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.

EVANSTON, ILL. RECEIVED JANUARY 8, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

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

BY H. F. WALTON

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.

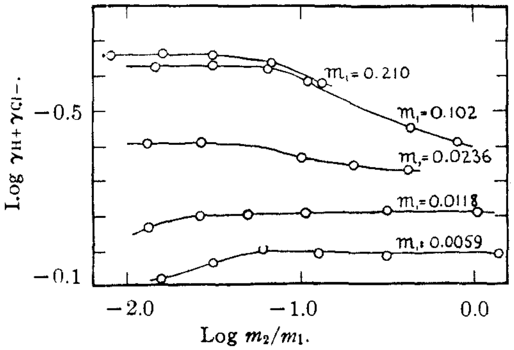

Fig. 1.—Activity coefficient product of hydrochloric acid in solutions of dodecanesulfonic acid of the constant molalities shown: m_1 = molality of sulfonic acid; m_2 = molality of hydrochloric acid.

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).

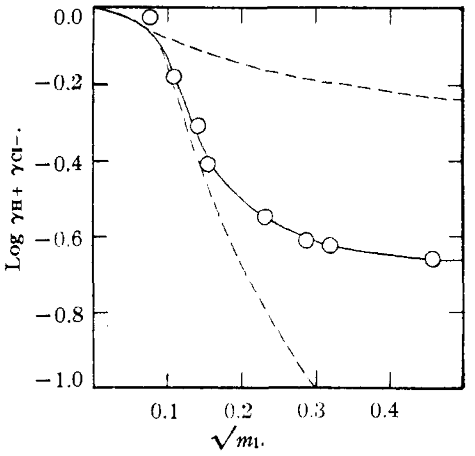

Fig. 2.—Limiting activity coefficient product of hydrochloric acid as a function of dodecanesulfonic acid concentration; temperature, 25°; upper broken curve, log $\gamma_{H^+}\gamma_{Cl^-}$ for pure HCl (Harned); lower broken curve, log $\gamma_\pm$ for dodecanesulfonic acid (preceding paper.)

thymol blue (pK = 1.65) in 0.0186 *M* sulfonic acid gave a redder color than it did in 2 *M* hydrochloric acid, though the true *p*H was about 2.

Discussion

(i) **The Hydrogen Ion Activity.**—From the limiting values of $\gamma_{H^+}\gamma_{Cl^-}$ we can estimate γ_{H^+} if we can assume values for γ_{Cl^-}. McBain[3] suggests that activity coefficients of free, non-associated ions are about the same in solutions of dodecanesulfonic acid as in hydrochloric acid solutions of equal molality; if we further suppose that γ_{Cl^-} in these solutions is equal to $\gamma_\pm$ for an equimolal solution of hydrochloric acid, we derive the values of log γ_{Cl^-} and a_{H^+} given in columns 3 and 4 of Table I. These are lower than the a_{H^+} values of McBain and Betz, and in better agreement with the freezing point depressions. The liquid junction potential that would be necessary in the cell of McBain and Betz to reconcile the two estimates of the hydrogen ion activity are given in the sixth column.

TABLE I

ESTIMATES OF HYDROGEN ION ACTIVITY IN DODECANESULFONIC ACID

Molality, m_1	This work log $\gamma_H\gamma_{Cl}$	log γ_{Cl^-}	a_{H^+}	McBain and Betz[1] a_{H^+}	Liquid junction potential, volt
0.020	−0.310	−0.005	0.0111	0.0108	+0.001
.083	− .610	− .092	.0252	.0374	− .010
.200	− .660	− .116	.0585	.0931	− .012

