[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Relative Acid Strengths in Normal Butyl Alcohol[1]

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The study of acid strengths in non-aqueous solvents has necessitated a more critical use of the colorimetric method. This paper is a report of the use of a photoelectric colorimeter in the determination of acid strengths in the basic solvent *n*-butyl alcohol. A recent report of relative strengths of acids in this solvent by an electrometric method affords a basis for comparison of the two methods.[2]

Indicators behave just as do other acids and bases and the protolysis constant for the transfer of a proton from the acid A to the basic form of the indicator I_B to give the acid form of the indicator I_A and the base B is written

$$K_{A_1I_B} = C_{B_1}C_{I_A}/C_{A_1}C_{I_B} \qquad (1)$$

For the reverse reaction we would have $K_{I_AB_1}$ as the acid is written first.

The concentration of the acid or basic form of the indicator can be determined colorimetrically and $K_{A_1I_B}$ computed from the stoichiometric concentrations. From the protolytic constants with indicators the classical dissociation constants or the protolytic constants of a series of acids referred to a common base (in this case the solvent) can be obtained.

Upon addition of hydrogen chloride to the weak base normal butyl alcohol the reaction

$$HCl + ROH \longrightarrow ROH{\cdot}H^+ + Cl^- \qquad (2)$$

probably goes practically to completion and we can take the concentration of $ROH{\cdot}H^+$ as equal to the stoichiometric concentration of the hydrochloric acid. This assumption is in agreement with the results of catalytic studies by Brönsted and Vance[3] who show that both hydrochloric and hydrobromic acids are probably practically completely dissociated in isoamyl alcohol. The reaction with the indicator base is

$$ROH{\cdot}H^+ + I_B \rightleftarrows ROH + I_A \qquad (3)$$

for which the protolysis constant is

$$K'_{(ROH\cdot H^+)I_B} = C_{ROH}C_{I_A}/C_{(ROH\cdot H^+)}C_{I_B} \qquad (4)$$

Now, since the concentration of the solvent is practically constant, this equation becomes

$$K_{(ROH\cdot H^+)I_B} = C_{I_A}C_{I_B}C_{ROH\cdot H^+} \qquad (5)$$

It follows from (1) and (5) that the protolysis constant of any acid and the solvent *n*-butyl alcohol may be expressed by the equation

$$K_{A(ROH)} = \frac{K_{AI_B}}{K_{(ROH\cdot H^+)I_B}} = \frac{C_BC_{I_A}}{C_AC_{I_B}}\,\frac{C_{I_B}C_{ROH\cdot H^+}}{C_{I_A}} = \frac{C_BC_{ROH\cdot H^+}}{C_A} \qquad (6)$$

If an indicator is very sensitive to acids it is impossible to determine $K_{(ROH\cdot H^+)I_B}$ with accuracy, and if the indicator is not very sensitive to acids it is equally impossible to determine K_{AI_B} with precision if the acid is weak. This difficulty is overcome by a stepwise procedure. $K_{A(ROH)}$ can be determined for an acid with an indicator which is fairly insensitive to acids. With this value another indicator more sensitive toward acids is used and $K_{(ROH\cdot H^+)I_B}$ for this second indicator is found, and now with another acid, A_1, and this same indicator, $K_{A_1(ROH)}$ is computed from the experimentally determined $K_{A_1I_B}$. A continuation of this stepwise procedure makes possible the evaluation of acidity constants that could not be reached by direct measurement.

Experimental Procedure

All colorimetric determinations of acid strength were carried out by measuring the concentration of a colored form of the indicator and then by substitution in equation (1), K_{AI_B} was found. With $K_{(ROH\cdot H^+)I_B}$ determined by means of previous measurements, $K_{A(ROH)}$ was evaluated.

The colorimetric determinations were based directly upon Beer's law, which states that the light transmitted by a solution is an exponential function of the thickness of the solution and of the concentration of the light-absorbing molecules. This expressed mathematically is

$$I_T = I_0e^{-kcx} \qquad (7)$$

where I_T is the transmitted light, I_0 the incident light, e the natural base of logarithms, k a constant, c the concentration of the light-absorbing molecules and x the thickness of the solution through which the light traveled. Here it should be emphasized that this equation is applicable for light of one and only one wave length. The extinction coefficient k has a definite value for each particular wave length and if any agreement with Beer's law is to be expected, which in turn means great accuracy for the determinations, only monochromatic light should be used.

