It remains to present data on the adsorption of labeled potassium palmitate on thin films of polystyrene. The technique of making these measurements is described in a previous section. Data are presented in Table V; c = concentration of potassium palmitate.

TABLE V

10^5c (moles/l.)	$10^{10}\Gamma$ (moles/cm.^{2})
1.17	0.6
2.34	1.0
4.68	1.7
7.02	2.6
9.36	3.6
11.7	4.0
17.3	4.2
23.4	3.8

It is of interest that in this case, too, saturation of the interface occurs at a concentration of soap considerably below the critical micelle concentration.

Acknowledgment.—The authors desire to acknowledge the technical assistance of Mr. Frank Grosseibl, who made most of the surface tension measurements reported in the foregoing paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

The Ionization Constant of Metanilic Acid from 0 to 50° by Means of E.M.F. Measurements

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RECEIVED APRIL 19, 1954

The ionization constant of metanilic acid has been determined from 0 to 50° by the use of cells without liquid junction. The equation $-\log K = 1327.59/T + 0.00281319T - 1.55334$ expresses the experimental data as a function of temperature in the above temperature range with a standard deviation of 0.00054 in $-\log K$ for eleven experimental points. An exceedingly small value of ΔS^0 for the ionization reaction, −0.57 e.u. at 25°, is found.

Introduction

The ionization constant of metanilic acid has been measured by several investigators. Of these investigations all but one[1] are results of conductivity measurements and were interpreted without taking interionic attractions into account. The resulting values are as follows:

Investigator	$K \times 10^4$	t, °C.
Ostwald[2]	1.85	25
White and Jones[3]	0.90	0
	1.33	12
	1.99	25
	2.62	35
Boyle[4]	2.11	25
Zollinger, Büchler and Wittwer[1]	2.24	25

It has been shown by Carr and Shutt[5] from measurements of the change of dielectric constant with *p*H of sulfanilic acid solutions that sulfanilic acid is a zwitterion. Considering that metanilic is even weaker than sulfanilic acid, it is reasonable to suppose the former acid also exists in solution as a zwitterion. Hence the ionization constant is for the reaction

$$^{+}H_3NC_6H_4SO_3^{-} = H_2NC_6H_4SO_3^{-} + H^{+}$$

It is the object of this investigation to present accurate values of the ionization constant of metanilic acid determined over the temperature range 0 to 50° by the measurement of the electromotive force of cells without liquid junction following the general method developed by Harned and co-workers.[6]

The cells were of the type Pt, H_2/HMet(m_1), NaMet(m_2), NaCl(m_3)/AgCl–Ag, where HMet and NaMet are metanilic acid and its sodium salt and m_1, m_2 and m_3 are molalities. By elimination of $m_{H^+}\gamma_{H^+}$ from the cell potential equation

$$E = E^0 - \frac{2.3026RT}{F} \log m_{H^+}m_{Cl^-}\gamma_{H^+}\gamma_{Cl^-} \qquad (1)$$

and the thermodynamic ionization constant expression

$$K = \frac{m_{H^+}m_{Met^-}\gamma_{H^+}\gamma_{Met^-}}{m_{HMet}\gamma_{HMet}} \qquad (2)$$

there results the following relation

$$\frac{(E - E^0)F}{2.3026RT} + \log \frac{m_{HMet}m_{Cl^-}}{m_{Met^-}} = -\log K - \log \frac{\gamma_{HMet}\gamma_{Cl^-}}{\gamma_{Met^-}} \qquad (3)$$

The ionization constant was calculated from equation 3 using a method similar to that developed by Hamer[7] and identical with that of MacLaren and Swinehart[8] used in the determination of the ionization constant of sulfanilic acid.

The values of the molal electrode potentials, E^0, of the silver–silver chloride electrode have been determined by Harned and Ehlers[9] and recalculated by Swinehart.[10] The values of the function $2.3026RT/F$ in absolute volts have also been calculated by Swinehart[10] using the constants of Bearden and Watts.[11]

Experimental

The materials and reagents were purified and analyzed in a similar manner to that indicated by MacLaren and Swinehart.[8] It may be noted, however, that in their experiments, stock solutions of sulfanilic acid showed a yellow color upon standing for a week or more. This coloration was attributed to a trace of oxygen remaining in the solution. How-

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[1] H. Zollinger, W. Büchler and C. Wittwer, *Helv. Chim. Acta*, **36**, 1711 (1953).

