

Determination of Very Weak Acids and Bases by Means of Electrolytic Conductivity Measurements.

By

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As is well known, the ordinary method of acidimetry and alkali-metry is not applicable to the determination of very weak acids and bases. Preliminary experiments gave evidencce that in such a case electrolytic conductivity measurement might conveniently be used; and the method of procedure has been investigated.

A. The Electrolytic Conductivity of a Mixture of a Weak Base and a Strong Acid.

As representative of a weak base aniline was chosen, and the electrolytic conductivities of mixtures of aniline and hydrochloric acid in different proportions were measured in the following way.

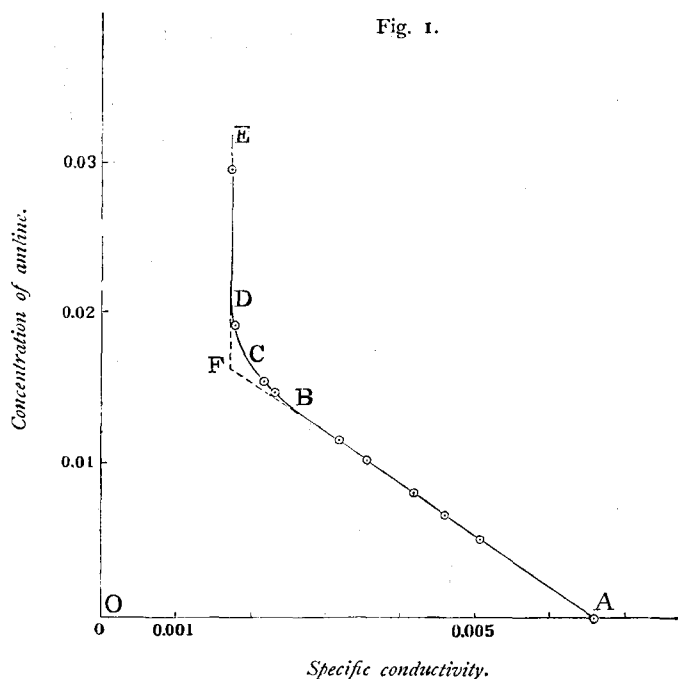
20 cc. of hydrochloric acid of a known concentration were mixed with 5 cc. of an aqueous solution of aniline in different concentrations, the mixture was put in a conductivity vessel which was immersed in a thermostat at 25.0°C. and the electrolytic conductivities were determined. Ordinary distilled water was used in the preparation of these solutions, because the specific conductivity of the distilled water in our laboratory was less than 4.10^{-6} reciprocal ohms, and this order of conductivity was negligible for the present investigation.

TABLE I.

Concentration of aniline used.	Concentration of aniline in conductivity vessel.	Concentration of hydrochloric acid in conductivity vessel.	Specific conductivity.
0	0	0.01645	0.006653
0.02603	0.005206	„	0.005119
0.03472	0.006944	„	0.004590

0.04166	0.008332	0.01645	0.004156
0.05207	0.01041	„	0.003505
0.05946	0.01189	„	0.003077
0.07425	0.01485	„	0.002284
0.07680	0.01536	„	0.002150
0.09670	0.01934	„	0.001730
0.1485	0.0297	„	0.001697

The curve representing the change of the specific conductivity of the mixture with the change of the aniline concentration is shown in Fig. 1, specific conductivity being taken as abscissa and concentration



of aniline as ordinate. As seen in the figure, the specific conductivity of the solution is a linear function of the concentration of aniline, becoming smaller and smaller as the concentration increases. This is represented by a straight line AB , OA being the specific conductivity of the pure hydrochloric acid solution. When the concentration of aniline approaches that of the hydrochloric acid, however, the rate of decrease of the conductivity becomes greater and greater and the straight line turns to a curve convex to the axes, as BCD . When

aniline is present in excess, the specific conductivity varies very slightly with its concentration; and the relation is again represented by a straight line DE , which is almost parallel to the ordinate axis. The point F , the intersection of the elongations of the two straight lines AB and DE , is the point corresponding to a concentration of aniline exactly equivalent to the hydrochloric acid in the solution.

Now let κ_m and κ_a be respectively the specific conductivities of the mixture and the pure acid solution, and C_b be the concentration of the base added; then the straight line AB in Fig. 1. may be represented by an equation as follows:

$$\kappa_m = PC_b + \kappa_a \quad (1)$$

where P is a constant. It is easily seen that the change of the conductivity of the solution with the addition of aniline is due to two different causes, firstly the conductivity is decreased by the gradual disappearance of free hydrochloric acid and secondly it is increased by the gradual formation of the neutral salt. Thus the factor P must consist of the two parts corresponding to these two terms.

