\mu_\infty$; △ is freezing point.

Before comparing the graphs on each figure, it is necessary to recall how they arise. Those for e. m. f. call for no comment, except that we have omitted the most concentrated solution for myristyl sulfonic acid on account of precipitation at the salt bridge. Those for undecyl sulfonic acid, judging from the dilute solutions, appear somewhat too high.

The first part of the conductivity curve, with points marked by circles, is the degree of dissociation according to the modern ionic attraction theory; but it passes through a minimum and leaves thereafter no basis for the calculation, since the results are already affected by the transition from simple electrolyte to colloidal electrolyte. Below and parallel to the last two circles lie the crosses representing Arrhenius conductivity ratios, $\mu\nu/\mu_\infty$ (where $\mu_\infty = \mu_{\text{Cl}}$) showing how much is the dual effect of interionic attraction and of the assumption that hydrochloric acid is fully dissociated. The graph of circles is continued by us as a dashed line parallel to the crosses. This gives us an approximate value for the hydrogen-ion concentration, on the assumption that the steadily increasing correction upward for interionic attraction is balanced by the steadily increasing correction downward due to the steady increase in mobility of the ionic micelle from that of chloride ion to that of hydroxyl ion.

It is to be noted that these two curves for concentration of hydrogen ion or degree of dissociation practically coincide. Within the experimental error, conductivity and electromotive force have given the same result. The concentration of hydrogen ion increases faster than the total concentration. The degree of dissociation —doubtless into a changing product—increases with concentration, contrary in appearance to Le Chatelier's principle.

As regards freezing point lowering, there are only two curves because of the insolubility of myristyl sulfonic acid below 15°. In dilute solution they have no direct significance on this diagram because freezing point counts all molecules and ions, not merely hydrogen ion. Only after the transition to colloidal electrolyte is complete does freezing point measure hydrogen ion alone, because no simple molecules and no simple ions other than hydrogen ion are present.

We may therefore for these more concentrated solutions calculate the degree of dissociation of the total sulfonic acid into hydrogen ion and corresponding equivalents of ionic micelle by making use of exactly the same assumptions that we have employed in calculating e. m. f. If we assume that $f_{\text{H}^+} = f_{\text{Cl}^-} = f_\pm$ for hydrochloric acid, and if we assume that the activity coefficient of the hydrogen ion from the sulfonic acid is identical with that of hydrogen ion in hydrochloric acid solution containing exactly the same concentration of hydrogen ion, we need only compare the actual lowering of freezing point, Θ, of the sulfonic acid with one-half the lowering observed for solutions of hydrochloric acid itself, as recorded in "I. C. T.," in order to identify the concentration of hydrogen ion causing the whole of the freezing point lowering of the sulfonic acid and causing exactly one-half the lowering in the hydrochloric acid solution. In other words, we have assumed that the effect of interionic attraction upon hydrogen ion in the sulfonic acid solution is exactly the same as in hydrochloric acid solution of the same actual concentration of the hydrogen ion. We find per cent. dissociation at once by dividing this concentration so obtained by the molality of the sulfonic acid solution. In dilute solutions, where the colloidal electrolyte is breaking down into a simple electrolyte, this relation can no longer hold and the results are not included in the figures.

