[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Determination of the Degree of Dissociation of Micelles of 1-*n*-Dodecanesulfonic Acid by Use of the Acid-catalyzed Reaction between Iodine and Acetone[1]

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Hydrogen ions in water (hydronium ions) have a rate constant in the catalyzed reaction between acetone and iodine of 5.0×10^{-5} sec.$^{-1}$ at 30°, while hydrogen ions associated with micelles of dodecanesulfonic acid have a greater rate constant of 10.0×10^{-5} sec.$^{-1}$. From results obtained on the rate of reaction in solutions of 1-*n*-dodecanesulfonic acid and similar solutions containing free hydrochloric acid an expression has been derived which allows the calculation of the ratio of hydrogen ions to sulfonate ions in the micelle. A value of 0.74 was found for this ratio which was constant above the critical concentration up to a concentration of 0.14 *M*. This value is in good agreement with values calculated from e.m.f. and freezing point data reported in the literature. Micellized dodecaneammonium chloride has no effect on the rate constant of the hydrogen ion catalyzed reaction between acetone and iodine.

A knowledge of the concentration of osmotically active single ions in solutions of colloidal electrolytes is of considerable interest in gaining a better understanding of the physico-chemical properties of these solutions. Various methods have been used to estimate the concentration of free single ions, which are present as counter ions on the surface of oppositely charged detergent micelles, or the related quantity, the "degree of dissociation of the micelle." Freezing point lowering,[2] vapor pressure lowering[3] methods, e.m.f. of cells,[4,5] conductivity data and transport numbers[6,7] and membrane potentials of ion selective membranes[8] have been used to obtain estimates of the free ion concentration. McBain and co-workers[2,5,9,10] have measured the freezing point lowering, the e.m.f. of cells, and conductivity of solutions of the straight chain paraffin sulfonic acids. These studies and the earlier ones of Reychler[11] have shown these acids to be strong acids until the critical concentration is reached, while at higher concentrations their behavior is typical of colloidal electrolytes.

McBain and Betz[5] measured the e.m.f. at 25° of cells such as

$$\mathrm{Pt,H_2} \mid \text{Dodecanesulfonic acid } (C_1) \mid \mathrm{KCl}\ (3.5\ M) \mid \mathrm{KCl}\ (0.1)\ \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}$$

and compared the e.m.f. obtained with the e.m.f. of cells in which the sulfonic acid was replaced by hydrochloric acid. Neglecting liquid junction potentials, which may be the cause of considerable uncertainty, the activity of the hydrogen ion will be the same in any two solutions which give the same e.m.f. Thus for one cell containing dodecanesulfonic acid and another containing hydrochloric acid which give the same e.m.f. the activity of the hydrogen ion in the sulfonic acid in the first cell is taken equal to the activity of the hydrogen ion in the hydrochloric acid used in the second cell. On this basis McBain and Betz calculated the degree of dissociation of dodecanesulfonic acid as a function of the concentration.

The freezing point data were interpreted by McBain[12] by comparison of the data in aqueous dodecanesulfonic acid solutions to the freezing point lowering in aqueous hydrochloric acid solutions. In solutions of dodecanesulfonic acid at concentrations which are high relative to the critical concentration the contribution to the freezing point lowering of single ions other than the hydrogen ions was neglected. Due to their large molecular weight the contribution to the freezing point lowering made by the micelles may also be neglected. On the basis of the assumption that in a hydrochloric acid solution the activity coefficient of the hydrogen ion is equal to the activity coefficient of the chloride ion, the freezing point lowering for a solution of hydrochloric acid should be twice the freezing point lowering for a solution of dodecanesulfonic acid ($\theta_{\mathrm{HCl}} = 2\theta_{\mathrm{sulfon.}}$) if the hydrogen ion concentration were the same in the two solutions. The degree of dissociation was calculated by McBain on the basis of the above assumptions.

In the concentration range 0.15 to 0.8 *M* the degree of dissociation as calculated by either method was found to be essentially constant. From the e.m.f. data this constant value of the degree of dissociation was found to be about 0.5 whereas from the freezing point lowering the degree of dissociation in this concentration range was found to be about 0.2.

The e.m.f. of a different type cell free of a liquid junction potential was measured by Walton[13] to obtain an estimate of the hydrogen ion concentration in dodecanesulfonic acid solutions

$$\mathrm{Ag.AgCl} \mid \mathrm{HCl}\ (0.1\ M) \mid \text{glass} \mid \mathrm{C_{12}H_{25}SO_3H}\ (m_1 + \mathrm{AgCl}\ (m_2) \mid \mathrm{AgCl\text{-}Ag}$$

Holding m_1 constant the value of m_2 was varied, the e.m.f. of the cell being obtained for each value of m_2. The limiting value (as m_2 approached zero) of the term $\log \gamma_{\mathrm{H^+}}\gamma_{\mathrm{Cl^-}}$, in which γ denotes activity coefficient, was obtained by extrapolation. Taking $\gamma_{\mathrm{Cl^-}}$ in these solutions as equal to $\gamma_\pm$ the value of a_+ can be calculated. These results were in better agreement with the freezing point depression

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(2) (a) J. W. McBain, E. Laing and A. F. Titley, *J. Chem. Soc.*, **115**, 1219 (1919); (b) J. W. McBain and M. Betz, THIS JOURNAL, **57**, 1909 (1935).

