for the alcohols are used to calculate the chlorides deviations of 0.5% or less are obtained with one exception, propylbutylamylchloromethane. A few values for branched chain hydrocarbons have been reported.[9] Using the same position values deviations of the same magnitude are indicated. It is suggested that further measurements may permit the construction of a CH_2 position table for tertiary structures not limited to any one type of compounds.

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[9] O. R. Quayle, R. A. Day and George Brown, THIS JOURNAL, 66, 938 (1944).

Summary

1. The refractive indices, densities, surface tensions and parachors for nine supplementary tertiary chlorides have been reported, at three temperatures.

2. The predicted and experimental values of the parachors have been shown to be in close agreement.

3. A table has been constructed for use in calculating the parachor of any tertiary chloride having normal alkyl groups.

EMORY UNIVERSITY, GEORGIA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Acidity of Buffered and Unbuffered Sulfuric Acid Solutions in Nitromethane[1]

BY LOUIS C. SMITH[2] AND LOUIS P. HAMMETT[2]

Studies of the behavior of electrolytes in nitromethane solution thus far have been largely restricted to conductivity measurements. Because of its relatively high dielectric constant (37), it is to be expected that nitromethane should favor the dissociation of dissolved salts. The recent conductivity studies of Wright, Murray-Rust and Hartley[3] and of Walden and Birr[4] demonstrate that this is not the case, and do in fact indicate that many salts are associated in this solvent even at very great dilutions.

According to the calculations of Walden and Birr, nitromethane shows relatively little tendency to solvate ions, particularly cations, and only the larger ions studied in the above investigations were found to approach ideal electrolytes in their behavior. Wright, Murray-Rust and Hartley found that the addition of 0.1% of water resulted in a very great increase in the conductivity of those electrolytes which deviated most greatly, while tetraethylammonium salts, which were normal in their behavior, were relatively unaffected by added water. This indicates that the effect of the water was to solvate the ions, thus decreasing the degree of association.

Nitromethane is a very weak base, as is shown by the work of Hantzsch[5] and of Wright, Murray-Rust and Hartley.[3] Hantzsch found by cryoscopic measurements that nitromethane was soluble but not ionized in absolute sulfuric acid. The conductivity measurements of Wright, Murray-Rust and Hartley showed that 0.02–0.05 molar solutions of sulfuric, thiocyanic, benzenesulfonic and nitric acids have an equivalent conductivity of 1–5 units, while hydrochloric acid had no effect at all on the conductivity of nitromethane. Perchloric acid, on the other hand, was found to have an equivalent conductivity of about 70 units, indicating that this is a relatively strong acid in nitromethane.

Because of its low basicity, nitromethane seemed well suited for making acidity measurements on strong acids, and the present work was undertaken for that purpose. The measurements were made colorimetrically, using the indicators of Hammett and Deyrup.[6]

The distribution of some of the indicators between nitromethane and water and benzene and water was also measured, and the results are given.

Apparatus

A Klett–Beaver[7] colorimeter was used. The scales, readable to 0.1 mm., were calibrated and found to have no error exceeding 0.2 mm. One of the conventional sets of cups and plungers was removed and replaced with a closed cup, which was used for the test solutions. This cup consisted of a glass cylinder closed at one end with an optically plane glass surface, and fitted at the other end with a standard taper ground glass joint. The inner member of this joint formed the plunger, and this also was closed by an optically plane surface. The distance between the two surfaces was measured both directly against the colorimeter scale, and by placing a dye solution in both the open and closed cups and comparing in the colorimeter. The distance was found by both methods to be 50 mm. well within the limits of experimental error.

The standard solutions were placed in the open cup. Although nitromethane evaporates quite rapidly, no drift was observed in the readings, indicating that the rate of evaporation of solvent from the open cup was not large enough to affect the results. . Beer's law was shown to hold for the indicators in nitromethane solution at the concentrations used.

Weights and volumetric ware were calibrated wherever necessary. All volumetric ware used was cleaned and dried out overnight at 110° and allowed to cool while being flushed out with a stream of dry air. After cooling to room temperature, flasks were stoppered until used.

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[1] Dissertation submitted by Louis Charles Smith in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Present address: 4800 Forbes St., Pittsburgh, Pa.

[3] Wright, Murray-Rust and Hartley, *J. Chem. Soc.*, 199 (1931).

[4] Walden and Birr, *Z. physik. Chem.*, **A163**, 263, 321 (1932).

[5] Hantzsch, *ibid.*, **65**, 41 (1908).

[6] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[7] The Klett Manufacturing Co., New York; J. J. Beaver, *J. Optical Soc. Am.*, **18**, 41 (1929).

Burets were cleaned and allowed to dry at room temperature. They were then flushed out with dry air before use. Stopcocks on the burets and nitromethane stock bottle were lubricated with a minimum amount of vaseline, which appears to be insoluble in nitromethane. Burets and stock bottle were equipped with calcium chloride tubes. All runs were made at room temperature, 26 ± 4°. The thermostat used in the distribution experiments was of conventional design, and was kept at 25.00 ± 0.02°.

