

**157.** *The Acid-Base Function in Non-aqueous Media. Part II. The Relative Strengths of Acids in Chlorobenzene.*

By D. C. GRIFFITHS.

An indicator method has been used for the determination of the relative strengths of a number of organic acids in the solvent chlorobenzene. It has been found that there is for uncharged acids a very close parallelism between the relative strengths in water and those in chlorobenzene. Measurements have been made at (a) constant salt concentration and (b) constant "total acid" concentration. It has been found possible to allow for association by the method of LaMer and Downes.

ACCORDING to the classical ionisation theory of acids and bases, these exercised their functions when they gave rise respectively to hydrogen and to hydroxyl ions. Chlorobenzene is non-polar and non-ionising in the accepted sense, and there is certainly no way in which a base such as ammonia could on the classical theory exercise its basic function in chlorobenzene.

The situation was clarified by Brönsted's suggestion (*Rec. Trav. chim.*, 1923, 42, 718; *J. Physical Chem.*, 1926, 30, 777) that acids and bases could be defined by the relation Acid = Base + Proton. Later he gave an expression (*Ber.*, 1928, 61, 2049) which serves as a measure of relative acidity in a given solvent. For the reaction represented by the equation,  $HA + B = HB + A$ , where B is a base, chosen as standard for the solvent employed, HA the acid used, HB the acid corresponding to the base B, and A the base corresponding to the acid HA,  $K = c_{HB}c_A/c_Bc_{HA}$  serves as a measure of acidity in a given solvent. Already this has led to interesting results: not only has it been found possible to get a qualitative picture of the function of acids and bases in aprotic media, but investigation has started on the quantitative measurement of the relative strengths of acids and bases in such media. Brönsted (*loc. cit.*) made preliminary qualitative measurements of the order of the strengths of several indicators and acids in benzene, and LaMer and Downes (*Chem. Reviews*, 1933, 13, 47) carried out more quantitative work in the same solvent.

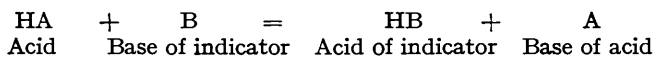
In the investigation described below, a solvent of considerably higher dielectric constant than benzene (2.26) was chosen. (For a discussion of the effect of dielectric constant on the association of solutes, see Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, 55, 2387.) Chlorobenzene has a dielectric constant of 10.95, but in spite of this the effect of association is quite marked, and it is possible to apply the method of LaMer and Downes in the interpretation of the results.

The relative strengths of a wide series of organic acids have been measured, and the results are fully in conformity with the view predicted by theory that the order and, apart from small deviations, the relative numerical values of the strengths of these acids in chlorobenzene are the same as in water. Owing to the insolubility of their salts in chlorobenzene it was not possible to compare the relative strengths of bases in this solvent as, for instance, has been done in *m*-cresol (Brönsted, Delbanco, and Tovborg-Jensen, *Z. physikal. Chem.*, 1934, 169, 361).

#### EXPERIMENTAL.

*Purification of Reagents.*—Commercially pure chlorobenzene was shaken with 10% sodium hydroxide solution, washed, shaken with dilute sulphuric acid, again washed, dried over phosphoric oxide, and distilled in an all-glass apparatus at low pressure. After use it was repurified by the same process. The other reagents had been purified by previous workers in this laboratory.

*Selection of Indicators.*—Preliminary semi-quantitative experiments were first made to determine the suitability of different indicators to be employed as indicated below. In order to compare the strength of an acid with that of an indicator, the experimental requirements were the determinations of the ratios of the concentrations of the acid and base forms of the indicator ( $c_{HB}$  and  $c_B$ ) and of the acid and base forms of the acid ( $c_{HA}$  and  $c_A$ ) in various acid-base mixtures. The equilibrium studied was



The concentration of the base, *e.g.*,  $C_6H_5\text{-COO}^-$ , is fixed if the titration base B' is sufficiently strong to convert its equivalent of benzoic acid into the benzoate ion:  $B' + C_6H_5\text{-CO}_2H = C_6H_5\text{-COO}^- + B'H^+$ . The concentration of the free acid was found simply by difference.

If one form of the indicator is colourless, the relative concentration of the two forms follows simply from the measurement of the extinction coefficients at suitable wave-lengths. When both forms show an absorption at all wave-lengths, but the relative extinction is widely different at some wave-lengths, then measurements are still possible, and the algebraic relationships are only a little more complicated. The indicators found suitable for use in the present investigation were 2:6-dinitrophenol and bromophenol-blue.