[2] W. Ostwald, *Z. physik. Chem.*, **3**, 406 (1889).

[3] G. F. White and H. C. Jones, *Am. Chem. J.*, **44**, 159 (1910).

[4] M. Boyle, *J. Chem. Soc.*, **115**, 1505 (1919).

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

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

[7] W. J. Hamer, THIS JOURNAL, **56**, 860 (1934).

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

[9] H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 2179 (1933).

[10] D. F. Swinehart, *ibid.*, **74**, 1100 (1952).

[11] J. A. Bearden and H. M. Watts, *Phys. Rev.*, **81**, 73 (1951).

TABLE I

ELECTROMOTIVE FORCE OF THE CELL

Pt, H_2/HMet(m_1), NaMet(m_2), NaCl(m_3)/Ag-AgCl

	Absolute volts										
μ(approx.)	0.01	0.01	0.02	0.03	0.04	0.04	0.06	0.06	0.08	0.08	0.1
m_1	0.005009	0.004991	0.009937	0.015251	0.019741	0.019990	0.030068	0.030111	0.040164	0.039884	0.050475
m_2	.005021	.004991	.009946	.015305	.019958	.019969	.030040	.030040	.040124	.039859	.050450
m_3	.005021	.004974	.009934	.015306	.019961	.019994	.030039	.030002	.040127	.039859	.050442
t(°C.)											
0	.58322	.58325	.56671	.55661	.55074	.55032	.54102	.54094	.53440	.53477	.....
5	.58329	.58333	.56641	.55608	.55008	.54967	.54018	.54006	.53344	.53383	.52844
10	.58322	.58328	.56594	.55542	.54929	.54889	.53919	.53910	.53229	.53266	.52724
15	.58298	.58307	.56534	.55459	.54833	.54784	.53801	.53795	.53097	.53138	.52583
20	.58265	.58271	.56460	.55359	.54723	.54666	.53671	.53663	.52955	.52995	.52427
25	.58222	.58230	.56376	.55250	.54598	.54550	.53531	.53521	.52798	.52835	.52259
30	.58171	.58173	.56285	.55129	.54476	.54421	.53377	.53368	.52631	.52671	.52080
35	.58105	.58108	.56170	.54998	.54320	.54268	.53209	.53199	.52451	.52490	.51888
40	.58033	.58034	.56054	.54853	.54163	.54114	.53029	.53018	.52258	.52297	.51682
45	.57949	.57957	.55923	.54699	.53994	.53948	.52839	.52826	.52054	.52091	.51456
50	.57855	.57862	.55780	.54531	.53812	.53764	.52632	.52623	.51828	.51874	.51229

ever, it was discovered in this investigation that solutions of metanilic acid were very photochemically sensitive, direct sunlight turning the solutions a deep red within a few minutes. The presence or absence of oxygen had no apparent effect on the time required for coloration. A check with sulfanilic acid showed that this was also the cause of the yellow color observed in that case.

Recrystallization of Matheson metanilic acid was carried out two to four times under an atmosphere of carbon dioxide in a semi-darkened room. The resulting white needles of the hydrate, m-$^{+}NH_3C_6H_4SO_3^{-}\cdot 1.5H_2O$, were ground in a mortar and dried over 90% sulfuric acid in a vacuum desiccator for about a week. Analyses were carried out by weight buret titration with sodium hydroxide solution which had been standardized against Bureau of Standards potassium acid phthalate, yielding an average of 99.92% metanilic acid. The remainder was assumed to be water. Each batch was analyzed separately.

That the metanilic acid was not contaminated with its isomers as impurities was shown by the complete absence of a precipitate of tribromoaniline when bromine water was added to a 1-g. sample in a water solution. Addition of 0.1% sulfanilic or orthanilic acid to the sample resulted in a precipitate immediately on the addition of bromine water.[12]

The cells, electrodes, measuring instruments and procedure of the measurements were the same as those described by MacLaren and Swinehart.[8]

Results

The data are given in Table I. Each potential difference is the average of sixteen potential measurements obtained from two cells, run in duplicate, except those at ionic strengths 0.01 and the second column at ionic strength 0.04. These are the results of averaging eight measurements from one cell only. In general, the reproducibility of the silver-silver chloride electrodes was ±0.02 mv., that of the hydrogen electrodes ±0.05 mv. In obtaining the averages listed in Table I, the maximum deviation from the mean was less than 0.05 mv. in a majority of cases. In only six of the more than one hundred such averages did the maximum deviation from the mean exceed 0.10 mv. and in no instance did it exceed 0.15 mv.

