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pH VALUES OF ACID-SALT MIXTURES OF SOME AROMATIC SULFONIC ACIDS AT VARIOUS TEMPERATURES AND A CRITERION OF COMPLETENESS OF DISSOCIATION

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ABSTRACT

A method is described to differentiate between completely and incompletely dissociated acids by means of measurements of the emf of galvanic cells without liquid junctions. Hydrogen and silver-silver-chloride electrodes and solutions of the acid, its sodium or potassium salt, and sodium or potassium chloride are used. The activity coefficients of hydrochloric acid in such mixtures are calculated by the equation relating the emf to the activity of hydrochloric acid in known concentrations of the acid and salts. If the mean values of the activity coefficient of hydrochloric acid in the mixtures are higher than those predicted by the limiting law of Debye and Hückel, the acid is then considered to be completely dissociated. If they are lower, the acid is incompletely dissociated. By this method it was found that the sulfonic acid group in *p*-phenolsulfonic and 4-chlorophenol-2-sulfonic acids may be regarded as completely dissociated into sulfonate and hydrogen ions at temperatures of 10°, 25°, 40°, and 60° C.

Solutions containing *p*-phenolsulfonic acid, its sodium or potassium salt, and sodium or potassium chloride and solutions containing 4-chlorophenol-2-sulfonic acid, its sodium salt, and sodium chloride are suitable for use as pH standards. Their pH values range from 1.2 to 2.5 and vary only slightly with temperature changes. Directions for their preparation are given.

The significance of the complete dissociation of the sulfonic acid group in the calculation of the ionization constants and pH values of sulfonate buffers and indicators is discussed in terms of the tautomeric relations and the theory of color changes of indicators.

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I. INTRODUCTION

In measurements of acidity, knowledge of the degree of dissociation of a sulfonic acid group in indicators or buffers is important. Wingfield and Acree [1]¹ have reported that the changes in the molar absorption index of β -naphthoquinonesulfonic acid upon the addition of different amounts of hydrochloric acid and various salts can best be

¹ Figures in brackets indicate the literature references at the end of this paper.

interpreted by assuming that the sulfonic acid group is almost completely dissociated into ions. However, their attempts to determine the degree of dissociation of the sulfonic acid from pH measurements with a glass electrode and a saturated calomel half-cell involved a number of uncertainties and led to the conclusion that β -naphthoquinonesulfonic acid might have an ionization constant as low as 0.03 to 0.10. On the other hand, conductivity measurements indicate that sulfonic acids are completely dissociated. This inconsistency may be attributed partly to the neglect of corrections for the potential of the liquid junction between the solutions of sulfonic acid and saturated potassium chloride of the calomel half-cell. Hamer and Acree [2] have shown that values of the ionization constants of weak acids determined from cells with liquid junction may be in error by as much as 46 percent, depending upon the method used to estimate the values of the liquid-junction potentials. Errors would be even greater for acids of large ionization constants [3]. Additional uncertainties may be attributed to salt errors of the glass electrode. This electrode was employed because β -naphthoquinonesulfonic acid is readily reduced at a hydrogen electrode.

As the above methods are complicated, it is the purpose of this report to describe a procedure using galvanic cells without liquid junction for determining whether the dissociation of strong acids is essentially complete. The method is illustrated by data on *p*-phenol-sulfonic and 4-chlorophenol-2-sulfonic acids. These acids were chosen because they are not reduced at the hydrogen electrode; are obtained in a fair state of purity; may be used as pH standards for the two pH ranges covered by the sulfonic and phenolic groups; have a structure similar to those of many indicators; and give spectrophotometric curves resembling those of sulfonphthalein indicators in the ultraviolet.

II. TAUTOMERIC EQUILIBRIA OF PHENOL-SULFONIC ACIDS

In order to determine the pH values of sulfonphthalein indicators and *p*-phenolsulfonate buffers, it is necessary to know the ionization constants of their sulfonic acid and phenolic groups. Both ionization constants must be determined by means of a mass-action equation, including the activities of the hydrogen and organic ions obtained by potentiometric, spectrophotometric, or other methods. The expressions involving tautomeric equilibria must also be considered, since the evidence so far obtained from spectrophotometric data, alkylation reactions, and pH measurements indicates that the free acids and salts of the above indicators and buffers must be treated as tautomeric compounds, such as are illustrated in figure 1.

The mathematical methods for correlating dissociation and equilibrium constants of tautomers have already been developed [4, 5, 6]. The fractional transformation, α , of the indicator or buffer into bivalent ions, and the change in color,² with increase in neutralization with alkali and corresponding rise in pH are represented by eq 1,

² The *p*-phenolsulfonates and indicators give absorption index bands in the ultraviolet that are as different for acid and alkaline solutions as are the visible bands for indicators. The molar absorption indices are used as a measure of the concentrations of the molecules and ions of these organic compounds [6, 8, 9]. The equations apply regardless of the number of uni- and bivalent electromers or electronic states giving the corresponding index bands [5, p. 220].

which is a simplification of the general equations governing such tautomeric compounds [4, 6].

$$H\alpha/(1-\alpha) = [K_{1Q}K_{2Q}R + K_{1P}K_{2P}]/[(K_{1P}+H) + R(K_{1Q}+H)]. \quad (1)$$

In eq 1 the apparent ionization and equilibrium constants are the classical ones and contain terms for the activity coefficients for each reaction shown in figure 1; α is the sum of the concentrations of the resonant bivalent ions ($P^= + Q^=$) obtained from the data for the absorption indices or otherwise; and H is the hydrogen-ion concentration. This equation is similar in form to those for dibasic acids having no tautomeric properties.