*Experiments with 2:6-Dinitrophenol.*—This indicator, in chlorobenzene as in water, exists in two forms, one coloured and one colourless, *viz.*,  $C_6H_3(NO_2)_2\text{-O}^-$  and  $C_6H_3(NO_2)_2\text{-OH}$ , respectively. A solution of the indicator in chlorobenzene is turned yellow on addition of a drop of a strong base. By adding sufficient quantities of a strong base, such as *isobutylamine*, in small amounts, a solution of constant molecular absorption was obtained. This was a solution of the indicator in the completely yellow basic form. In the absorption measurements

a Pulfrich-Zeiss colorimeter, and in some cases also a Hilger spectrophotometer, was used. The former instrument was graduated to give directly the percentage of light transmitted by the indicator solutions at the different wave-lengths of the colour filters. The molecular extinction coefficients are given by the relation  $\epsilon_m = \log D/lm$ , where  $l$  is the length (in cm.) of the containing vessel,  $m$  the molar concentration of the indicator, and  $D$  the fraction of light transmitted.

It was not necessary to find the absolute values of the extinction coefficients, for, in a solution containing both forms of which one shows no absorption at the particular wave-length selected, the ratio of the molecular concentrations of the two forms is given by

$$c_{\text{HB}}/c_{\text{B}} = (\log D_2 - \log D_1)/(-\log D_1)$$

if the lengths of the tubes are the same, where  $D_1$  is the fraction of light transmitted by the solution when the indicator is completely in the basic form, and  $D_2$  that measured. In the above expressions Beer's law is assumed. For the ranges of concentration studied, the deviations were well within the limits of experimental error.

In each experiment the actual values of  $D$  for the completely yellow solution were determined, rather than the alternative procedure of evaluating it from previous absorption measurements.

An approximately  $10^{-4}$   $m$ -solution of the indicator was made by dissolving about 0.05 g. in 25 c.c. of pure chlorobenzene and diluting 1 g. of this solution 100-fold by weighing. All the acid and base solutions employed were made up in this indicator solution: there was therefore no doubt about the constancy of the total indicator concentration.

In the experiments, 1.50—3.00 c.c. portions of 0.01  $m$ -isobutylamine were measured from a burette into a series of tubes, and sufficient acid solution (of appropriate concentration) was added to cause a visible diminution in the yellow colour of the solution. Readings of the value of  $D$  at 4300 Å. (the wave-length of the light transmitted by the yellow colour filter) were taken for a series of mixtures into which various quantities of the acid solution had been measured. The results for a number of acids are tabulated below.

The following symbols are used for the substances concerned in the equilibrium  $A_1 + I_B = B_1 + I_A$ :  $A_1$  is the titration acid,  $B_1$  its conjugate base (in all the cases considered  $B_1$  is the negative ion of the salt of  $A_1$ ),  $I_B$  is the basic (yellow) form of the indicator,  $I_A$  the colourless acid form, and  $B_2$  the titration base (isobutylamine).

#### *Propionic acid.*

Mixtures:  $A_1 = 0.0606m$ ;  $B_2 = 0.01202m$ .

$A_1$ , c.c.	$B_2$ , c.c.	$[A_1]$ .	$[B_1]$ .	D, %.	$\log [I_B]/[I_A]$ .	$\log [B_1]/[A_1]$ .
. . . . .	. . . . .	Yellow form . . . . .		17.8	. . . . .	. . . . .
5.00	1.50	0.0438	0.00277	48.7	-0.148	-1.199
7.00	1.50	0.0478	0.00212	54.5	-0.265	-1.325
8.00	1.50	0.0491	0.00190	60.8	-0.392	-1.412
10.00	1.50	0.0511	0.00157	65.0	-0.479	-1.513

#### *Acetic acid.*

Mixtures:  $A_1 = 0.0218m$ ;  $B_2 = 0.01060m$ .

$A_1$ , c.c.	$B_2$ , c.c.	$[A_1]$ .	$[B_1]$ .	D, %.	$\log [I_B]/[I_A]$ .	$\log [B_1]/[A_1]$ .
. . . . .	. . . . .	Yellow form . . . . .		17.9	. . . . .	. . . . .
2.50	1.50	0.00965	0.00397	21.6	0.909	-0.386
3.00	1.50	0.01100	0.00353	22.2	0.847	-0.494
5.00	1.50	0.0143	0.00245	31.1	0.335	-0.766
7.00	1.50	0.0161	0.00187	41.1	0.033	-0.935
8.00	1.50	0.0166	0.00168	43.5	-0.027	-0.995
10.00	1.50	0.0176	0.00138	51.0	-0.192	-1.106

#### *Benzoic acid.*

Mixtures:  $A_1 = 0.0100m$ ;  $B_2 = 0.01038m$ .