(3) J. W. McBain and C. S. Salmon, *ibid.*, **42**, 426 (1920).

(4) C. S. Salmon, *J. Chem. Soc.*, **117**, 530 (1920).

(5) J. W. McBain and M. Betz, THIS JOURNAL, **57**, 1913 (1935).

(6) G. S. Hartley, B. Collie and G. S. Samis, *Trans. Faraday Soc.*, **32**, 785 (1936).

(7) A. P. Brady and D. J. Salley, THIS JOURNAL, **70**, 914 (1948).

(8) C. W. Carr, W. F. Johnson and I. M. Kolthoff, *J. Phys. Chem.*, **51**, 636 (1947).

(9) J. W. McBain and M. Betz, THIS JOURNAL, **57**, 1905 (1935).

(10) J. W. McBain and R. C. Williams, *ibid.*, **55**, 2250 (1933).

(11) A. Reychler, *Kolloid-Z.*, **13**, 252 (1913).

(12) J. W. McBain, THIS JOURNAL, **57**, 1916 (1935).

(13) H. F. Walton, *ibid.*, **68**, 1182 (1946).

measurements of McBain and Betz[2] than with the e.m.f. measurements of these authors.

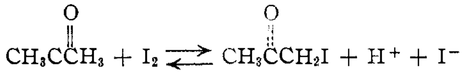
In an effort to decide which of the above methods gives the most reliable estimate of the "degree of dissociation" of the micelle solution we have determined the hydrogen ion concentration in dodecanesulfonic acid solutions by measuring the rate of an acid-catalyzed reaction between iodine and acetone. The reaction has been carefully studied by Dawson and co-workers[14–17] and by others.[18,19]

The rate of the reaction between iodine and acetone has been shown[14] to be zero order with respect to the iodine concentration and first order with respect to acetone concentration. The reaction is catalyzed by many ionic and molecular species.[16,17] In a solution of the weak acid, HA, the over-all rate of disappearance of iodine is given by

$$v = d(I_2)/dt = (\text{acetone})\{k_{H^+}(H^+) + k_A(A^-) + k_{HA}(HA) + k_{H_2O}(H_2O) + k_{OH^-}(OH^-)\} \quad (1)$$

where the various k's are the rate constants for the various species present. By using buffer solutions of varying concentration, in which the ratio of (A^-) to (HA) was kept constant Dawson and Key[17] were able to evaluate the various rate constants in equation (1) for a number of weak acids. From this work it is found that the minimum rate of reaction between iodine and acetone occurs at a pH of approximately 5 in acetate buffers.

The reaction between iodine and acetone is reversible and at high acid concentrations in the presence of appreciable iodide ion a condition of equilibrium is easily attained. The reaction liberates hydriodic acid according to the equation



$$CH_3\overset{\overset{O}{\|}}{C}CH_3 + I_2 \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}CH_2I + H^+ + I^-$$

The acid so liberated can act to make the reaction autocatalytic or at high acid concentration to bring the reaction to an equilibrium state if much iodide ion is present. These difficulties were overcome by working with very dilute iodine solutions in the presence of very small concentrations of iodide, or with no added iodide.

To determine a possible general effect of micelles on the rate of this reaction a preliminary study was made in dodecaneammonium chloride solutions. No hydrogen ions are associated with this cationic type of micelle. The micelles of this detergent solubilize iodine and possibly also acetone. Therefore, it was necessary to know whether this type of micelle affects the rate of the catalyzed reaction before reliable calculations could be made from rate measurements in micellized solutions of dodecanesulfonic acid.

Materials

The dodecaneammonium chloride was prepared by neutralizing an alcoholic solution of dodecaneamine (Armour and Co. product) with concentrated hydrochloric acid and twice recrystallizing the salt from an ethyl ether–ethanol solution.

The dodecanesulfonic acid was a sample kindly supplied by the late Dr. A. W. Ralston of Armour and Co. This sample had become discolored while being dried and it was found necessary to purify it. As originally received, the dodecanesulfonic acid contained a trace of some impurity which reacted with iodine. This impurity was rendered harmless by treating an aqueous solution of the acid with bromine water. The bromine was expelled by boiling until a portion of the solution did not liberate iodine when added to a potassium iodide solution. The aqueous solution of dodecane sulfonic acid was then acidified with sulfuric acid and the dodecanesulfonic acid extracted with peroxide and aldehyde-free diethyl ether. The ethereal solution of the acid was treated with activated charcoal to remove colored impurities and after filtering off the charcoal the sulfonic acid was crystallized by cooling the solution to Dry Ice–ethanol temperature. The acid was filtered off and dried under a pressure of about 1 mm. The product obtained was a white crystalline powder. Solutions were prepared by dissolving the sulfonic acid in water and standardizing the solution by titration of samples in ethanol solution to a phenolphthalein end-point with standard sodium hydroxide solution. The acid prepared in this manner consumed a negligible amount of iodine.