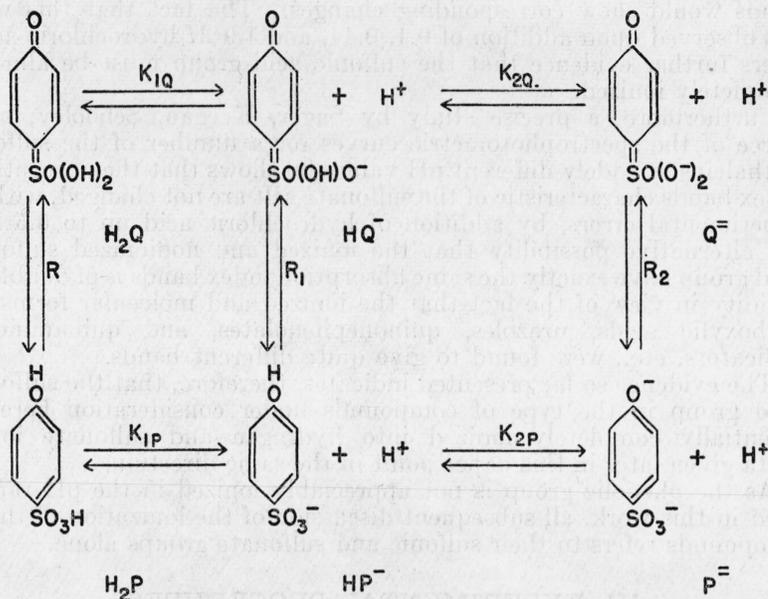


FIGURE 1.—Tautomeric and electromeric forms of *p*-phenolsulfonates

H_2Q , HQ^- , and $Q^=$ represent the molecular, univalent, and bivalent forms of the quinoidal structure.

H_2P , HP^- , and $P^=$ represent the molecular, univalent, and bivalent phenolic structures.

R , R_1 , and R_2 represent the ratios H_2Q/H_2P , HQ^-/HP^- , and $Q^=/P^=$.

K_{1Q} and K_{2Q} represent the primary and secondary ionization constants of the quinoidal form.

K_{1P} and K_{2P} represent the primary and secondary ionization constants of the phenolic form.

The apparent ionization constants and ionization relations of the phenol and sulfonic acid groups in sulfonophthaleins and phenol-sulfonates are thus very complex in that they involve activity coefficients and several equilibrium and ionization constants. The value of $H\alpha/(1-\alpha)$ for any given hydrogen-ion concentration depends greatly on the relative magnitudes of the first and second ionization constants. If the sulfonic acid group is almost completely ionized under all conditions, as usually assumed for strong mineral acids and bases, and K_{1P}/K_{2P} and K_{1Q}/K_{2Q} , therefore large, eq 1 reduces to eq 2

$$H\alpha/(1-\alpha) = K_2, \quad (2)$$

which is the form for the second ionization constant of *p*-phenol-

sulfonates and sulfonphthalein indicators, involving only the dissociation of the phenolic group, as follows:



Use of the mass law (eq 2) and emf data by Bates, Siegel, and Acree [7], including the corresponding values of the activity coefficients of the ions, gave a good second ionization constant for phenolsulfonic acid. Practically the same value was obtained by Sager, Schooley, and Acree by spectrophotometric methods [8]. If the sulfonic acid group were incompletely ionized, however, more of its molecules would be formed upon the addition of a strong acid to either the sulfonate salt or the free sulfonic acid, and the spectral absorption bands would show corresponding changes. The fact that this was not observed upon addition of 0.1, 0.44, and 1.9 *M* hydrochloric acid offers further evidence that the sulfonic acid group must be almost completely ionized.

Furthermore, a precise study by Sager, Keegan, Schooley, and Acree of the spectrophotometric curves for a number of the sulfonphthaleins at widely different pH values [9] shows that the absorption index bands characteristic of the sulfonate salt are not changed, within experimental errors, by addition of hydrochloric acid up to 0.5 *M*. An alternative possibility that the ionized and nonionized sulfonic acid group have exactly the same absorption index bands is of doubtful validity in view of the fact that the ionized and molecular forms of carboxylic acids, urazoles, quinonephenolates, and quinaminone indicators, etc., were found to give quite different bands.

The evidence so far presented indicates, therefore, that the sulfonic acid group in the type of compounds under consideration here is essentially completely ionized into hydrogen and sulfonate ions. Data given later in this paper point in the same direction.

As the phenolic group is not appreciably ionized in the pH range used in this work, all subsequent discussion of the ionization of these compounds refers to their sulfonic and sulfonate groups alone.

III. EXPERIMENTAL PROCEDURES

1. MATERIALS

Sodium *p*-phenolsulfonate obtained from a commercial source was recrystallized four times from distilled water and dried to constant weight at 105° C. The purity of the material was found to be 98 percent by bromometric assay [7, 8]. The original sample contained traces of sulfate and phenol, which were absent in the purified material. Impurities in the recrystallized material are probably cresol sulfonate and phenoldisulfonate. In the pH range 1.2 to 2.5 used in the work neither of these impurities could affect the conclusions.

Potassium *p*-phenolsulfonate obtained from a commercial source was dissolved in distilled water, treated three times with activated carbon to remove colored impurities, recrystallized four times from distilled water, and dried at 110° C. By bromometric assay it was

found to have a purity of 100.1 percent. Differential titration with carbonate-free sodium hydroxide [7] indicated a purity of 100.1 percent. Both methods of assay have an estimated uncertainty of 0.1 percent.

Sodium 4-chlorophenol-2-sulfonate obtained from a commercial source was dissolved in distilled water, digested with four successive portions of activated carbon to remove colored impurities, recrystallized twice from distilled water, and dried at 105° C. Whereas the original material contained traces of sulfate, the purified material was found to be free of this impurity.