Since hydrochloric acid and its neutral salt may be taken as having the same dissociation degree in dilute solutions, we have the following equations:

$$\kappa_a = a_a C_a \quad (2)$$

where κ_a and C_a denote respectively the specific conductivity of hydrochloric acid and the concentration of the acid and a_a is a constant for hydrochloric acid.

Similarly we have the following expression for the neutral salt,

$$\kappa_s = a_s C_s \quad (3)$$

when any hydrolysis of the salt is negligible.

If the relations (2) and (3) hold, the coefficient P can be dissolved into two terms such as,

$$P = (-a_a + a_s)$$

then, we have

$$\kappa_m = (-a_a + a_s)C_b + \kappa_a \quad (4)$$

This equation was derived under the assumption that no hydrolytic dissociation took place, but in fact it becomes remarkable only when the free acid is greatly decreased and the curved part BCD of Fig. 1 is the result. When aniline is present in excess, the conduc-

tivity is almost entirely due to the neutral salt in the solution, and the conductivity, due to the free weak base itself in the presence of its neutral salt, may be neglected. This explains the fact that an excess of aniline has no noticeable effect on the conductivity of the solution.

Calculation of the Factor α_a .

TABLE II.

Concentration of hydrochloric acid.	Specific conductivity.	$\alpha_a = \frac{\kappa_a}{C_a}$	Concentration of hydrochloric acid (calc.).
0.03296	0.01314	0.400	0.03252
0.01645	0.006635	0.405	0.01643
0.01028	0.004190	0.408	0.01037
0.00685	0.002819	0.412	0.00698

The factor α_a changes a little with the concentration of the acid; but taking α_a as a constant, say $\alpha_a \doteq 0.404$, the calculated values of the concentrations from the observed specific conductivities are not very different from the actual values, as shown in the 4th column of Table II. For equation (4), however, the observed value and not $0.404 \times C_a$ must be used, because a small error in α_a will remarkably affect the calculated concentration of the base.

Calculation of the Factor α_s .

If the relation (4) holds for the point F , which is the intersection of the two straight lines, and represents concentration of aniline equivalent to the hydrochloric acid in the mixture, we get the following relation:

$$\kappa_a - \alpha_a C_b = 0$$

and the equation (4) becomes:

$$\kappa_m = \alpha_s C_b = \alpha_s C_a.$$

As the straight line EF is almost parallel to the ordinate axis, the conductivity of the mixture may be put equal to κ_m in the above equation when large excess of aniline is present, and thus the value of α_s is easily found.

The specific conductivity of the mixture formed from 20 cc. of hydrochloric acid of 0.02056 norm. and 5 cc. of aqueous solution of aniline of 0.09676 norm. was 0.00173 reciprocal ohms, therefore we have

$$0.00173 = a_s \frac{0.02056 \times 4}{5}$$

$$a_s = 0.105.$$

Again, the specific conductivity of the mixture formed from 20 cc. of hydrochloric acid of 0.05120 norm. and 5 cc. of aqueous aniline solution of 0.1934 norm. was 0.00349 reciprocal ohms, therefore we have

$$0.00349 = a_s \frac{0.04120 \times 4}{5}$$

$$a_s = 0.106.$$

Thus we may put as the mean

$$a_s = 0.1055$$

$$\begin{aligned} \text{then } P &= -a_a + a_s = -0.404 + 0.1055 \\ &= -0.2985. \end{aligned}$$

Lastly we have the equation:

$$x_m = -0.2985 C_b + x_a.$$

The Experimental Verification of the Equation.

TABLE III.

The concentration of hydrochloric acid used: 0.04120.

The concentration of hydrochloric acid in the conductivity vessel:

$$\frac{4}{5} \times 0.04120 = 0.03296.$$

The specific conductivity of the acid: 0.01314.

Therefore

$$x_m = -0.2985 C_b + 0.01314.$$

Concentration of aniline used.	Concentration of aniline in cond. vessel.	Specific conductivity.	Concentration of aniline (calc.).	Error.
0.09670	0.01934	0.007345	0.01942	+0.00006
0.06447	0.01289	0.009224	0.01306	+0.00017

TABLE IV.

The concentration of hydrochloric acid used : 0.02056.

The concentration of hydrochloric acid in the conductivity vessel :

$$\frac{4}{5} \times 0.02056 = 0.01645.$$

The specific conductivity of the acid : 0.006635.

