$\gamma^*_\pm$, were based upon a reference state of unit mean ionic activity coefficient of the acid at infinite dilution in pure water. For this latter value it was necessary to employ the standard molal potentials reported by Harned and Hamer.[4]

Since electromotive force measurements could not be made in concentrations below 0.05 molal, the usual extrapolation technique for determining the standard electrode potentials for cells containing these solutions could not be successfully employed. Instead the E^0 values quoted in Tables II and III were arrived at by the method used by Crockford and Wideman.[5]

Curves obtained by plotting the values of $\gamma_\pm$ and $\gamma^*_\pm$ against the square root of the molality show a similar shape to those obtained for sulfuric acid in pure water.

Plots of the ln $\gamma_\pm$ for each molality in both the 5 and 10% by weight 2-propanol–water solutions against the absolute temperature indicate a straight line function. Using the method of least squares, the slope, $\partial \ln \gamma_\pm/\partial T$, for each curve was determined. By means of the equation

$$\bar{L}_2 = -3RT^2(\partial \ln \gamma_\pm/\partial T)$$

the relative partial molal heat content of sulfuric acid has been calculated for each molality listed in Tables II and III over the temperature range 5 to 25°.

TABLE IV

THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF SULFURIC ACID IN 5% 2-PROPANOL–WATER SOLUTION RELATIVE TO INFINITE DILUTION

$m(H_2SO_4)$	$\bar{L}_2(5°)$	$\bar{L}_2(10°)$	$\bar{L}_2(15°)$	$\bar{L}_2(20°)$	$\bar{L}_2(25°)$
0.05	4738	4910	5085	5263	5444
.10	5105	5290	5479	5671	5866
.20	5322	5515	5712	5911	6115
.30	5438	5636	5837	6041	6249
.40	5500	5700	5903	6110	6320
.50	5545	5746	5951	6160	6372
.60	5557	5758	5964	6172	6385
.70	5565	5767	5972	6182	6394
.80	5577	5779	5985	6195	6408
.90	5585	5788	5994	6204	6417
1.00	5690	5897	6107	6321	6539

TABLE V

THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF SULFURIC ACID IN 10% 2-PROPANOL–WATER SOLUTIONS RELATIVE TO INFINITE DILUTION

$m(H_2SO_4)$	$\bar{L}_2(5°)$	$\bar{L}_2(10°)$	$\bar{L}_2(15°)$	$\bar{L}_2(20°)$	$\bar{L}_2(25°)$
0.05	4109	4258	4410	4564	4722
.10	4393	4552	4715	4880	5048
.20	4720	4891	5065	5243	5423
.30	4892	5070	5251	5438	5622
.40	4983	5163	5348	5535	5725
.50	5030	5213	5399	5588	5780
.60	5062	5245	5432	5622	5816
.70	5082	5267	5455	5646	5840
.80	5091	5275	5464	5655	5850
.90	5113	5298	5487	5680	5875
1.00	5156	5344	5534	5728	5925

The values of $\bar{L}_2$, as read from the best smooth curve on a large scale plot of the calculated $\bar{L}_2$ values against $m^{1/2}$, are reported in Tables IV and V. Isothermal curves obtained by plotting $\bar{L}_2$ against the square root of the molality show a similar shape to those reported in the literature for sulfuric acid in pure water, but the respective values for $\bar{L}_2$ are greater over the concentration range studied in the 2-propanol–water solutions as compared to pure water as the solvent.

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[4] H. S. Harned and W. J. Hamer, THIS JOURNAL, **57**, 27 (1935).

[5] H. D. Crockford and S. A. Wideman, *J. Phys. Chem.*, **50**, 418 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE, COLUMBIA UNIVERSITY]

The Ionization Constants of Taurine and its Activity Coefficient in Hydrochloric Acid Solutions from Electromotive Force Measurements

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The electromotive forces of cells with hydrogen and silver–silver chloride electrodes that contained either taurine–sodium taurinate–sodium chloride buffers (cell I) or taurine–hydrochloric acid mixtures (cell II) have been measured at 5° intervals from 10 to 50°. From the data for cell I the thermodynamic ionization constant, K_2, associated with the ionization of the ammonium group has been calculated. The values fit the equation $-\log K_2 = (2458.49/T) - 0.0997 + 0.0030689T$ and from this have been derived the changes in free energy, enthalpy, entropy and heat capacity associated with the ionization. The measurements on cell II were used to find the effect of taurine upon the activity coefficient of hydrochloric acid and the activity coefficient of taurine (γ_1) in the hydrochloric acid solutions. The limiting slope for the variation of log γ_1 with the concentration of hydrochloric acid is used in connection with a theory of Kirkwood to calculate the dipole moment of taurine in solution. For either a spherical or an ellipsoidal model of the taurine molecule the calculated dipole moment was 18 ± 1 which is of the right order of magnitude. The salting-out effect cannot be neglected in discussing the behavior of taurine in hydrochloric acid solutions. The measurements on cell II were also used in an attempt to determine the ionization constant (K_1) of the sulfonic acid group, but it was found to be only possible to state that K_1 is larger than one.