In order to have the readings free from personal error a photoelectric colorimeter was constructed. Approximately monochromatic light was obtained by passing light from an automobile head lamp, operated by a six-volt

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[1] Abstracted from the dissertation of Ralph Burgess Mason presented December 1, 1935, to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

[3] Brönsted and Vance, *Z. physik. Chem.*, **A163**, 240 (1932).

storage battery, through a Hilger constant deviation spectroscope. This source was used in preference to a lamp operating on the a. c. line because its intensity was more constant, since Partridge[4] has shown that one of the greatest limitations of the photoelectric cell is the variable voltage of the light source. He states that the intensity of a tungsten filament lamp is

$$I = kv^{3.6}$$

where I is the intensity, k a constant and v the voltage across the lamp. This equation shows that a large change in light intensity results from a small change in voltage, which means a large variation in the photoelectric current also.

The prism was on a turntable and by turning a calibrated drum a beam of light of any wave length could be obtained. The prism was first adjusted at 5890 and 6705 Å. by means of sodium and lithium flames. The light obtained from the incandescent bulb was approximately monochromatic (covering a range of 30 Å. units) after resolution by the prism.

The light from the spectrometer passed through the solution cell to the photoelectric cell, and as shown in Fig. 1 photoelectric currents were amplified by means of the amplifier of Razek and Mulder.[5] The solution cell was a quartz cell with clear quartz end-plates which were not sealed to the cylindrical part of the cell but were ground to fit. By means of an outer metal jacket the end-plates were held in place making a liquid-tight container. It was possible to have varying lengths of cell simply by removing an end-plate and attaching an extension to a 2-cm. tube. The extension had a concave grind at one end, a convex at the other and the concave grind fitted into the convex grind at the end-plate, the convex into the concave grind of the 2-cm. cell. With extensions it was possible to obtain cell lengths of 2, 4, 6, 8 and 10 cm. Most of the work, however, was carried out in the 2-cm. section.

Two types of photoelectric cells were used, a potassium hydride which is sensitive in the blue portion of the spectrum, and a cesium cell which has its maximum sensitivity in the longer wave lengths of the spectrum. These cells were housed in a copper box and were so arranged that the cesium cell could be used for yellow or red light and the potassium hydride cell for blue light. Neither of these cells shows much response to green light.

The apparatus was balanced by adjusting P_1 and P_2 so that the milliammeters would read the same (5 or 6 m. a.), and with the galvanometer fully protected by the galvanometer shunt R_G the switch was closed. Now by gradually increasing R_G more current flowed through the galvanometer causing a deflection. When this took place the plate currents of the two tubes were not the same but were brought into better adjustment by the variable resistance R′, and for very fine balance the variable resistance R was employed. The apparatus balanced by this means did not remain so unless the filament voltages of the two tubes were compensated, which was brought about by fixing the settings of the resistors at P_7 and P_8 and by finding the points where a small change in the setting of P_9 would result in no change of the galvanometer reading. With the apparatus thus balanced and adjusted it was ready for use. When the photoelectric voltage was superimposed on the grid of one tube, the galvanometer showed a deflection which was proportional to the photoelectric current which in turn was proportional to the intensity of the light striking the photoelectric cell. Although the galvanometer readings were only relative and not absolute measurements of the light intensity, nevertheless these deflections could be used to obtain the concentrations of the colored forms of the indicators, as will now be shown. Equation (7) may be put into the form

$$\log I_T = \log I_0 - (kcx/2.3) \qquad (8)$$

If Beer's law is obeyed the logarithm of the intensity of the transmitted light will be found to be a linear function of c, the concentration of the light-absorbing substance. The slope of the line is $-kx/2.3$. Since the galvanometer readings are proportional to the intensity of the light striking the photoelectric cell, galvanometer readings may be plotted as ordinates in place of I_T.