$A_1$ , c.c.	$B_2$ , c.c.	$[A_1]$ .	$[B_1]$ .	D, %.	$\log [I_B]/[I_A]$ .	$\log [B_1]/[A_1]$ .
. . . . .	. . . . .	Yellow form . . . . .		18.7	. . . . .	. . . . .
2.50	1.50	0.00235	0.00390	25.1	0.671	0.220
3.00	1.50	0.00319	0.00347	27.1	0.546	0.037
5.00	1.50	0.00529	0.00240	35.9	0.196	-0.343
6.00	1.50	0.00582	0.00208	38.0	0.135	-0.447
8.00	1.50	0.00678	0.00164	45.1	-0.043	-0.616
10.00	1.50	0.00735	0.00135	53.5	-0.224	-0.745

Salicylic acid.

Mixtures:  $A_1 = 0.01043m$ ;  $B_2 = 0.01047m$ .

$A_1$ , c.c.	$B_2$ , c.c.	$[A_1]$ .	$[B_1]$ .	D, %.	$\log [I_B]/[I_A]$ .	$\log [B_1]/[A_1]$ .
2.30	2.00	0.000707	0.00487	23.0	0.164	0.838
2.40	2.00	0.000930	0.00476	42.0	-0.060	0.706
2.50	2.00	0.001141	0.00465	50.0	-0.222	0.610
2.60	2.00	0.001343	0.00455	67.0	-0.456	0.530
3.00	2.00	0.002071	0.00419	80.0	-0.745	0.306

Monochloroacetic acid.

Mixtures:  $A_1 = 0.01292m$ ;  $B_2 = 0.01153m$ .

		$[A_1]$ .	$[B_1]$ .	D, %.	$\log [I_B]/[I_A]$ .	$\log [B_1]/[A_1]$ .
3.40	3.00	0.00146	0.00540	47.8	-0.308	0.568
3.50	3.00	0.00164	0.00533	59.2	-0.505	0.511
3.70	3.00	0.00197	0.00516	66.9	-0.653	0.418
4.00	3.00	0.00244	0.00494	77.2	-0.879	0.306

In the absence of association (or of some other effect) the expression  $K = B_1I_A/A_1I_B$  would be constant for a given acid and indicator. That this expression is not constant is evident from the experimental data. For instance, in the case of salicylic acid the value of  $K$  increases from 4.91 to 11.07 in the series taken. Again, no definite effect due to salt concentration on the value of  $K$  could be found.

However, when allowance was made for association by the method suggested by LaMer and Downes, *i.e.*, when  $\log [I_B]/[I_A]$  was plotted against  $\log [B_1]/[A_1]$ , straight-line graphs were obtained. The intercepts on the  $\log [B_1]/[A_1]$  axes were taken as a measure of the strengths of the acids relative to the indicator acid, 2 : 6-dinitrophenol.

When a comparison was made of the relative strengths in water and in chlorobenzene, the first six values in the table on p. 823 were obtained on a logarithmic scale. The dissociation constants of the acids in water are taken from Landolt-Börnstein "Tabellen," and those of the indicator from Koltthoff's "Säure-Basen-Indikatoren," Berlin, 1934. The constants are defined as

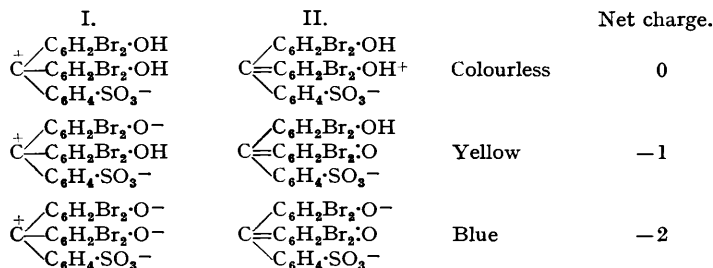
$$K_{A.M. \text{ conventional}} = c_{\text{base}}c_{H_2O}/c_{\text{acid}} \text{ for water}$$

$$K_{A.F^-} = c_{\text{base}}c_{I_A}/c_{\text{acid}}c_{I_B} \text{ for } c_{I_B}/c_{I_A} = 1 \text{ in chlorobenzene}$$

$$K_{A.F^-} = c_{\text{base}}c_{I_A}/c_{\text{acid}}c_{I_B} \text{ in water}$$

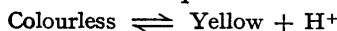
There is clearly a parallelism between the relative strengths of these acids in chlorobenzene and in water.