In recent papers values of the ionization constants of sulfamic[1,2] and sulfanilic[3] acids have been reported. The electrolytic behavior of taurine, the aminosulfonic acid analogous to β-alanine, is the subject of the present communication. Its low ionization constant (8.69×10^{-10} at 25°), its high dielectric increment (41),[4] and the absence from its infrared spectrum of the absorption band near 1.04 μ

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[1] E. G. Taylor, R. P. Desch and A. J. Catotti, THIS JOURNAL, **73**, 74 (1951).

[2] E. J. King and G. W. King, *ibid.*, **74**, 1212 (1952).

[3] R. O. MacLaren and D. F. Swinehart, *ibid.*, **73**, 1822 (1951).

[4] G. DeVoto, *Gazz. chim. ital.*, **61**, 897 (1931).

that is associated with the uncharged amino group[5] show that taurine occurs in solution as the dipolar ion, $^+NH_3CH_2CH_2SO_3^-$. The second thermodynamic ionization constant, K_2, corresponding to the reaction represented by $^+NH_3CH_2CH_2SO_3^- \rightleftarrows NH_2CH_2CH_2SO_3^- + H^+$ has been obtained by a familiar method from the electromotive forces of the cell

$$H_2 \mid {}^+NH_3CH_2CH_2SO_3^- (m_1),\ NH_2CH_2CH_2SO_3Na\ (m_2),\ NaCl\ (m_3) \mid AgCl\text{–}Ag \quad \text{I}$$

If the sulfonic acid group is completely ionized, taurine will be almost completely in the dipolar ion form in hydrochloric acid solutions. Accordingly, the effect of the dipolar ion on the mean molal activity coefficient ($\gamma_\pm$) of hydrochloric acid was found from measurements on cells of the type

$$H_2 \mid {}^+NH_3CH_2CH_2SO_3^- (m_1),\ HCl\ (m_2) \mid AgCl\text{–}Ag \quad \text{II}$$

These activity coefficients can then be used to derive the activity coefficient of taurine in the hydrochloric acid solutions. This is of interest in connection with Kirkwood's theory of ion–dipolar ion interaction.[6] The measurements on cell II can also be examined under the assumption of complete ionization of hydrochloric acid but partial removal of hydrogen ions by the sulfonic acid group. An attempt was made to estimate the first ionization constant, K_1, corresponding to the reaction represented by $^+NH_3CH_2CH_2SO_3H \rightleftarrows {}^+NH_3CH_2CH_2SO_3^- + H^+$.

Experimental

Apparatus.—The general features of the apparatus have been described previously.[2,7] Hills and Ives[8] have recently reported that the potential of a hydrogen electrode is affected by the depth at which hydrogen is introduced into the solution. The cells which have been used in this and the previous work[2,7,9] have hydrogen inlets approximately 10 cm. below the surface of the solution and, on the basis of the data of Hills and Ives, should give readings that are high by 0.05 mv. The existence of this effect and its magnitude were confirmed by some experiments. As would be expected from the nature of the effect, it is independent of *p*H and ionic strength and varies only slightly with temperature.[10] Since the standard electromotive forces (E^0) of these cells were obtained under similar conditions,[11] the absolute error in the electromotive forces recorded in this paper from this source is undoubtedly less than 0.05 mv. and no correction has been made for this effect.

Materials.—The sodium chloride has been described in an earlier paper.[7] Carbonate-free sodium hydroxide solution was prepared by dilution of the saturated solution and was standardized against potassium acid phthalate from the National Bureau of Standards with a precision of ±0.02%. At the conclusion of the measurements on cell I the base was restandardized and its concentration was found to be within 0.06% of that previously obtained. Constant-boiling hydrochloric acid was prepared from reagent-grade concentrated acid according to the customary procedure.[12] It was used directly in the preparation of the 0.2 and 0.5 molal acid solutions. The other hydrochloric acid solutions were made from a one molal stock solution that had been prepared from the constant-boiling acid. The concentration of the stock solution was checked gravimetrically and found to be within 0.05% of that calculated from the dilution data. Two samples of taurine, A. P. grade, were obtained from Amino Acid Manufacturers. Their purity was checked by formol titration, their water content was determined by the Karl Fischer method,[13] and several of the semi-quantitative tests of Stoddard and Dunn[14] and a sulfate test[15] were carried out. The sample used in cell I was 99.88% pure (precision ±0.02%) and contained 0.04% water; that used in cell II was 99.84 ± 0.05% pure and contained 0.03% water. The first sample contained about 0.004% heavy metals, the second still less; both samples contained less than 0.004% chloride, ammonia, phosphate, iron and sulfate.