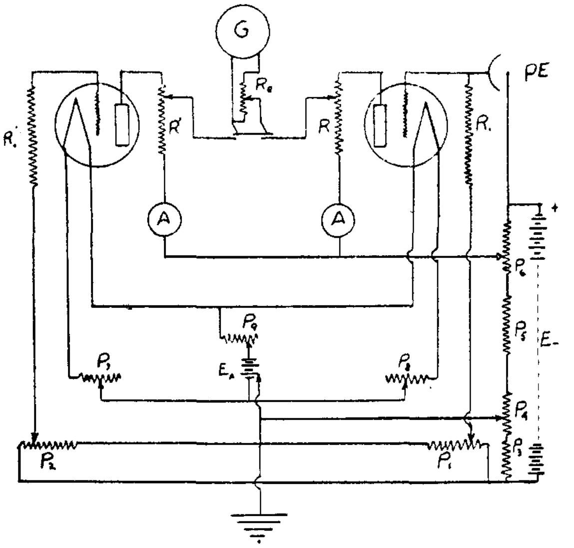

Fig. 1.—Electric circuit, meaning of symbols: A, milliammeters (10-m. a. range); G, Leeds and Northrup type R galvanometer No. 2500e; R_G, variable resistor, 1500 ohms; R_1, resistor, 100 megohms; R_1', resistor, 100 megohms; R, resistor, total of 1030 ohms (1000 ohms with variable portion of 30 ohms); R′, resistor, total of 1100 ohms (850 ohms with variable portion of 250 ohms); P_1 and P_2, potentiometers, 3000 ohms each; P_3, potential divider, 1500 ohms; P_4, potential divider, 1500 ohms; P_5, potential divider, 7000 ohms; P_6, potential divider, 3000 ohms; P_7 and P_8, variable resistors, 6 ohms each; P_9, variable resistor, 1 ohm; E_A, filament battery (6-volt storage); E_T, six 45-volt B batteries connected with two series of three in parallel; Cunningham 112A vacuum tubes were used.

The experimental procedure consisted of making one form of the indicator at various concentrations, which was done by preparing indicator solutions of the desired concentration and then adding a sufficient quantity of acid or base to produce the completely acidic or basic form of the

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[4] H. M. Partridge, *Ind. Eng. Chem., Anal. Ed.*, **2**, 207 (1930).

[5] Joseph Razek and P. J. Mulder, *J. Opt. Soc. Am.* and *Rev. Sci. Instruments*, **19**, 390 (1929).

indicator. The necessary amount of acid or base was determined experimentally, that is, acid or base was added to the indicator solution until an additional amount caused no change in the galvanometer reading. The basic forms of brom phenol blue and brom cresol green were solutions of their lithium salts, while the basic form of picric acid was prepared by the addition of lithium butylate until an increase of one drop caused no color change in the solution. The basic forms of brom cresol green, brom phenol blue and picric acid were used and the acidic forms of dimethyl yellow and benzene-azodiphenylamine. Different amounts of the colored form of each of these indicators were put into the solution cell, light passed through and the galvanometer read. The logarithms of these readings plotted against the concentration, lay on a straight line as required by Beer's law. From such curves the concentration of the colored form of the indicator in an unknown solution, corresponding to a given galvanometer deflection, could be read off. Owing, however, to the fact that it was difficult to keep the amplifier balanced over a long period of time, our practice was to construct a calibration curve of two points only at the time of the colorimetric analysis of the unknown solution. With experience it was possible to locate one of these points on each side of the unknown solution.

Beer's law as expressed in equation (7) is applicable only when the light-absorbing molecules are identical. For indicators presenting one color there are no obstacles to be met because the light-absorbing molecules are all the same and colored light which is preferentially absorbed may be used. For example, the fact that picric acid solutions are yellow means that the light absorption is greater in the violet range of the spectrum. In this work a blue light of 4600 Å. was employed for picric acid solutions because of the deficiency of violet light in the source. Although with a two-color indicator there are two kinds of light-absorbing molecules, it is sometimes possible to find a wave length at which only one form of the indicator absorbs light. The yellow forms of dimethyl yellow and benzene-azodiphenylamine absorb negligible amounts of light at 5900 Å. wave length while their red forms absorb a fair amount. By using light of 5900 Å. wave length, it was possible to treat these indicators like one-color indicators. The use of light of 5750 Å. made the same procedure possible in the case of brom phenol blue (yellow-blue).

With brom cresol green it was not possible to find a wave length at which one form of the indicator absorbed no light. While there was a minimum absorption at 5800 Å. by the yellow form, it was nevertheless appreciable. In this case Beer's law has the form

$$I_T = I_0 e^{-k_A c_A x} e^{-k_B c_B x} \qquad (9)$$

where k_A is the extinction coefficient and c_A the concentration of the acid form and k_B and c_B the extinction coefficient and concentration, respectively, of the basic form.

The procedure with brom cresol green was as follows. The extinction coefficient of the indicator wholly in its acid form, k_A, was obtained by measurement of the intensity of the light transmitted by solutions of concentrations c_1 and c_2. From (8) it follows that

$$k_A = \frac{2.3}{(c_2 - c_1)x} \log \frac{I_{T_1}}{I_{T_2}} \qquad (10)$$

Table I shows the extinction coefficient of the acid form of brom cresol green at 5800 Å.

Table I

Extinction Coefficient of Yellow Form of Brom Cresol Green at 5800 Å.

Cell length = 10 cm.

$c \times 10^5$	I_T = k' Galv. defl.	k
0.0	20.5	
1.459	18.7	630
2.918	17.0	630
5.836	14.5	600
14.59	8.5	610
		Mean k = 617

An approximate value of the concentration of the basic form in the unknown solution was found in the customary manner. The corresponding approximate concentration of the acid form was then obtained by difference and $e^{-k_A c_A x}$ was computed. Dividing the galvanometer reading by $e^{-k_A c_A x}$ gave a corrected intensity, I'_T, from which a more reliable value of c_B was computed.

