

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Straight-Chain Sulfonic Acids in Water. III. Electromotive Force¹

BY J. W. MCBAIN AND MARGARET D. BETZ

Before attempting to determine concentration of hydrogen ion using a hydrogen electrode separated from a 0.1 *N* calomel electrode by a 3.5 *N* potassium chloride bridge, it is advisable to refer to the standard data on hydrochloric acid² and to compare them with the predicted values from $E = E_0 + E_D + 0.05915 \log 1/N_w f_H$ at 25°.

E_0 has been shown by Guggenheim and Schindler³ to be equal to 0.3337 volt, E_D is calculable from the two extreme formulas, that of Henderson for a diffuse boundary

$$E_D = \frac{-RT}{F} \frac{C_1(U_1 - V_1) - C_2(U_2 - V_2)}{C_1(U_1 + V_1) - C_2(U_2 + V_2)} \log \frac{C_1(U_1 + V_1)}{C_2(U_2 + V_2)}$$

where $-RT/F = -0.05915$; $C_1 = C_{\text{KCl}} = 3.5$; $U_1 = 73.50$; $V_1 = 76.32 = V_2$; $C_2 = C_{\text{HCl}}$; $U_2 = 349.72$; and the transcendental equation of Planck for a sharp boundary $E_D = 0.05915 \log \xi$ where ξ is defined by the equation

$$\frac{\xi C_1 V_1 - C_2 V_2}{C_1 V_1 - \xi C_2 V_2} = \frac{\log(C_1/C_2) - \log \xi}{\log(C_1/C_2) + \log \xi} \times \frac{\xi C_1 - C_2}{C_1 - \xi C_2}$$

which may be solved by a short series of approximations. Both formulas neglect the actual laws of diffusion as revealed experimentally and in particular the acceleration, retardation and collision⁴ effects exerted by different diffusion columns upon each other, which may even reverse the direction of diffusion.

It is interesting to note the large values of computed diffusion potentials and the minima and changes of sign in Table I. The familiar Bjerrum correction, subtracting values for saturated and half saturated salt bridges from each other, is not well supported by the data of the table, for the two formulas differ from each other and the last two columns of the table likewise differ. For dilute solutions, the Henderson formula agrees

(1) Experiments by Miss Betz.

(2) All the best data are collected in "Abhandlungen der Deutsche Bunsen-Gesellschaft"; *Messungen Elektromotorischer Kräfte galvanischer Zellen*, No. 5, 116 (1911); *Erster Ergänzungsheft*, 22 (1915); *Zweiter Ergänzungsheft*, 71, 72, 73 and 74 (1929).(3) E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 533 (1934). If Scatchard's maximum difference between flowing junctions and diffused junctions, 3.5 millivolts, be subtracted from his chosen value, -0.3373 volt, for E_0 with flowing junction, the result for a diffused boundary is 0.3338 volt, in excellent agreement with Guggenheim [G. Scatchard, *THIS JOURNAL*, **47**, 707 (1925)]. We used a calomel electrode of Guggenheim's pattern and hydrogen electrodes used in 1914 by McBain and Martin. All results were corrected to 760 mm. pressure of hydrogen.(4) For references see J. W. McBain and C. R. Dawson, *THIS JOURNAL*, **56**, 52 (1934).

with the Bjerrum value within one millivolt if the Scatchard value for KCl/KCl be adopted, but then the Planck equation deviates from Bjerrum by +1 to -1.5 millivolts. The deviation for normal acid is very large in all cases.

TABLE I
COMPUTED VALUES FOR DIFFUSION POTENTIALS OF THE LIQUID JUNCTIONS HCl/KCl AND HCl/KCl/0.1 KCl

N_w HCl	HCl/KCl			HCl/KCl/0.1 KCl		
	1.75 KCl, m. v.	3.5 KCl, m. v.	Difference	1.75 KCl, m. v.	3.5 KCl, m. v.	Difference
By Henderson's Formula						
0.991	21.1	15.2	-5.9	19.7	13.5	-6.2
.09812	6.8	4.9	-1.9	5.4	3.2	-2.2
.009715	3.2	3.0	-0.2	1.8	1.3	-0.5
.001	4.0	3.5	-.5	2.6	1.8	-.8
.0001	4.2	4.6	+.4	2.8	2.9	+.1
By Planck's Equation						
1.0	21.9	16.0	-5.9	20.5	14.3	-6.2
0.1	8.0	5.7	-2.3	6.6	4.0	-2.6
.01	3.9	2.7	-1.2	2.5	1.0	-1.5
.001	3.9	3.9	-0.0	2.5	2.2	-0.3
.0001	5.0	4.6	-.4	3.6	2.9	-.7
.000001		7.4			5.7	