The basic buffers were prepared from weighed amounts of redistilled water, sodium chloride, taurine and sodium hydroxide solution; the solutions for cell II were prepared from weighed amounts of redistilled water, hydrochloric acid and taurine. Oxygen was removed from all solutions and a special effort was made to exclude carbon dioxide from the solutions of cell I. The solutions were prepared a day before the measurements were made. Buoyancy corrections were made to all weighings. For this purpose the density of solid taurine was taken to be about 1.6 g. per cc. The error in the concentrations is believed to be not greater than 0.1%.

Procedure.—The method of making electromotive force measurements over the temperature range was generally the same as that used in the study of sulfamic acid.[2] Agreement between successive readings at 25°, usually four in number, was used as a criterion of the performance of the cells. The standard deviations between duplicate measurements were ±0.036 mv. for cell I and ±0.023 mv. for cell II. The standard deviations between initial and final readings at 25°, usually taken about 30 hours apart, was ±0.14 mv. for cell I and ±0.11 mv. for cell II. When measurements were carried over a period of two days, the results of the second day were corrected to make them consistent with those of the first.[7]

The electromotive forces have been corrected to a hydrogen pressure of one atmosphere. Small corrections have also been applied to the electromotive forces of cell II to make them correspond to rounded molalities. Only one of these corrections exceeded 0.05 mv. The electromotive forces can be represented as a function of temperature by the equation

$$E_t = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (1)$$

The parameters of this equation for electromotive forces in absolute volts are given in Tables I and II. The standard deviation between the observed values and those calculated from the equation is ±0.057 mv. for cell I and ±0.022 mv. for cell II.

TABLE I

PARAMETERS OF EQUATION (1) FOR CELL I

m_1	m_2/m_1	m_3/m_1	E_{25}	$a \times 10^5$	$b \times 10^6$
0.01524	0.5001	0.5077	0.86597	6.50	−2.94
.01953	.5074	.5029	.86063	4.65	−2.90
.02212	.5091	.5030	.85749	3.30	−2.65
.02509	.5001	.5077	.85365	1.80	−2.80
.02664	.5091	.5030	.85285	1.70	−2.73
.02890	.5074	.5029	.85091	1.00	−2.65
.03134	.5058	.5021	.84893	0.20	−2.77
.03287	.5091	.5030	.84775	−0.40	−2.53
.03480	.5001	.5077	.84557	−1.30	−2.59
.03928	.5058	.5021	.84338	−1.70	−2.77
.04499	.5074	.5029	.83999	−3.05	−2.55
.05463	.5058	.5021	.83532	−4.50	−2.65

Results and Discussion

A. The Second Ionization Constant.—The function $pK_2' = (\mathfrak{F}/2.3026RT)(E_1 - E^0) + \log[m_3 \cdot (m_1 + m_{OH})/(m_2 - m_{OH})]$ can be calculated from

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[5] M. Freymann and P. Rumpf, *Compt. rend.*, **201**, 606 (1935).

[6] J. G. Kirkwood, Chapter 12 in E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," Reinhold Publ. Corp., New York, N. Y., 1943; *cf.* also *Chem. Revs.*, **19**, 275 (1936).

[7] E. J. King, THIS JOURNAL, **73**, 155 (1951).

[8] G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 305 (1951).

[9] E. J. King, THIS JOURNAL, **67**, 2178 (1945).

[10] G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **45**, 322 (1950).

[11] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); **55**, 652, 2179 (1933).

[12] C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923); A. C. Titus and D. E. Smith, *ibid.*, **63**, 3266 (1941).

[13] K. Fischer, *Angew. Chem.*, **48**, 394 (1935).

[14] M. P. Stoddard and M. S. Dunn, *J. Biol. Chem.*, **142**, 329 (1942).

[15] J. E. Ricci and B. Selikson, THIS JOURNAL, **69**, 995 (1947).