Materials

The nitromethane used was obtained from the Commercial Solvents Corporation. The principal impurities appeared to be water, aldehydes, hydrogen cyanide, and some unidentified material which gives the solvent a yellow color. Fractionation from 95% sulfuric acid (50 ml. of acid to 1500 ml. of solvent) yields a middle cut (1100 ml.) boiling over a 2° range, colorless, high in hydrogen cyanide content, low in aldehydes, and a residue of two layers, one a dark brown sirup containing most of the acid, and a lighter less colored nitromethane residue. The distillate was treated in 500–600 ml. quantities with 75- and 50-ml. portions of 1% silver nitrate solution, 50–100 ml. of water, and then dried thirty-six hours over magnesium sulfate. The solvent was then filtered by suction directly into a 2-liter standard taper flask, 60–70 g. of phosphorus pentoxide was added (considerable heat is developed), and the mixture allowed to cool with frequent shaking. The solvent was then fractionated at about 100 mm. pressure, taking a small forerun and a middle cut of about 900 ml. The product contained no aldehyde (Schiff test) and no or very little hydrogen cyanide. The residue remained milky white or only slightly colored throughout the distillation. A 30-cm. Vigreux column equipped with standard taper joints was used in both distillations, which were carried out at a rate of about 1–2 drops per second. The middle cut was distilled directly into a one-liter flask equipped with a standard taper joint and a stopcock through which the solvent could be drawn off as needed. The solvent was always used within a few days after the final distillation.

To check for the presence of water, 25 g. of phosphorus pentoxide was added to about 600 ml. of purified solvent. No heat was developed, and the mixture quickly became orange, red and finally dark brown. Distillation of the mixture at 100 mm. pressure yielded about 200 ml. of distillate and a semi-solid residue which appeared to be a gel of phosphorus pentoxide in nitromethane.[8] The acidity of unbuffered sulfuric acid in the distillate was 0.1–0.2 unit lower than in the original purified solvent.

The density at 25.00° was somewhat low, 1.1278 g./cc. compared with values of about 1.130 reported in the literature.[3,8,9,10]

Sulfuric Acid.—One hundred per cent. sulfuric acid was prepared by distilling sulfur trioxide from fuming sulfuric acid into Baker C. P. grade 95% acid in an all-glass apparatus. The pure fuming acid so obtained was diluted with more 95% acid to maximum freezing point. The acid was stored in a tightly glass-stoppered bottle in a desiccator. The titer was checked periodically against Bureau of Standards phthalate. The titer of the freshly prepared acid indicated 100.0%.

Pyridine.—Eimer and Amend C. P. grade pyridine was dried over barium oxide and fractionally distilled. The distillate was then fractionally distilled from phosphorus pentoxide, taking the middle third, b. p. 115.3–115.6°. The distillate was stored in a glass-stoppered bottle containing barium oxide, and was kept in a desiccator.

2-Nitro-4-chloroaniline.—Eastman Kodak Co. yellow label 2-nitro-4-chloroaniline was recrystallized four times from 50% alcohol to constant specific color intensity and constant m. p. 116.1–116.4°.

4-Nitrodiphenylamine.—Eastman Kodak Co. white label 4-nitrodiphenylamine was recrystallized four times from alcohol, twice from 75% acetic acid; test of purity, constant specific color intensity, constant m. p. 135.1–135.7°.

2,4-Dichloro-6-nitroaniline.—This was prepared by the chlorination of 2-nitro-4-chloroaniline by the method of Witt.[11] The product was recrystallized three times from 80% methyl alcohol; test of purity, constant specific color intensity, constant m. p. 100.9–101.2°.

***o*-Nitroaniline.**—Eastman Kodak Co. white label *o*-nitroaniline was recrystallized three times from 50% alcohol, once from 95% alcohol; test of purity, constant specific color intensity, constant m. p. 71.6–72.4°.

Hydrogen Chloride.—This was prepared by dropping concd. sulfuric acid into a mixture of sodium chloride and concd. hydrochloric acid. The gas was first bubbled through sulfuric acid and then passed through a Dry Ice trap.

Methanesulfonic Acid.—This was prepared by a modification of the procedure of Hemilian.[12] Methyl iodide was heated under reflux with ammonium sulfite solution until all the iodide had reacted. Excess barium hydroxide was added and the mixture boiled until no more ammonia was liberated. The larger part of the barium ion was removed by precipitating it out with sulfuric acid, and the iodine then precipitated by slow addition of 15% hydrogen peroxide with good stirring. It was necessary to cool the solution during the addition of the peroxide. The filtered solution was then cautiously treated with dilute sulfuric acid to remove the remainder of the barium ion, filtered and evaporated down to a sirupy consistency. It was then distilled at 0.6 mm. pressure, b. p. 138°. Titration against Bureau of Standards phthalate indicated 99.7%.

Benzene.—Merck & Co. pure benzene was redistilled, b. p. 79.8–80.0°.

Sodium Chloride.—Eimer and Amend C. P. grade.

Method

In the acidity measurements on sulfuric and methanesulfonic acids, the acid was weighed into a 100-ml. volumetric flask and diluted up to the mark with solvent. The pyridine solutions were made up in the same way. The standard solutions so obtained were transferred to calibrated burets. The calculated quantities of standard acid and base were drawn off into 25-ml. volumetric flasks, 1 ml. of indicator solution was added, and the solutions diluted up to the mark. The concentration of indicator in the final solutions was about 0.0001 *M*. The test solutions were placed in the closed cup in the colorimeter and compared against known standards. The standard solutions in each case contained the same concentration of pyridine acid sulfate as the test solutions to compensate for any salt effect on the color of the indicator. In this way a series of six to ten measurements could be made from one set of standard solutions. Such a series will hereafter be referred to as a "run."