Therefore

$$\kappa_m = -0.2985 C_b + 0.006635.$$

Concentration of aniline used.	Concentration of aniline in cond. vessel.	Specific conductivity.	Concentration of aniline (calc.)	Error.
0.02603	0.005206	0.005119	0.005140	-0.000066
0.03472	0.006944	0.004590	0.006911	-0.000033
0.04166	0.008332	0.004156	0.008366	+0.000034
0.05207	0.010414	0.003505	0.01054	+0.00013

As seen from the above tables, the agreements between observed and calculated values are quite satisfactory.

Application in Chemical Analysis.

From the above experiments, it is evident that a weak base such as aniline, which can not be determined by the ordinary method of alkalimetry, may easily be estimated by the measurement of the conductivity of mixtures of the aniline solution and hydrochloric acid.

Let c be the concentration of the aniline and κ be the specific conductivity of this mixture, then

$$c = -\frac{\kappa - \kappa_a}{0.2895}$$

in which the observed value of κ_a is to be used. This equation is valid, with the constant factor 0.2895, between the limit $\frac{1}{50} - \frac{2}{50}$ norm. of hydrochloric acid, in excess of aniline. It is to be remarked here that the solution may contain some indifferent substances such as chloroform, without affecting the result.

Calculation of the Degree of the Hydrolysis.

We can calculate the degree of the hydrolysis of a salt by means of equation (4).

If we have the following data :

the concentration of hydrochloric acid in the conductivity vessel :

$$\frac{1}{5} \times 0.08234,$$

the concentration of aniline in the conductivity vessel : $\frac{1}{5} \times 0.07425,$

the specific conductivity of this mixture : 0.002284,

then $0.002284 = -0.2985 c + 0.006635$

$$c = 0.07316 \times \frac{1}{5}.$$

Therefore we have :

the concentration of aniline hydrochloride in the mixture :

$$0.07316 \times \frac{1}{5},$$

the concentration of free aniline : $(0.07425 - 0.07316) \times \frac{1}{5},$

the concentration of free hydrochloric acid : $(0.08234 - 0.07316) \times \frac{1}{5}.$

If K be the constant of the hydrolysis, then

$$K = \frac{[\text{Base}][\text{Acid}]}{[\text{Salt}]} = \frac{(0.07425 - 0.07316)(0.08234 - 0.07316)}{5 \times 0.07316} \\ = 2.74 \times 10^{-5}.$$

Moreover the following results were obtained.

Concentration of hydrochloric acid.	Concentration of aniline.	Specific conductivity.	Concentration of aniline hydrochloride (calc.).	K
$0.1648 \times \frac{1}{5}$	$0.1536 \times \frac{1}{5}$	0.004063	$0.1522 \times \frac{1}{5}$	2.26×10^{-5}
$0.08234 \times \frac{1}{5}$	$0.07680 \times \frac{1}{5}$	0.002150	$0.07543 \times \frac{1}{5}$	2.51×10^{-5}

The constant of the hydrolysis of aniline hydrochloride at 25.0°C. given in literature is as follows :

2.25×10^{-5}	Bredig ¹
2.29×10^{-5}	Denison and Steele ²
2.16×10^{-5}	Denham ³

¹ Zs. physik. Chem., **13**, 322 (1894).

² J. Chem. Soc., **89**, 1008 (1906).

³ *Ibid.*, **93**, 48 (1908).

B. The Electrolytic Conductivity of a Mixture of a Weak Acid and a Strong Base.

As representative of a weak acid phenol was taken, and the conductivities of the mixtures of phenol and sodium hydroxide were studied in the same way as the mixture of aniline and hydrochloric acid. In this case, however, distilled water free from carbonic acid was used and during the operations of the conductivity measurement, the utmost care was taken to avoid the absorption of carbonic acid from the air. The experiments were carried out in a thermostat at 25.0°C.

TABLE V.