TABLE II

PARAMETERS OF EQUATION (1) FOR CELL II

m_2	m_1	E_{25}	$a \times 10^5$	$b \times 10^6$
0.01	0.01	0.46440	18.1	−2.62
.01	.02	.46450	18.0	−2.70
.01	.03	.46464	18.3	−2.68
.01	.045	.46477	18.3	−2.68
.02	.01	.43048	7.05	−2.69
.02	.02[a]	.43050	7.05	−2.69
.02	.03	.43066	7.20	−2.78
.02	.05	.43081	7.05	−2.71
.05	.01	.38611	− 6.95	−2.72
.05	.015	.38614	− 7.00	−2.77
.05	.02	.38617	− 7.00	−2.77
.05	.03	.38624	− 7.00	−2.77
.05	.05	.38632	− 7.00	−2.67
.05	.075	.38647	− 6.70	−2.75
.1	.01	.35267	−17.6	−2.65
.1	.015[a]	.35265	−18.6	−2.25
.1	.02	.35292	−17.2	−2.78
.1	.03	.35275	−17.1	−2.82
.1	.05	.35285	−17.3	−2.72
.1	.075[a]	.35292	−17.3	−2.60
.1	.1	.35303	−17.3	−2.72
.2	.01	.31895	−27.4	−2.79
.2	.02	.31895	−27.8	−2.62
.2	.03	.31898	−27.7	−2.58
.2	.05	.31903	−27.4	−2.65
.2	.1	.31911	−27.7	−2.60
.5	.02	.27243	−40.8	−2.51
.5	.05	.27240	−41.0	−2.55
.5	.1	.27244	−41.0	−2.55

[a] No measurements were made at 10, 15 and 20°.

the electromotive force data after a rough estimate of the very small hydroxyl ion concentration, m_{OH}, has been made.[16] In this and all subsequent calculations the most recently approved values[17] of the physical constants have been used. The values of the standard electromotive force, E^0, given by Harned and Ehlers[11] were increased by 0.06 to 0.08 mv. to put them on the same basis.[18] The negative logarithm of the second ionization constant is the intercept at zero ionic strength of a plot of pK_2' against the ionic strength, $m_2 + m_3 + m_{OH}$. Values of pK_2, with a standard deviation of ±0.0013, as obtained by linear extrapolation are: 10°, 9.4520 (4); 15°, 9.3161 (−2); 20°, 9.1855 (−6); 25°, 9.0614 (6); 30°, 8.9402 (0); 35°, 8.8236 (−3); 40°, 8.7121 (2); 45°, 8.6042 (3); 50°, 8.4993 (−4). The numbers in parentheses following the values of pK_2 are the differences in the fourth decimal place between these values and those calculated from the Harned and Robinson equation[19]

$$pK_2 = (2458.49/T) - 0.0997 + 0.0030689T \quad (2)$$

The changes in free energy (ΔF_2^0), enthalpy (ΔH_2^0), entropy (ΔS_2^0) and heat capacity (ΔC_{p2}^0) associated with the ionization reaction in the standard state can be derived from this equation by familiar thermodynamic methods. The values of these functions at 25° are, respectively, 12,361.6 cal. mole^{-1}, 10,000 cal. mole^{-1}, −7.91 cal. mole^{-1} deg.$^{-1}$ and −8.37 cal. mole^{-1} deg.$^{-1}$. The measurements reported in the next section indicate a mounting discrepancy above 25° between the activity coefficients of hydrochloric acid given by Harned and Ehlers[11] and those obtained from cell II. If the values of E^0 obtained by Harned and Ehlers are taken to be correct, this means that the values of pK_2 calculated above will be too high above 25°, the maximum error being about 0.004 in pK_2 at 50°. The thermodynamic properties at 25° therefore may be too low by 37 cal. for $\Delta H_2^{\prime}$, 0.12 unit for ΔS_2^0, and 1.84 for ΔC_{p2}^0.

There are no values of the thermodynamic ionization constant recorded in the literature. Various investigators have obtained apparent constants from titration curves,[20-22] and hydrolysis measurements using cells with liquid junction[23] and conductance[24] methods. These constants are

$K_2 \times 10^{10}$	Temp., °C.	Investigator
18	25	Andrews and Schmidt
16	25	Winkelblech
6.3	Not given	Rumpf
5	20 (?)	Carr and Shutt
5.77	18	Josephson
5.79	18	King
6.52	20	King
8.69	25	King

B. The Effect of Taurine on the Activity Coefficient of Hydrochloric Acid.—The stoichiometric mean molal activity coefficient of hydrochloric acid was calculated from the electromotive force measurements of cell II by means of the fundamental equation

$$-\log \gamma_\pm = (\mathfrak{F}/4.6052RT)(E_{II} - E^0) + \log m_2 \quad (3)$$

Both hydrochloric acid and the sulfonic acid group of taurine were assumed to be completely ionized. Values of $-\log \gamma_\pm$ from equation (2) were plotted against the concentration of taurine, m_1, at constant concentration of hydrochloric acid, m_2, and the plots were extrapolated to $m_1 = 0$ to obtain $-\log \gamma_\pm^0$ for hydrochloric acid in pure water. The extrapolations at 25°, which are representative of the whole set, are shown in Fig. 1. The effect of taurine on the logarithm of the activity coefficient of hydrochloric acid is seen to be linear up to 0.1 molal, the highest concentration of taurine used, and to decrease as the concentration of hydrochloric acid increases.