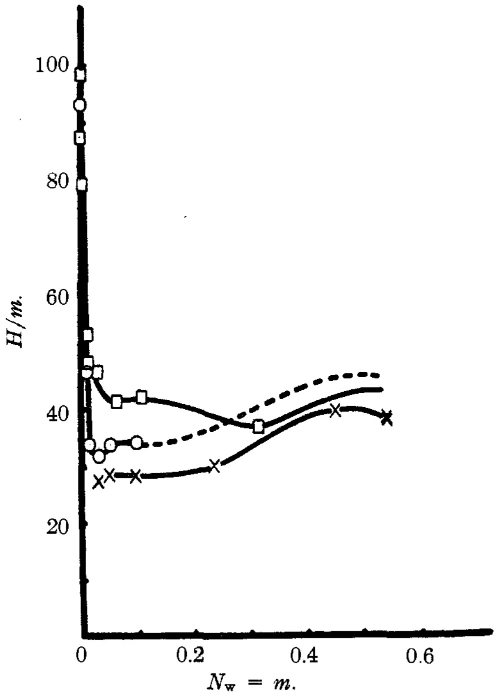

Fig. 3.—Hydrogen-ion concentration of myristyl sulfonic acid: □ is e. m. f.; ○ is conductivity, $100\mu\nu/\mu_\epsilon$; × is Arrhenius ratio, $100\ \mu\nu/\mu_\infty$.

It will be noted in the foregoing that precisely the same basis of assumption is made in calculating e. m. f. and freezing points. Incidentally, we take advantage of the direct proportionality between Θ and g, derived as follows, using the nomenclature of Guggenheim $g \ln 1/N_0 = L_F^0\Theta/RT^{\circ 2}$ with good approximation for aqueous solutions.

$$g \ln \frac{1}{N_0} \equiv \ln \frac{1}{N_0 f_0} \equiv g \left(N_S + \frac{N_S^2}{2} + \frac{N_S^2}{3} + \text{etc.} \right) = g\ N_S = gm$$

since $N_0 = 1 - N_S$. Whence $g = \Theta/\lambda m$.

The freezing point lowering is only about three-fifths that required for the concentration of hydrogen ion shown to be present by conductivity and electromotive force. This contradiction has to be accepted as a fact because it is far beyond any possible error of experiment, and we see no way of explaining it away as unreal without introducing some fantastic and unjustified assumption, such as that the actual conductivity observed is partly metallic or that some new class of impurity is present which does not lower freezing point but yet has a high conductivity. It cannot be due to any non-electrolyte or electrolyte present as impurity because the effect would be in the opposite direction of that here observed. It must be recalled that all three measurements were made on identical solutions.

Similarly, with 0.5 *N* cetyl sulfonic acid[1] at 90° the hydrogen-ion concentration, according to e. m. f., appeared nearly double that deduced from vapor pressure lowering. The only other authenticated instance is that of thymonucleic acid as studied by the Hammarstens, to which we shall return.

No such discrepancy has ever been observed between the many methods used to measure ordinary soaps.

So-Called "Hammarsten Effects."—Confusion has arisen through calling different things, some of them long since known,[2] "Hammarsten effect." Unquestionably, it is wholly legitimate to follow the usage of Linderstrøm-Lang[3] in defining as genuine "Hammarsten effect" the fact that the osmotic coefficient of thymonucleates depends upon the size of the cation. Thus the Bjerrum osmotic coefficient, $g, = i/v = \Theta/v\lambda m$, which is approximately equal to the osmotic pressure observed divided by the osmotic pressure of an ideal non-electrolyte of the same concentration, was observed by E. and H. Hammarsten[4] to be as follows

Cation	H^+	Na^+	NH_4^+	$(CH_3)_3NH^+$	$(CH_3)_4N^+$	$(C_2H_3)N^+$	$(C_3H_7)_3NH^+$
	0.70	0.80	1.20	1.35	1.45	1.50	1.74

Linderstrøm-Lang, however, did not agree with Hammarsten's explanation which assumed that "the small ions, I_1, are able to penetrate into the I_n ions and thus become osmotically inactive, whereas large ions I_2, are not capable of this." He concluded "that there must be far different and more profound causes and that Hammarsten's explanation, though perhaps necessary, is not sufficient." Jorpes and Hillgrew[5] also observed this kind of Hammarsten effect with various salts of Congo red.