Tables II, III and IV illustrate how the calculations for *o*-toluic acid with brom cresol green were carried out.

Table II

Galvanometer Readings for *o*-Toluic Acid

Unknowns		Comparison standards		
Flask	I_T	Flask	I_T	$C_{I_B} \times 10^6$
35	12.5	22	10.7	2.817
		10	19.0	1.812
45	12.4	22	10.5	2.718
		10	18.7	1.812
61	12.5	22	10.6	2.718
		10	18.6	1.812

The computations from the preceding data are summarized in Table III; the columns headed "C_{I_B}" give the concentration of the basic form of the indicator as read from the calibration curve.

Table III

Correction for Light Absorption by Yellow Form of Brom Cresol Green

Flask	35	45	61
$C_{I_B} \times 10^5$	2.47	2.45	2.46
$C_{I_A} \times 10^5$	1.16	1.17	1.16
$e^{-k_A c_A x}$	0.985	0.985	0.985
I_T	12.5	12.4	12.5
$I'_T = I_T/e^{-k_A c_A x}$	12.7	12.6	12.7
$C_{I_B} \times 10^5$	2.45	2.43	2.44
$C_{I_A} \times 10^5$	1.18	1.20	1.19

The concentration of the indicator was comparable to that of the buffered solution of the acid, so in calculating the acid strength constants a correction had to be made for the acid that was used to convert the indicator. That is to say, the acid was added to the basic form of the indicator and the concentration of the undissociated acid became the original acid concentration minus the concentration of the acid form of the indicator, while the concentration of the *o*-toluate ion increased the concentration of the acid form of the indicator. The values of the protolysis constant for *o*-toluic acid and the basic form of brom cresol green are given in Table IV.

TABLE IV

K_{AI_B} FOR *o*-TOLUIC ACID WITH BROM CRESOL GREEN AS INDICATOR

Flask	35	45	61
$C_{0A} \times 10^5$	22.54	45.08	67.62
$C_{0B} \times 10^5$	22.54	45.08	67.62
$C_{0I} \times 10^5$	3.625	3.625	3.625
$C_{I_B} \times 10^5$	2.45	2.43	2.44
$C_{I_A} \times 10^5$	1.18	1.20	1.19
K_{AI_B}	0.534	0.522	0.505
Mean K_{AI_B}			.520

Brom cresol green was the only indicator with which it was necessary to make a correction because of absorption of light by both acid and basic forms. With the other two-color indicators it was possible to find a wave length at which absorption by one form was negligible.

As was previously mentioned, the method of determining the protolysis of the indicators least sensitive to acids was to add a definite amount of hydrochloric acid and then measure the change in color of the indicator. This procedure was followed with dimethyl yellow, but since benzeneazodiphenylamine hydrochloride could be prepared pure, the hydrochloride was added to the solution in this case.

Preparation of Materials.—The *n*-butyl alcohol was purified by treating a commercial grade of the alcohol with sulfuric acid, distilling and refluxing over sodium hydroxide. This treatment was followed by refluxing over lime and subsequent distillation in a 17-ball Snyder column.

Lithium butylate was prepared by dissolving lithium in the pure *n*-butyl alcohol in an inert atmosphere. The solution was standardized against Bureau of Standards benzoic acid.

Lithium Chloride.—Our original plan included the study of the effect of ionic strength on the acid strength constants and a few measurements were carried out using fused lithium chloride. Difficulties with the alkalinity of the salt led us to defer that part of the work.

Acids.—Acetic acid was purified by the method of Bousfield and Lowry.[6] Monochloroacetic acid was twice crystallized from benzene, dichloroacetic acid was fractionally distilled. Picric acid was recrystallized from an aqueous solution of hydrochloric acid. The *o*-chlorobenzoic acid was purified in connection with solubility studies of Osol and Kilpatrick.[7] The other acids were Kahlbaum products which upon drying were found, by titration with standard base, to be sufficiently pure.

Bases.—The hydrochlorides of ethylamine, piperidine and aniline were dried *in vacuo* over sulfuric acid for a period of four weeks and used without further purification. Each of these was a Kahlbaum product.

Indicators.—The indicators brom cresol green and brom phenol blue were purified samples used in connection with other studies.[8] The lithium salts were prepared by adding two equivalents of lithium ethoxide to the acid dissolved in ethyl alcohol and evaporating to dryness.

The dimethylaminoazobenzene was purified by recrystallization from an alcoholic solution. The purified product melted at 117°. The benzeneazodiphenylamine was recrystallized from alcohol until the product had a melting point of 82°. The hydrochloride was prepared by the method of Witt, that is, the free base was dissolved in benzene and the hydrochloride precipitated by passing dry hydrogen chloride into the solution.[9]

Experimental Results

The experimental results are given in Tables V, VI, VII, VIII and IX, and summarized in Table

TABLE V

K_{AI_B} WITH BROM CRESOL GREEN (AT 5800 Å.)