The data were treated as indicated in the introduction. Representative extrapolations for the evaluation of the ionization constant at three temperatures are shown in Fig. 1.

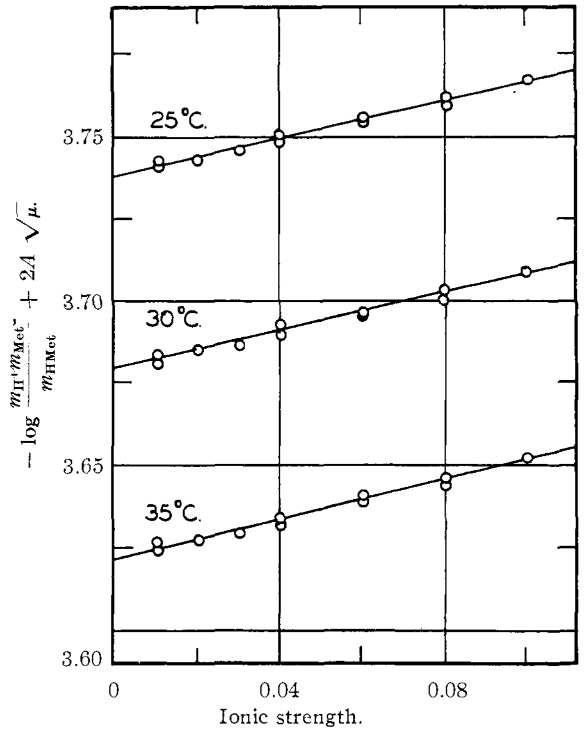

Fig. 1.—Representative extrapolations for the evaluation of −log K.

The results showing K at various temperatures are given in Table II. The experimental values of $-\log K$ were fitted by least squares by the empirical equation $-\log K = A/T + CT - D$, yielding the values 1327.59, 0.00281319 and 1.55334 for A, C and D, respectively. The calculated values of $-\log K$ using these constants are given in the fourth column of Table II. The standard deviation of the calculated values from the experimental ones is 0.00054 in $-\log K$. This quantity is calculated from

$$\text{Standard deviation} = \left(\frac{\Sigma\Delta^2}{n - c}\right)^{1/2}$$

where Δ is the deviation of the point from the fitted

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(12) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 404.

line in the direction of the $-\log K$ axis, n is the number of experimental points and c is the number of constants in the equation.[13] Most previous results in work of this sort have reported precision in terms of the average deviation which results in an overly optimistic estimate of the precision.

TABLE II

THE IONIZATION CONSTANT OF METANILIC ACID IN WATER FROM 0 TO 50°

Av. dev. of $-\log K$(obsd.) = 3.2×10^{-4}; standard dev. of $-\log K$(obsd.) = 5.4×10^{-4}

t, °C.	$K \times 10^4$	$-\log K$ Obsd.	$-\log K$ Calcd.	$\Delta \times 10^4$
0	0.8408	4.0754	4.0753	−1
5	0.9956	4.0018	4.0019	+1
10	1.170	3.9319	3.9317	−2
15	1.366	3.8647	3.8644	−3
20	1.585	3.7987	3.7999	+12
25	1.828	3.7381	3.7381	0
30	2.096	3.6794	3.6787	−7
35	2.390	3.6217	3.6217	0
40	2.710	3.5671	3.5670	−1
45	3.059	3.5147	3.5144	−3
50	3.436	3.4635	3.4639	+4

Discussion

Standard thermodynamic quantities for the ionization reaction may be calculated from the above constants by well-known relations.[14] It may be noted that $\Delta C_p^0 = -2(2.3026)CRT$ gives −7.68 cal. mole^{-1} deg.$^{-1}$ at 25°. This compares with −6.3 cal. mole^{-1} deg.$^{-1}$ for sulfanilic acid.[8] These values are surprisingly low, being somewhat below that value predicted on empirical grounds by Harned and Owen[15] for the standard heat capacity change for the ionization of a zwitterion.