For this genuine Hammarsten effect we may advance here a new explanation. The formation of neutral micelles is a process of association of molecules through orderly array of like parts. It is the organic radical which possesses this property. This close packing of parallel molecules can only occur if the cationic radicals, such as hydrogen, are so small as not to interfere. When these "heads" of the molecules, as they are commonly referred to in the literature on insoluble monomolecular films, become too large, their bulk interferes with the association of molecules to form neutral micelle. Meanwhile, the formation of ionic micelle, stripped of these cations, proceeds as usual. Thus the effect of large heads is to leave in the solution more ions and more simple molecules even if formation of ionic micelle is somewhat favored. Hence the lowering of freezing point or any other expression of *g* is measurably increased, the original genuine Hammarsten effect. This would explain the series of thymonucleates and the series of Congo reds.

The same principle or genuine Hammarsten effect also serves for the first time to explain many phenomena known to soap boilers who blend their raw materials to yield soaps of definite physical properties.[6] It also explains why hydrogen soaps

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(1) J. W. McBain and R. C. Williams, THIS JOURNAL, **55**, 2256 (1933).

(2) Van Rysselberghe's use of the term which he defines as observing a value of van't Hoff's *i* of the order of 1 or less, was in fact the basis of the older work on dyes and soaps and the reason for recognizing the existence of colloidal electrolytes and their most characteristic feature, the ionic micelle. His suggestion [*J. Phys. Chem.*, **38**, 645 (1934)] that the ionic micelle may be treated as an ordinary polyvalent ion was based upon lack of data for other measurements and appears to be invalidated by the data referred to in the previous parts of this series. Similarly, F. G. Donnan's new definition "that the value of *g* may be affected by the action of the Coulomb field of the G^+ ions on the Cl^- ions, or by a variety of actions (Hammarsten effect)" likewise appears to be invalidated by its postulation of significant interionic attraction at great distances apart of ions.

(3) K. Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **16**, 1 (1926).

(4) E. and H. Hammarsten, *Arch. Kemi. Geol. og. Mineralogi. Medd. Kngl. Vetensk. Akad.*, **8**, No. 27 (1913); E. Hammarsten, *Biochem. Z.*, **144**, 383 (1924); H. Hammarsten, *ibid.*, **147**, 481 (1924).

(5) E. Jorpes and G. Hillgrew, *Biochem. Z.*, **145**, 57 (1925).

(6) Compare J. L. Bowen and R. Thomas, *Trans. Faraday Soc.*, **31**, 172 (1935).

are more colloidal than those of sodium and potassium.

Following Pauli and his collaborators,[7] McBain and Williams,[1] and Adair and Adair[8] conferred the name "Hammarsten effect" upon the divergence observed where the total freezing point lowering or osmotic coefficient g, is far less than that necessary to account for the hydrogen ion alone as measured by e. m. f. The only example was that of thymonucleic acid itself, not its salts, studied by E. Hammarsten in 1924.[4] Now, with four sulfonic acids, we have five examples altogether.[9] Linderstrøm-Lang's explanation[3] has been shown to be untenable. We shall now suggest a general explanation.

The Activity Coefficients of Individual Ions.—Guggenheim convincingly emphasized that activity coefficients of single ions had no meaning, since in measurements of activity hitherto the results had been a function of both ions, not separated from each other. However, this is not to say that the ions do not exist and do not each contribute a partial molal free energy, but merely that the individual activity coefficients had not been experimentally isolated.

Guggenheim himself, however, has defined an activity coefficient of hydrogen ion f_{H^+} which is arbitrarily set equal to $f_{\pm}$ or f_{HCl} the mean activity coefficient of the salt, and in which the definition is used only for dilute solutions. This is a different convention from that of MacInnes and Scatchard, who set f_{K^+} equal to f_{Cl^-} and equal to $f_{\pm}$ or f_{KCl}.

We will now show that if the experimental data here presented are valid they lead to a more definite evaluation of f_{H^+} which is not a mere arbitrary convention but which is fixed by the data themselves.

This is a direct result and explanation of McBain and Pauli's "Hammarsten effect," which otherwise has recently been referred to as "an affront to the second law of thermodynamics." This so-called Hammarsten effect is that hydrogen-ion concentration measured by e. m. f. with a liquid junction salt bridge appears far greater than as measured by freezing point or osmotic pressure.