$C_{0A} \times 10^5$	$C_{0B} \times 10^5$	$C_{I_B} \times 10^5$	$C_{I_A} \times 10^5$	K_{AI_B}
		Benzoic Acid		
19.29	19.29	2.54	1.09	0.48
38.58	38.58	2.52	1.12	.47
			Mean	.475
		Acetic Acid		
52.88	52.88	2.78	0.85	0.316
105.80	105.80	2.78	.85	.308
158.70	158.70	2.79	.84	.304
			Mean	.309
		o-Chlorobenzoic Acid		
18.87	56.61	1.32	2.303	6.20
28.30	84.90	1.28	2.345	6.16
			Mean	6.18
		Piperidinium Ion		
380.2		1.05	2.575	0.0167
570.3		0.915	2.610	.0133
380.2		1.05	2.575	.0167
			Mean	.0155
		Ethylammonium Ion		
304.6		0.755	2.870	0.036
304.6		.755	2.870	.036
456.9		.660	2.985	.030
			Mean	.034

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(6) Bousfield and Lowry, *J. Chem. Soc.*, **99**, 1440 (1911).

(7) Osol and Kilpatrick, THIS JOURNAL, **55**, 4430 (1933).

(8) Chase and Kilpatrick, *ibid.*, **54**, 2284 (1932); Kilpatrick, *ibid.*, **56**, 2048 (1934).

(9) Witt, *Ber.*, **12**, 259 (1879).

X. All measurements were made at approximately 25°.

TABLE VI

$K_{\mathrm{AI_B}}$ WITH BROM PHENOL BLUE AS INDICATOR (MEASUREMENTS AT 5700 Å.)

$C_{0\mathrm{A}} \times 10^5$	$C_{0\mathrm{B}} \times 10^5$	$C_{\mathrm{I_B}} \times 10^6$	$C_{\mathrm{I_A}} \times 10^5$	$K_{\mathrm{AI_B}}$
		o-Chlorobenzoic Acid		
24.69	24.69	0.835	0.642	0.807
49.38	49.38	.82	.65	.817
			Mean	.812
		m-Nitrobenzoic Acid		
37.38	37.38	0.734	0.739	1.03
56.07	56.07	.736	.737	1.04
			Mean	1.035
		Monochloroacetic Acid		
31.16	93.48	0.691	0.782	3.52
62.32	186.9	.687	.786	3.51
			Mean	3.515
		Cyanoacetic Acid		
37.11	148.5	0.406	1.061	10.8
74.22	297.0	.406	1.061	10.5
11.3	445.3	.406	1.061	10.6
			Mean	10.6
		Dichloroacetic Acid		
38.78	97.0	0.612	0.861	3.75
58.17	145.1	.578	.895	3.92
58.17	145.1	.578	.895	3.92
			Mean	3.86

TABLE VII

$K_{\mathrm{AI_B}}$ WITH DIMETHYL YELLOW AS INDICATOR (MEASUREMENTS AT 5900 Å.)

$C_{0\mathrm{A}} \times 10^4$	$C_{\mathrm{I_A}} \times 10^4$	$C_{\mathrm{I_B}} \times 10^4$	$K_{\mathrm{AI_B}} \times 10^6$
	Dichloroacetic Acid		
518.4	0.185	9.30	2.03
777.6	.23	9.25	2.10
		Mean	2.065
	Trichloroacetic Acid		
234.4	0.35	4.39	19.7
234.4	.35	4.39	19.7
	Anilinium Ion		
21.1	0.45	4.29	95,000
63.3	.785	3.96	108,000
		Mean	102,000
	Solvated Hydrogen Ion		
2.482	0.49	42,500	57,000,000
4.694	.91	39,700	57,000,000

TABLE VIII

$K_{\mathrm{AI_B}}$ WITH BENZENE-AZODIPHENYLAMINE (MEASUREMENTS AT 5900 Å.)

$C_{0\mathrm{A}} \times 10^4$	$C_{\mathrm{I_A}} \times 10^5$	$C_{\mathrm{I_B}} \times 10^6$	$K_{\mathrm{AI_B}} \times 10^{-1}$
	Solvated Hydrogen Ion		
6.798	1.42	66.56	3.12
7.554	1.77	73.77	3.09
		Mean	3.10

TABLE IX

DISSOCIATION CONSTANT OF PICRIC ACID (MEASUREMENTS AT 4600 Å.)