The hydrochloric acid solutions used to determine the rate constant at 30° and for experiments with dodecaneammonium chloride were standardized against potassium iodate. The hydrochloric acid solutions used to determine the rate at high hydrochloric acid concentrations and in the experiments in which both hydrochloric acid and dodecanesulfonic acid were present were prepared by adding constant boiling hydrochloric acid of known concentration from a weight pipet directly to the reaction mixture before it was diluted to volume.

Merck's Analytical Reagent grade acetone was distilled through a fractionating column, the middle fraction which boiled over a one-tenth degree range being taken. This fraction was then used to prepare a sample of pure acetone by the sodium iodide method.[20] The final product was dried with anhydrous sodium carbonate and kept stored in the dark under a nitrogen atmosphere over anhydrous sodium carbonate. Standard solutions of acetone were prepared by weighing a stoppered one-hundred ml. volumetric flask which contained approximately 30 ml. of water. Approximately the desired weight of acetone was added by pipet, the flask swirled to mix the acetone and water and the flask plus solution weighed; the solution was then made up to volume.

Experimental

Analysis for Unreacted Iodine.—Analysis of samples of the reaction mixtures for unreacted iodine by titration with standard sodium thiosulfate solution was possible only for the reactions run in solutions of 1-n-dodecanesulfonic acid in the absence of added hydrochloric acid. In all other reaction mixtures, electrolytes (hydrochloric acid or salt) were present in addition to the colloidal electrolyte. When samples of these solutions were titrated with standard sodium thiosulfate solution the colloidal electrolyte precipitated. This precipitate interfered with the detection of the end-point, preventing accurate analysis of the samples for unreacted iodine. Two methods were tried for the detection of the end-point of the titration, one was the classical starch method and the other the amperometric technique with a rotating platinum wire electrode. Neither of these methods gave an accuracy of better than 10% in the presence of precipitated colloidal electrolyte.

The titration of iodine in the presence of 1-n-dodecanesulfonic acid presented no appreciable difficulties. The sample of iodine and 1-n-dodecanesulfonic acid solution was added to twice its volume of 50% ethanol which was 0.05 M in sodium acetate and 0.05 M in acetic acid and 0.1 M in potassium iodide and the mixture titrated with standard sodium thiosulfate solution, the end-point being determined amperometrically. The titration of 5.00-ml. samples of 4.99×10^{-4} M iodine which were 0.0683 M in dodecanesulfonic acid required 2.493, 2.496, 2.493, 2.498 and 2.510 ml. of 1.001×10^{-3} sodium thiosulfate solution. The average per cent. error was 0.2.

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(14) H. M. Dawson and F. Powis, *J. Chem. Soc.*, **103**, 2135 (1913); H. M. Dawson and C. K. Reiman, *ibid.*, **107**, 1426 (1915).

(15) H. M. Dawson and T. W. Crann, *ibid.*, **109**, 1262 (1916).

(16) H. M. Dawson and J. S. Carter, *ibid.*, **109**, 2282 (1926); H. M. Dawson and N. C. Dean, *ibid.*, **109**, 2872 (1926).

(17) H. M. Dawson and A. Key, *ibid*, **109**, 543 (1928).

(18) F. O. Rice and M. Kilpatrick, This Journal, **45**, 1401 (1923).

(19) F. O. Rice, C. F. Fryling and Wesolewski, *ibid.*, **46**, 2405 (1924).

(20) K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

When the reaction between iodine and acetone could not be followed by titration methods, the rate of change of the diffusion current of the iodine at a constant speed rotating platinum wire electrode was measured. These experiments were performed in reaction vessels similar to the reaction vessel shown in Fig. 1. The electrode bearing was constructed from a 5-ml. hypodermic syringe. This bearing is gas tight and thus losses of iodine from this cell due to volatization were minimized. The volume of solution used in this cell was 25 ml. If the equilibrium vapor pressure of iodine were attained in the air space above the solution, the maximum error in these experiments would be approximately 1%. The stirring paddle on the bottom of the electrode shaft served to ensure rapid mixing of the acetone solution which was added at the start of the reaction. This small paddle did not interfere with the constancy of the diffusion current. The electrode was driven at a speed of 720 r.p.m. by a synchronous electric motor through a set of reduction gears.

The electrode was maintained at a potential of +0.1 v. with respect to the saturated calomel electrode at which potential no oxygen reduction occurs. The diffusion current was measured with a calibrated galvanometer in the cell circuit. The rate of change of the diffusion current, which is proportional to the rate of disappearance of iodine, was measured by reading the galvanometer at regular time intervals. The slope of the galvanometer deflection *vs.* time curve multiplied by the proportionality constant between galvanometer deflection and iodine concentration gave the rate of disappearance of iodine.