The hydrochloric acid standard solutions were made up as follows. Hydrogen chloride was bubbled through nitromethane in a volumetric flask. When approximately the calculated weight desired had been taken up, the solution was diluted to about 100 ml. Ten ml. of this solution was pipetted into 25 ml. of 95% alcohol and titrated with standard base, using brom phenol blue as indicator. This method of titrating hydrochloric acid in the presence of nitromethane was found to be accurate to within one part per thousand. The standard hydrochloric acid solution was then transferred to the buret and used as outlined above.

The distribution experiments were carried out as follows. In the nitromethane experiments, the solvent was shaken with saturated sodium chloride solution in a large separatory funnel at 25.00°. Just sufficient water was then added to redissolve the precipitated sodium chloride, the layers separated, and placed in glass-stoppered bottles in the thermostat.

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(8) Williams, THIS JOURNAL, **47**, 2644 (1925); Williams and Skogstrom, *J. Phys. Chem.*, **30**, 1170 (1926).

(9) Schumacher and Hunt, *Ind. Eng. Chem.*, **34**, 701 (1942).

(10) "Int. Crit. Tables," Vol. III, p. 28.

(11) Witt, *Ber.*, **8**, 820 (1875).

(12) Hemilian, *Ann.*, **168**, 145 (1873); see also Strecker, *ibid.*, **148**, 90 (1868); and Wagner and Reid, THIS JOURNAL, **53**, 3407 (1931).

A solution of indicator was then made up in this nitromethane and diluted stepwise to obtain the various concentrations. Twenty-five ml. of each of these solutions was shaken with 25.0 ml. of the saturated salt solution obtained above in 125-ml. separatory funnels, whose outlets had been closed with short pieces of plugged rubber tubing. The funnels were placed in the thermostat, and shaken intermittently. After coming to 25.00°, the funnels were removed from the thermostat and the aqueous layer drawn off into a colorimeter cup and compared in the colorimeter against a known standard. The standard was made up in saturated sodium chloride solution to compensate for any salt effect on the indicator.

In the case of the experiments with benzene, the indicator solutions were made up in the benzene, and the procedure outlined above followed. Distilled water was used in place of the sodium chloride solution. In the benzene experiments, it was found necessary to leave the separatory funnels in the thermostat for about five hours to obtain complete separation of layers. A slight cloudiness in the water layer disappeared in this time.

Errors

In the acidity measurements, there were two significant sources of error. The larger of these was the visual error in making the color balance. A mean of nine independent settings of the colorimeter was taken on each solution. The average deviation of the ratio varied from 1 to 4%. Hammett and Deyrup's[6] conclusions on the precision of matching *versus* concentration of indicator were verified, particularly in the distribution experiments, where it was desired to keep the concentration of indicator in the organic layer as low as possible. It was found that at indicator concentrations below 10^{-5} molar, the precision of matching fell off rapidly.

The other significant though smaller error in the acidity measurements was inherent in the method of making up the solutions. The volumes of standard acid and base measured out of the burets varied from about 1 ml. to about 20 ml. Since this can be done with a precision of only 0.01–0.02 ml., the accuracy in making up the solutions could vary from about 4 to 0.1%. In general the volumes used were between 3 and 10 ml., where an accuracy of better than 1% could be expected.

Results

The acidity of unbuffered sulfuric acid solutions was measured from 0.005 to 0.03 M using 4-nitrodiphenylamine and 2,4-dichloro-6-nitroaniline as indicators. The results are shown in Fig. 1. The data (Table I) lie on a straight line of slope 1.76. The log R in this and the succeeding tables is log $[HI^+]/[I]$ where HI^+ and I are the acid and base forms of the indicator, respectively. The acidity of unbuffered hydrochloric acid solutions was also measured, these at concentrations varying from 0.02 M to 0.15 M. These data (Table I) also lie on a straight line of slope 1.76 (Fig. 1). The position of this curve is somewhat in doubt, as the high vapor pressure of hydrogen chloride in nitromethane solution results in a loss of solute amounting to several per cent. during the process of making up the solutions. However, the slope of the curve seems well defined, and exhibits remarkable agreement with that for sulfuric acid.

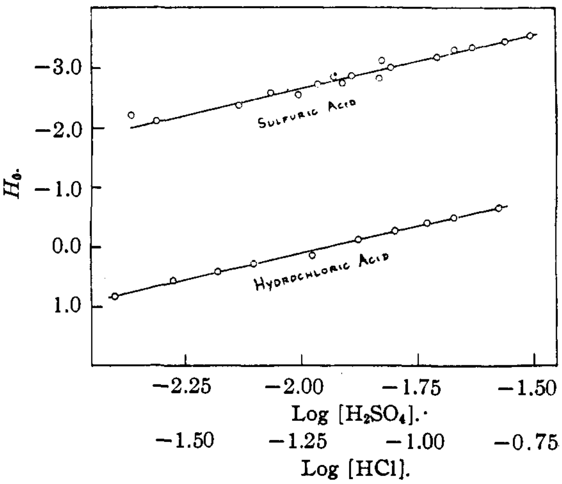

Fig. 1.

These curves are of interest in view of the fact that even at very low dilutions the slopes are considerably greater than would be predicted. The slope does not vary with the concentration of acid over the range studied. The curve for sulfuric acid defines certain limits for other of the data.