The hydrochloric acid solution was prepared by dissolving hydrogen chloride gas in conductivity water [10]. The strength of the acid was determined by weight titration with a standardized solution of carbonate-free sodium hydroxide, using phenolphthalein as the indicator. Determinations agreed within 0.05 percent.

2. SOLUTIONS

Stock solutions were prepared from a known weight of the dry sodium or potassium salt and the requisite weight of hydrochloric acid. The more dilute solutions were prepared from known weights of stock solution and conductivity water.

Three different stock solutions containing different ratios of acid to salt were used for the measurements on *p*-phenolsulfonic acid. One contained equal molal quantities of sodium *p*-phenolsulfonate, *p*-phenolsulfonic acid, and sodium chloride. A second contained the same constituents in the ratio of 3:1:3. In the third, the potassium salts were used in the corresponding ratio of 5:2:5. For the measurements on 4-chlorophenol-2-sulfonic acid, only one stock solution containing sodium 4-chlorophenol-2-sulfonate, 4-chlorophenol-2-sulfonic acid, and sodium chloride in the ratio 1:1:1 was employed.

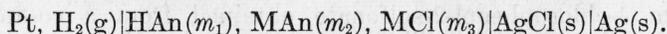
3. APPARATUS AND METHOD

Galvanic cells with hydrogen and silver-silver-chloride electrodes were employed. These cells are of the type used in this Bureau in work on pH standards and have been described in previous papers [3, 11, 12]. Measurements were made at 10°, 25°, 40°, and 60° C in order to determine the effect of temperature upon the degree of dissociation of the acids. Solutions containing mixtures of the acid, its sodium or potassium salts, and sodium or potassium chloride were employed rather than solutions of the pure acids alone. The addition of the chloride is a prerequisite for the use of the silver-silver-chloride electrode in such mixtures.

The details of the apparatus employed in this investigation, including the cells, bubble tubes, electrodes, thermostat, and the emf recording instruments, have been described by Hamer and Acree [12]. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within 0.01° C at the four temperatures, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell.

IV. ELECTROMOTIVE-FORCE MEASUREMENTS

The galvanic cell employed for these measurements may be represented by



An designates the sulfonate anion, and M represents either sodium or potassium. Molality was chosen as the concentration unit.

The emf of this cell at a pressure of 1 atmosphere of hydrogen is given by

$$E = E^\circ - \frac{RT}{F} \ln(a_{\text{H}}a_{\text{Cl}}) = E^\circ - \frac{RT}{F} \ln(f_{\text{H}}f_{\text{Cl}}m_{\text{H}}m_{\text{Cl}}), \quad (1)$$

in which E is the measured emf in international volts; E° is the potential of the silver-silver-chloride electrode in international volts for unit activity of hydrochloric acid; a , m , and f represent, respectively, the activity, molality, and activity coefficient of the ionic species denoted by subscripts; and R , T , and F have their usual significance.

TABLE 1.—*Electromotive force of the galvanic cell Pt, H₂(g)|HAn(m₁), MAn(m₂), MCl(m₃)|AgCl(s)|Ag at 10°, 25°, 40°, and 60° C*

Concentrations of solutions in moles of solutes per 1,000 g of water		emf in volts at—			
$m_1 = m_3$	m_2	10° C	25° C	40° C	60° C
Mixtures of 4-chlorophenol-2-sulfonic acid, the sodium salt and sodium chloride					
0.10093	0.10094	0.35790	0.35597	0.35288	0.34724
.07513	.07514	.37164	.37036	.36801	.36302
.05147	.05147	.38902	.38866	.38703	.38347
.02569	.02569	.42080	.42203	.42204	.42055
.009676	.009676	.46421	.46754	.46936	.47009
.008138	.008138	.47240	.47615	.47806	.47928
.006236	.006236	.48430	.48867	.49166	.49440
.004343	.004343	.50171	.50702	.51117	.51511
Mixtures of <i>p</i> -phenolsulfonic acid, the sodium salt and sodium chloride					
0.10090	0.09552	0.35732	0.35540	0.35244	0.34699
.06862	.06497	.37543	.37437	.37225	.36799
.05057	.04787	.38962	.38929	.38790	.38448
.03490	.03304	.40697	.40751	.40700	.40465
.009558	.009049	.46604	.46943	.47179	.47314
.007992	.007566	.47453	.47849	.48120	.48335
.10093	.03366	.35677	.35476	.35177	.34628
.06271	.02092	.37871	.37798	.37591	.37160
.04389	.014637	.39536	.39534	.39419	.39104
.024710	.008240	.42188	.42310	.42339	.42203
.009350	.003118	.46650	.46976	.47167	.47372
.008496	.002833	.47086	.47441	.47651	.47900
.006449	.002151	.48382	.48796	.49112	.49427
.004350	.001451	.50277	.50777	.51184	.51689
Mixtures of <i>p</i> -phenolsulfonic acid, the potassium salt and potassium chloride					
0.10093	0.04070	0.35739	0.35547	0.35245	0.34675
.02870	.02367	.38241	.38170	.37994	.37582
.04216	.01700	.39752	.39763	.39661	.39353
.02926	.01180	.41415	.41500	.41481	.41271
.010018	.004040	.46338	.46676	.46896	.47021
.008320	.003355	.47176	.47546	.47799	.47975
.006217	.002507	.48524	.48969	.49292	.49562
.003990	.001609	.50649	.51192	.51652	.52090

In table 1 values of the observed emf corrected to unit hydrogen pressure in the usual manner [13] are given for the temperatures of 10°, 25°, 40°, and 60° C and for the various solutions of concentrations recorded in columns 2 and 3. After each experiment the solutions were withdrawn from the cells and analyzed for *p*-phenolsulfonic acid by the bromate method and tested for sulfinic acid, a possible reduction product, by the addition of dilute potassium permanganate. The sulfonate concentrations of all the solutions agreed with their original values within 0.2 percent and sulfinic acid was not detected. The steadiness of the emf over a considerable time period was also evidence that no reduction of the sulfonates had occurred. The values of the emf recorded are the average of duplicate measurements, all of which agreed within 0.10 millivolt.