The accuracy of the present measurements can be checked by comparison of the mean activity coefficients of hydrochloric acid as obtained by extrapolation with the values given by Harned and

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(16) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, pp. 506–507.

(17) F. D. Rossini, F. Gucker, Jr., H. Johnston, L. Pauling and G. Vinal, THIS JOURNAL, **74**, 2699 (1952).

(18) The recalculated values of E^0 reported by D. Swinehart, *ibid.*, **74**, 1100 (1952), are 0.01 mv. higher than those used in this paper.

(19) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(20) S. Andrews and C. L. A. Schmidt, *J. Biol. Chem.*, **73**, 651 (1927).

(21) P. Rumpf, *Compt. rend.*, **204**, 592 (1937).

(22) W. Carr and W. J. Shutt, *Trans. Faraday Soc.*, **35**, 579 (1939).

(23) B. Josephson, *Acta Med. Scand.*, **68**, 284 (1928); *C. A.*, **22**, 2579 (1928).

(24) K. Winkelblech, *Z. physik. Chem.*, **36**, 546 (1901).

Ehlers,[11] Shedlovsky and MacInnes,[25] and Hills and Ives.[26] The activity coefficients of Harned and Ehlers have been recalculated on the basis of the new constants[17] from their smoothed electromotive forces. The other two sources used the constants given by Birge[27]; the correction to the new basis[17] is not more than two units in the fourth decimal place of the activity coefficient and has been neglected. The agreement between the activity coefficients obtained in this investigation and those from the other sources as shown in Table III is seen to be excellent at 25°. The agreement with the activity coefficients of Harned and Ehlers is also very good below 25°, but above this temperature the activity coefficients obtained in this study fall progressively further and further below those of Harned and Ehlers until at 50° they differ by the equivalent of 0.29 mv. Although the cause of this discrepancy is not known, it fortunately does not affect the activity coefficent ratio, $\gamma_\pm/\gamma^0_\pm$, which is about to be discussed. Its effect on the second ionization constant has already been considered.[28]

TABLE III

THE MEAN MOLAL ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID AT 25°

m_{HCl}	Ref. 11	Ref. 25	Ref. 26	King
0.01	0.9041	0.9049	0.9040	0.9051
.02	.8758	.8757	.8747	.8754
.05	.8302	.8301	.8296	.8295
.1	.7969	.7938	.7958	.7952
.2	.7674			.7661
.5	.7579			.7574

The effect of taurine on the activity coefficient of hydrochloric acid is most conveniently expressed by the negative logarithm of the activity coefficient ratio, $-\log\ (\gamma_\pm/\gamma^0_\pm)$. Values of this quantity obtained in this investigation are very small, the largest being only 0.0046. They also show no apparent trend with temperature. The data for each solution have been averaged over the whole temperature range and fitted to the equation $-\log\ (\gamma_\pm/\gamma^0_\pm) = Sm_1$. The slopes, S, and their standard deviations are: 0.0911 ± 0.0016, 0.0734 ± 0.0013, 0.0467 ± 0.0004, 0.0340 ± 0.0005, 0.0182 ± 0.0005, and 0.0001 ± 0.0004 for 0.01, 0.02, 0.05, 0.1, 0.2 and 0.5 molal hydrochloric acid, respectively. These slopes were, in their turn, smoothed against m_2 by the method of least squares and the following relation resulted

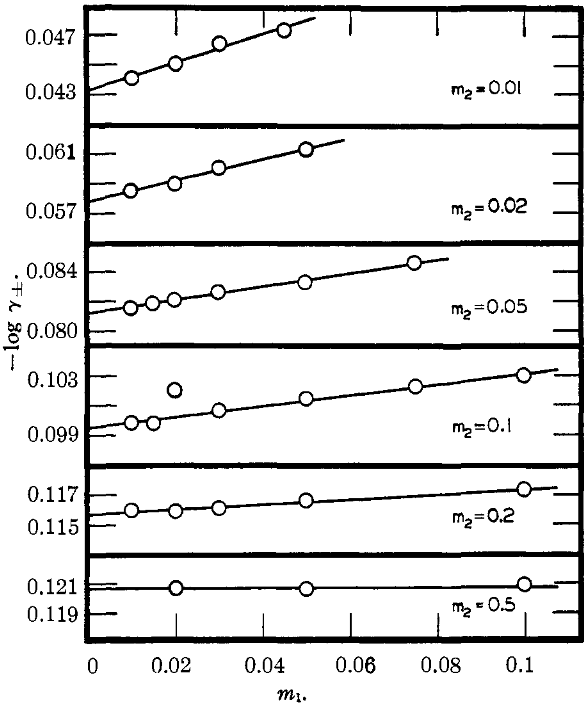

Fig. 1.—Effect of taurine upon the activity coefficient of hydrochloric acid at 25°. Diameters of the circles represent 0.10 mv. in the electromotive forces.