TABLE I

Run	Indicator	C (acid)	Log R	H_0
	UNBUFFERED SULFURIC ACID			
1	4-Nitrodiphenylamine	0.0043	−0.14	−2.22
		.0049	− .25	−2.11
		.0073	.01	−2.37
		.0086	.22	−2.58
		.0099	.18	−2.54
		.0108	.36	−2.72
		.0123	.38	−2.74
		.0129	.50	−2.86
		.0148	.45	−2.81
		.0150	.75	−3.11
		.0223	.94	−3.30
2	2,4-Dichloro-6-nitroaniline	.0117	− .46	−2.85
		.0157	− .31	−3.00
		.0197	− .13	−3.18
		.0235	.04	−3.35
		.0274	.13	−3.44
		.0314	.22	−3.53
	UNBUFFERED HYDROCHLORIC ACID			
18	*o*-Nitroaniline	0.0224	−0.94	0.84
		.0300	− .66	.56
		.0373	− .52	.42
		.0449	− .38	.28
		.0595	− .23	.13
		.0746	.00	− .10
		.0900	.15	− .25
		.105	.28	− .38
		.120	.39	− .49
		.149	.54	− .64

The acidity of buffered sulfuric acid solutions has been studied as a function of three variables:

concentration of buffer ("buffer" curve), concentration of acid at constant base (*i. e.*, HSO_4^-) concentration ("acid" curve), and concentration of base at constant acid concentration ("base" curve).

The data (Table II) from the first of these studies lie on a straight line of slope 1.87 (Fig. 2).

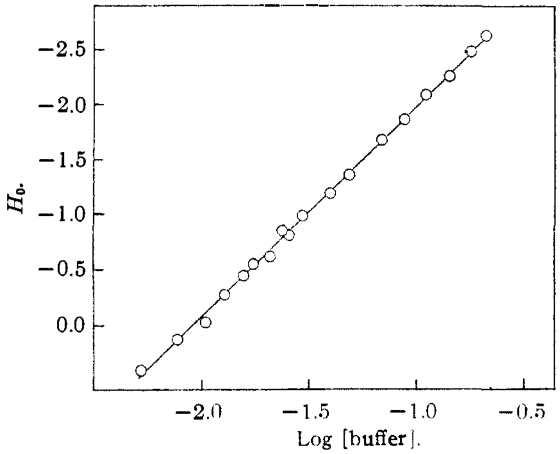

Fig. 2.

Concentrations studied range from 0.005 to 0.2 *M*, a forty-fold variation. It would of course be expected that there should be no change in acidity since the ratio concentration of acid to concentration of base is constant. This curve is in fact nearly parallel to the unbuffered acid curve.

TABLE II

ACIDITY AS A FUNCTION OF CONCENTRATION OF BUFFER

Run	Indicator	*C* (acid)	*C* (base)	Log *R*	H_0
15	*o*-Nitroaniline	0.0052	0.0052	−0.49	0.42
		.0077	.0078	−.21	.14
		.0104	.0104	.06	−.01
		.0129	.0129	.19	−.26
		.0158	.0156	.37	−.44
		.0207	.0208	.54	−.61
		.0256	.0250	.73	−.80
5	2-Nitro-4-chloroaniline	.0122	.0124	−.45	−.40
		.0173	.0173	−.31	−.54
		.0247	.0247	−.01	−.84
		.0296	.0295	.13	−.98
		.0396	.0396	.33	−1.18
		.0495	.0492	.50	−1.35
8	4-Nitrodiphenylamine	.0684	.0675	−.65	−1.67
		.0900	.0900	−.47	−1.85
		.113	.113	−.24	−2.08
		.145	.146	−.07	−2.25
		.181	.180	.15	−2.47
		.216	.214	.30	−2.62

The acid curve (Fig. 3) obtained at 0.025 *M* base concentration starts out linearly in the lower concentration range with a slope of 4.12, which holds in the range of about 0.01 to 0.04 *M*. Between 0.04 and 0.08 *M* there is a downward curvature, after which the curve again becomes linear with a slope of 3.35. The data (Table III) extend to slightly over 0.2 *M*.

Another acid curve was obtained at a base concentration of 0.05 *M* (Fig. 3) (Table III). The slope of this curve appears to be greater than that obtained at 0.025 *M* base by about 0.5 unit.

TABLE III

ACIDITY AS A FUNCTION OF CONCENTRATION OF ACID

Run	Indicator	*C* (acid)	*C* (base)	Log *R*	H_0
14	*o*-Nitroaniline	0.0107	0.0249	−0.75	0.67
		.0132	.0250	−.42	.34
		.0157	.0250	−.19	.11
		.0184	.0248	.09	−.17
		.0208	.0251	.35	−.43
		.0232	.0250	.61	−.69
		.0260	.0250	.85	−.93
3	2-Nitro-4-chloroaniline	.0173	.0251	−.72	−.13
		.0191	.0250	−.54	−.31
		.0212	.0251	−.40	−.45
		.0222	.0249	−.34	−.51
		.0240	.0249	−.16	−.69
		.0286	.0251	.19	−1.04
		.0336	.0251	.47	−1.32
		.0387	.0248	.73	−1.58
12	4-Nitrodiphenylamine	.0405	.0251	−.70	−1.64
		.0455	.0251	−.42	−1.92
		.0508	.0250	−.29	−2.05
		.0609	.0251	.06	−2.40
		.0706	.0252	.19	−2.53
		.0806	.0249	.42	−2.76
		.0909	.0251	.54	−2.88
12a	4-Nitrodiphenylamine	.0424	.0251	−.68	−1.72
		.0558	.0252	−.20	−2.20
		.0693	.0250	.12	−2.52
		.0829	.0251	.38	−2.78
		.0962	.0253	.58	−2.98
		.109	.0250	.68	−3.08
16	2,4-Dichloro-6-nitroaniline	.0753	.0252	−.77	−2.47
		.100	.0253	−.22	−3.02
		.124	.0251	.13	−3.37
		.150	.0253	.39	−3.63
		.175	.0253	.64	−3.88
		.213	.0251	.89	−4.13
9	2-Nitro-4-chloroaniline	.0251	.0503	−.89	0.04
		.0302	.0497	−.52	−.33
		.0340	.0504	−.34	−.51
		.0405	.0500	−.01	−.84
		.0452	.0500	.20	−1.05
		.0502	.0502	.47	−1.32
		.0601	.0503	.86	−1.71