$C_0 \times 10^3$	$C_{\mathrm{B^-}} \times 10^4$	$K_{\mathrm{A(ROH)}} \times 10^6$
2.54	3.69	6.30
2.64	3.76	6.30
3.17	4.11	6.15
	Mean	6.25

TABLE X

SUMMARY OF $K_{\mathrm{AI_B}}$ VALUES

	$K_{\mathrm{AI_B}}$
1. Brom cresol green	
1. Benzoic acid	0.475
2. Acetic acid	.390
3. *o*-Chlorobenzoic acid	.18
4. Piperidinium ion	.0155
5. Ethylammonium ion	.034
6. *o*-Toluic acid	.520
2. Brom phenol blue	
1. *o*-Chlorobenzoic acid	0.812
2. *m*-Nitrobenzoic acid	1.03
3. Monochloroacetic acid	3.515
4. Cyanoacetic acid	10.6
5. Dichloroacetic acid	3.86
3. Dimethyl yellow	
1. Dichloroacetic acid	2.07×10^{-6}
2. Trichloroacetic acid	1.97×10^{-4}
3. Anilinium ion	1.02
4. Solvated hydrogen ion	5.7×10^2
4. Benzene-azodiphenylamine	
1. Solvated hydrogen ion	3.10×10^1
Picric acid	
1. Solvated hydrogen ion	1.60×10^4

The accuracy of the results obtained depends upon the accuracy of the composition of the solutions, upon the validity of Beer's law, and upon the constant amplification of the photoelectric current. It will be noted that with the corresponding lithium salt, no deviations greater than ±2% were obtained. In other cases the deviations ran as high as 6%. To ensure constant amplification of the photoelectric current, a new calibration curve was made at the time each unknown solution was analyzed. By means of equation (6) the values of the dissociation constants were found. With dimethyl yellow as indicator $K_{\mathrm{AI_B}}$ was determined for four acids including the solvated hydrogen ion. From these data $K_{\mathrm{A(ROH)}}$ was obtained for each of these acids. With $K_{\mathrm{A(ROH)}}$ for dichloroacetic acid $K_{\mathrm{(ROH)I_B}}$ was found from brom phenol blue and continuing in this manner $K_{\mathrm{A(ROH)}}$ for each acid in the table was found. It is to be noted that $K_{\mathrm{A(ROH)}}$ for an indicator is $K_{\mathrm{I_A(ROH)}}$ which is the reciprocal of $K_{(\mathrm{ROH \cdot H^+})\mathrm{IB}}$. The values of $K_{\mathrm{A(ROH)}}$ are summarized in Table XI; their logarithms and the logarithms of the corresponding dissociation constants in aqueous solution are also given.

TABLE XI

DISSOCIATION CONSTANTS

	Acid	*n*-Butyl alcohol 25° approximate $K_{\mathrm{A(ROH)}}$	Log $K_{\mathrm{A(ROH)}}$	Water 25° Log $K_{\mathrm{A(H_2O)}}$
1	Brom cresol green (yellow to blue)	1.21×10^{-10}	$\overline{10}.082$	$\overline{5}.06$[a]
2	Benzoic acid	5.75×10^{-11}	$\overline{11}.760$	$\overline{5}.80$[b]
3	Acetic acid	3.74×10^{-11}	$\overline{11}.572$	$\overline{5}.24$[c]
4	*o*-Chlorobenzoic acid	7.48×10^{-10}	$\overline{10}.873$	$\overline{3}.08$[d]
5	Piperidinium ion	1.89×10^{-12}	$\overline{12}.276$	$\overline{12}.87$[e]
6	Ethylammonium ion	4.11×10^{-12}	$\overline{12}.614$	$\overline{11}.33$[e]
7	*o*-Toluic acid	6.33×10^{-11}	$\overline{11}.802$	$\overline{4}.10$[f]
8	Brom phenol blue (yellow to blue)	9.5×10^{-10}	$\overline{10}.978$	$\overline{5}.77$[g]
9	*m*-Nitrobenzoic acid	9.5×10^{-10}	$\overline{10}.978$	$\overline{4}.54$[f]
10	Monochloroacetic acid	3.25×10^{-9}	$\overline{9}.512$	$\overline{3}.14$[h]
11	Cyanoacetic acid	9.79×10^{-9}	$\overline{9}.990$	$\overline{3}.57$[f]
12	Dichloroacetic acid	3.58×10^{-8}	$\overline{8}.554$	$\overline{2}.70$[f]
13	Azobenzene dimethylammonium ion	1.71×10^{-3}	$\overline{3}.233$	$\overline{4}.71$[i]
14	Trichloroacetic acid	3.41×10^{-7}	$\overline{7}.533$	$\overline{1}.30$[j]
15	Anilinium ion	1.8×10^{-4}	$\overline{4}.254$	$\overline{5}.34$[f]
16	Benzene-azodiphenylammonium ion	3.12×10^{-2}	$\overline{2}.494$	$\overline{2}.54$[k]
17	Picric acid	6.23×10^{-5}	$\overline{5}.794$	$\overline{1}.20$[f]