V. DISSOCIATION OF *p*-PHENOLSULFONIC AND 4-CHLOROPHENOL-2-SULFONIC ACIDS

It is well known that the determination of ionization constants of the order of 0.01 to 0.10 is a complicated procedure and involves several successive approximations for the determination of the hydrogen-ion concentration [11]. A briefer and more direct method was devised to circumvent these extensive calculations. According to eq 1, the emf of the galvanic cell is a function of known constants E° , R , T , and F , and the unknown quantities m and f . Upon rearrangement, eq 1 becomes

$$\frac{E - E^\circ}{2.3026RT/F} + \log(m_{\text{H}}m_{\text{Cl}}) = -\log(f_{\text{H}}f_{\text{Cl}}) \quad (2)$$

or

$$J = -\log(f_{\text{H}}f_{\text{Cl}}) = -2 \log f_{\pm} \quad (3)$$

where

J equals $(E - E^\circ)/(2.3026RT/F) + \log(m_{\text{H}}m_{\text{Cl}})$, and f_{\pm}

denotes the mean activity coefficient. If it is assumed that the acid and salts are completely dissociated into ions, values of $J/2$ can be calculated, which give the mean activity coefficients of hydrochloric acid in the mixtures studied. Furthermore, by making this assumption, the values of $J/2$ must be similar to those for acids and salts which are completely dissociated into ions, and will be higher than those predicted by the limiting law of Debye and Hückel [14]. On the other hand, if the values of $J/2$ do not conform to those for a completely dissociated acid or salt, it will then be necessary to revert to the more complicated method of successive approximations in order to determine the degree of dissociation of the acids or salts. To illustrate, values of $J/2$ were calculated from data given in the literature for a typical strong electrolyte (hydrochloric acid) and for a number of typical weak electrolytes which were investigated by a similar type of galvanic cell, using the values of E° determined by Harned and Ehlers [15] and the numerical values of R , T , and F given in a previous report [11]. Values of $J/2$ at 25° C for hydrochloric acid, the bisulfate ion ($K=0.0120$) formic acid ($K=1.772 \times 10^{-4}$), acetic acid ($K=1.754 \times 10^{-5}$), and malonic acid (second step in its ionization) ($K=2.014 \times 10^{-6}$) obtained respectively by Harned and Ehlers [15], Hamer [16], Harned

and Embree [17], Harned and Ehlers [18], and Hamer, Burton and Acree [11] are shown plotted in figure 2 as functions of the square root of the ionic strength. The dotted line (curve *C*) corresponds to the theoretical values of $J/2$ predicted by the limiting law of Debye and Hückel. The data for hydrochloric acid fall above the dotted line, whereas the data for the weak acids (curves *D*, *E*, *F*, and *G*) fall below the dotted line. The weaker the acid, the farther are its values of $J/2$ below the dotted line. In other words, the activity coefficients of those acids or salts which are completely dissociated into ions are greater than those predicted by the Debye-Hückel equation, whereas those

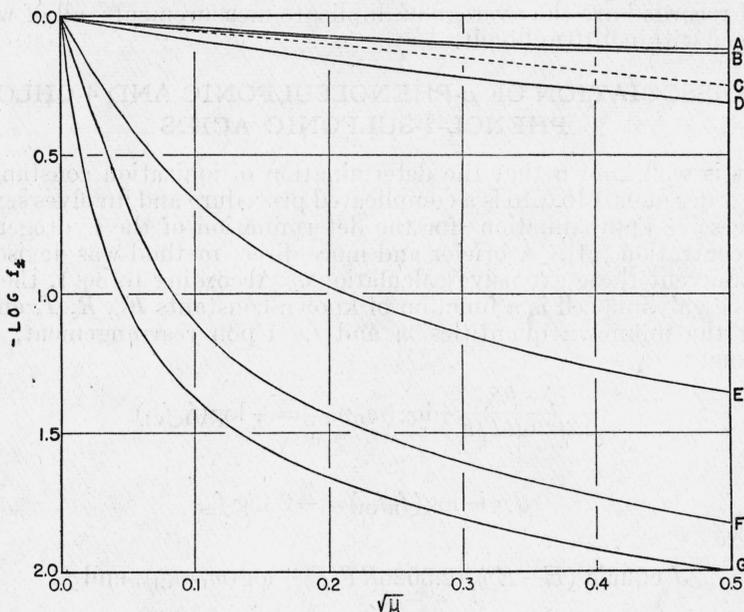


FIGURE 2.—Plots of the negative of the common logarithm of the mean activity coefficient of hydrochloric acid, or values of $J/2$, in solutions of various acid-salt mixtures against the square root of the ionic strength at 25° C.

