**156.** *The Acid–Base Function in Non-aqueous Media. Part I. The Autoprotolytic Constant of* m-Cresol.

By D. C. GRIFFITHS.

A potentiometric method, similar to that used in the classical researches on the determination of the autoprotolytic constant of water, has been devised for measurements with *m*-cresol. The effect of small concentrations of water is considered.

ACCORDING to the new theory of acids and bases, first clearly stated by Brönsted (*Rec. Trav. chim.*, 1923, **42**, 718; *J. Physical Chem.*, 1926, **30**, 777), the fundamental reaction in all acid–base equilibria is not dissociation but protolysis. In a pure hydrolytic solvent such a reaction can proceed automatically; for instance, in the case of water the reaction can be represented by the equation

$$2H_2O = H_3O^+ + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
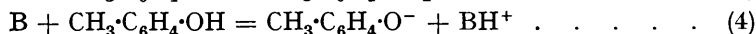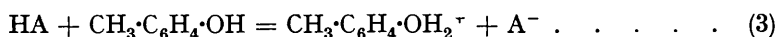
and the process is called "autoprotolysis."

The law of mass action is applied to this reaction and the active mass of the neutral water is assumed constant. Then, by definition, the autoprotolytic constant of water is given by

$$K_W = c_{H_3O^+} \cdot c_{OH^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Recent studies on the behaviour of acids and bases in *m*-cresol (Brönsted, Delbanco, and Tovborg-Jensen, *Z. physikal. Chem.*, 1934, **169**, 361) indicate that this solvent enters into protolytic reactions with the acids (HA) and bases (B) :

$$HA + CH_3 \cdot C_6H_4 \cdot OH = CH_3 \cdot C_6H_4 \cdot OH_2^+ + A^- \quad . \quad . \quad . \quad . \quad (3)$$
$$B + CH_3 \cdot C_6H_4 \cdot OH = CH_3 \cdot C_6H_4 \cdot O^- + BH^+ \quad . \quad . \quad . \quad . \quad (4)$$

Autoprotolysis is a special case of such equilibria, and it is logical to assume that it occurs in *m*-cresol :

$$2CH_3 \cdot C_6H_4 \cdot OH = CH_3 \cdot C_6H_4 \cdot OH_2^+ + CH_3 \cdot C_6H_4 \cdot O^- \quad . \quad . \quad . \quad (5)$$
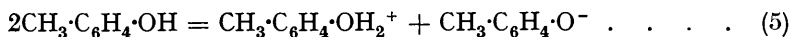
for which the autoprotolytic constant is given by

$$K_{W \text{ (cresol)}} = c_{CH_3 \cdot C_6H_4 \cdot OH_2^+} \cdot c_{CH_3 \cdot C_6H_4 \cdot O^-} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In the present work this constant has been measured by a method similar to one of those employed for the same determination in the case of water. Use is made of the fact that the concentration of hydrogen ions in an alkaline solution can be determined by measuring the *E.M.F.* of an acid–alkali cell (Ostwald, *Z. physikal. Chem.*, 1893, **11**, 521; Arrhenius, *ibid.*, p. 805; Loewenherz, *ibid.*, 1894, **14**, 155).

In a cell of the type represented by the scheme

$$H_2 \mid \text{acid solution} \mid \text{base solution} \mid H_2$$
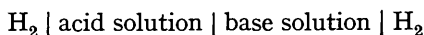
the *E.M.F.* is given by

$$E = 0.057 \log c_a/c_b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$
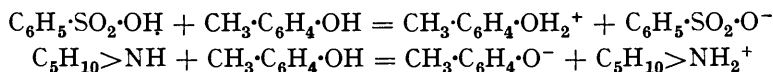
where $c_a$ and $c_b$ represent the solvated hydrogen-ion concentrations on the acid and the base side, respectively, if the complications due to diffusion and liquid–liquid junction potentials are ignored. Attention must be paid to the elimination or minimisation of these factors, and at the same time it is desirable to increase the conductivity of the system. This can be brought about by the use of a suitable salt solution as medium (see p. 817).

