[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Activity of 1-*n*-Dodecanesulfonic Acid in Aqueous Solutions

BY H. F. WALTON

Introduction

1-*n*-Dodecanesulfonic acid or lauryl sulfonic acid is a typical colloidal electrolyte in aqueous solution and has been studied extensively by McBain and others.[1,2,3] Osmotic and activity coefficients have been calculated from freezing point data,[1] and they show the sharp drop above a certain critical concentration which is typical of colloidal electrolytes. The aim of the present work was to determine the activity coefficient by an electromotive force method, and to study the effect of temperature and added electrolyte.

Experimental

The electromotive force of this cell was measured

$$\text{Ag-AgCl} \mid \text{HCl}(0.1M) \mid \text{glass} \mid C_{12}H_{25}SO_3H \mid Hg_2(C_{12}H_{25}SO_3)_2\text{-Hg } (+)$$

Mercurous dodecanesulfonate is sparingly soluble and with metallic mercury gives an electrode reversible to the dodecanesulfonate ion. Unfortunately the stability and reproducibility of this electrode was not all that could be desired, but it was enough for the purpose. The glass electrode on the other hand was very stable and reproducible in dodecanesulfonic acid solutions, as separate tests showed. Its asymmetry potential, which was checked before and after each run, was about a millivolt. The electromotive forces reported in this paper have been corrected to zero asymmetry potential.

The glass electrode was checked against the hydrogen electrode in the cell

$$(\text{Pt-}H_2 \text{ or Ag-AgCl-HCl-glass}) \mid C_{12}H_{25}SO_3H + HCl \mid \text{AgCl-Ag}$$

With 0.1 *M* dodecanesulfonic acid the glass electrode gave a cell e. m. f. smaller by about 2 millivolts than would correspond to the experimental hydrogen electrode e. m. f. However, the hydrogen electrode was unsteady and there is no reason to consider its potentials more authentic than those of glass. The glass electrode was preferred because of its convenience and greater stability, and also because the hydrogen stream would keep finely divided mercurous dodecanesulfonate in suspension and reduce it to mercury.

The cell was of conventional design. The mercury pool had a diameter of 3.0 cm.; the glass electrode was Leeds and Northrup Std. 1199, with bulb diameter about 22 mm. The silver-silver chloride electrode was made by silver plating a coil of 22-gage platinum wire and chloridizing anodically. The volume of solution in the cell was about 25 ml. The different concentrations needed were obtained by starting with the highest concentration, then diluting by withdrawing 12.5 ml. and adding 12.5 ml. of redistilled water. Withdrawals and additions were made with specially calibrated pipets. Each sample withdrawn was centrifuged to remove suspended mercurous salt and titrated with sodium hydroxide. It was difficult to start with exactly 25 ml. in the cell, but by titrating three or more consecutive samples a dilution factor was established which could be used to calculate the concentrations after successive dilutions had made the solutions too dilute for titration.

Since the mercury electrode was rather slow in coming to equilibrium, each solution had to stand for some time (usually an hour or more) before a final e. m. f. reading could be taken. Standing also allowed most of the suspended mercurous dodecanesulfonate to settle out before performing the next dilution. The electromotive force was read to 0.1 millivolt, using a Leeds and Northrup student potentiometer, direct current amplifier (L. & N. No. 7673) and type P galvanometer. The temperature was controlled manually to ±0.2°, variations of this magnitude not being enough to affect the results.

Materials

1-*n*-Dodecanesulfonic Acid.—Lauryl bromide (Eastman Kodak Co) was redistilled (b. p. 145° at 24 mm.) and converted to sodium dodecanesulfonate by heating with sodium sulfite and water under pressure at 200° for ten hours.[4,4a] The purified sodium salt was dissolved in hot water and lead acetate added to precipitate the lead salt. From the lead salt pure dodecanesulfonic acid monohydrate was made by the procedure of Noller and Gordon.[4b] The product melted at 32–33.5° and was 98.5% pure by titration. (On long standing over phosphorus pentoxide the monohydrate lost water and became apparently 105% pure.)