*Experiments with Bromophenol-blue.*—In water this indicator can exist in two forms, one blue and the other yellow; the  $p_H$  of the colour change is 2.8—4.6. In certain other solvents it can exist in three or even four modifications: four forms are known in *m*-cresol (Brönsted, Delbanco, and Tovborg-Jensen, *loc. cit.*). When bromophenol-blue was dissolved in chlorobenzene the solution was practically colourless, and on addition of acids no colour was produced. On adding a weak base, such as *p*-toluidine, a yellow colour was produced, and if a strong base was added in sufficient quantity a green and eventually a blue colour was obtained. Thus, bromophenol-blue can exist in at least three forms in chlorobenzene. The three forms can be represented by the following alternative formulæ.



The colourless form is a strong acid. The blue form is not very soluble in chlorobenzene and is precipitated on standing, so it is not convenient to use the blue-yellow change for indicator

purposes. Since the colourless form is a strong acid, it is quite suitable for investigations with strong acids in chlorobenzene. The indicator equilibrium is:



The experimental procedure was almost identical with that employed in the case of 2 : 6-dinitrophenol. Allowance had to be made for the insolubility of the blue form of the indicator in chlorobenzene. A suitable concentration of indicator for measurements in the 1-cm. tube was produced by dissolving 0.05 g. in 25 c.c. of chlorobenzene and diluting the solution 50-fold. The indicator concentration was then approximately  $6 \times 10^{-5}m$ . As before, all the acid and base solutions were made up in this indicator solution. Readings were taken in the violet region. In order to produce the yellow colour, small quantities of *p*-toluidine were added to the indicator solution until a constant reading was obtained in the spectrophotometer. Since it was not practicable, owing to the insolubility of the blue form of the indicator, to make up solutions of the pure base, *isobutylamine*, in the indicator solution in chlorobenzene, the base was dissolved in a solution of the acid in the indicator solution. In this way two solutions were obtained: A<sub>1</sub>, acid in indicator solution; M, acid + base in indicator solution.

*Monochloroacetic acid.* In order to determine if there was any variation in the value of *K* at (1) constant salt concentration, (2) constant "total acid" concentration, the following experiments were carried out.

(1) In this series, three solutions, *viz.*, the pure indicator solution, an acid solution, and a solution of the base in acid solution, were used. The total volume and also the volume of M were maintained constant by adding pure solution of the indicator. When the salt concentration was maintained constant at 0.00193*m*, and the acid (A<sub>1</sub>) concentration was decreased from 0.480 to 0.029*m*, the value of *K* increased from 0.00229 to 0.00327. The variations in *K* found in other experiments are thus not due to a salt effect alone. By plotting  $\log \frac{[B]}{[A]}$  against  $\log \frac{[B]}{[A]}$ , a straight line was obtained cutting the  $\log \frac{[B]}{[A]}$  axis at -2.69.

(2) In order to maintain the total acid (free acid + salt) constant when the salt concentration was varied, two acid solutions and one solution of the base in one of the acid solutions were made up. The total volume was again kept constant, as well as the volume of the more concentrated acid solution. The acid concentration varied slightly (from 0.734 to 0.737*m*). The salt concentration was decreased from 0.00401 to 0.00120*m*. Meanwhile, *K* increased gradually from 0.00161 to 0.00202. By plotting logarithms as before, the value -2.68 was obtained.

In a series in which the concentration both of the salt and of the total acid was varied, the following results were obtained.

*Monochloroacetic acid.*

Mixtures: A<sub>1</sub> = 0.1204*m*-acid; M<sub>1</sub> = 0.1204*m*-acid + 0.01055*m*-*isobutylamine*.

A <sub>1</sub> , c.c.	M <sub>1</sub> , c.c.	[A].	[B].	D, %.	$\log \frac{[B]}{[A]}$	$\log \frac{[B]}{[A]}$
		Yellow form		24.7		
2.0	2.0	0.1151	0.00528	26.3	1.332	-1.338
3.0	2.0	0.1162	0.00422	26.6	1.255	-1.440
5.0	2.0	0.1174	0.00301	28.2	0.985	-1.591
8.2	2.0	0.1183	0.00211	29.6	0.872	-1.749

*Dichloroacetic acid.*

Mixtures: A<sub>1</sub> = 0.0503*m*-acid; M<sub>1</sub> = 0.0503*m*-acid + 0.01055*m*-*isobutylamine*.