$$\log\ (\gamma_\pm/\gamma^0_\pm) = -0.120m_1 + 0.357m_1m_2^{1/2} - 0.268m_1m_2 \qquad (4)$$

The standard deviations of the constants in this equation are ±6, 9 and 15%, respectively. The standard deviation of observed from calculated values of $\log\ (\gamma_\pm/\gamma^0_\pm)$ is ±0.00030 or the equivalent of ±0.035 mv. in the electromotive forces. Roberts and Kirkwood[29] have used an expression similar to equation (4) to express the logarithm of the activity coefficient ratio of potassium chloride in the presence of glycine. Since their measurements covered concentrations of glycine up to 0.5 molal, they found it necessary to include a term in the square of the dipolar ion concentration.

C. The Stoichiometric Activity Coefficient of Taurine in Hydrochloric Acid.—The activity coefficients of hydrochloric acid and taurine (γ_1) must satisfy the requirement

$$2(\partial \ln \gamma_\pm/\partial m_1)_{\mathrm{T,p,}m_2} = (\partial \ln \gamma_1/\partial m_2)_{\mathrm{T,p.m}m_1} \qquad (5)$$

When this is applied to equation (4) an expression is obtained for the logarithm of the activity coefficient of taurine in hydrochloric acid solutions

$$\log \gamma_1 = -0.240\ m_2 + 0.476\ m_2^{3/2} - 0.268\ m_2^2 \qquad (6)$$

It is of interest to examine the limiting slope, −0.240, in connection with Kirkwood's theory of ion–dipolar ion interaction.[6] Two models of the taurine dipolar ion will be considered: a spherical model and an ellipsoidal model with the charges at the foci.

For the spherical model Kirkwood has shown[6]

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[25] T. Shedlovsky and D. A. MacInnes, THIS JOURNAL, **58**, 1970 (1936); T. Shedlovsky, *ibid.*, **72**, 3680 (1950).

[26] G. J. Hills and D. J. G. Ives, *J. Chem. Soc.*, 318 (1951).

[27] R. Birge, *Rev. Modern Phys.*, **13**, 253 (1941).

[28] The activity coefficients given by Hills and Ives[26] and Shedlovsky and MacInnes[25] do not depend upon the standard electrode potential of the silver–silver chloride electrode. The excellent agreement between the activity coefficients from all four sources can be taken as evidence in favor of the value of the standard potential at 25° obtained by Harned and Ehlers[11] and used in the present calculations. Hills and Ives[26] and D. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, pp. 186–187, had recalculated the results of Harned and Ehlers and obtained standard potentials more than 0.10 mv. higher. C. W. Davies, H. W. Jones and C. B. Monk, *Trans. Faraday Soc.*, **48**, 921 (1952), have also concluded that the lower value was to be preferred. It is unfortunate, in view of the discrepancy between the results of Harned and Ehlers and those in this communication, that activity coefficients of hydrochloric acid at temperatures above 25° are not available from measurements which do not involve the silver–silver chloride electrode.

[29] R. M. Roberts and J. G. Kirkwood, THIS JOURNAL, **63**, 1373 (1941).

that at 25° the limiting slope, $-K_{R1}$, can be expressed by the equation[30]

$$-K_{R1} = -(5.44 \times 10^{-3}\mu^2/a) + 4.64 \times 10^{-3}(V_1/a)\alpha(\rho) \tag{7}$$