Mercurous Dodecanesulfonate.—This was prepared in two ways; firstly, by electrolyzing a solution of dodecanesulfonic acid (about 0.05 *M*) in the experimental cell, with the mercury as anode and a platinum foil cathode and a current of 20 milliamperes; secondly, from mercurous nitrate solution and a slight excess of dodecanesulfonic acid solution, followed by thorough washing of the precipitate. The results obtained with the two preparations were indistinguishable.

Mercury and **potassium nitrate** were C. P. products, the former redistilled.

Results and Discussion

The electromotive force data are shown graphically in Fig. 1. The ordinates are $E + 4.606\ RT/F \log m = E^0 - 4.606\ RT/F \log \gamma_\pm$, where E = electromotive force, m = molality, $\gamma_\pm$ = molal activity coefficient. The abscissa are $\sqrt{m}$. The points for low concentrations are extrapolated to $m = 0$ by the Debye–Hückel limiting law. Lack of reproducibility, as already explained, is to be blamed on the mercury electrode rather than the glass.

In Fig. 2, activity coefficients are shown, these being calculated from the interpolation curves of E. The values of McBain[2] found from freezing point depression are included for comparison. These data and the electromotive force data for 0° do not agree. The discrepancy of about 0.2 in log $\gamma_\pm$ is outside experimental error, which

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(1) McBain and Betz, THIS JOURNAL, **57**, 1905, 1909, 1913, 1916 (1935).

(2) M. E. L. McBain, Dye and Johnston, *ibid.*, **61**, 3210 (1939).

(3) M. E. L. McBain, *J. Phys. Chem.*, **47**, 196 (1943).

(4) Tartar and Wright, THIS JOURNAL, **61**, 539 (1939).

(4a) Acknowledgment is made to A. S. Wexler and J. M. Longfellow for performing this preparation.

(4b) Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

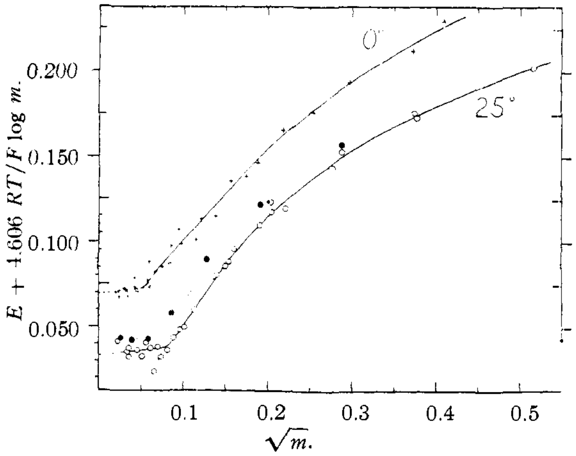

Fig. 1.—Electromotive force data: crosses, 0°; open circles, 25°; filled circles, with 0.020*m* potassium nitrate at 25°. Ordinate figures apply to data at 25°; points for 0° have been displaced upward by 0.025 volt.

would have to be 20 millivolts in e. m. f., or 0.02 to 0.03° in freezing point in the dilute range, to reconcile the two sets of data. Solubilization of mercurous dodecanesulfonate, which might have caused uncertainty, was found to be undetectably small.

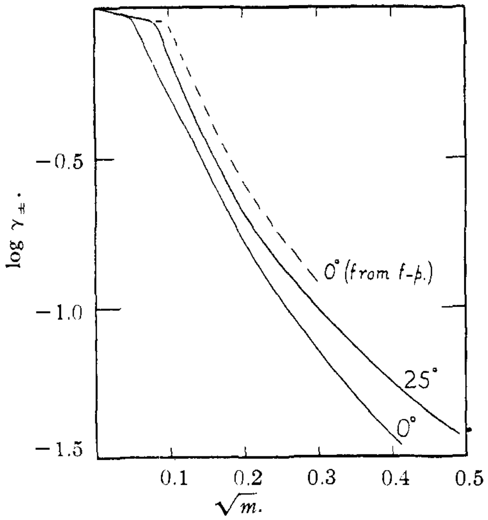

Fig. 2.—Activity coefficient of dodecanesulfonic acid: full curves, results of this paper; broken curve, calculated from freezing point measurements of McBain, Dye and Johnston, THIS JOURNAL, **61**, 3210 (1939).