In the opposite direction come the diffusion potentials of 3.5 KCl/0.1 KCl, 1.72 millivolts from the Henderson formula, 2.7 from the Cummings modification; 2.4 to 2.7 Scatchard,⁵ 1.85 Guggenheim and Schindler,³ and for 1.75 KCl/0.1 KCl, 1.38 by the Henderson formula. $n_{\text{KCl}} = 0.510$ from $m = 0$ to 0.5.

Our e. m. f. values for hydrochloric acid as compared with the best data for the nearest round concentrations are 0.991 N_w , 0.3400 (0.3427, 0.3423); 0.0981 N_w , 0.4010 (0.4020, 0.4012, 0.4010, 0.4004, 0.4000, 0.3998, 0.3995); 0.00972 N_w , 0.4584 (0.4582, 0.4579); 0.000962 N_w , 0.5165; 0.0000952 N_w , 0.5739 volt.

f_{HCl} is taken from the calculations of Randall and Young.⁵ If the assumption is made that $f_{\text{H}^+} = f_{\text{HCl}} = f_{\text{Cl}^-}$, we are able to compare the computed values with the best observed values for e. m. f. of hydrochloric acid in Table II, which shows a discrepancy of no less than 10 millivolts for N hydrochloric acid. Either the activity of the hydrogen ion in hydrochloric acid solution has been very greatly overestimated or the diffus-

(5) M. Randall and L. E. Young, *ibid.*, **50**, 989 (1928).

TABLE II
COMPUTED VALUES FOR E. M. F. OF HCl SOLUTIONS AT 25°
 $E = E_0 + E_D + 0.05915 \log 1/N_w f_H$ for the cell

(Pt)₂H₂ | HCl | KCl | KCl, HgCl | Hg, where E₀ = 0.3337

N_w	N_w	$f_H =$ activity	$0.05915 \times$ $1/N_w f_H$	H ^a	E _D	P ^b	H ^a	Total	P ^b	Observed
1.0	1.019	0.843	0.0044	0.0135		0.0143	0.3516		0.3524	0.3417
0.1	0.1004	.802	.0648	.0032		.0040	.4017		.4025	.4006
.01	.01	.906	.1208	.0013		.0010	.4558		.4555	.4582
.001	.001	.966	.1783	.0018		.0022	.5138		.5142	.5163
.0001	.0001	.99	.2369	.0029		.0029	.5735		.5735	.5739

^a Henderson formula. ^b Planck equation.

sion potential is very different from that calculated from either the Planck or Henderson formula. The e. m. f. data for more dilute solutions agree with the computed values only within 2 millivolts.

E. m. f. Data for Sulfonic Acids and their Mixtures with Hydrochloric Acid.—Before presenting the e. m. f. data for the sulfonic acids themselves, we give Table III to show that as a first approximation the addition of hydrochloric acid to water and to a solution of sulfonic acid produces the same effect upon e. m. f. In other words, the activity of hydrochloric acid is not profoundly affected by the presence of the ionic micelle of the sulfonic acid. This is a result of general significance confirming similar previous findings with soaps and cetyl sulfonic acid, for it would indicate that in all mixtures containing polyvalent organic compounds or any other ions or particles where the charges are not concentrated in a point the effect of multivalence almost wholly disappears. Ordinarily the Debye-Hückel theory would postulate an ionic strength sufficient almost

completely to obliterate the lowering of freezing point or the production of e. m. f. by any univalent ions present. Hence the principle of ionic strength as regards valency definitely does not apply; even the data for pH for the sulfonic acid solutions alone would serve to substantiate this important truth.