The first term in equation (7) corresponds to salting-in of the dipolar ion by the electrolyte and the second term to salting-out as a result of a repulsion between the ions and their image in the cavity of the dipolar ion. In equation (7) μ is the dipole moment in debyes, b is the radius of the dipolar ion, a is the sum of b and the radius of the real ion, ρ is the ratio b/a, $\alpha(\rho)$ is a tabulated function,[6] and V_1 is the partial molal volume of taurine at infinite dilution corrected for solvent electrostriction. The limiting partial molal volume of taurine at 25° is 72.3 cc.[31] If we assume that taurine and β-alanine have the same electrostriction correction, namely, 14.4 cc.,[32] then $V_1 = 86.7$ cc. per mole. From this b is found to be 3.25 Å. If the ions are treated as spheres of the same size and the average ionic radius is taken to be 1.75 Å., $a = 5.00$ Å., $\rho = 0.65$, and $\alpha(\rho) = 1.29$. From these values and the experimental limiting slope, -0.24, the dipole moment is calculated from equation (7) to be 18 debyes. There are various methods of estimating the dipole moment from the dielectric increment. Using a value of 41 for that quantity,[4] we obtain dipole moments of 16, 20 and 21 by the methods of Wyman,[33] Cohn[34] and Kirkwood,[6] respectively. Structural considerations would lead us to expect the dipole moment to be between 15 for the tightly coiled molecule and 23 for the fully extended chain. The value 18 calculated from the present measurements is thus of the right order of magnitude. The value is particularly sensitive to errors in K_{R1} and a. The limiting slope is probably known within ±20% and if ±0.50 Å. is taken as a possible error in estimating the mean ionic radius, the probable error in the dipole moment will be of the order of ±1 debye.

The ellipsoidal model with the charges located at the foci remains to be considered. Unfortunately, it is necessary to make some drastic simplifying assumptions in this treatment. If the ionic volume and image repulsion are neglected, the slope is given by[6]

$$K'_{R1} = 0.245\epsilon\, g(\epsilon)[V_1/(1 - \epsilon^2)]^{1/3} \tag{8}$$

and the dipole separation by

$$R = 1.47 V_1^{1/3}\epsilon(1 - \epsilon^2)^{-1/3} \tag{9}$$

In these equations ϵ is the eccentricity of the ellipsoid and $g(\epsilon)$ is a tabular function.[6] From Equation (8) with $K'_{R1} = 0.24$ and $V_1 = 86.7$ cc. per mole, we find $\epsilon = 0.37$ and $g(\epsilon) = 0.54$. The separation of the charges is then found to be 2.65 Å. corresponding to a dipole moment of 13 debyes, a value which is certainly too low. An approximate correction for image repulsion can be made[6] by subtracting from the right-hand side of equation (8) the term $4.64 \times 10^{-3}\ (V_1/l)\ \alpha(\rho)$ in which l is a length intermediate between the semi-major and semi-minor axes of the ellipsoid. If l is taken to be about 3.5 Å., $R = 3.80$ Å., and $\mu = 18$ debyes, the same as that found from the spherical model. The salting-out term in the limiting slope obviously is an important one for taurine. Because of the limitations of the theory and the fairly large experimental error in K_{R1}, it is not possible to make a decision between the two models for taurine. Nor is it possible to check the temperature coefficient of K_{R1} predicted by theory because the magnitude of the effect is less than the experimental error.

D. The First Ionization Constant of Taurine.—The discussion of the electromotive force data for cell II has, to this point, been based on the assumption that the sulfonic group is completely ionized. This is a reasonable assumption, for sulfonic acids are generally regarded as "strong" acids. Evidence to support this assertion can be cited from various sources. It has been found that the addition of hydrochloric acid in concentrations up to 2 *M* has no appreciable effect on the spectral absorption bands of the sulfonaphthaleins[35] or of *p*-phenolsulfonic acid.[36] The logarithm of the mean activity coefficient of hydrochloric acid in various buffers containing *p*-phenolsulfonic acid or 4-chlorophenol-2-sulfonic acid[36] never falls below the Debye–Hückel limiting slope. The equivalent conductance of ethanesulfonic acid[37] approaches the Onsager limiting slope from above.

Taurine, with a positive charge on its nitrogen, should have a sulfonic acid group which is no less strongly ionized. The ionization constant of this group has been estimated to be 0.03[20] from the isoelectric condition $p\mathrm{I} = (1/2)\ (pk_1 + pk_2)$ and 0.008[22] from a titration curve, but these methods are not reliable for this strong an acid. Winkelblech[24] has measured the conductivities of equimolar mixtures of hydrochloric acid and taurine and found them to be somewhat less than those of hydrochloric acid alone. This cannot be a result of the change in dielectric constant caused by the presence of taurine, for the concentrations of that substance were too low to cause any appreciable change in that property. The decrease in conductance is most probably a result of the transformation of some hydrogen ions to the less mobile positive taurine ion. The addition of taurine to the hydrochloric acid does not change the ional concentration and, since the concentration of positive taurine ion formed must be low, the mobility of the remaining hydrogen and chloride ions should not be appreciably affected. Bjerrum,[38] apparently on the basis of the data of Winkelblech,[24] estimated the first ionization constant to be 1, but no confidence can be placed in this because of the low precision of the conduction data and the failure to make activity coefficient corrections.

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(30) This is the limiting slope for activity coefficients on the molar concentration scale. The difference between the molar and molal activity coefficients is below the experimental error in the slope.