(ii) **The Ratio** $\gamma_{Cl^-}/\gamma_{C_{12}H_{25}SO_3^-}$.—This ratio of activity coefficients can be evaluated without any assumptions from the activity coefficients of hydrochloric acid reported in this paper and from the activity coefficients of dodecanesulfonic acid itself, and is of interest for the picture it gives of the association of the sulfonate anion. Taking the values of $\gamma_{C_{12}H_{25}SO_3H}$ at 25° reported in the preceding paper, and plotted as the lower broken curve in Fig. 2 of this paper, one finds that above m = 0.07, $\gamma_{Cl^-}/\gamma_{C_{12}H_{25}SO_3^-} = 2400m^{1.9}$ Unless the activity coefficient of the chloride ion is rising rapidly with concentration in this range, which is unlikely, this means that the activity of the dodecanesulfonate ion is actually decreasing as the concentration rises. This agrees with a suggestion made by Murray[4] to account for the anomalous rise in surface tension of colloidal electrolyte solutions with concentration and also for certain solubility effects.

(iii) **The Effect of Salts on** γ_{HCl}.—The addition of a salt to a solution increases its ionic strength, so if potassium nitrate is added to a solution of dodecanesulfonic acid containing hydrochloric acid, the activity of the hydrochloric acid should be decreased. Instead, it is increased quite considerably, as is seen from Fig. 3. A decrease in cell e. m. f. corresponds to an increase in activity of hydrochloric acid. The simplest way to account for this increase is to suppose that the alkali metal cations displace hydrogen ions from the micelles. At m = 0.0064, there are no micelles present before addition of salt, and so the salt has its expected effect of lowering the activity of hydrochloric acid because of the increase of ionic strength.

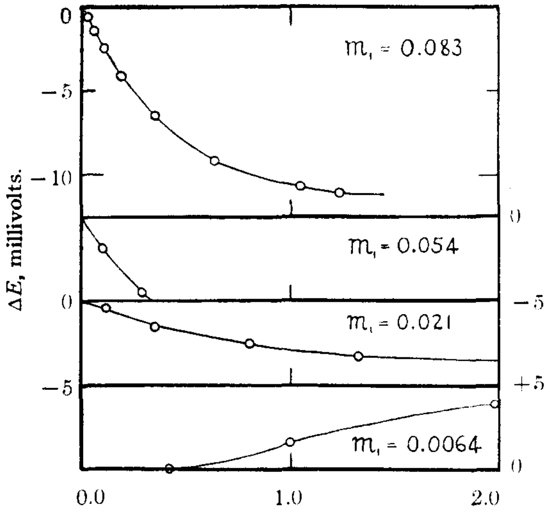

Fig. 3.—Displacement of hydrogen ions by added salt; e. m. f. increase *versus* ratio of salt to sulfonic acid. Salts used are 0.083*m* KNO_3 and $CsNO_3$ (points shown for $CsNO_3$); 0.054 and 0.0064*m* $NaClO_4$; 0.021*m* KNO_3.

Accepting this explanation of the effect, we can calculate approximately the proportion of hydrogen ions bound in the micelle and displaced by added salt. Excess of potassium or cesium

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[3] McBain in Alexander, "Colloid Chemistry," Vol. 5, Reinhold Publishing Corp., New York, N. Y., 1944, p. 115; see also ref. 1.

[4] Murray, *Trans. Faraday Soc.*, **31**, 206 (1935); Murray and Hartley, *ibid.*, **183**.

nitrate added to 0.083 *m* dodecanesulfonic acid which was also 0.0035 *m* in hydrochloric acid caused a drop in e m. f. of 11.2 millivolts (Fig. 3, upper curve), corresponding to an increase in log $\gamma_{H^+}\gamma_{Cl^-}$ of 11.2/59.1 = 0.190. Neglecting, as a first approximation, the increase of ionic strength caused by the salt addition, and ascribing this increase simply to the displacement of hydrogen ions from the micelles, the concentration of free hydrogen ions has been multiplied by (antilog 0.190) or 1.55. If, after adding excess of salt, the concentration of free hydrogen ions is equal to the stoichiometric concentration, which is 0.087 *m*, the concentration of free hydrogen ions before adding the salt was 0.087/1.55 = 0.056 *m*. The proportion of hydrogen ions of the sulfonic acid which are bound in the micelle is (0.087 − 0.056)/0.083, or 37%.