Since it is difficult exactly to predict what the hydrogen-ion concentration of a mixture of colloidal electrolytes with hydrochloric acid should be, we have inserted as a guide the last two columns as a comparison with the observations. One gives the mean of the two concentrations before mixing and the other assumes that the weight normality of the hydrogen ion referred to the solvent water in each of the separate solutions is maintained constant apart from the actual increase in the amount of water present; that is, that the degree of dissociation of neither sulfonic acid nor hydrochloric acid nor their activities is affected by mixing. Upon referring to the table, it will be seen that the concentration of hydrogen ion observed, with two exceptions, actually ex-

TABLE III
HYDROGEN-ION CONCENTRATION OF MIXTURES OF EQUAL VOLUMES OF SULFONIC ACID SOLUTIONS WITH HYDROCHLORIC ACID SOLUTIONS AT 25°

HCl N_w	N_w	Sulfonic acid alone E. m. f.	N_w of H	E. m. f.	Mixture N_w of H	Mean of Columns 1 and 4	Mean N_w
Undecyl							
0.00972	0.0324	0.4303	0.0290	0.4382	0.0214	0.0194	0.0193
.00972	.112	.4100	.0661	.4273	.0327	.0379	.0376
.0981	.112	.4097	.0668	.4023	.0902	.0825	.0826
.0981	.238	.3939	.126	.3947	.1216	.1120	.1117
Lauryl							
0.01	0.01	0.4615	0.00845	0.4580	0.00966	0.00923	0.00923
.1	.1	.4152	.0537	.4109	.0634	.0769	.0771
1.0	.810	.3655	.389	.3463	.838	.695	.719
Myristyl							
0.01	0.029	0.4498	0.0135	0.4513	0.0127	0.0117	0.0117
.1	.1066	.4197	.0447	.4081	.0713	.0723	.0727
.1	.313	.3962	.115	.3975	.108	.107	.107

ceeds both of these values. The acidity of the mixture and the activity of the hydrogen ion is greater than that predicted, even though we have completely ignored in the computation any driving back of the dissociation of the incompletely dissociated colloidal electrolyte and also any effect of valency. Apparently, both of these items are insignificant in comparison even with the relatively minor effect of hydration.

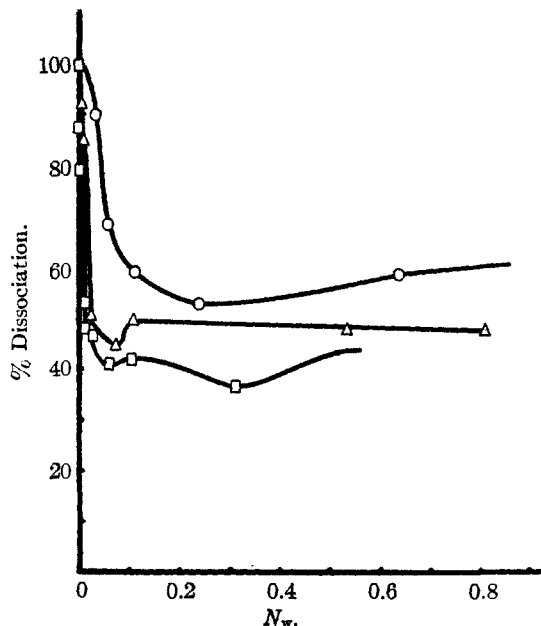


Fig. 1.—Degree of dissociation of undecyl (O), lauryl (Δ), and myristyl (□), sulfonic acids at 25°.

The method of calculation of hydrogen-ion concentration used in Table II is justified by its

TABLE IV
HYDROGEN-ION CONCENTRATION OF SULFONIC ACID SOLUTIONS FROM E. M. F. MEASUREMENTS AT 25°, WITH 0.1 N CALOMEL ELECTRODE

N_w	E. m. f.	N_w of H^+	% Dissociation
Undecyl			
0.0324	0.4303	0.0292	90.0
.0595	.4220	.0407	68.5
.112	.4097	.0668	60.0
.112	.4100	.0661	59.0
.238	.3939	.126	52.9
.637	.3666	.374	58.7
1.138	.3515	.684	60.1
Lauryl			
0.0061	0.4716	0.00562	92.2
.01	.4615	.00849	84.9
.025	.4515	.0126	50.4
.075	.4266	.0335	44.7
.1085	.4152	.0537	49.5
.535	.3762	.256	47.8
.814	.3655	.389	47.8