The base curve was obtained at an acid concentration of 0.025 *M* (Fig. 4) (Table IV). As the concentration of base is decreased in the region of 0.01 *M*, the curve begins to flatten off somewhat, so that it is approaching a limit of acidity of about −3.4, as obtained from the unbuffered acid curve. The central portion of the curve is more or less linear, with a slope of about −2.43. At a concentration of about 0.05 *M*, an upward curvature sets in, which is about the same place that the acid curve acquires a downward curvature. A

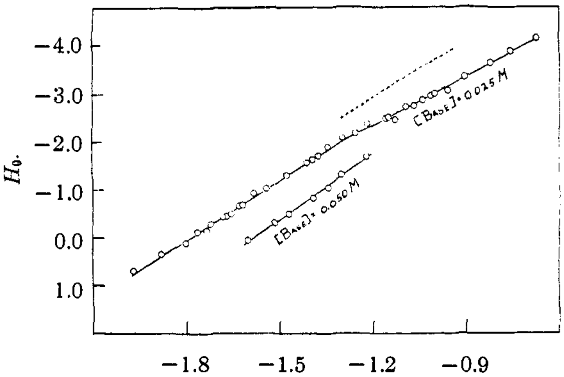

Fig. 3.

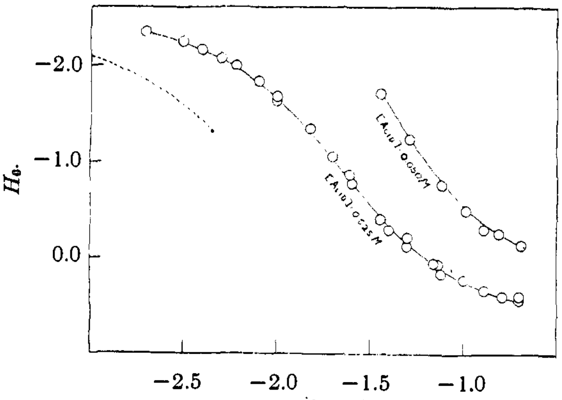

Fig. 4.

base curve was also obtained at an acid concentration of 0.05 *M* over a small range (Fig. 4) (Table IV). This appears to start out with a somewhat steeper slope, then curves upward to become nearly parallel with the other base curve.

TABLE IV

ACIDITY AS A FUNCTION OF CONCENTRATION OF BASE

Run	Indicator	*C* (acid)	*C* (base)	Log *R*	H_0
11	4-Nitrodiphenylamine	0.0250	0.0020	0.04	−2.34
		.0250	.0030	− .14	−2.24
		.0251	.0040	− .22	−2.16
		.0250	.0050	− .31	−2.07
		.0251	.0060	− .38	−2.00
		.0250	.0080	− .54	−1.84
		.0250	.0100	− .70	−1.68
4	2-Nitro-4-chloroaniline	.0250	.0101	.80	−1.65
		.0248	.0150	.50	−1.35
		.0251	.0201	.21	−1.06
		.0248	.0252	− .08	−0.77
		.0250	.0352	− .45	− .40
		.0252	.0502	− .64	− .21
13	*o*-Nitroaniline	.0251	.0248	.73	− .86
		.0252	.0503	− .01	− .12
		.0246	.0753	− .30	.17
		.0252	.100	− .36	.23
		.0251	.130	− .48	.35
		.0250	.161	− .54	.41
		.0254	.200	− .58	.45
13a	*o*-Nitroaniline	.0247	.0402	.15	− .29
		.0254	.0699	− .20	.06
		.0250	.100	− .37	.23
		.0255	.130	− .50	.36
		.0254	.200	− .55	.41
10	2-Nitro-4-chloroaniline	.0496	.0359	.86	−1.71
		.0495	.0512	.38	−1.23
		.0501	.0767	− .09	−0.76
		.0509	.102	− .36	− .49
		.0494	.128	− .56	− .29
		.0496	.154	− .60	− .25
		.0504	.204	− .72	− .13

The data for the buffered solutions form two sets of three curves, each set having a common point of intersection. At these points of intersection the sum of the slopes of the acid and base curves about equals the slope of the buffer curve. Thus at 0.025 *M*, 4.12 − 2.43 is 1.69, which is 0.18 unit less than the slope of the buffer curve. At 0.05 *M* the sum of the slopes is 1.61, which is 0.26 unit low. These differences are probably not significant, as a very small change in the direction of any of the curves results in a very large difference in slope, and some of the curves were obtained over small ranges, and in others curvature makes an accurate estimation of the slope difficult. This agreement means merely that for the variations concerned

$$dH_0 = \frac{\partial H_0}{\partial[\mathrm{A}]}\,d[\mathrm{A}] + \frac{\partial H_0}{\partial[\mathrm{B}]}\,d[\mathrm{B}]$$

$$i.\ e.,\ H_0 = f([\mathrm{A}],\ [\mathrm{B}])$$

where [A] is concentration of acid (H_2SO_4) and [B] concentration of base (HSO_4^-).