The rate of reduction of iodine at the electrode is negligible in comparison to the rate of reaction of iodine with acetone and consequently no correction need be applied to the observed rate of disappearance of iodine for the rate of electrode reduction of iodine.

Experiments with Dodecaneammonium Chloride.—The procedure used in the experiments with dodecaneammonium chloride was as follows. A solution containing known concentrations of dodecaneammonium chloride, potassium iodide and hydrochloric acid was prepared and 25 ml. of this solution transferred by pipet to the reaction vessel which was in the 30° thermostat. Two ml. of standard potassium iodate solution was added from a calibrated pipet, the vessel stoppered, and the solution stirred by turning on the electrode for about two minutes. The reaction mixture was allowed to stand in the thermostat for about 15 minutes to attain temperature equilibrium. The electrode was again started, the stopper removed, and 2 ml. of standard acetone solutions (at 30°) was added rapidly from a pipet, the vessel stoppered, and the galvanometer deflection read at 15 second intervals.

To make use of this method it is necessary that the diffusion current be proportional to the iodine concentration under the condition of the experiment. This was easily tested for these particular solutions. To a solution containing known concentrations of potassium iodide, dodecaneammonium chloride, and hydrochloric acid, measured volumes of standard potassium iodate solution were added from a buret, the galvanometer deflection being read after each addition. For a given concentration of dodecaneammonium chloride it was found that the current was proportional to the concentration of iodine, but that a different proportionality constant was obtained with varying concentrations of the detergent. Experiments in which no dodecaneammonium chloride was present were run intermittently with the runs in which detergent was present to assure that the electrode remained unchanged. A factor D is defined as $D = (i_d)_a/(i_d)_p$, where $(i_d)_p$ is the diffusion current obtained in the presence of a given concentration of dodecaneammonium chloride and $(i_d)_a$ is the diffusion current obtained in the absence of dodecaneammonium chloride both solutions containing the same concentration of iodine. The value of D varied from 1.00 in 0.00458 M dodecaneammonium chloride to 13.4 in 0.229 M dodecaneammonium chloride. As was to be expected the diffusion current and, therefore, also the diffusion coefficient of the solubilized iodine is much smaller than that of the iodine dissolved in the water.

A reaction temperature of 30.0° was chosen since it is above the critical solution temperature of dodecaneammonium chloride.[21] No data were available for the rate constant for the iodine–acetone reaction at 30° and so preliminary investigation was made to determine this rate constant. The reaction was followed by means of the change of diffusion current with time. The data for these runs are presented in Table I.

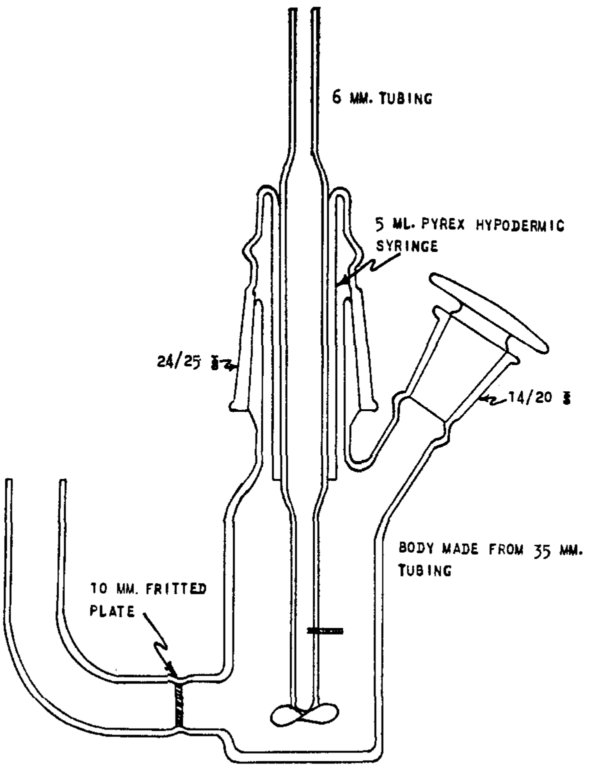

Fig. 1.—Reaction vessel.

TABLE I

RATE CONSTANT OF THE IODINE–ACETONE REACTION AT 30.00 ± 0.05° IN ABSENCE AND PRESENCE OF KCl

Concn. HCl (mole/liter)	Concn. KI (mole/liter)	Concn. acetone (mole/liter)	Analytical concn. I_2 (mole/liter)	Concn. KCl (mole/liter)	Rate constant $k \times 10^6$
0.0869	0.0895	0.242	1.36×10^{-4}	...	47.9
.00869	.0895	.242	1.36×10^{-4}	...	52.5
.0869	.0895	.242	6.80×10^{-4}	...	56.3
.0869	.0895	.242	4.08×10^{-4}	...	49.4
.00869	.00895	.242	1.36×10^{-5}	...	49.4
.00869	.000895	.0605	1.36×10^{-5}	...	49.5
.00869	.000895	.0605	1.36×10^{-5}	...	50.5
.00869	.000895	.0605	2.72×10^{-5}	...	50.3
.00869	.000895	.0605	2.72×10^{-5}	0.037	47.6
.00869	.000895	.0605	2.72×10^{-5}	.037	47.4
.00972	.00099	.0675	1.51×10^{-5}	.050	48.2

The rate constant, k, is defined by the equation $k_H = V/(H^+)(\text{acetone})$, where V is the rate of disappearance of iodine expressed in moles per liter per second. The average value of 49.9×10^{-6} mole liter^{-1} sec.$^{-1}$ for the rate constant at 30° agrees very well with the value of 50.8×10^{-6} mole liter^{-1} sec.$^{-1}$ obtained by interpolation from values given by Rice and Kilpatrick[17] at an ionic strength of about 0.1.