In the equations (3) and (4), if the acid HA or the base B is sufficiently strong, the reactions proceed to the right almost completely : in the present work HA was a strong organic acid and B a strong organic base. If, however, the base is not sufficiently strong in *m*-cresol, reaction (4) does not proceed completely from left to right and the concentration of the ion $CH_3 \cdot C_6H_4 \cdot O^-$ is given by $c_B p/100$, where $p$ is the percentage protolysis. Professor Brönsted (private communication), by conductivity measurements, has found the protolysis of 0·01*m-iso*amylamine to be *ca.* 30% in *m*-cresol. Direct evidence on the absolute strength of benzenesulphonic acid in *m*-cresol is lacking, but such evidence as there is (Brönsted and Volqvartz, private communication), which is based on conductivity determinations of benzenesulphonates, indicates that this acid is very strong compared with trichloroacetic acid.

In the present investigation the E.M.F. of the cell

$$H_2 \mid 0\cdot01m\text{-benzenesulphonic acid} \mid 0\cdot01m\text{-piperidine} \mid H_2$$
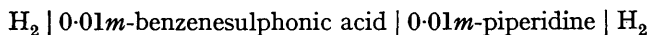
(all in $0\cdot1m$-*iso*amylamine benzenesulphonate in $m$-cresol) was measured. The reactions concerned are represented by the equations

$$C_6H_5 \cdot SO_2 \cdot OH + CH_3 \cdot C_6H_4 \cdot OH = CH_3 \cdot C_6H_4 \cdot OH_2^+ + C_6H_5 \cdot SO_2 \cdot O^-$$
$$C_5H_{10} > NH + CH_3 \cdot C_6H_4 \cdot OH = CH_3 \cdot C_6H_4 \cdot O^- + C_5H_{10} > NH_2^+$$

The concentration of the solvated hydrogen ion is given by that of the acid added; that of the solvated hydrogen ion in the basic solution can then be calculated by use of equation (7).

<div align="center">EXPERIMENTAL.</div>

*Purification of Reagents.*—Benzenesulphonic acid was recrystallised from water, collected on a Buchner funnel surrounded by ice, and dehydrated at 50° over phosphoric oxide under reduced pressure. Analysis by titration against standard base indicated that less than 0·03 mole of water was present per mole of acid.

*iso*Amylamine benzenesulphonate was prepared by mixing the components in equivalent amounts, *viz.*, 32 g. of acid and 15 g. of base. The product was dissolved in alcohol, cooled, and reprecipitated by addition of ether. This operation was repeated, 13·5 g. of the salt being obtained.

Kahlbaum's $m$-cresol was shaken with solid sodium hydroxide, the liquid decanted into a bottle containing phosphoric oxide and again well shaken, and then distilled in an all-glass apparatus from a suspension of the dehydrating agent.

The cell used consisted of a $\cup$-tube somewhat constricted near the bends, stoppered at both ends, and provided also with an entry and an exit tube for hydrogen. A pair of platinum electrodes passed through each stopper. They were carefully insulated from each other, and in this way the potential of any electrode could be compared with each of the others in turn. (I am indebted to Mr. E. Guntelberg for suggesting this arrangement.) By this method any individual eccentricity of an electrode could be detected. The potentiometer was of the direct reading type, standardised by a Weston cell. " Electrolytic hydrogen " from a cylinder was passed over heated copper, bubbled through concentrated sulphuric acid, and finally passed through dry $m$-cresol. The stream of gas was equally divided.

The electrodes were tested in hydrochloric acid, and hydrogen passed through until the differences were of the order of 0·001 volt. The electrodes were replatinised several times during the course of the experiments. Great care was taken to remove the platinising liquor. After equilibrium had been attained in acid solution in water, the electrodes were well washed in water and then in alcohol and ether or in dry $m$-cresol. Both methods gave the same results. In acid solutions in $m$-cresol maximum differences of 0·002 volt were noted, and in basic solution in the same solvent maximum differences of 0·005 volt.