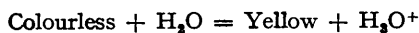
		Yellow form		5.9		
1.00	2.00	0.0430	0.00733	15.9	0.261	-0.770
1.60	2.00	0.0422	0.00611	21.5	0.070	-0.857
2.00	2.00	0.0448	0.00550	22.9	0.030	-0.910
2.50	2.00	0.0454	0.00489	26.6	-0.061	-0.967
3.00	2.00	0.0459	0.00440	30.3	-0.141	-1.014
5.00	2.00	0.0482	0.00314	41.1	-0.342	-1.177

*Trichloroacetic acid.* In order to see if the results could be reproduced under diverse conditions, several series of experiments were conducted with this acid, and good agreement was obtained when the intercepts on the *y* axes were compared as before. The description of one such experiment will suffice.

Mixtures: A<sub>1</sub> = 0.0186*m*-acid; M<sub>1</sub> = 0.0186*m*-acid + 0.01055*m*-*isobutylamine*.

		Yellow form		8.4		
1.1	2.0	0.00406	0.00680	15.1	0.507	0.224
2.0	2.0	0.00558	0.00528	25.7	0.084	-0.024
3.0	2.0	0.00664	0.00422	39.4	-0.161	-0.197
4.0	2.0	0.00734	0.00352	47.6	-0.369	-0.320
5.0	2.0	0.00785	0.00301	57.5	-0.542	-0.416

No value can be given for the strength of the colourless form of bromophenol-blue in water, since this form is immediately hydrolysed according to the scheme :



By comparison with colourless bromophenol-blue, the strengths on the logarithmic scale were :

Monochloroacetic acid . . . . .	-2.69	Trichloroacetic acid . . . . .	-0.09
Dichloroacetic acid . . . . .	-0.94	Bromophenol-blue (yellow form) . . . . .	0.00

Since monochloroacetic acid also appears on the 2 : 6-dinitrophenol scale, the two series can be linked up and so one obtains the last three values in the following table.

Acid.	Water.		Chloro- benzene. log $K_{AF^-}$ .	Acid.	Water.		Chloro- benzene. log $K_{AF^-}$ .
	log $K_{AM}$ .	log $K_{AF^-}$ .			log $K_{AM}$ .	log $K_{AF^-}$ .	
Propionic .....	5.13	-1.07	-1.08	Monochloroacetic ...	3.17	0.97	0.77
Acetic .....	5.25	-0.95	-1.00	Dichloroacetic .....	3.70	2.50	2.52
Benzoic .....	5.81	-0.39	-0.58	Trichloroacetic .....	—	—	3.37
Dinitrophenol ...	4.2	0.00	0.00	Bromophenol-blue...	—	—	3.46
Salicylic .....	3.02	0.82	0.74				

Some of the above results were confirmed by similar experiments in which the Hilger-Nutting spectrophotometer was employed in the determination of the ratio of the two forms of the indicator. One example is quoted here.

*Monochloroacetic acid with 2 : 6-dinitrophenol.*

Mixtures :  $A_1$ , acid = 0.1022*m*,  $B_2$ , isobutylamine = 0.1039*m*. I = indicator in pure solvent.

$A_1$ , c.c.	$B_2$ , c.c.	I, c.c.	[A].	[B].	log $[I_B]/[I_A]$ .	log $[B]/[A]$ .
7.0	6.0	3.0	0.0056	0.0390	0.076	0.843
7.6	6.0	2.4	0.0095	0.0390	-0.173	0.613
8.0	6.0	2.0	0.0120	0.0390	-0.248	0.512
8.5	6.0	1.5	0.0151	0.0390	-0.389	0.412
10.0	6.0	0.0	0.0248	0.0390	-0.555	0.196

When the logarithms are plotted as before, one finds the constant for this acid to be 0.79, which is in good agreement with the value obtained by use of the other apparatus.

All the acids are not associated to the same extent relative to the indicator, and for an individual acid the slopes are different on the curves drawn, but the point of intersection of the vertical axis was practically the same for any one acid. This would indicate that the figures given fairly accurately represent the relative strengths of acids in chlorobenzene, and the close parallelism between these values and those in water indicates, further, that the activity coefficients of the acids undergo almost parallel changes in passing from water to benzene or chlorobenzene.

It is shown that trichloroacetic acid and bromophenol-blue, both just "strong" acids in water, are about ten times as strong as dichloroacetic acid in chlorobenzene.

Thanks are due to Professor J. N. Brønsted, at whose suggestion this work was started and under whose guidance it was continued, first in his laboratory in Copenhagen and later in Cardiff. I am also indebted to Professor T. Graham Brown, F.R.S., and Dr. John Pryde for providing me with laboratory facilities.

UNIVERSITETETS FYSISK-KEMISKE INSTITUT, COPENHAGEN.  
THE INSTITUTE OF PHYSIOLOGY, NEWPORT ROAD, CARDIFF.

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