The very small entropy changes for the ionization reaction are particularly significant. At 25°, $\Delta S^0 = 2.3026R(D-2CT) = -0.57$ cal. mole^{-1} deg.$^{-1}$, increasing to +0.08 cal. mole^{-1} deg.$^{-1}$ at 0°. This compares with −0.37 and +0.15 cal. mole^{-1} deg.$^{-1}$ at 25 and 0° respectively, for sulfanilic acid,[8] these values being several entropy units less negative than ΔS^0 values for other zwitterions listed by Harned and Owen.[16]

When neutral molecules or ions dissolve in water, large entropy losses occur.[17] According to the semi-quantitative theory of Frank and Evans,[18] part of the entropy loss is due to the restriction of the molecule or ion to a very small volume or cage and part is due to the loss in freedom of motion of the water molecules in the surrounding layers, *i.e.*, the water molecules are frozen in place around the solute particle. Thus when a weak acid ionizes, one neutral molecule becomes two ions and much entropy is lost. Many weak acids show standard entropies of ionization in the range of 20 to 30 entropy units. In the case of the zwitterions of the amino acids, much orientation has already occurred around the dipolar (but still neutral) acid molecules. Thus less entropy is lost upon ionization of glycine[16] ($\Delta S^0_{298} = -6.9$ cal. mole^{-1} deg.$^{-1}$).

It appears that this effect is even greater for metanilic and sulfanilic acids. Here the dipole moments are very large. The charges on the zwitterion are sufficiently separated that nearly all the orientation of water molecules has already occurred around the separated charges so that little or no further orientation occurs on ionization. This results in very small entropies of ionization, being less than one entropy unit at 25° and both values actually becoming positive at 0°.

Since the charge separation in the zwitterion of orthanilic acid will be much smaller than that for its two isomers, it seems safe to predict that the entropy of ionization of this acid should be much nearer that of glycine and should show a loss of 5 to 10 entropy units. The standard heat capacity change should be correspondingly larger.[19]

The influence of the -SO_3^- group upon the ionization of the anilinium ion is also of interest. In terms of the parameters of the Hammett equation,[20] $\log K - \log K_0 = \sigma\rho$, values of σ for the *p*- and *m*-SO_3^- groups equal to 0.49 and 0.30, respectively, are obtained. In a review of the Hammett equation by Jaffe[21] a value of 0.381 is given for σp, based upon the ionization constant of phenol. No value based upon a "normal" acid, *i.e.*, one other than phenol or anilinium ion, is given. However, Zollinger, Büchler and Wittwer[1] show that two values of σp are required, one for phenol and anilinium ion and another for benzoic acid. This is interpreted as indicating an appreciable resonance effect of the *p*-SO_3^- group with the benzene ring, involving a ten- or twelve-electron structure for sulfur. Bordwell and Cooper[22] interpret the effect of the *p*-CH_3SO_2 group on the acidity of phenol and anilinium ion in this same manner. They show that two values of σp are also required for this group.

A summary of the available data for the determination of σ for the -SO_3^- group is given in Table III.

TABLE III

VALUES OF σ FOR SO_3^- GROUP

	pK_0	ρ^a	pK	σ
Sulfanilic acid[8]	4.58	2.767	3.227	0.49
Sulfanilic acid[1]	4.58	2.767	3.32	.46
p-Phenolsulfonic acid[1]	9.92	2.113	8.96	.45
p-Phenolsulfonic acid[21]	9.847	2.113	9.03	.39
p-Sulfobenzoic acid[1]	4.20	1.00	4.11	.09
Metanilic acid (this paper)	4.58	2.767	3.738	.30
Metanilic acid[1]	4.58	2.767	3.80	.28
m-Phenolsulfonic acid[1]	9.92	2.113	9.30	.29
m-Sulfobenzoic acid[1]	4.20	1.00	4.15	.05

[a] Jaffe's[21] values. These are different from Zollinger's[1] values for phenol and anilinium ion.

Acknowledgment.—This research was supported by a grant from the Graduate Council of the University of Oregon and by the Society of the Sigma Xi.

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[13] T. B. Crumpler and J. H. Yoe, "Chemical Computations and Errors," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 222.

[14] Reference 6, p. 583.

[15] Reference 6, p. 533.

[16] Reference 6, p. 514.

[17] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

[18] H. S. Frank and M. W. Evans, *ibid.*, **13**, 507 (1945).

[19] D. F. Swinehart, paper presented at the Northwest Regional Meeting of the A.C.S., Pullman, Wash., June 12-13, 1953.

[20] L. P. Hammett, THIS JOURNAL, **59**, 96 (1937).

[21] H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

[22] F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).