The concentration of hydrochloric acid is the concentration of free acid left after reaction with iodate and iodide.

The average value (49.9×10^{-6}) of the true rate constant in solutions of dodecaneammonium chloride is in good agreement with the rate constant obtained in the absence of this colloidal electrolyte. Evidently, the micelles do not affect the reaction, even though most of the iodine is solubilized.

Experiments with Dodecanesulfonic Acid.—When applying the kinetic method to solutions of dodecanesulfonic acid it is essential not to add any foreign electrolyte except acids, in order to prevent an exchange between hydrogen ion held

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[21] A. W. Ralston and C. W. Hoerr, THIS JOURNAL, **64**, 2824 (1942).

TABLE II

RATE CONSTANTS OF THE IODINE–ACETONE REACTION IN DODECANEAMMONIUM CHLORIDE SOLUTION (DDA·HCl) AT 30.00 ± 0.05°

Concn. HCl (mole/l.)	Concn. KI (mole/l.)	Concn. Acetone (mole/l.)	Anal. concn. I_2 (mole/l.) × 10^5	Concn. DDA. HCl (mole/l.)	Apparent rate const. × 10^6	Factor D^a	True rate const. KD × 10^6
0.00869	0.00895	0.0605	1.36	0.00458	49.7	1.00	49.7
.00869	.000895	.0605	1.36	.0229	8.31	6.05	50.6
.00869	.000895	.0605	1.36	.0458	7.00	7.02	50.3
.00972	.00099	.0675	1.51	.0916	5.75	8.85	50.8
.00972	.00099	.0675	1.51	.2290	3.50	13.75	48.2

[a] Ratio of iodine diffusion current in absence of DDA·HCl to diffusion current in presence of DDA·HCl.

by the micelle and foreign cations. The rate experiments in these solutions were therefore made in the absence of any potassium iodide.

The rate of disappearance of iodine in solutions of 1-*n*-dodecanesulfonic acid in the absence of added hydrochloric acid was measured by titrating after various times samples of the reaction solution. To a 50-ml. volumetric flask were added by pipet an appropriate volume of standardized dodecanesulfonic acid solution and 25 ml. of standard iodine solution and water until the volume below the mark was just slightly greater than two ml. The flask was suspended in the 30° thermostat to allow temperature equilibrium to be established. The iodine solution used contained no iodide. It was prepared by shaking resublimed iodine with water at room temperature until the solution was approximately saturated. This iodine solution was standardized immediately before use by amperometric titration with 0.001 *N* sodium thiosulfate using the rotating platinum electrode to detect the end-point. After the flask had remained in the bath for 15 min., 2.00 ml. of standard acetone solution (at 30°) was added, and water to make the solution up to volume, the flask was stoppered and shaken thoroughly and returned to the thermostat. At time intervals ranging from 6 to 15 minutes 2.00-ml. samples were removed and titrated amperometrically. The time interval was chosen so that about ten points could be obtained during a given run. The rate of disappearance of iodine in solution of dodecanesulfonic acid and acetone as a function of the concentration of the acid is given in Table III.

The rate calculated to the basis of one molar acetone concentration is given in column 4 of Table III. This gives the rate on a comparable basis since the concentration of acetone was not the same in all of the experiments. In the following we will refer to the rate calculated on the basis of one molar acetone as the rate of the reaction. The values of the rate given in column 4 of Table III are plotted *vs.* concentration of sulfonic acid in Fig. 2.

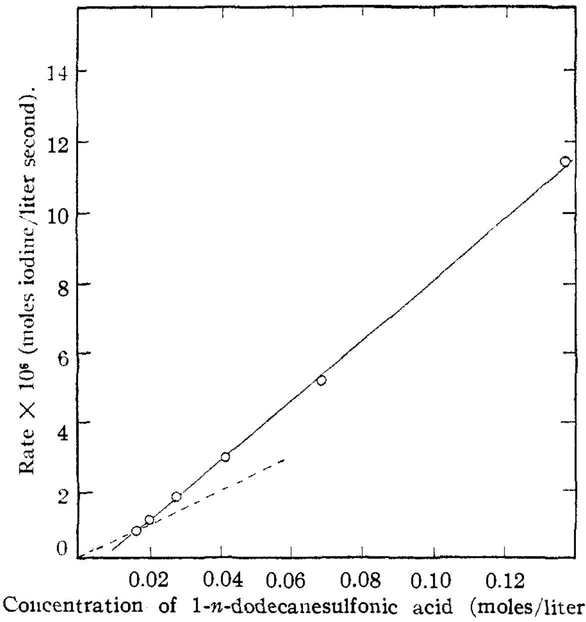

Fig. 2.—Rate of the iodine acetone reaction at 30° in solutions of 1-*n*-dodecanesulfonic acid *vs.* concentration of 1-*n*-dodecanesulfonic acid.