The reason is, as was shown in deriving Figs. 1 and 2, that the conventional assumption was made that f_{H^+} equals f_{HCl} in these more concentrated solutions. Since added hydrochloric acid affects e. m. f. and freezing point of these solutions by approximately the same amount as it does in water, it was, and is, approximately correct to identify the concentration of hydrogen ion of a sulfonic acid solution with that of a solution of hydrochloric acid giving the same e. m. f. However, as regards freezing point lowering, although f_{H^+} may be taken as approximately the same for both cases, the freezing point lowering was quite arbitrarily ascribed equally to hydrogen and chlorine ions. That is, it was assumed that f_{H^+} equals f_{Cl^-} and this resulted in finding that the concentration of hydrogen ion so arrived at was only 60% of that corresponding to the e. m. f. data.

To reconcile freezing point with e. m. f. and explain away such "Hammarsten effect," it is only necessary to assume that f_{H^+} is only about one-half f_{Cl^-} and that the freezing point lowering of these more concentrated solutions is therefore more largely due to the chlorine ion than to the hydrogen ion. This brings up the values for hydrogen-ion concentration derived from freezing point to approximate equality to those from e. m. f. for the latter remain unchanged.

It is evident that this new approach toward measuring the activity coefficient of a single ion lends itself to further experimental test, since all data with single electrodes must conform if they are real. It is also evident that no information is obtainable from cells without liquid junctions because they measure, like freezing point in ordinary solutions, the geometric mean of both ions or the stoichiometric activity coefficient of the salt itself.

It is not without interest that in the preceding section devoted to e. m. f. it was shown that the existing data for e. m. f. of 1 N hydrochloric acid differ by no less than 10 millivolts from the value predicted on the assumption that $f_{H^+} = f_{HCl}$. This would corroborate the conclusion thus reached that $f_{H^+} < f_{HCl} < f_{Cl^-}$.

Constitution Diagram.—The constitution diagrams of these solutions resemble those of the soaps such as published by Miss Norris[10] for cetyl sulfonic acid, or more closely that of potas-

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[7] W. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929, p. 258; *Kolloid-Z.*, **48**, 1 (1929); **57**, 312 (1931); **62**, 162 (1933); **66**, 312 (1934).

[8] G. S. Adair and M. E. Adair, *Trans. Faraday Soc.*, **31**, 131 (1935).

[9] Possibly also gum arabic should be added to the list (D. R. Buggs, "Symposium on Quantitative Biology," Cold Springs Harbor, **1**, 152 (1933); *J. Phys. Chem.*, **38**, 873 (1934); Thomas and Murray, *ibid.*, **32**, 676 (1928); H. B. Oakley, *Trans. Faraday Soc.*, **31**, 146 (1935).

[10] M. H. Norris, *J. Chem. Soc.*, **121**, 2161 (1922).

sium oleate at 18,[11] except that in previous diagrams boundaries should be raised by a few per cent. to allow for interionic attraction and 100% dissociation of hydrochloric acid. The middle line of the diagram is given from e. m. f. and conductivity data of Figs. 1, 2 and 3. Most of the transition between simple crystalloidal and colloidal electrolytes takes place between 0.05 and 0.15 *N* for undecyl and lauryl sulfonic acids and in still more dilute solution in myristyl sulfonic acid. Above 0.1 or 0.2 *N* there can be but little else than colloid and hydrogen ions. The concentration of ionic micelles will be equal to that of the hydrogen ion, the remaining sulfonic acid forming neutral micelles.

Summary

Hydrogen-ion concentration deduced from conductivity, freezing point lowering, and electromotive force for solutions of simple sulfonic acids above 0.1 *N* are compared.

Conductivity and e. m. f. (single electrode) agree in showing that the dissociation of the colloidal electrolyte is about 50%.

