At the half-neutralization point

$$C_{X^-} = C_{HX} \quad (4)$$

so that

$$pK = (pH)_{1/2} - \log \gamma_\pm \quad (5)$$

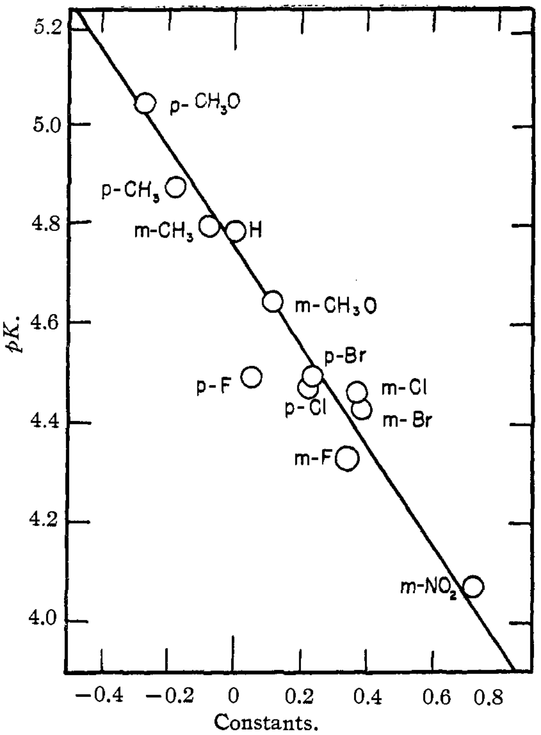

Fig. 2.—Plot of *pK* *vs.* Hammett's substituent constants.

Since

$$-\log \gamma_\pm = 0.505 Z_a^2 \sqrt{\mu} \quad (6)$$

this term has the value 0.025 under our experimental conditions, which leads to

$$pK = (pH)_{1/2} + 0.025 \quad (7)$$

A plot of the *pK* values at 25° is made against Hammett's substituent constants (σ values) in Fig. 2 and it is seen that a good approximation to a straight line results. The best straight line through the points has a slope of 1.0 which indicates that the ionization constants of the benzeneseleninic acids have the same susceptibility toward substituents as do the benzoic acids which were the source of the σ values.

The *pK* values of the benzeneseleninic acids are rather insensitive to changes of temperature. The five acids investigated were the parent acid, *p*-CH_3, *m*-CH_3, *p*-Cl and *m*-Cl. In all cases the *pK* increased approximately 0.02 unit per 10° rise in temperature in the range 25–40°.

Summary

1. Thirteen benzeneseleninic acids have been prepared, six of which are new. Methods of preparation are described.

2. The ionization constants (as *pK*) of these acids have been determined by potentiometric titration using a Beckman *p*H meter. The *pK* values thus found are a linear function of Hammett's σ values.

3. Approximate temperature coefficients of the *pK* values have been noted for five of the acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

The Surface Tension of Aqueous Sulfuric Acid Solutions at 25°

BY R. M. SUGGITT, P. M. AZIZ AND F. E. W. WETMORE

Introduction.—In this Laboratory we required values of the surface tension of sulfuric acid solutions at 25° up to the concentration corresponding to maximum conductivity. Morgan and Davis[1] reported values obtained by the drop-weight method; later Harkins and Brown[2] showed that certain corrections must be applied in using this method, but until now the corrected values have not been reported. More recently Sabinina and Terpugow[3] presented data obtained by the method of capillary rise, but gave no experimental details and reported no values for solutions less than 23% by weight acid.

The differential maximum bubble pressure technique described by Sugden[4] was chosen for our measurements, not only because it involves bubble formation which parallels the experimental arrangement for which we required the data, but also because choice of this technique would afford comparison of data obtained by three different methods.

Experimental

The solutions were made from C. P. sulfuric acid and twice-distilled water. The individual solutions were standardized by precipitation of barium sulfate and by titration against freshly prepared sodium carbonate.

The apparatus, as shown in Fig. 1, consisted of a pressure generator G and reservoir R (20 liters) connected to the bubble-forming tubes immersed in the liquid, and a sensitive manometer M attached as closely as possible to the tubes. The pressure generator consisted simply of a fine oil stream admitted to a bottle at controlled rate; thus the head required to form bubbles could be maintained at any slow rate of air flow to the tubes. The reservoir minimized pressure fluctuations during the measurements. A connection C to the compressed air line served for setting the initial pressure roughly. The manometer was a water-filled 6 mm. i.d. U-tube enclosed in a thermally lagged box. A glass scale ruled at 0.5 mm.

[1] Morgan and Davis, THIS JOURNAL, **38**, 555 (1916).

[2] Harkins and Brown, *ibid.*, **41**, 499 (1919).

[3] Sabinina and Terpugow, *Z. physik. Chem.*, **A173**, 237 (1935).