TABLE III

THE RATE OF REACTION FOR THE REACTION BETWEEN IODINE AND ACETONE IN AQUEOUS SOLUTIONS OF 1-*n*-DODECANESULFONIC ACID AT 30.0°

Concn. sulfonic acid (mole/liter)	Acetone concn. (moles/liter) × 10^2	V(obsd.) × 10^9 moles I_2/(liter)(sec.)	V × 10^6	(H^+)calcd.
0.0153	1.11	8.64	0.778	0.0156
.0191	1.20	14.28	1.19	.0238
.0274	1.133	20.4	1.80	.0360
.0410	1.140	33.1	2.91	.0580
.0682	1.133	58.2	5.12	.1023
.1366	1.140	130	11.4	.228
.0682[a]	1.133	45.8	4.03[a]	.0807

[a] Solution also 0.2 *M* in KCl.

A series of experiments was also run in which the concentration of dodecanesulfonic acid was kept constant but in which various large excesses of hydrochloric acid were present. To make corrections for ionic strength some experiments were made with comparable concentrations of hydrochloric acid but without dodecanesulfonic acid. The rate of the reaction was followed by measuring the change in diffusion current.

The linearity of the relation between diffusion current and iodine concentration in solutions of 1-*n*-dodecanesulfonic acid was first checked. The procedure used was similar to that used with dodecaneammonium chloride with the exception that hydrogen peroxide was used to oxidize iodide to iodine. It was found that the diffusion current was a linear function of the iodine concentration at a given sulfonic acid concentration.

The desired volume of standard sulfonic acid solution was added by volumetric pipet to a 25-ml. volumetric flask calibrated to contain and also to deliver; hydrochloric acid was then added as previously described. Finally 15.0 ml. of iodine solution (containing no potassium iodide and standardized immediately before use) was pipetted into the flask and the volume made up to 25.0 ml. All the solutions used were stored in the thermostat at 30.0°. The solution was transferred into the reaction vessel, the electrode started, and 2.00 ml. of standard acetone solution added. The initial concentration of the various compounds present was calculated assuming the volumes of the acetone solution and the acid solution were additive. The rate of disappearance of iodine in these solutions is given in Table IV.

TABLE IV

RATE OF REACTION BETWEEN IODINE AND ACETONE IN HYDROCHLORIC ACID SOLUTIONS IN THE PRESENCE AND ABSENCE OF 1-*n*-DODECANESULFONIC ACID AT 30.0°

Concn. sulfonic acid (mole/liter)	Concn. HCl (moles/liter)	Concn. acetone (moles/liter) × 10^2	Rate V (moles I_2 liter^{-1} sec.$^{-1}$) × 10^5	$V_{cor.}$ × 10^5
0.0629	1.365	2.13	9.83	7.41
.0629	0.697	2.13	5.50	4.26
.0629	0.489	2.13	3.76	2.99
.0629	0.366	1.011	3.30	2.65
.0862	1.210	2.10	9.57	7.24
.0862	1.034	2.10	8.22	6.29
.0862	0.915	2.06	7.31	5.62
.0862	0.617	2.25	5.19	4.08
.0862	0.563	2.06	4.88	3.85
.0862	0.268	2.06	2.87	2.44
None	1.514	1.011	10.90	..
None	1.312	1.011	8.87	..
None	0.592	1.011	3.99	..
None	0.477	1.011	3.23	..

Discussion

The apparent hydrogen ion concentration in dodecanesulfonic acid solutions may be calculated from the equation $H^+ = V/50 \times 10^{-6}$, where V is the rate of reaction (on the basis of one molar acetone). The value of 50×10^{-6} is the rate constant for catalysis by the hydrogen ion. The assumption is made when using this expression that the hydrogen ion is the only catalyzing species present in the solution. The values of the hydrogen ion concentration as calculated by the above formula are given in Table III. It is seen that at all concentrations of sulfonic acid the concentration of the hydrogen ions thus calculated exceeds the stoichiometric concentration of the sulfonic acid. The ratio between the calculated hydrogen ion concentration and the concentration of the acid increases as the concentration of the sulfonic acid increases. The presence of potassium chloride causes a decrease in the calculated hydrogen ion concentration which cannot be attributed to a change in ionic strength since increasing ionic strength should lead to an increase in rate of reaction and consequently to an increase in calculated hydrogen ion concentration.