[a] Kilpatrick, *Chem. Rev.*, **16**, 57 (1935). [b] Brockman and Kilpatrick, THIS JOURNAL, **56**, 1483 (1934). [c] Harned and Ehlers, *ibid.*, **55**, 652 (1933). [d] Saxton and Meier, *ibid.*, **56**, 1918 (1934). [e] Hall and Sprinkle, *ibid.*, **54**, 3478 (1932). [f] Landolt–Börnstein, "Tabellen." [g] Kilpatrick, THIS JOURNAL, **56**, 2048 (1934). [h] Wright, *ibid.*, **56**, 314 (1934). [i] Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928). [j] Hall, *Chem. Rev.*, **8**, 191 (1931). [k] Hammett and Paul, THIS JOURNAL, **56**, 827 (1934).

The data of Table XI are summarized graphically in Fig. 2 in which log $K_{\mathrm{A(ROH)}}$ is plotted against log $K_{\mathrm{A(H_2O)}}$. Both lines in Fig. 2 are drawn with unit slope. In general we believe that these slopes may vary from unity.

For both types of acid, the logarithm of the dissociation constant in *n*-butyl alcohol is proportional to the logarithm of the dissociation constant in water. As in other cases the change in strength with change[10] in dielectric constant is in qualitative agreement with the theory.

Brönsted in a consideration of the effect of charge and medium on[11] the equilibrium constants of protolytic reactions arrives at the equation

$$\ln K_{\mathrm{A_1B_2}} = \ln K_{\mathrm{a_2}} + \ln K_{\mathrm{b_2}} + \frac{\epsilon^2}{2kTD}\left[\frac{2Z_{\mathrm{A_1}} - 1}{r_1} - \frac{2Z_{\mathrm{A_2}} - 1}{r_2}\right]$$

where $K_{\mathrm{A_1B_2}} = C_{\mathrm{B_1}}C_{\mathrm{A_2}}/C_{\mathrm{A_1}}C_{\mathrm{B_2}}$ is the equilibrium constant for the transfer of a proton from $\mathrm{A_1}$ to $\mathrm{B_2}$, $K_{\mathrm{a_1}}$ and $K_{\mathrm{b_2}}$ the constants $a_{\mathrm{H^+}}\ (a_{\mathrm{B_1}}/a_{\mathrm{A_1}})$ and $\frac{1}{a_{\mathrm{H^+}}}\frac{a_{\mathrm{A_2}}}{a_{\mathrm{B_2}}}$, respectively, ϵ the electronic charge, k the Boltzmann constant, T the absolute temperature, D the dielectric constant, Z the valence and r_1 and r_2 the effective radii of the first and second protolytes. If $\mathrm{A_2}$ is taken as the standard acid, $K_{\mathrm{A_1B_2}}$ becomes K_r in the symbols of Wynne-Jones.[12]

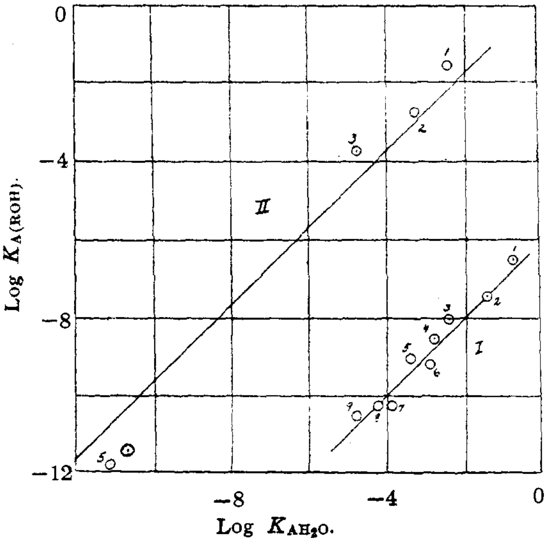

Fig. 2.—Log $K_{\mathrm{A(ROH)}}$ plotted against log $K_{\mathrm{AH_2O}}$. I. Carboxylic acids: 1, trichloroacetic acid; 2, dichloroacetic acid; 3, cyanoacetic acid; 4, monochloroacetic acid; 5, *m*-nitrobenzoic acid; 6, *o*-chlorobenzoic acid; 7, *o*-toluic acid; 8, benzoic acid; 9, acetic acid. II. Ammonium ion type acids: 1, benzene-azodiphenylammonium ion; 2, azobenzene-dimethylammonium ion; 3, anilinium ion; 4, ethylammonium ion; 5, piperidinium ion.