Myristyl			
0.00032	0.5466	0.000279	87.3
.00122	.5104	.00120	98.5
.00259	.4970	.00205	79.2
.0126	.4673	.00668	53.0
.01317	.4689	.00631	47.9
.029	.4498	.0135	46.5
.0625	.4336	.0257	41.1
.1066	.4197	.0447	41.9
.313	.3962	.115	36.7
.543	.3672	.366	67.3

results, especially in view of the foregoing discussion of diffusion potentials. What we have done is to assume that the activity of the hydrogen ion is the same in solutions of hydrochloric acid as in solutions of sulfonic acids or their mixtures with hydrochloric acid that give the same e. m. f. This assumes equality of diffusion potential in both cases and also 100% dissociation of hydrochloric acid. We therefore plotted the best values for e. m. f. of hydrochloric acid against the logarithm of the concentration N_w and read off the concentration of hydrochloric acid and therefore of hydrogen ion responsible for each value of e. m. f. observed in all further experiments. The data are given in Table IV and the degrees of dissociation shown in Fig. 1. Less accurate data for 0° are given in Fig. 2, where if anything the hydrogen-ion concentrations appear greater.

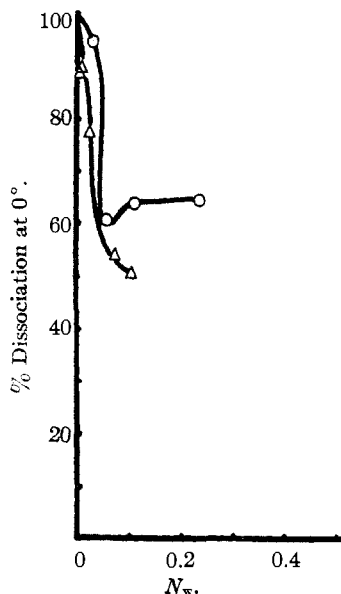


Fig. 2.—Degree of dissociation of undecyl (O), and lauryl (Δ), sulfonic acids at 0°.

Summary

Existing e. m. f. data for hydrochloric acid with

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.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED JUNE 18, 1935

[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

tend to rise with concentration. The data are collected in Figs. 1, 2 and 3.

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 my-

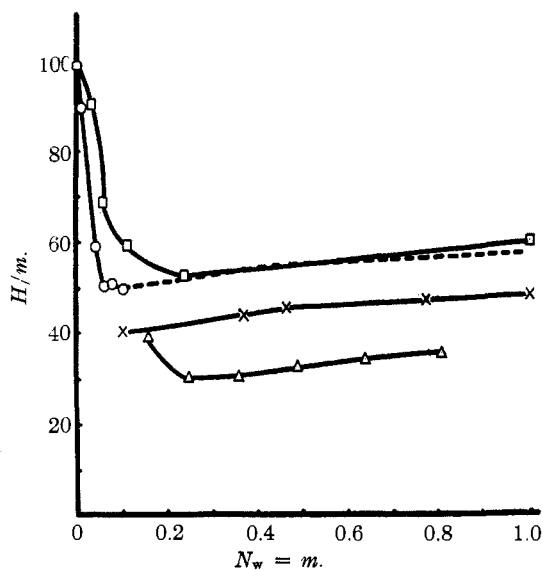


Fig. 1.—Hydrogen-ion concentration of undecyl sulfonic acid: \square is e. m. f.; \circ is conductivity, $100\mu\nu/\mu_0$; \times is Arrhenius ratio, $100\mu/\mu_\infty$; \triangle is freezing point.

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

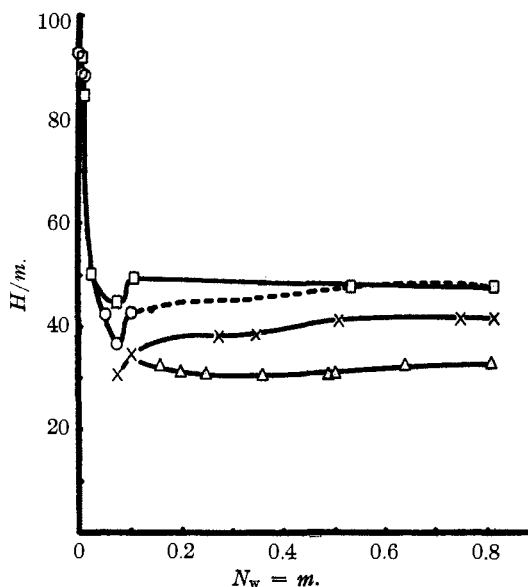


Fig. 2.—Hydrogen-ion concentration of lauryl sulfonic acid: \square is e. m. f.; \circ is conductivity, $100\mu\nu/\mu_0$; \times is Arrhenius ratio, $100\mu/\mu_\infty$; \triangle is freezing point.

ristyl 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