A, Hydrochloric acid; B, sulfonate-acid mixtures; C, values calculated by means of the limiting law of Debye and Hückel; D, sodium acid sulfate-hydrochloric acid mixtures; E, sodium formate-hydrochloric acid mixtures; F, sodium acetate-hydrochloric acid mixtures; and G, disodium malonate-hydrochloric acid mixtures.

which are incompletely dissociated into ions are lower. Values of $J/2$ obtained for the sulfonate mixtures investigated in this work are given in table 2 and are shown plotted as curve *B* in figure 2 at 25° C. All the data for the different sulfonate solutions lie on curve *B* within the limits of the scale used in constructing this figure. These values, like pure hydrochloric acid, fall above the dotted line. On the basis of this criterion, it follows that the sulfonic acid groups are completely dissociated into ions. In figure 3 the data for the three different *p*-phenolsulfonate solutions are shown plotted with respect to the square root of the ionic strength at 10°, 25°, 40°, and 60° C. The data all fall above those for the limiting law (straight line) and hence *p*-phenolsulfonic acid is completely dissociated at the four temperatures. In figure 4, similar data are plotted for 4-chlorophenol-2-

sulfonic acid mixtures. Obviously, similar conclusions regarding complete dissociation for these mixtures may be made.

TABLE 2.—Activity coefficient of hydrochloric acid in sulfonate solutions at 10°, 25°, 40°, and 60° C

Concentrations of solutions in moles of solutes per 1,000 g of water		Activity coefficients at—							
HCl	Salt	10° C		25° C		40° C		60° C	
		obs.	calc.*	obs.	calc.*	obs.	calc.*	obs.	calc.*
Mixtures of 4-chlorophenol-2-sulfonic acid, the sodium salt and sodium chloride									
0.10093	0.20187	0.740	0.739	0.735	0.736	0.728	0.728	0.713	0.713
.07513	.15027	.750	.749	.747	.745	.739	.738	.727	.724
.05147	.10294	.766	.766	.763	.766	.759	.755	.744	.743
.02569	.05138	.800	.803	.799	.803	.794	.794	.781	.784
.009676	.019352	.873	.856	.874	.853	.877	.849	.875	.842
.008138	.016275	.877	.865	.879	.862	.888	.858	.886	.852
.006236	.012472	.897	.878	.899	.875	.900	.872	.889	.866
.004343	.008686	.901	.894	.903	.892	.900	.889	.889	.884
Mixtures of <i>p</i> -phenolsulfonic acid, the sodium salt and sodium chloride									
0.10090	0.19642	0.749	0.742	0.744	0.742	0.735	0.734	0.716	0.716
.06862	.13359	.759	.755	.756	.753	.748	.746	.731	.731
.05057	.09844	.770	.768	.767	.766	.760	.760	.744	.747
.03490	.06794	.782	.788	.780	.785	.773	.779	.758	.768
.009558	.018607	.851	.858	.853	.856	.849	.852	.840	.845
.007992	.015557	.855	.867	.855	.865	.853	.861	.840	.855
.10093	.13459	.757	.749	.753	.748	.744	.731	.725	.725
.06271	.08363	.777	.769	.771	.767	.765	.761	.751	.748
.04389	.05853	.789	.788	.786	.785	.779	.779	.764	.768
.02471	.03295	.814	.820	.813	.817	.805	.812	.791	.803
.003350	.012469	.862	.871	.866	.868	.870	.865	.850	.859
.008496	.011329	.867	.875	.871	.873	.875	.869	.853	.864
.006449	.008600	.876	.888	.881	.886	.879	.882	.861	.877
.004350	.005801	.880	.904	.888	.902	.888	.899	.861	.895
Mixtures of <i>p</i> -phenolsulfonic acid, the potassium salt and potassium chloride									
0.10093	0.14163	0.748	0.748	0.743	0.747	0.734	0.740	0.719	0.724
.05870	.08237	.770	.771	.766	.769	.759	.762	.745	.750
.04216	.05916	.786	.788	.782	.786	.775	.780	.762	.769
.02926	.04106	.805	.808	.804	.806	.797	.800	.786	.791
.010018	.014058	.857	.866	.857	.863	.854	.860	.843	.854
.008320	.011675	.869	.875	.871	.873	.869	.869	.860	.863
.006217	.008724	.883	.888	.884	.886	.882	.883	.872	.878
.003990	.005599	.890	.907	.894	.905	.888	.902	.875	.898

* Calculated by eq 4.

The values of $J/2$ or $-\log f_{\pm}$ recorded in the tables vary with the ionic strength in a manner typical of strong electrolytes. This variation may be represented by the Hückel extension [19] of the Debye-Hückel equation for univalent ions, namely,

$$-1/2 \log(f_{\text{H}}f_{\text{Cl}}) = -\log f_{\pm} = \frac{A\sqrt{\mu}}{1 + Ba\sqrt{\mu}} + \beta\mu, \quad (4)$$

where A and B are constants whose numerical values depend upon various natural constants, β is an empirical constant expressing in part the interactions of the nonpolar hydrogen and chloride ions with

the polar phenolsulfonate ions [8, 9, 32] analogous to Kirkwood's treatment of ampholytes [20], a_1 is the so-called closest distance of approach of the ions; and μ is the ionic strength of the mixtures. Molality was used as the concentration unit in this equation, following the suggestion of Scatchard [21]. Values of a_1 and β were determined for each series in the usual manner by substituting two measured values of $-\log f_{\pm}$ and their corresponding ionic strengths in the above equation and then solving the two simultaneous equations for the unknowns. It was found that the best value for a_1 was 3.5 \AA for the four series and that β has values at the temperatures of 10°, 25°, 40°, 60°,