If the data for thymonucleic acid and for undecyl, lauryl, myristyl, and cetyl sulfonic acids are valid, it is shown that the activity coefficients of single ions may be measured. For example, in more concentrated solutions of hydrochloric acid, the activity coefficient of the hydrogen ion appears to be about half that of the chlorine ion and $f_{H^+} < f_{HCl} < f_{Cl^-}$ where $f_{H^+} f_{Cl^-} = f_{HCl}$.

A new explanation of the genuine Hammarsten effect is given, based upon steric hindrance to close packing.

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[11] J. W. McBain and R. C. Bowden, *J. Chem. Soc.*, **123**, 2427 (1923).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Nitroso Compounds. III. Reactions of Organo-metallic Compounds with Alpha Halo Nitroso Compounds[1]

BY JOHN G. ASTON AND DAVID F. MENARD

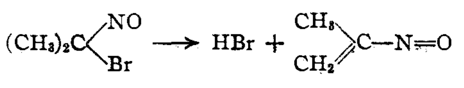
Introduction

This investigation originated in an attempt to obtain true nitroso hydrocarbons by the action of zinc alkyl on compounds of the type $CR_1R_2Br(NO)$ in a way similar to that by which Bewad had obtained nitro compounds from their alpha bromo derivatives.[2]

Although this attempt failed, certain reactions involving the nitroso group were observed which were interesting from the standpoint of possible analogies between true nitroso compounds and aldehydes or ketones.

Splitting Out of the Hydrogen Halide

When 2,2-bromonitrosopropane was treated with anhydrous ammonia, only ammonium bromide resulted along with acetoxime. To explain this splitting out of hydrobromic acid the first step in the reaction may be tentatively written

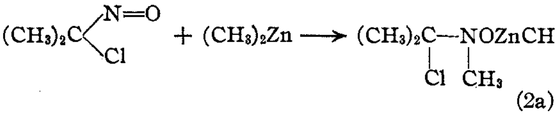


$$(CH_3)_2C{<}^{NO}_{Br} \longrightarrow HBr + {}^{CH_3}_{CH_2}{>}C{-}N{=}O \quad (1)$$

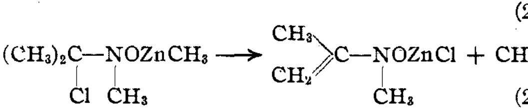
inasmuch as the unsaturated nitroso compound might well react to give acetoxime. It is not surprising therefore that the alpha halo nitroso compounds with dimethylzinc yield methane almost quantitatively by inducing the splitting out of hydrogen bromide and then reacting with it.

Reaction with Zinc Alkyls

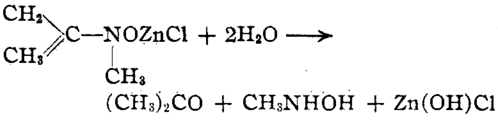
In the reaction of one mole of dimethylzinc and one mole of 2-chloro-2-nitrosopropane, one mole of methane is evolved per mole of chloronitroso compound. In the products of hydrolysis of the solid addition product methylhydroxylamine, acetone and acetoxime were observed. The first two arise from addition. The net reaction may be written



$$(CH_3)_2C{<}^{N=O}_{Cl} + (CH_3)_2Zn \longrightarrow (CH_3)_2\underset{Cl}{C}{-}\underset{CH_3}{N}OZnCH_3 \quad (2a)$$



$$(CH_3)_2\underset{Cl}{C}{-}\underset{CH_3}{N}OZnCH_3 \longrightarrow {}^{CH_3}_{CH_2}{>}C{-}\underset{CH_3}{N}OZnCl + CH_4 \quad (2b)$$



$${}^{CH_2}_{CH_3}{>}C{-}\underset{CH_3}{N}OZnCl + 2H_2O \longrightarrow (CH_3)_2CO + CH_3NHOH + Zn(OH)Cl \quad (2c)$$

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[1] From a thesis presented by David F. Menard in partial fulfilment of the requirements for the Ph.D. degree, June, 1934.

[2] Bewad, *J. prakt. Chem.*, [2] **48**, 368 (1893).