The above results are easily interpreted if it is assumed that in micellized solutions of dodecanesulfonic acid in addition to the hydronium ions not associated with the micelle the hydrogen ions associated with the micelle (counter ions) exert a catalytic effect, and that the rate constant of the hydrogen ions associated with the micelles is considerably greater than that of the free hydronium ions. In agreement with this it is found that up to the critical concentration of the sulfonic acid the kinetically determined hydrogen ion concentration is equal to the total concentration of the acid. These experiments also show that the sulfonate ions do not affect the rate constant. Addition of potassium chloride (see Table II) replaces hydrogen ions on the micelle with potassium ions, consequently the rate constant should decrease, as has been found. The results can be interpreted quantitatively on the basis of the assumptions: (1) the catalytic activity of the hydrogen ions associated as counter ions on the micelle is directly proportional to the concentration of these ions, (2) the concentration of free sulfonate ions is constant in solutions which are micellized and equal numerically to the critical concentration, (3) the ratio of hydrogen ions to sulfonate ions in the micelle is constant and independent of the concentration of the sulfonic acid, (4) the hydrogen ions in the diffuse double layer behave kinetically like free hydrogen ions.

The rate of the reaction can be written as

$$V = k_{\mathrm{H}}\,[\mathrm{H}^+]_{\mathrm{s}} + k_{\mathrm{m}}[\mathrm{H}^+]_{\mathrm{m}} \qquad (2)$$

where $[\mathrm{H}^+]_{\mathrm{s}}$ is the concentration of free hydrogen ions, $[\mathrm{H}^+]_{\mathrm{m}}$ the concentration of hydrogen ions associated with the micelle, k_{H} the rate constant for free hydrogen ions, k_{m} the rate constant for the hydrogen ions on the micelle. The micelle may be represented by the formula

$$\mathrm{H}_{n}\mathrm{R}_{m}^{\,(m-n)-}\ \vdots\ \underset{\text{diffuse layer}}{(m-n)\mathrm{H}^+}$$

and a ratio, β, defined as

$$\beta = \frac{n}{m} = \frac{[\mathrm{H}^+]_{\mathrm{m}}}{C - C_0} = \text{constant} \qquad (3)$$

where C is the stoichiometric concentration of the sulfonic acid and C_0 is the critical concentration. Substituting equation (3) into equation (2) and making use of the relation

$$[\mathrm{H}^+]_{\mathrm{s}} = C - [\mathrm{H}^+]_{\mathrm{m}}$$

the rate of reaction for concentrations of sulfonic acid greater than the critical concentration is given by

$$V = k_{\mathrm{H}}C + (k_{\mathrm{m}} - k_{\mathrm{H}})\beta(C - C_0) \qquad (4)$$

The values of β and k_{m} must be evaluated to make use of this equation, but only the value of the product $(k_{\mathrm{m}} - k_{\mathrm{H}})\beta$ can be evaluated from the measurement of the reaction rate as a function of the concentration of dodecanesulfonic acid.

To obtain the values of these constants, the conditions of the experiment must be changed in such a manner as to vary one constant in a known manner while holding the other constant. Variations in β can be produced by varying the total hydrogen ion concentration in the solution while holding the total sulfonate ion concentration constant. This was done by adding various amounts of hydrochloric acid to solutions containing a constant concentration of sulfonic acid. As the concentration of hydrochloric acid is made much larger than the concentration of dodecanesulfonic acid, β should approach unity and the value of k_{m} should then be readily obtainable. The results of experiments of this type have been given in Table IV. Values for the rate of reaction corrected for the large ionic strength effect by means of the rates determined in the absence of dodecanesulfonic acid are given in the last column of Table IV.

By plotting the rate of reaction in solutions being 0.0862 *M* in dodecanesulfonic acid and containing an excess of hydrochloric acid as a function of the concentration of hydrochloric acid concentration and extrapolating to zero concentration of hydrochloric acid the rate of reaction is obtained in a 0.0862 *M* dodecanesulfonic acid solution which should be completely micellized and for which β equals unity. The large concentration of hydrochloric acid decreases the critical concentration to very low values and saturates the micelles with hydrogen ions. The rate of reaction *vs.* concentration curve is given in Fig. 3. Values of the rate which were corrected for ionic strength effect by means of the curve run in the absence of sulfonic acid are also plotted. The extrapolated value of the rate is the same for the corrected and uncorrected curves and is 0.86×10^{-5} mole liter^{-1} sec.$^{-1}$. When using the extrapolated rate to calculate the value of k_{m} we must assume that k_{m} is independent of the ionic strength. On this basis

$$k_{\mathrm{m}} = 0.86 \times 10^{-5}/0.086 = 1.00 \times 10^{-4}\ \text{sec.}^{-1}$$

The value of β may be found by differentiating equation (4) with respect to C which yields the equation

$$\mathrm{d}V/\mathrm{d}C = k_{\mathrm{H}} + (k_{\mathrm{m}} - k_{\mathrm{H}})\beta \qquad (5)$$