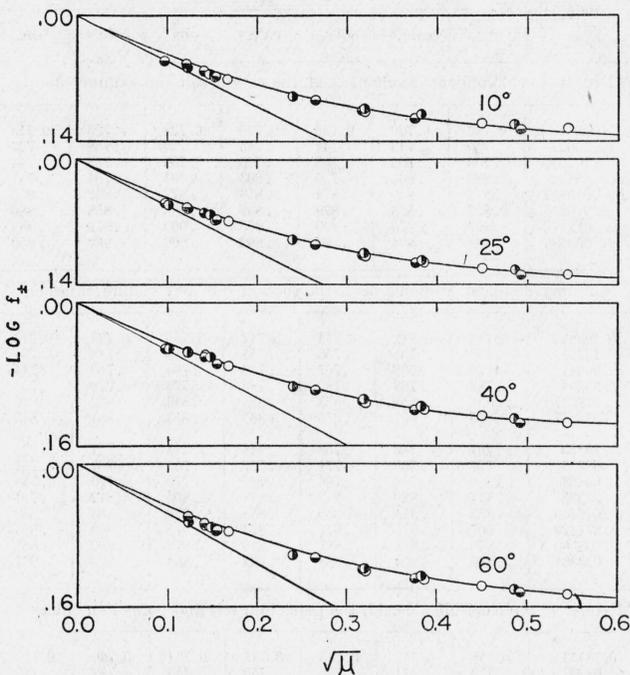


FIGURE 3.—Plots of the negative of the common logarithm of the mean activity coefficient of hydrochloric acid, or values of $J/2$, in solutions of sodium and potassium *p*-phenolsulfate, sodium and potassium chloride, and *p*-phenolsulfonic acid against the square root of the ionic strength.

○, ●, and ⊙ represent, respectively, values of 2:1, 4:3, and 7:5 for the ratio of sulfonate concentration to hydrochloric acid concentration. The curved line represents the calculated values and the straight line corresponds to the values given by the limiting law of Debye and Hückel.

and 60°, respectively, of 0.121, 0.126, 0.127, and 0.117 for 4-chlorophenol-2-sulfonic acid and 0.125, 0.137, 0.137, and 0.124 for *p*-phenolsulfonic acid. Values of $-\log f_{\pm}$ calculated by eq 4 are given in table 2. At all the temperatures, the calculated and observed values of $-\log \pm f_{\pm}$ agree with a mean deviation of ± 0.002 for the concentrated and ± 0.023 for the most dilute solutions of the 4-chlorophenol-2-sulfonate series, and ± 0.006 for all the concentrations of the sodium and potassium *p*-phenolsulfonate series. It is apparent, however, that a smooth curve drawn through the observed values for the most dilute solutions of the *p*-phenolsulfonates would be slightly concave toward the axis of abscissas. Robinson [22] observed a similar be-

havior for pure salts of sulfonic acids, which may be attributed in part to the presence of "ion pairs" arising from the resonant, polar structure of the phenolsulfonates [8, 9, 32]. The value of a_1 found here is nearly equal to Bjerrum's [23] critical value and may indicate, although not conclusively, that "ion pairs" are present. Their presence, however, does not alter the conclusion that these sulfonic acids are almost completely dissociated into hydrogen and sulfonate ions, since "ion pairs" result from electrostatic forces.

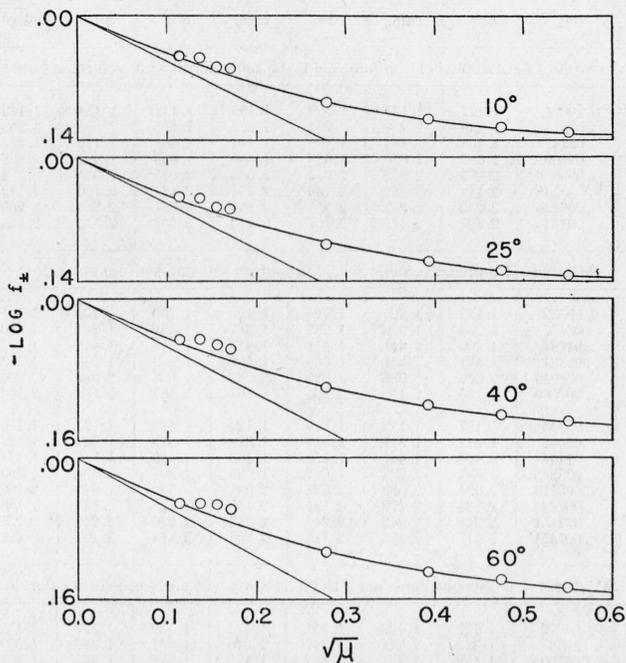


FIGURE 4.—Plots of the negative of the common logarithm of the mean activity coefficient of hydrochloric acid, or values of $J/2$, in solutions of sodium 4-chlorophenol-2-sulfonate, sodium chloride and 4-chlorophenol-2-sulfonic acid against the square root of the ionic strength.

Circles represent the experimental values, the curved line represents the calculated values, and the straight line corresponds to the values given by the limiting law of Debye and Hückel.

VI. CALCULATIONS OF THE pH VALUES OF THE ACID-SALT MIXTURES

The pH value of a solution is defined as the common logarithm of the reciprocal of the hydrogen ion activity, expressed by the equation

$$\text{pH} = -\log a_{\text{H}} = -\log(m_{\text{H}}f_{\text{H}}). \quad (5)$$

In section V, values of f_{\pm} for the acid-salt mixtures were given. With the assumption that $f_{\text{H}} = f_{\pm}$ in these mixtures, it is possible to calculate their pH values. They were computed at the four temperatures by using both the experimental and calculated values of the mean activity coefficients and the known values of the hydrogen-ion concentrations (i. e., of the hydrochloric acid) in these mixtures and are given in table 3. The pH values computed from the experimental

and calculated values of the activity coefficients agree within ± 0.004 at the four temperatures.