[4] Sugden, "The Parachor and Valency," George Routledge and Sons, London, 1930, p. 208.

intervals was set directly behind the U-tube; at the front a vertical square bar carried two vertically adjustable channels in which were set micrometer telescopes on ground slides for forward adjustment. The liquid level was determined by focussing a telescope on the meniscus and reading the micrometer graticule; the telescope was then run forward to bring the glass scale into focus and readings on the graticule taken for the nearest scale lines above and below the meniscus reading. By interpolation the meniscus level was referred to the glass scale. Readings of level difference could be made to 0.001 mm., an order of magnitude better than required.

Precision-bore Pyrex tubing was used for the bubble-forming tubes. The ends to be immersed were ground normal to the bore with very fine carborundum on a rotating linen disc; during this grinding the possibility of crushing or flaring of the bore was avoided by filling the end of the tube with deKhotinsky cement. The chipped edges left from the manufacturer's grinding were thus removed until microscopic examination showed a sharply circular bore. The outside diameter of both tubes was about 6 mm., the internal diameters, respectively, 0.227 and 0.454 mm., as measured with a microscope and graticule and with the ratio confirmed by the data obtained for water. The manufacture of precision-bore tubing in recent years has made possible the happy choice of tubes with bore ratio 2:1. The tubes were held in universally adjustable supports mounted in a framework which in turn was attached to a large cylindrical post with a clamping sleeve. By means of this arrangement the tubes were set vertically parallel; later they could be removed from liquid and reimmersed without change of slant or relative height. The small difference in level of the tips of the two tubes was determined with a micrometer telescope by measurement of the distance from each tip to the surface of a pool of mercury. The difference was confirmed during the runs. The liquid under test was maintained at 25.00 ± 0.02° with a conventional thermostat T. The temperature was determined with a thermometer calibrated by comparison with a platinum resistance thermometer.

With sufficiently slow formation of bubbles the maximum bubble pressure is independent of the rate of formation. Following preliminary tests the rate was set at one bubble every seven seconds (not critical). The pressure reading of the manometer slowly rose as the bubble nucleus expanded, dropping suddenly when the bubble exceeded the critical size; the maximum pressure was recorded. Every determination on a solution was preceded by one on water. Only with meticulously cleaned tubes could the readings be duplicated from one day to another.

Experimental Results

In Table I are recorded duplicate readings of pressure differences found for the two tubes, in terms of the solution at 25° as the manometric liquid. With the exception of one number patently in error, no readings were found outside the limits of the duplicates shown. Values of the surface tension γ were calculated through the method of successive approximation recommended by Sugden and the average value for each solution is recorded in Table 1. These values are based on the assumption that the surface tension of water at 25°, γ_0, is 71.97 dynes/cm.[5] The increment of the surface tension of a solution over that of pure water, $\Delta = \gamma - \gamma_0$, is given as the more suitable recording of the data, since it is independent of small variations in γ_0 and will serve at any later time for calculating γ by adding it to the then acceptable value of γ_0.

TABLE I

SURFACE TENSION OF AQUEOUS SULFURIC ACID AT 25°

Acid, %	Press. diff. in mm.		γ	Δ
4.11	63.24	63.24	72.21	0.24
8.26	61.85	61.83	72.55	0.58
12.18	60.48	60.46	72.80	0.83
17.66	58.86	58.84	73.36	1.39
21.88	57.66	57.66	73.91	1.94
29.07	55.66	55.65	74.80	2.83
33.63	54.42	54.43	75.29	3.32

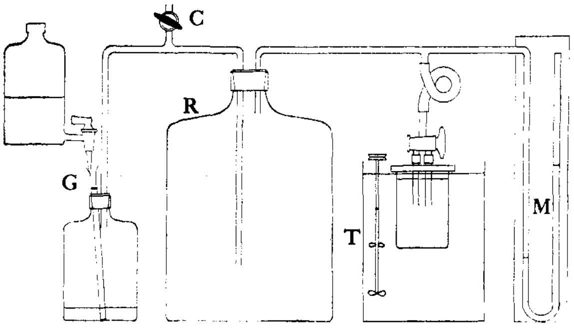

Fig. 1.—Experimental arrangement.