This author finds that if one plots the logarithm of K_r against $1/D$ for the three solvents ethyl alcohol, methyl alcohol and water the linear relationship permits an extrapolation to $D = \infty$, and an evaluation of $K_{r\infty}$ or the intrinsic acid strength. The results in the present paper are at sufficiently low ionic strengths to afford a test of the validity of this relationship.

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(10) Brönsted, Delbanco and Tovborg-Jensen, *Z. physik. Chem.*, **A169**, 361 (1934).

(11) Brönsted, *ibid.*, **A169**, 52 (1934).

(12) Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

TABLE XII

LOG K_r FOR CARBOXYLIC ACIDS IN VARIOUS SOLVENTS

Solvent	Water	Acetonitrile	Methyl alcohol	Ethyl alcohol	*n*-Butyl alcohol (a)	*n*-Butyl alcohol (b)	*m*-Cresol
Dielectric constant	80	37	33	25	17	17	13
Benzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acetic acid	− .56	− .69	− .1	.0	− .19	− .05	.20
o-Toluic acid	.30	.19	...	...	.04	.02	..
m-Nitrobenzoic acid	.74	..	...	1.1	1.22	1.09	.78
o-Chlorobenzoic acid	1.28	1.09	...	1.0	1.11	1.00	..
Monochloroacetic acid	1.34	1.48	...	...	1.75	1.71	1.63
Cyanoacetic acid	1.77	..	...	...	2.23	..	2.15
Dichloroacetic acid	2.9	2.73	3.0	3.1	2.79	3.1	2.96
Trichloroacetic acid	3.50	3.88	4.3	4.4	3.77	4.1	3.88

In Table XII are listed the values of log K_r (K_r is the ratio of the dissociation constant in question to that of a benzoic acid) for a number of carboxylic acids in various solvents.

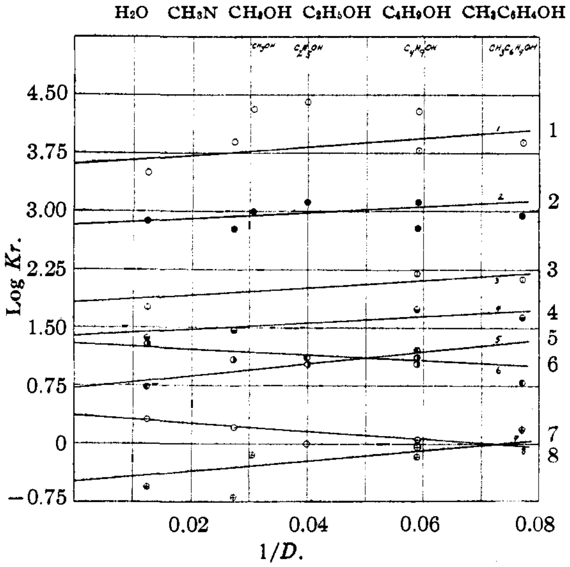

Fig. 3.—Graphic presentation of the Wynne-Jones relationship: 1, trichloroacetic acid; 2, dichloroacetic acid; 3, cyanoacetic acid; 4, monochloroacetic acid; 5, *m*-nitrobenzoic acid; 6, *o*-chlorobenzoic acid; 7, acetic acid; 8, *o*-toluic acid.

A negative value for log K_r means that the acid is weaker than benzoic acid. For aqueous solutions the K_r's were computed from the dissociation constants given in Table XI.

The values for K_r in *m*-cresol were calculated from the results of Brönsted, Delbanco and Tovborg-Jensen.[10] The source of the data for methyl and ethyl alcohol is given by Wynne-Jones. The results in acetonitrile are from the unpublished data of M. and M. L. Kilpatrick. For comparison with the results of the present study the column marked (b) under *n*-butyl alcohol gives the values from the data of Wooten and Hammett.[2] These data were obtained in the presence of 0.05 molar lithium chloride and are not strictly comparable with our data obtained at low ionic strengths. These differences are not greater than those which might be attributed to specific salt effects.

An inspection of Table XII and the graphic presentation in Fig. 3 indicates at best a qualitative agreement with the relationship of Wynne-Jones. The slopes of the lines for *o*-toluic and *o*-chlorobenzoic acid are in accord with his observations on ortho substituted acids. No correlation with the relationship was found for the ammonium type acids. Wooten and Hammett have given a different interpretation of the variation in relative strength of the carboxylic acids.

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Summary

1. A photoelectric colorimeter has been constructed.

2. The dissociation constants of seventeen acids in *n*-butyl alcohol have been determined.

3. The results have been compared with other results in the same solvent and the acid strengths relative to benzoic acid have been compared in different solvents.

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