In a typical experiment 100 c.c. of $0\cdot1m$-*iso*amylamine benzenesulphonate were prepared, and 15 c.c. portions of $0\cdot01m$-benzenesulphonic acid and of piperidine severally were made up in this salt solution. A few c.c. of the *iso*amylamine benzenesulphonate solution were introduced into the cell, and clean dry sand was carefully added in such a way that no air bubbles were embedded in the mass. Sand was added until the viscous mass came up to the level of the constrictions in the cell. The excess of solution was removed with filter-paper. The sand bridge effectively prevented appreciable diffusion. Equal measured amounts of the $0\cdot01m$-benzenesulphonic acid solution and of the $0\cdot01m$-piperidine solution were poured simultaneously into the two halves of the cell.

The following is a record of the readings (in volts) obtained at various times with different electrodes.

| Electrodes. | | 60 mins. | 80 mins. | 100 mins. |
|---|---|---|---|---|
| 4 . . . . . . . 1 | | 0·5750 | 0·5757 | 0·5752 |
| 4 . . . . . . . 2 | | 0·5752 | 0·5752 | 0·5759 |
| 3 . . . . . . . 1 | | 0·5760 | 0·5762 | 0·5758 |
| 3 . . . . . . . 2 | | 0·5760 | 0·5757 | 0·5755 |

<div align="center">Mean value of E.M.F. 0·575 volt.</div>

Next, the basic solution was removed by a pipette and replaced by fresh basic solution.

After (*a*) 45 mins. and (*b*) 90 mins., the readings were as tabulated below. When the acid side was similarly replenished, the readings were (*c*) after a 45-mins. interval.

| Electrodes. | | (*a*). | (*b*). | (*c*). |
|---|---|---|---|---|
| 4 . . . . . . . 1 | | 0·5720 | 0·5720 | 0·5840 |
| 4 . . . . . . . 2 | | 0·5728 | 0·5720 | 0·5842 |
| 3 . . . . . . . 1 | | 0·5720 | 0·5717 | 0·5820 |
| 3 . . . . . . . 2 | | 0·5718 | 0·5715 | 0·5820 |

The results may be summarised as below, the bridge in each experiment being a 0·1*m*-salt solution :

| | 1 | 2 |
|---|---|---|
| Expt. ................................................................. | 1 | 2 |
| Temp. ................................................................. | 23° | 19° |
| Soltn. 1 : Concn. (*m*) of $Ph\cdot SO_3H$ in 0·1*m*-salt soltn. ... | $10^{-2\cdot22}$ | $10^{-1\cdot89}$ |
| „ 2 : „ „ $C_5H_{11}N$ „ „ „ ... | $10^{-1\cdot96}$ | $10^{-1\cdot91}$ |
| Mean value of *E*, volt ............................................. | 0·575 | 0·584 |
| *K* ................................................................. | $10^{-14\cdot66}$ | $10^{-14\cdot41}$ |

In the evaluation of the constants (*K*) it was assumed that the protolysis of the base was 30% and that of the acid 100%. ·

In order to determine if a small concentration of water in the *m*-cresol had much effect on the *E.M.F.* measurements, the following preliminary measurements were carried out. A uniform solution of benzenesulphonic acid was added to each side of the sand bridge. When a solution of water in *m*-cresol was added to one side of the cell until the concentration of water on this side was 0·01*m*, the change in *P.D.* was less than a millivolt. With a concentration as high as 0·05*m*, the difference only amounted to about 0·002 volt. Under the conditions of the final experiments no definite regularities could be found when successive drops of a solution of water in *m*-cresol were added, but since the influence of water is clearly so small, such effects do not have much bearing on the accuracy of the measurement of the autoprotolytic constant.

The values of the constant are strictly only valid under the given conditions of concentration and temperature. It is regarded as significant that the figures obtained are very nearly the same as those obtained for water under similar conditions. In this investigation salt effects have not been considered. These can only be studied when data over a much wider range of concentration have been collected. It is considered outside the scope of this paper to consider to what extent the ions associate to form electrostatic molecules.