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An attempt was made to use the data for cell II to find K_1. The calculations involve the relations

$$-\log m_{\mathrm{H}} = (\mathfrak{F}/2.3026RT)(E_{\mathrm{II}} - E^0) + \log m_2 + \log \gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} \quad (10)$$

$$pK'_1 = pK_1 + \mathrm{f}(m_2) = -\log[m_{\mathrm{H}}(m_2 - m_{\mathrm{H}})/(m_1 + m_{\mathrm{H}} - m_2)] \quad (11)$$

The activity coefficients required by equation (10) are not known but can be approximated by those of hydrochloric acid in pure water. From these relations and the smoothed data for cell II, values of pK'_1 were calculated for several ratios of m_1 to m_2. Extrapolation of pK'_1 to zero ionic strength gave $pK_1 = -0.33$ at 25° regardless of which constant value of m_1/m_2 was used in the extrapolation. Errors in the concentrations and electromotive forces have such a large effect on this intercept that it is not possible to place much confidence in the value given above. But it seems fair to state that these calculations indicate that the first ionization constant is certainly greater than one.

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The Acid Dissociation Constants of Aromatic Phosphonic Acids. I. Meta and Para Substituted Compounds[1]

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The acid dissociation constants of 25 meta and para substituted benzenephosphonic acids have been determined by potentiometric titration in water and in 50% ethanol. The data show that Hammett's equation applies, and that the reaction constants are close to unity. Comparison of the reaction constants with those for the ionization of the benzoic, the arylboric, and the arylarsonic acids leads to the conclusion that ρ-values depend on the polarizabilities of the central atoms of the acid functions. Several substituent constants not in Hammett's original tabulation are evaluated, and the structures of aminophosphonic acids are discussed.

As part of a systematic study of the properties of organophosphorus compounds, we have determined the acid dissociation constants of 25 meta and para substituted benzenephosphonic acids by potentiometric titration in water and 50% ethanol. This investigation was undertaken to evaluate quantitatively the effect of substituents on the strength of such acids. From measurements of five phosphonic acids, Lesfauries and Rumpf[2] had concluded previously that the effect of substituents in benzoic and in benzenephosphonic acids are very similar. This conclusion suggests that Hammett's equation[3] applies, and that the reaction constants (ρ) for the two series are almost the same. The data presented by the previous authors[2] are inadequate to test these points. It is shown in the present paper that the two assumptions are correct.

Experimental

Materials.—Practically all the phosphonic acids were prepared in this Laboratory and have been reported previously.[4] *p*-Ethylmercapto-, *p*-ethoxy- and 3,4-methylenedioxybenzenephosphonic acids were kindly made available to us by Drs. L. D. Quinn and Arthur Roe of the Department of Chemistry, University of North Carolina.[5]

m-Carboxybenzenephosphonic acid[6] was prepared from *m*-carboxybenzenediazonium fluoborate by the general method described previously.[4a] The phosphonic acid was purified by procedure A,[4a] and the yield was 43%; m.p. > 300°.[6] No phosphinic acid was obtained.

Anal. Calcd. for $C_7H_7O_5P$: P, 15.33; neut. equiv., 67.4. Found: P, 14.89; neut. equiv., 68.0.

Procedure.—Approximately one millimole of the acid was dissolved in 10 ml. of the appropriate solvent and titrated with 0.25 *N* sodium hydroxide. After each addition of the alkali the *p*H was determined by means of a Cambridge "Electron-Ray" Research Model *p*H meter in conjunction with a Beckman 1190-90 glass electrode and a saturated calomel electrode. Each *p*K was calculated by standard methods[7] from 7 to 10 *p*H determinations. The *p*K values obtained in this manner agreed to ±0.05 unit, and were averaged. Duplicate titrations were made in a few cases, and agreed to within ±0.05 unit. Activity corrections and liquid junction potentials were neglected throughout, and hence the experimental values are non-thermodynamic dissociation constants.

Results and Discussion

Table I lists both the first and second *p*K of the phosphono group ($-PO_3H_2$) for the acids investigated. The σ-values for some of the substituents (R) are included in Table I; only values appearing in Hammett's original table[3] are given. From these data reaction constants (ρ) and their standard errors were calculated by the method of least squares and are summarized in Table II. The correlation coefficients (r)[8] are also given in Table II, and serve as a measure of the fit of the data to Hammett's equation. The same table further gives $-\log K^\circ$ derived from the equation, and the number (n) of compounds used in the calculation of ρ. Although the aromatic phosphonic acids are much stronger acids than either the benzoic acids[3] or the aromatic arsonic acids,[9] the reaction con-

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(1) Presented before the Division of Organic Chemistry at the 122nd Meeting of the A.C.S., Atlantic City, N. J., September, 1952.

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