Two preliminary runs were made on methanesulfonic acid, one holding acid concentration constant at 0.025 *M* while varying base concentration below 0.01 *M*, the other at 0.025 *M* base concentration, varying the acid concentration around 0.1 *M*. The data are shown as dotted lines on the corresponding sulfuric acid graphs. The scale for the methanesulfonic acid is arbitrary, the data having been shifted upward by several units for purposes of comparison. It is seen that the data closely parallel those for sulfuric acid.

The effect of added water on the acidity of the solutions was also measured to determine how serious an effect absorption of water from the air by the solutions would have on the results. Two sets of data (Table V) (Fig. 5) were obtained, one in which the concentration of water was varied while holding the concentration of buffer constant at 0.025 *M* acid–0.025 *M* base, the other in which the concentration of buffer was varied while holding the concentration of water constant at 0.025 *M*. Added water has a definite effect on the acidity, as shown by the curves. The effect increases with the concentration of water (Curve 1) and appears to be independent of the concentration of buffer (Curve 2) over the range studied.

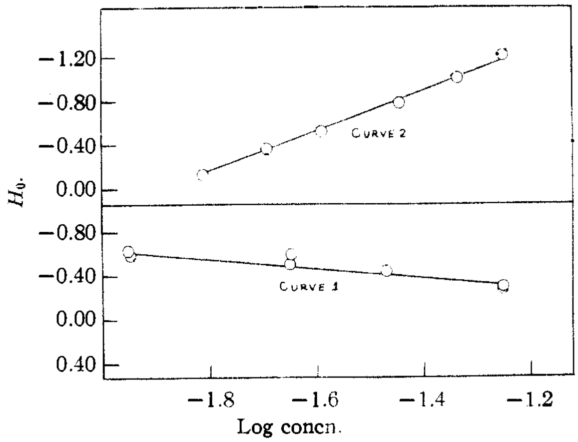

Fig. 5.

Thus 0.025 *M* water decreases the acidity of the buffered solution by about 0.3 unit.

TABLE V

THE EFFECT OF ADDED WATER

Indicator: 2-nitro-4-chloroaniline

Run	*C* (water)	*C* (acid)	*C* (base)	Log *R*	H_0
6	0.0000	0.0250	0.0251	−0.11	−0.74
	.0113	.0250	.0250	− .27	− .58
	.0226	.0249	.0249	− .36	− .49
	.0339	.0252	.0250	− .42	− .43
6a	.0000	.0249	.0251	− .09	− .76
	.0112	.0251	.0249	− .22	− .63
	.0224	.0251	.0249	− .29	− .56
	.0560	.0250	.0250	− .57	− .28
	.0560	.0253	.0251	− .58	− .27
7	.0254	.0154	.0151	− .68	− .17
	.0254	.0203	.0202	− .49	− .36
	.0254	.0257	.0251	− .30	− .55
	.0254	.0359	.0351	− .04	− .81
	.0254	.0462	.0453	.19	−1.04
	.0254	.0563	.0552	.37	−1.22

To determine whether there was any variation in acidity with concentration of indicator, the acidities of 0.025 *M* acid–0.025 *M* base solutions, to which varying concentrations of indicator had been added, were determined. The data are given in Table VI.

TABLE VI

ACIDITY AS A FUNCTION OF CONCENTRATION OF INDICATOR

Indicator: 2-nitro-4-chloroaniline

C (acid)	*C* (base)	*C* (ind.)	Log *R*	Δ Log *R*	Log *R* (cor.)
0.0250	0.0251	6.78×10^{-5}	−0.13	0.02	−0.11
.0250	.0251	1.36×10^{-4}	− .14	.02	− .12
.0249	.0251	2.71×10^{-4}	− .15	.03	− .12
.0251	.0250	4.07×10^{-4}	− .16	.03	− .13
.0250	.0252	5.42×10^{-4}	− .18	.05	− .13
.0252	.0249	6.78×10^{-4}	− .18	.05	− .13

The Δ log *R* in this table is a correction on the observed acidity which is made for two reasons. First, in making up the solutions of acid and base, it was not always possible to get exactly the concentrations desired. Thus, a concentration of 0.0250 *M* acid–0.0250 *M* base might be desired, while the actual stoichiometric concentrations as calculated from the concentrations of the standard solutions and from the buret readings, might be 0.0253 *M* acid and 0.0248 *M* base. This is easily brought back to the desired concentration, however, by making use of the slopes of the acid and base curves as obtained from a large number of points over a large range. These corrections never exceeded a few hundredths of a unit. A second correction in this particular set of data is necessary because of the fact that the concentration of indicator in some of the measurements is appreciable in comparison to the concentration of base and acid. In making this correction, the amount of indicator converted to the indicator ion was calculated from the colorimeter reading and the observed acidities corrected as explained above. The effect of making these corrections is seen by reference to the table. While the column headed log *R* would indicate a definite dependence of observed acidity on indicator concentration, the corrected values are all constant within the limits of experimental error. A summary of the runs made is given in Table VII.