This is a lower limit to the proportion of bound hydrogen ions, since no account was taken of the increase of ionic strength caused by salt addition. It is consistent with the upper limit estimates of 50% from e. m. f., and 70% from freezing point, made by McBain and Betz.[1]

It is noteworthy that hydrogen ions seem to be displacable from the micelles over the whole concentration range studied. This gives no evidence either for or against the view of McBain[5] that there are two or more kinds of micelle whose proportions change with concentration.

Acknowledgment.—This investigation was supported by a grant from the Abbott Fund of Northwestern University. The assistance of Lyle Powell and Evelyn Sholtes is gratefully acknowledged.

Summary

1. The activity coefficient of hydrochloric acid in solutions of 1-*n*-dodecanesulfonic acid has been measured by an electromotive force method. The activity coefficient–concentration curve is of the form characteristic of colloidal electrolytes.

2. The ratio of activity coefficients of chloride ion and dodecanesulfonate ion in these solutions has been evaluated.

3. Addition of neutral salt causes an increase in the activity of hydrochloric acid. This is interpreted as a displacement of hydrogen ions from the colloidal micelles and, from the magnitude of the effect, a lower limit of 37% for the proportion of bound hydrogen ions in 0.083 *m* sulfonic acid is estimated.

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[5] McBain, Laing and Titley, *J. Chem. Soc.*, **115**, 1279 (1919), also ref. 3.

EVANSTON, ILL. RECEIVED JANUARY 8, 1946

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Absorption Spectra of Some Para Substituted Aniline Derivatives. The Presence of *x'* Bands

BY W. D. KUMLER

Lewis and Calvin[1] and Lewis and Bigeleisen[2] have given evidence for the existence of second order *x* bands in carotinoids, polyenes and several types of dyes. These second order *x* bands have been designated *x'* bands and result from an electronic oscillation along the long axis of the molecule but are an "octave" higher than the main *x* band. The compounds in which such bands have been found absorb mainly in the visible and are symmetrical or nearly so.

In this communication evidence is presented for the existence of *x'* bands in a series of highly unsymmetrical compounds all but two of which absorb mainly or entirely in the ultraviolet. All of these compounds are of the type  in which A is an electron donating group and B is an electron attracting group. The A group in the series is amino or alkyl substituted amino and the B group is nitroso, nitro, aldehyde, acetyl, carboxyl and sulfonamide.

Evidence for *x'* Bands.—Two criteria for *x'* bands have been set up by Lewis and co-workers[1,2] by noting the characteristics of an oscillator of varying anharmonicity. One criterion is that the ratio of the frequencies of the short to the long wave length band $\bar{\nu}'/\bar{\nu}$ should be less than two and increase in a series of compounds as the wave length λ increases, the other that the ratio of the extinction coefficients ϵ'/ϵ should decrease as $\bar{\nu}'/\bar{\nu}$ increases.

For a perfect harmonic oscillator $\bar{\nu}'/\bar{\nu}$ is two but ϵ'/ϵ would be zero because the probability of the 0–2 jump is zero. As the anharmonicity increases $\bar{\nu}'/\bar{\nu}$ would decrease from two and ϵ'/ϵ increase from 0. The relative anharmonicity depends on the amplitude of the electronic oscillations relative to the dimensions of the molecule. The amplitude depends on the polarizability and the latter is greater for those compounds whose bands come at long wave length. Hence $\bar{\nu}'/\bar{\nu}$ should decrease and ϵ'/ϵ increase as we go down a series of compounds arranged in descending order of λ.

The spectra of the eighteen compounds studied are given in Figs. 1–6. In spite of the fact that the compounds contain B groups that have quite different chemical properties, the spectra of all these compounds are very similar, being characterized by two bands, a long wave length band of

[1] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[2] Lewis and Bigeleisen, THIS JOURNAL, **65**, 2107 (1943).