TABLE 3.—pH values of sulfonate solutions at 10°, 25°, 40°, and 60° C

Concentrations of solutions in moles of solutes per 1,000 g of water		pH values at—							
		10° C		25° C		40° C		60° C	
$m_1 = m_3$	m_2	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Mixtures of 4-chlorophenol-2-sulfonic acid, the sodium salt and sodium chloride									
0. 10093	0. 10094	1. 127	1. 127	1. 129	1. 129	1. 134	1. 134	1. 143	1. 143
. 07513	. 07514	1. 249	1. 250	1. 251	1. 252	1. 255	1. 256	1. 262	1. 264
. 05147	. 05147	1. 404	1. 404	1. 406	1. 404	1. 408	1. 410	1. 417	1. 417
. 02569	. 02569	1. 687	1. 686	1. 688	1. 686	1. 690	1. 691	1. 698	1. 696
. 009676	. 009676	2. 073	2. 082	2. 073	2. 083	2. 071	2. 085	2. 072	2. 089
. 008138	. 008138	2. 146	2. 152	2. 146	2. 154	2. 141	2. 156	2. 142	2. 159
. 006236	. 006236	2. 252	2. 262	2. 251	2. 263	2. 251	2. 265	2. 256	2. 267
. 004343	. 004343	2. 407	2. 411	2. 407	2. 412	2. 408	2. 413	2. 413	2. 416
Mixtures of <i>p</i> -phenolsulfonic acid, the sodium salt and sodium chloride									
0. 10090	0. 09552	1. 122	1. 126	1. 125	1. 126	1. 130	1. 130	1. 141	1. 141
. 06862	. 06497	1. 283	1. 286	1. 285	1. 287	1. 289	1. 291	1. 300	1. 299
. 05057	. 04787	1. 409	1. 411	1. 411	1. 412	1. 415	1. 416	1. 425	1. 423
. 03490	. 03304	1. 564	1. 561	1. 565	1. 562	1. 569	1. 566	1. 577	1. 572
. 009558	. 009049	2. 090	2. 086	2. 089	2. 087	2. 091	2. 089	2. 096	2. 093
. 007992	. 007566	2. 165	2. 159	2. 165	2. 161	2. 167	2. 162	2. 173	2. 166
. 10093	. 03366	1. 117	1. 122	1. 119	1. 122	1. 125	1. 127	1. 136	1. 136
. 06271	. 02092	1. 312	1. 317	1. 316	1. 318	1. 319	1. 322	1. 327	1. 329
. 04389	. 01464	1. 460	1. 461	1. 462	1. 463	1. 466	1. 466	1. 474	1. 472
. 02471	. 008240	1. 697	1. 693	1. 697	1. 695	1. 701	1. 698	1. 709	1. 702
. 009350	. 003118	2. 094	2. 089	2. 091	2. 091	2. 090	2. 092	2. 100	2. 095
. 008496	. 002833	2. 133	2. 129	2. 131	2. 130	2. 129	2. 132	2. 140	2. 134
. 006449	. 002151	2. 248	2. 242	2. 245	2. 243	2. 246	2. 245	2. 255	2. 247
. 004350	. 001451	2. 417	2. 405	2. 413	2. 406	2. 413	2. 407	2. 427	2. 410
Mixtures of <i>p</i> -phenolsulfonic acid, the potassium salt and potassium chloride									
0. 10093	0. 04070	1. 122	1. 122	1. 125	1. 123	1. 130	1. 127	1. 139	1. 136
. 05870	. 02367	1. 345	1. 344	1. 347	1. 346	1. 351	1. 349	1. 359	1. 356
. 04216	. 01700	1. 480	1. 478	1. 482	1. 480	1. 486	1. 483	1. 493	1. 489
. 02926	. 01180	1. 628	1. 626	1. 629	1. 628	1. 632	1. 630	1. 638	1. 636
. 010018	. 004040	2. 063	2. 062	2. 066	2. 063	2. 068	2. 065	2. 073	2. 068
. 008320	. 003355	2. 141	2. 138	2. 140	2. 139	2. 141	2. 141	2. 146	2. 144
. 006217	. 002507	2. 259	2. 258	2. 260	2. 259	2. 261	2. 261	2. 266	2. 263
. 003990	. 001609	2. 450	2. 442	2. 448	2. 443	2. 451	2. 444	2. 457	2. 446

Although these solutions do not have as large a buffer capacity as do solutions prepared from a weak acid and its salt, they do have a slight buffer capacity, of approximately the same magnitude as hydrochloric acid-sodium chloride mixtures [24] frequently used for the same range of pH. When a solution containing 2 parts of sodium chloride and 1 part of hydrochloric acid is diluted from an ionic strength of 0.3 to 0.03, it shows a change in pH of +0.933. A change of +0.924 occurs for a similar dilution of a solution containing 2 parts of sodium 4-chlorophenol-2-sulfonate and 1 part of hydrochloric acid, and a change of +0.933 occurs for a similar dilution of a solution containing 2 parts of sodium *p*-phenolsulfonate and 1 part of hydrochloric acid.

The pH values of these solutions increase linearly with the temperature at a rate of 0.00025 to 0.00045 pH unit per degree, depending upon the concentration. This variation is in accord with the general behavior of buffer solutions in that the pH of solutions of low pH

increases with a rise in temperature and decreases for solutions of high pH [25, 26]. They are therefore very suitable for use as pH standards.