TABLE VII

SUMMARY OF RUNS

The indicator used is given in parentheses.

1	Unbuffered sulfuric acid (4-nitrodiphenylamine)
2	Unbuffered sulfuric acid (2,4-dichloro-6-nitroaniline)
3	0.025 *M* base, acid varied *ca.* 0.025 *M* (2-nitro-4-chloroaniline)
4	0.025 *M* acid, base varied *ca.* 0.025 *M* (same)
5	Buffer varied *ca.* 0.025 *M* (same)
6 & 6a	0.025 *M* buffer, water varied *ca.* 0.025 *M* (same)
7	0.025 *M* water, buffer varied *ca.* 0.025 *M* (same)
8	Buffer varied *ca.* 0.1 *M* (4-nitrodiphenylamine)
9	0.050 *M* base, acid varied *ca.* 0.05 *M* (2-nitro-4-chloroaniline)
10	0.050 *M* acid, base varied *ca.* 0.050 *M* (same)
11	0.025 *M* acid, base varied *ca.* 0.01 *M* (4-nitrodiphenylamine)
12 & 12a	0.025 *M* base, acid varied *ca.* 0.05 *M* (same)
13 & 13a	0.025 *M* acid, base varied *ca.* 0.1 *M* (*o*-nitroaniline)
14	0.025 *M* base, acid varied *ca.* 0.015 *M* (same)
15	Buffer varied *ca.* 0.01 *M* (same)
16	0.025 *M* base, acid varied *ca.* 0.1 *M* (2,4-dichloro-6-nitroaniline)
17	0.025 *M* buffer, indicator varied (2-nitro-4-chloroaniline)
18	Unbuffered hydrochloric acid (*o*-nitroaniline)

The relative pK'_b's of the indicators are obtained by shifting on the H_0 axis the plot of the colorimeter readings for one of the indicators until the data lie on an extension of the plot of similar data for the other indicator. The data permit this to be done several times for each of the indicators. All the indicators are referred back to 2-nitro-4-chloroaniline, which was used in greatest frequency. The results of this process are given in Table VIII, together with the combination of runs from which each value was obtained. Also given for comparison are the results of Hammett and Deyrup[6] for sulfuric acid–water and perchloric acid–water mixtures, as corrected by Hammett and Paul.[13] The data for perchloric acid–water mixtures have been shifted further by 0.06 unit to again give 2-nitro-4-chloroaniline the value −0.85, the value selected as the basis of comparison.

TABLE VIII

RELATIVE pK_b''S OF INDICATORS

Indicator	Runs	Solvent CH_3NO_2–H_2SO_4	 H_2SO_4–H_2O	 $HClO_4$–H_2O
o-Nitroaniline	4, 13	−0.13		
	3, 14	− .08		
	5, 15	− .07		
	4, 13a	− .14		
	Average	− .10 ± 0.03	−0.13	−0.13
2-Nitro-4-chloroaniline	Standard	−0.85	−0.85	−0.85
4-Nitrodiphenylamine	3, 12	−2.34		
	4, 11	−2.38		
	12a, 3	−2.40		
	5, 8	−2.32		
	Average	−2.36 ± 0.03	−2.38	....
2,4-Dichloro-6-nitroaniline	1, 2	−3.31		
	12, 16	−3.24		
	Average	−3.28 ± 0.04	−3.22	−3.12

The distribution experiments were made to determine whether the indicators might be associated in nitromethane. In these experiments it was desired to keep the concentration in the organic layer as near as possible to the concentrations used in making the acidity measurements. This was inconsistent with the fact that the concentration in the water layer was then so low as to make accurate colorimetric measurements impossible. Even at the concentrations used, in the case of the nitromethane experiments the matchings were not made at optimum concentration, as indicated by the variation in the distribution constant (Table IX).

The highly divergent values indicated by the parentheses were probably due to the fact that the nitromethane had a tendency to stick in the form of minute globules near the stopcock of the separatory. One of these may have been drawn off with the water (the heavier) layer. Since the concentration of the indicator in the nitromethane layer is about 1000 times as great as that in the aqueous layer, only a very small drop could cause a very great error. The data indicate that the indicators are not associated in nitromethane under the conditions of the experiment.

It was thought that a tendency of the indicators to associate in nitromethane might be overcome by the comparatively high concentration of water in the nitromethane layer at equilibrium. It was therefore decided to determine whether the indicator would be associated in benzene, which with its very low dielectric constant, and because of the low solubility of water in this solvent, would offer comparatively good opportunity for association. The data for this experiment are also given in Table IX. Because of the more favorable distribution constant, it was possible to make more precise colorimetric matchings than was the case with nitromethane. This fact is reflected in the close agreement of the values of the distribution constant. The data indicate that o-nitroaniline is not associated in benzene solution.