Correction of the Data of Morgan and Davis.—The values reported by Morgan and Davis were calculated from the formula $\gamma' = 936.0\ w$ (Eqn. 1), in which γ' is the uncorrected surface tension, 936.0 a quantity dependent on the radius of their tube, but not, by their assumption, on the composition of the liquid, and w is the average drop-weight in grams. Harkins and Brown suggested the form $\gamma = w\phi/r$ (Eqn. 2), in which γ is the corrected surface tension, r the radius of the tube, and ϕ is an empirical term depending on r and the cube root of the volume, v, of one drop. The value of v can be determined from the density of the liquid and the value of w calculated through Eqn. 1. It so happens that ϕ can be expressed as a linear function of the variable $r/v^{1/3}$ over a range sufficient for the calculations here: $\phi = A + Br/v^{1/3}$ (Eqn. 3), *e. g.*, for $r/v^{1/3} = 0.61$ to 0.64, $A = 207.6$ and $B = 70$. Thus r can be calculated by substituting in

TABLE II

SURFACE TENSION OF AQUEOUS SULFURIC ACID, CORRECTED DATA OF MORGAN AND DAVIS

	Δ			
Acid, %	0°	30°	50°	25° (calcd.)
4.67	−0.23	0.24	0.45	0.17
8.93	−0.17	0.49	0.83	0.39
16.40	0.42	1.21	1.67	1.09
22.73	0.98	2.08	2.63	1.92
28.18	1.60	2.68	3.45	2.49
32.90	2.06	3.28	4.26	3.06
37.05	2.28	3.75	4.81	3.50
40.71	2.41	4.13	5.31	3.84
45.46	2.47	4.41	5.74	4.08
49.51	2.03	4.39	5.88	4.01

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[5] "International Critical Tables," Vol. IV, p. 447. In a recent private communication Professor F. E. Bartell of the University of Michigan has kindly offered the value 72.00 at 25° as part of a corrected series to be published by him shortly. This corrected value will be useful in obtaining γ more accurately, but its use does not change the values of Δ cited here.

Eqn. 2 an acceptable value of γ and in Eqn. 2 and 3 the values of v and w found as shown above. The data of Morgan and Davis for water and the more acceptable values of γ_0[5] give r at 0, 30 and 50° as 0.2687, 0.2686 and 0.2685 cm., respectively; one would expect a small opposite thermal variation. The effective radius was taken as 0.2686 cm. and through Eqn. 1, 2 and 3 values of γ were calculated from the data of Morgan and Davis. In Table II are shown the corrected values of Δ, along with values for 25° obtained by parabolic interpolation of these data for 0, 30 and 50°.

Comparison of Data.—Table III shows the data of Sabinina and Terpugow for 10, 20, 30, 40 and 50°, as well as values for 25° obtained by graphical interpolation rather than the linear interpolation they used.

Table III

Surface Tension of Aqueous Sulfuric Acid, Data of Sabinina and Terpugow

Acid, %	Δ					
	10°	20°	30°	40°	50°	25° (calcd.)
23.80	1.56	1.90	2.45	3.08	3.75	2.16
38.00	3.09	3.66	4.33	5.00	5.75	3.99
40.61	3.24	3.88	4.53	5.36	6.10	4.19
45.43	3.39	4.04	4.75	5.68	6.53	4.38

Table IV

Surface Tension of Aqueous Sulfuric Acid at 25°, Mean Values

Acid, %	5	10	15	20	25	30	35
Δ	0.24	0.58	1.02	1.63	2.27	2.85	3.42

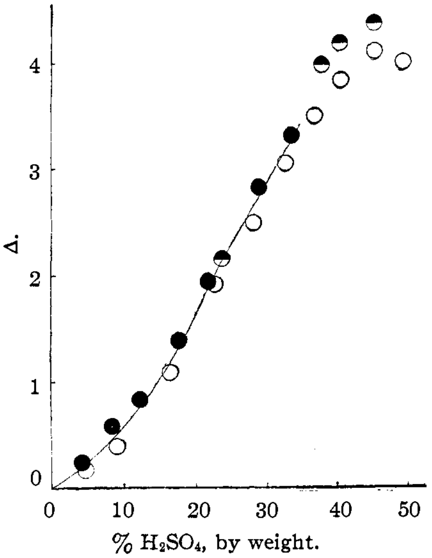

Fig. 2.—Surface tension of sulfuric acid at 25°: ○, Morgan and Davis; ◓, Sabinina and Terpugow; ●, Suggitt, Aziz and Wetmore.

In Fig. 2 the data for 25° from the three experimental methods are compared. The line has been drawn to give a minimum square deviation of the points, without weighting. The circles have radius equal to 0.07 unit, or about 0.1% of γ. In Table IV are given the values of Δ corresponding to the mean curve of Fig. 2. Over the range 0 to 35% acid the points show an average vertical deviation of 0.07 unit, or 0.1% of γ. It is quite apparent that the data from the work of Morgan and Davis lie consistently below the other two sets; a part of this difference may have arisen in the parabolic interpolation, but undoubtedly a part is due to difference in the experimental method used.

Summary

1. The surface tension of aqueous sulfuric acid at 25° has been determined over the range 0 to 33% acid by means of the differential maximum bubble pressure method.
2. The data of Morgan and Davis obtained by the drop-weight method have been recalculated in accordance with the corrections of Harkins and Brown.
3. Surface tension values obtained by three different methods have been compared.

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