VII. DISCUSSION

The conclusion that the sulfonic acid groups in *p*-phenolsulfonic and 4-chlorophenol-2-sulfonic acids are completely dissociated into hydrogen and sulfonate ions in solutions of an ionic strength of 0.3 or less and at temperatures of 10°, 25°, 40°, and 60° C agrees with results obtained by electrical conductivity and spectrophotometric measurements. It may be concluded that the same group in indicators of similar structure will likewise be completely dissociated in dilute solutions, a conclusion previously arrived at by Wingfield and Acree [1]. An extension of this conclusion to more complex compounds must be made with caution, however, since sulfonic acids of large molecular weight have a tendency to exhibit colloidal characteristics. Although the results of conductivity measurements on a series of straight-chain sulfonic acids [27] show that the sulfonic acid group is completely dissociated, they also indicate that there is a gradual transition from typically strong electrolytes to well-marked colloidal electrolytes consisting of "ion micelles" as the number of carbon atoms increases from 2 to 14, with heptyl and nonyl acids occupying an intermediate position. A similar study of a series of aromatic sulfonic acids [28] also indicates the complete dissociation of the sulfonic acid group but a smaller tendency to form ion micelles than for straight-chain sulfonic acids containing the same number of carbon atoms. Another series of measurements indicates that halogen substitution in the ring increases slightly the tendency to form ion micelles [29]. The critical concentration at which ion micelles first appear is generally very low and may be as small as 0.0004 *N* [30]. This critical concentration is also greatly decreased on the addition of neutral salts [31]. Hence in most cases ion micelles may be present in very dilute solutions of complex sulfonic acids, especially after addition of large concentrations of salts. The optical properties of solutions of less complex phenolsulfonate buffers and of sulfonaphthalein indicators show that the presence of ion micelles is highly improbable. Nevertheless, cognizance must be taken of their possible existence in the presentation of data on theories and use of indicators as pH standards.

VIII. REFERENCES

- [1] B. Wingfield and S. F. Acree, *J. Research NBS* **27**, 361 (1941) RP1424.
- [2] W. J. Hamer and S. F. Acree, *J. Research NBS* **17**, 605 (1936) RP930.
- [3] W. J. Hamer, *Trans. Electrochem. Soc.* **72**, 257 (1937).
- [4] S. F. Acree, *Am. Chem. J.* **38**, 1 (1907).
- [5] S. F. Acree, unpublished Lectures on pH Standards, *p.* 214 (1930, mimeographed).
- [6] R. T. Birge and S. F. Acree, *J. Am. Chem. Soc.* **41**, 1031 (1919). S. F. Acree, S. Nirdlinger, F. M. Rogers, H. C. Robertson, J. P. Harrison, and E. K. Marshall, *Am. Chem. J.* **49**, 121, 364, 485 (1913).
- [7] R. G. Bates, Gerda L. Siegel, and S. F. Acree, *J. Research NBS* **31**, 205 (1943) RP1559.
- [8] Elizabeth E. Sager, Marjorie Schooley, and S. F. Acree, *J. Research NBS* **31**, 197 (1943) RP1558, and unpublished work.
- [9] Elizabeth E. Sager, H. J. Keegan, and S. F. Acree, *J. Research NBS* **31**, 323 (1943) RP1569, and unpublished work.
- [10] S. F. Acree, and R. F. Brunel, *Am. Chem. J.* **36**, 117 (1906).

- [11] W. J. Hamer, J. O. Burton, and S. F. Acree, *J. Research NBS* **16**, 575 (1936) RP895; **24**, 269 (1940) RP1284.
- [12] W. J. Hamer and S. F. Acree, *J. Research NBS* **23**, 647 (1939) RP1261.
- [13] N. E. Loomis and S. F. Acree, *J. Am. Chem. Soc.* **38**, 2391 (1916).
- [14] P. Debye and E. Hückel, *Phys. Z.* **24**, 185, 305, 334 (1923).
- [15] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **55**, 2179 (1933).
- [16] W. J. Hamer, *J. Am. Chem. Soc.* **56**, 860 (1934).
- [17] H. S. Harned and N. D. Embree, *J. Am. Chem. Soc.* **56**, 1042 (1934).
- [18] H. S. Harned and R. W. Ehlers, *J. Am. Chem. Soc.* **54**, 1350 (1932); **55**, 652 (1933).
- [19] E. Hückel, *Phys. Z.* **26**, 93 (1925).
- [20] J. G. Kirkwood, *J. Chem. Phys.* **2**, 351 (1934); *Chem. Rev.* **24**, 233 (1939).
- [21] G. Scatchard, *Chem. Rev.* **19**, 309 (1936).
- [22] R. A. Robinson, *J. Am. Chem. Soc.* **57**, 1165 (1935).
- [23] N. Bjerrum, *Kgl. Danske Vidensk. Selsk. Math. fysik. Medd.* VII, No. 9 (1926).
- [24] H. S. Harned, *J. Am. Chem. Soc.* **57**, 1865 (1935).
- [25] R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree, *J. Research NBS* **29**, 183 (1942) RP1495.
- [26] W. J. Hamer, *J. Wash. Acad. Sci.* **29**, 551 (1939).
- [27] E. L. McBain, W. B. Dye, and S. A. Johnston, *J. Am. Chem. Soc.* **61**, 3210 (1939).
- [28] M. H. Norris, *J. Chem. Soc.* **121**, 2161 (1922).
- [29] T. R. Bolam and J. Hope, *J. Chem. Soc.* 843 (1941).
- [30] J. L. Moilliet, B. Collie, C. Robinson, and G. S. Hartley, *Trans. Faraday Soc.* **31**, 120 (1935).
- [31] K. A. Wright, A. D. Abbott, V. Sivertz, and H. V. Tartar, *J. Am. Chem. Soc.* **61**, 549 (1939).
- [32] G. G. Manov, R. G. Bates, W. J. Hamer, and S. F. Acree, *J. Am. Chem. Soc.* **65**, 1765 (1943).

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