The effect of temperature on activity coefficient in the colloidal region seems to be that log γ is raised by about 0.1 for the 25° rise studied. Using the equation[5]

$$\bar{L}_2 = -2 \times 2.303RT^2(\partial \log \gamma/\partial T)_m$$

$\bar{L}_2$, the relative partial molal heat content of dodecanesulfonic acid, is −3000 calories. This is probably of the same order of magnitude as the heat of association of individual molecules of the acid to form the micelle. This heat of association had been estimated as −7700 calories by Meyer and van der Wyk,[6] who, however, disregarded electrolytic dissociation in their estimate. The effect of temperature on the critical concentration for micelle formation (which is 0.003*M* at 0°, 0.0064*M* at 25°) is quite large, larger in proportion than that found by Wright and Tartar[7] for sodium dodecanesulfonate between 40 and 60°. Moreover, it is entirely different from the effect found by Brady[8] in conductivity measurements with dodecanesulfonic acid solutions; these measurements show critical concentrations of 0.010 *M* at 0° and 0.0072 *M* at 25°.

The addition of potassium nitrate promotes micelle formation as would be expected, since the increase of ionic strength would shift to the right an equilibrium of the type

$$\overline{nX^-} \rightleftarrows X_n^{-n}$$

The effect of 0.02 *M* potassium nitrate in reducing the critical concentration for micelle formation at 25° from 0.0064 to 0.0042 *M* suggests that the micelles first formed have a high charge, certainly greater than 2. This is also shown by the effect of high frequencies[9] and high field strengths[10] on the conductance of solutions of colloidal electrolytes. The number of ions uniting must in any case be large to make the drop in activity and conductance as sharp as it is. An exact calculation of the charge on the micelle from the effect of ionic strength on activity would be difficult, as we do not know how these small, highly charged micelles with widely separated charges would be affected by ionic strength.

The electromotive force values for the higher concentrations of dodecanesulfonic acid with potassium nitrate present have little quantitative significance, as the potassium ions are displacing hydrogen ions from the micelle. This was shown by tests to be described separately.

The graphs in Fig. 1 show the standard potentials of the mercury–mercurous dodecanesulfonate electrode against the glass electrode system chosen. Referred to the standard hydrogen electrode, the system $2Hg + 2C_{12}H_{25}SO_3^- \rightarrow Hg_2(C_{12}H_{25}SO_3)_2^- + 2e$ would have $(E^0)_H$ = 0.386 volt at 25°, 0.399 volt at 0°. Taking $(E^0)_H$ = 0.799 volt at 25° for 2Hg *M* Hg_2^{++} + 2e, the solubility product for mercurous dodecanesulfonate, $a_{Hg^{++}}\, a^2_{C_{12}H_{25}SO_3^-}$, is calculated to be 1×10^{-14} at 25°.

Summary

Electromotive force measurements are reported from which the activity of 1-*n*-dodecanesulfonic

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[5] Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 48.

[6] Meyer and van der Wyk, *Helv. Chim. Acta*, **20**, 1321 (1937).

[7] Wright and Tartar, THIS JOURNAL, **61**, 544, 549 (1939).

[8] Brady, Thesis, Stanford University, 1944. The writer is indebted to Professor J. W. McBain for bringing this work to his attention.

[9] Schmid and Larsen, *Z. Elektrochem.*, **44**, 651 (1938).

[10] Malsch and Hartley, *Z. physik. Chem.*, **A170**, 321 (1934).

acid in aqueous solutions has been calculated. Measurements have been made at 0 and 25° and in the presence of added potassium nitrate. Decrease of temperature and increase of ionic strength are seen to promote micelle formation. The activities found at 0° do not agree with previous determinations from freezing point depression. The solubility product of mercurous dodecanesulfonate at 25° is reported.