The value of $\mathrm{d}V/\mathrm{d}C$ is given by the slope of the line

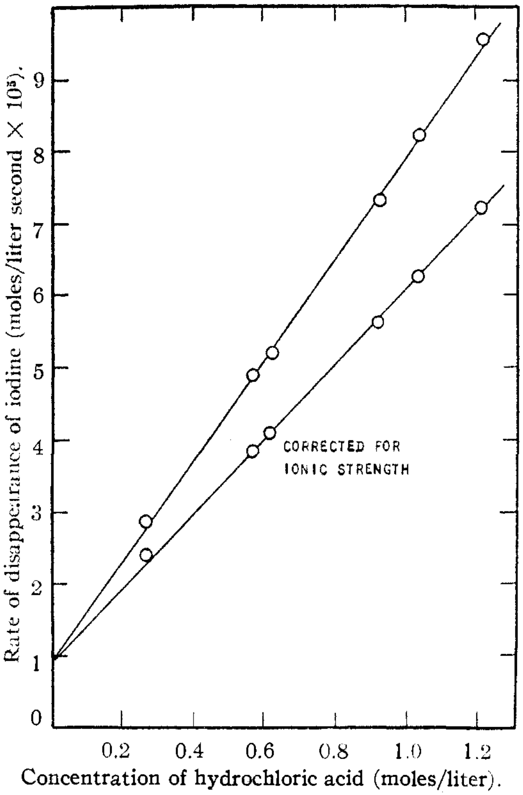

Fig. 3.—Rate of disappearance of iodine at 30.0° in 0.0862 *M* 1-*n*-dodecanesulfonic acid with various concentrations of hydrochloric acid present.

in Fig. 2, the numerical value being 8.58×10^{-5} sec^{-1}. On substituting this value for dV/dC and the value of k_m given above into equation (5) a value of 0.74 is found for β. The rate equation is then

$$V = (5.0 \times 10^{-5})C + (3.7 \times 10^{-5})(C - C_0) \quad (6)$$

The data for 0.0629 *M* dodecanesulfonic acid given in Table IV show too wide a scattering to be used for the evaluation of β. The data do confirm the result obtained in 0.0862 *M* dodecanesulfonic acid solutions in that they give a value of β lying between 0.5 and 0.7. The uncertainty in the value of β obtained in 0.0862 *M* solutions is of the order of 10%. This large uncertainty is caused by the fact that the uncertainty in β is about twice the uncertainty in k_m.

The value of β can be obtained from the freezing point depression of solutions of the sulfonic acid. Making the same assumption that was made in interpreting the kinetic data, that above the critical concentration the concentration of simple sulfonate ions remains constant and is equal to the critical concentration, and also assuming that the micelles are so large that they do not contribute to the freezing point lowering the constant, β, is given by the equation

$$\beta = 1 - \frac{1}{\lambda}\frac{d\theta}{dC}$$

where λ is the cryoscopic constant for water and $d\theta/dC$ is the slope of the freezing point lowering *vs.* concentration curve. An equation similar in nature has been given by Brady and Salley.[7] Using the freezing point data of McBain, Dye and Johnston[22] we have evaluated a constant value of β of 0.89 in the concentration range 0.01 to 0.10 *M*. From the data of McBain and Betz[2] for the freezing point lowering in more concentrated solutions we find by this method that for the concentration range 0.1 to 0.5 molal the value of β is 0.73, and for the range 0.5 to 0.9 the value of β is 0.64. As is to be expected, the latter value is in agreement with the value one obtains using the method of calculation originally suggested by McBain[12] since in this concentration range the contribution of unmicellized sulfonic acid may be neglected.

The values of a_{H^+} obtained by Walton[13] from e.m.f. measurements of cells without liquid junctions provide another method for estimating the value of β. Taking 0.007 *M* as the critical concentration,[23] β is given by the equation $\beta = [C - (a_{H^+}/H^+)]C - 0.007$; this equation is consistent with our previous assumptions. To obtain the activity coefficient of the hydrogen ions in dodecanesulfonic acid solutions, we have made the assumption that the activity coefficient of the hydrogen ion is the same in equimolar solutions of dodecanesulfonic acid and hydrochloric acid. This assumption has been used by McBain and Walton to interpret their data. Assuming that γ_{H^+} in hydrochloric acid solutions is equal to $\gamma_\pm$ we have evaluated γ_{H^+} in dodecanesulfonic acid solutions using values for the activity coefficient of hydrochloric acid solutions given by Harned and Owen.[24] The values of β calculated from the above equation are for $C = 0.020$, $\beta = 0.47$; for $C = 0.083$, $\beta = 0.68$; and for $C = 0.200$, $\beta = 0.64$.

The estimates of the ratio of bound hydrogen ions in the micelle from the e.m.f. of cells without liquid junctions, the kinetic data, and the freezing point data for solutions of a concentration greater than 0.1 molal are in good agreement, giving a value of β of about 0.7.

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[22] M. E. L. McBain, W. B. Dye and S. A. Johnston, This Journal, **61**, 3210 (1939).

[23] W. F. Walton, *ibid.*, **68**, 1180 (1946).

[24] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.