The concentration of sodium hydroxide in conductivity vessel :
 $0.04809 \times \frac{4}{5} = 0.03847.$

Concentration of phenol used.	Concentration of phenol in conductivity vessel.	Specific conductivity.
0	0	0.008570
0.02085	0.004190	0.007866
0.04171	0.008342	0.007206
0.06202	0.012404	0.006527
0.07657	0.015314	0.006089
0.08341	0.016682	0.005865
0.09305	0.01861	0.005546
0.1407	0.02814	0.004111
0.1532	0.03064	0.003762
0.1914	0.03828	0.002981
0.3063	0.06126	0.002732
0.3311	0.06622	0.002720
0.4253	0.08506	0.002642

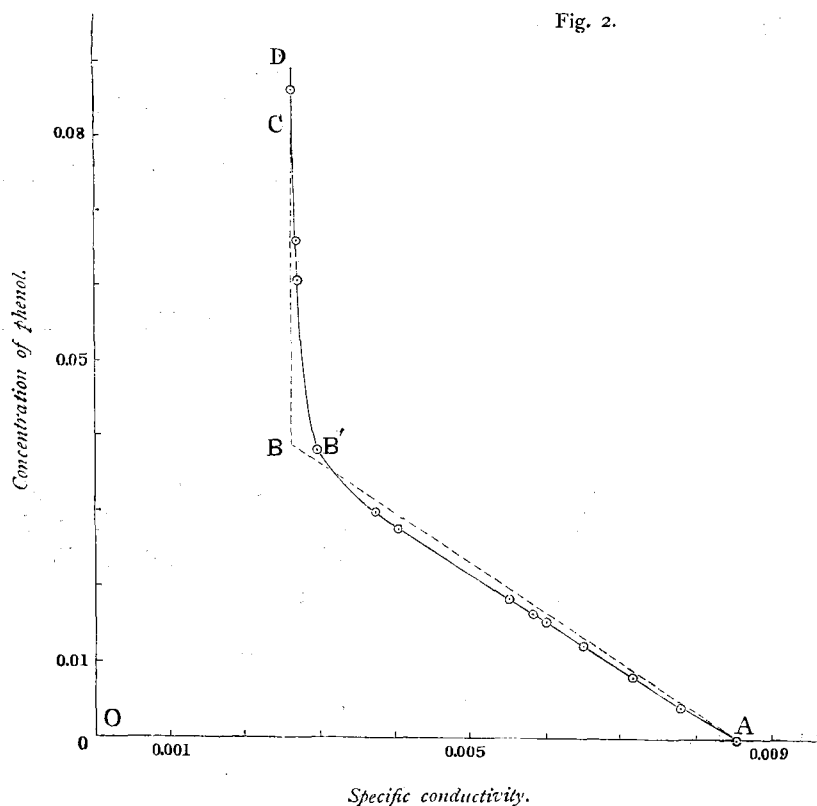
TABLE VI.

The conductivity of sodium hydroxide in conductivity vessel :
 $0.02405 \times \frac{4}{5} = 0.01924.$

Concentration of phenol used.	Concentration of Phenol in conductivity vessel.	Specific conductivity.
0	0	0.004363
0.01668	0.003336	0.003826

0.02085	0.004170	0.003673
0.04171	0.008342	0.003034
0.04652	0.009304	0.002844
0.07657	0.015314	0.001951
0.09305	0.01861	0.001599
0.1407	0.02814	0.001437
0.3311	0.06622	0.001405
0.5683	0.11366	0.001396

The curve representing the change of the specific conductivity of the mixture with the change of the phenol concentration is shown in Fig. 2. The decrease of the specific conductivity with the increase of



the concentration of phenol is not rectilinear, as shown $AB'C$ in the figure; and the curve proceeds parallel to the axis of ordinate as CD . Now elongate the straight line DC to the point B which corresponds to a concentration of phenol exactly equivalent to the concentration

of sodium hydroxide in the mixture, and connect the points B and A ; then it will be seen that the conductivity curve $AB'C$ deviates from the line AB at first to the left and then to the right as the concentration of phenol increases. These deviations may perhaps be ascribed to two causes, namely the hydrolysis of sodium phenolate and the slightrness of the electrolytic dissociation of sodium phenolate in an excess of the hydroxide, compared to that of the free base. From an assumption that the hydrolysis is negligible, we can derive a formula for the conductivity of the mixture as follows :

$$\kappa_m = PC_a + (C_b - C_a)^n \beta C_a + \kappa_b \quad (5)$$

where κ_m denotes the specific conductivity of the mixture,

C_a : the concentration of phenol,

C_b : the concentration of sodium hydroxide,

κ_b : the specific conductivity of sodium hydroxide alone,

P : a factor for this mixture,

and β is a factor for the dissociation degree of sodium hydroxide solution.

Calculation of the Factor P .