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The Activity of Hydrochloric Acid in Solutions of 1-*n*-Dodecanesulfonic Acid

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Introduction.—The original aim of this work was to investigate the so-called "Hammarsten effect" in solutions of long chain sulfonic acids, which is that electrometric *p*H measurements indicate a hydrogen ion activity which is greater than the maximum expected from freezing point measurements. Thus in a 0.108 molal solution of 1-*n*-dodecanesulfonic acid, McBain and Betz[1] found the hydrogen ion activity to be 0.0537 at 25°, and somewhat greater than this at 0°, by measuring the e. m. f. of the cell

$$\mathrm{Pt, H_2|C_{12}H_{25}SO_3H|KCl\ (3.5\mathit{M})|KCl\ (0.1\ \mathit{M})|Hg_2Cl_2, Hg}$$

The freezing point of 0.108 molal sulfonic acid was −0.060°, which would indicate a maximum hydrogen ion activity of 0.060/1.86 = 0.032, only two-thirds of that found potentiometrically. With solutions of hexadecanesulfonic acid the discrepancy is even greater.[2]

Estimates of single ion activities necessarily involve assumptions. In the work mentioned, the liquid junction potentials were assumed to be negligible. It seemed desirable, therefore, to try to estimate the hydrogen ion activity by a method which did not involve liquid junction potentials. The method chosen was to measure the activity of hydrochloric acid in dodecanesulfonic acid solutions containing a small proportion of added hydrochloric acid.

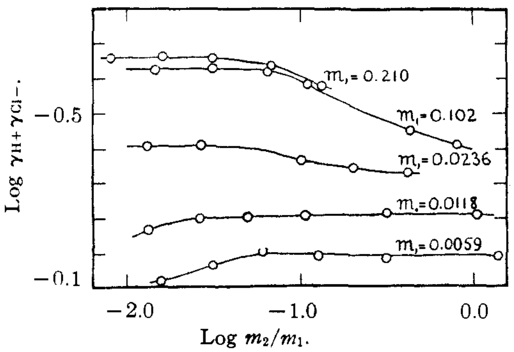

Fig. 1.—Activity coefficient product of hydrochloric acid in solutions of dodecanesulfonic acid of the constant molalities shown: m_1 = molality of sulfonic acid; m_2 = molality of hydrochloric acid.

Experimental

The electromotive force was measured of the cell

$$\mathrm{Ag\text{-}AgCl|HCl\ (0.1\ \mathit{M})|glass|C_{12}H_{25}SO_3H\ (\mathit{m}_1) + HCl(\mathit{m}_2)|AgCl\text{-}Ag}$$

The type of electrodes used, the electrical equipment, and the method of preparing the dodecanesulfonic acid were described in the preceding paper. The temperature was 25 ± 0.2°. Before and after every run the glass electrode–silver chloride electrode system was calibrated with hydrochloric acid solutions, and a graph plotted of log $a_{H^+}a_{Cl^-}$ against e. m. f. from which values of log $a_{H^+}a_{Cl^-}$ for the dodecanesulfonic acid solutions were read off. Although silver dodecanesulfonate is sparingly soluble, it is far more soluble than silver chloride, and the silver–silver chloride electrode was reversible to chloride ion.

Experiments were first made in which m_1, the molality of the sulfonic acid, was kept constant and m_2, the molality of hydrochloric acid, increased by successive small additions of standard acid from a capillary buret. Except at the lowest sulfonic acid concentrations, the molal stoichiometric activity coefficient product, $\gamma_{H^+}\gamma_{Cl^-}$, was independent of m_2 so long as m_2/m_1 was less than 0.1. The dependence of $\gamma_{H^+}\gamma_{Cl^-}$ on m_2/m_1 is shown in Fig. 1. The limiting values of $\gamma_{H^+}\gamma_{Cl^-}$ are plotted as a function of m_1 in Fig. 2.

A series of experiments was next made in which m_1 and m_2 were constant and a neutral salt was added a little at a time. With all but the most dilute solution the effect of the salt was to lower the e. m. f., as shown in Fig. 3. This corresponds to an increase of hydrochloric acid activity.

In a few preliminary tests a solution of sulfonic acid which contained alcohol was used. These tests gave values for $\gamma_{H^+}\gamma_{Cl^-}$ which were all higher than those in the absence of alcohol, which is not surprising, since alcohol is known to inhibit micelle formation.

Attempts were also made to use indicators to estimate the hydrogen ion activity of dodecanesulfonic acid solutions but, as was expected, preferential solubilization of one form of the indicator (the undissociated acid) by the micelles was so marked that the indicators tried were of no use whatever in estimating the *p*H. For example,

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[1] McBain and Betz, THIS JOURNAL, **57**, 1909, 1913 (1935).

[2] McBain and Williams, *ibid.*, **55**, 2250 (1933).