TABLE IX

DISTRIBUTION OF INDICATORS

Initial concn. in nitromethane	Concn. in water (obs.)	$K = \frac{C(H_2O)}{C(CH_3NO_2)}$
Nitromethane and Water		
Indicator: o-nitroaniline		
5.01×10^{-3}	0.85×10^{-5}	1.7×10^{-3}
1.00×10^{-3}	0.28×10^{-5}	(2.8×10^{-3})
9.93×10^{-3}	1.47×10^{-5}	1.5×10^{-3}
4.96×10^{-3}	0.77×10^{-5}	1.6×10^{-3}
2.48×10^{-3}	0.32×10^{-5}	1.3×10^{-3}
	Average	1.5×10^{-3}
Indicator: 2-nitro-4-chloroaniline		
5.78×10^{-3}	2.27×10^{-6}	3.92×10^{-4}
4.98×10^{-2}	2.47×10^{-5}	(4.96×10^{-4})
2.49×10^{-2}	1.00×10^{-5}	4.02×10^{-4}
1.25×10^{-2}	0.474×10^{-5}	3.79×10^{-4}
	Average	3.91×10^{-4}
Benzene and Water		
Indicator: o-nitroaniline		
8.20×10^{-3}	1.31×10^{-4}	1.62×10^{-2}
4.10×10^{-3}	6.65×10^{-5}	1.65×10^{-2}
2.05×10^{-3}	3.36×10^{-5}	1.66×10^{-2}
1.02×10^{-3}	1.67×10^{-5}	1.67×10^{-2}
	Average	1.65×10^{-2}

Discussion

These results lead to a consistent and relatively simple, yet extremely puzzling picture of the behavior of acids in the solvent nitromethane. Since

$$H_0 = \text{constant} + \log \frac{[\mathrm{I}]}{[\mathrm{IH}^+]} \tag{1}$$

where I is indicator base and IH^+ its conjugate acid, the data for the buffer solutions may be put in the approximate form

$$\frac{[\mathrm{IH}^+]}{[\mathrm{I}]} = K \frac{[H_2SO_4]^4}{[HSO_4^-]^2} \tag{2}$$

The actual exponent for the H_2SO_4 term varies from 3.35 to 4.6, that for the HSO_4^- term from 0.6 to 3.0. Furthermore the data for the unbuffered acid solutions are consistent if for such solutions

$$[HSO_4^-] \propto [H_2SO_4] \tag{3}$$

The results are completely foreign to those ob-

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[13] Hammett and Paul, THIS JOURNAL, 56, 827 (1934).

served in water and other hydroxylic solvents for which

$$\frac{[IH^+]}{[I]} = K\frac{[HA]}{[A^-]} \qquad (4)$$

and for which in a solution of an unbuffered weak acid

$$[A^-] \propto [HA]^{1/2} \qquad (5)$$

Similar phenomena in a restricted sense (for the condition that [HA] + [A⁻] = constant) have been observed with aprotic solvents of low dielectric constant, namely, benzene and chlorobenzene (La Mer and Downes,[14] Griffiths[15]) and attributed to association phenomena. In so far as the ions are concerned these effects should be of much less magnitude in a solvent of dielectric constant 37, and much experience indicates that they are of no such importance in alcohols of still lower dielectric constant as the phenomena now observed in nitromethane.

It is improbable that the abnormal effects in question arise from the indicator. The experiments in which the concentration of indicator was varied demonstrate that any association of the indicator base is paralleled by an equal association of its conjugate acid, and the distribution experiments made it highly unlikely that the base is associated. Further the ratios of the values of *K* in equation (2) for various indicators are the same for these solutions as in others which have been studied previously (see Table VIII).

With these limitations upon the reaction of the indicator there appears to be no stoichiometric equation consistent with equation (2) unless one makes the improbable assumption that the indicators are diacid in this system, in which case the reaction

$$4H_2SO_4 + I \rightleftharpoons IH_2^{++} + 2(HSO_4^- \cdot H_2SO_4)$$

would satisfy the conditions.

If this interpretation is discarded one is left only with the conclusion that some new and unexpected effect makes the activity coefficients of H_2SO_4 and HSO_4^- largely dependent upon the concentration. If, for instance

$$f_{H_2SO_4} \propto [H_2SO_4]^3$$

and

$$f_{HSO_4^-} \propto [HSO_4^-]$$

then the equation

$$\frac{[IH^+]}{[I]} = K\frac{[H_2SO_4]\,f_{H_2SO_4}}{[HSO_4^-]\,f_{HSO_4^-}}$$

is equivalent to equation (2). Whatever the nature of the effect it appears from the preliminary data obtained for hydrochloric and methanesulfonic acids to operate in the same way with these acids as with sulfuric acid.

In 0.01 *M* solution sulfuric acid is about 40,000 times stronger in nitromethane than in water; in 0.1 *M* solution the corresponding ratio for hydrochloric acid is approximately 20. The ratio of the acid strengths of sulfuric and hydrochloric acids in nitromethane is of the order of 1000.

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Summary

1. The acidities of buffered and unbuffered solutions of sulfuric acid in nitromethane have been measured colorimetrically.

2. The *o*-nitroaniline and 2-nitro-4-chloroaniline indicators used in the acidity measurements were found by distribution experiments to be unassociated in nitromethane, and *o*-nitroaniline was similarly found to be unassociated in benzene.

3. In buffer solutions of sulfuric acid and pyridine bisulfate the indicator acidity varies approximately as the fourth power of the sulfuric acid concentration and inversely as the second power of the bisulfate concentration; in unbuffered acid solutions it varies approximately as the square of the acid concentration. These effects point to the existence of new and unexpected phenomena in the behavior of acids in solvents of low basicity, even when they are of relatively high dielectric constant.

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(14) La Mer and Downes, THIS JOURNAL, **55**, 1840 (1933).

(15) Griffiths, *J. Chem. Soc.*, 818 (1938).