If the concentrations of phenol and sodium hydroxide be the same in the mixture, the expression (5) may be written,

$$\kappa_m = PC_a + \kappa_b. \quad (6)$$

In that case, the value of κ_m , the specific conductivity of pure sodium phenolate, will be given from the specific conductivity of a mixture containing a large excess of phenol. From the data of Table V, the factor P can be calculated as follows:

$$0.002640 = P \times 0.03847 + 0.008570$$

$$P = -0.154.$$

From Table VI

$$0.001400 = P \times 0.01924 + 0.004363$$

$$P = -0.154.$$

Therefore we can put $P = -0.154$ in the case where sodium hydroxide of $\frac{2}{50} - \frac{1}{50}$ norm. is used.

The Experimental Verification.

In the equation (5), if C_a be smaller than C_b , we can expand the factor $(C_b - C_a)^n$ according the binomial theorem; and, neglecting the higher terms, we obtain approximately,

$$x_m = PC_a + \beta C_b^n + x_b$$

or

$$C_a = \frac{x_m - x_b}{P + \beta C_b^n}. \quad (7)$$

Put $n = \frac{1}{2}$, and $\beta = 0.0433$, then from table V

$$\begin{aligned} C_a &= - \frac{x_m - 0.008570}{0.154 + 0.0433 \times 0.03848^{\frac{1}{2}}} \\ &= - \frac{x_m - 0.008570}{0.1625} \end{aligned}$$

Concentration of phenol.	Specific conductivity.	Concentration of phenol (calc.).	Error.
0.004190	0.007866	0.004332	+ 0.00014
0.008342	0.007206	0.008396	+ 0.000054
0.012404	0.006527	0.01257	+ 0.00017
0.015314	0.006089	0.01527	- 0.00004
0.016682	0.005865	0.01665	- 0.050017
0.01861	0.005546	0.01861	± 0.0

From Table VI, we have

$$\begin{aligned} C_a &= - \frac{x_m - 0.004363}{0.154 + 0.0433 \times 0.01924^{\frac{1}{2}}} \\ &= - \frac{x_m - 0.004363}{0.160} \end{aligned}$$

Concentration of phenol.	Specific conductivity.	Concentration of phenol (calc.).	Error.
0.003336	0.003826	0.003357	+ 0.000021
0.004170	0.003673	0.004311	+ 0.00014
0.008342	0.003034	0.008310	- 0.000032
0.009304	0.002844	0.009493	+ 0.00019

The agreements of the observed and calculated values are quite satisfactory, and therefore, if it is desired to estimate the concentration

of a dilute phenol solution, the conductivity of the mixture of the phenol solution and sodium hydroxide solution may be determined, and the concentration required calculated by the formula,

$$C_a = - \frac{x_m - x_b}{0.154 + 0.0433 \times C_b^{\frac{1}{2}}}$$

where C_b must lie between the limit $\frac{2}{50} - \frac{1}{50}$ norm. and the concentration of phenol be less than $\frac{1}{2} C_b$.

Calculation of the Degree of the Hydrolysis.

By the graphical representations of Table V and VI, the specific conductivities of equivalent solutions of phenol and sodium hydroxide are found.

i When the concentration of sodium hydroxide is

$$0.03877 : x_m = 0.00290.$$

ii When the concentration of sodium hydroxide is

$$0.01024 : x_m = 0.00158.$$

From equation (6), we get

$$i \quad C_a = \frac{0.00290 - 0.008570}{-0.154} = 0.00368,$$

$$ii \quad C_a = \frac{0.00159 - 0.004363}{-0.154} = 0.00180.$$

Therefore the concentrations of free alkali and phenol are altogether

$$i \quad 0.03877 - 0.00368 = 0.00020,$$

$$ii \quad 0.01924 - 0.00180 = 0.000124.$$

Then the constant of the hydrolytic dissociation is

$$i \quad \frac{(0.00020)^2}{0.00368} = 1.06 \times 10^{-4},$$

$$ii \quad \frac{(0.000124)^2}{0.00180} = 0.85 \times 10^{-4}.$$

The degrees of the hydrolysis of sodium phenolate at 25.0°C. given in literature are as follows :

Dilution.	Degree of hydrolysis.	
32 <i>l</i>	ca. 6%	Hantzsch ¹
10 <i>l</i>	„ 3%	Walker ²

From these data the constant of the hydrolytic dissociation is given respectively:

$$K = 1.20 \times 10^{-4},$$

$$K = 0.93 \times 10^{-4}.$$

Summary.

- (1) The conductivities of the mixture of aniline and hydrochloric acid, and of phenol and sodium hydroxide have been determined, and the empirical formulæ to represent the change of conductivity with concentrations derived.
- (2) A method of analysis of a weak base or acid by conductivity measurements has been described.
- (3) The constants of the hydrolytic dissociation of aniline hydrochloride and sodium phenolate has been calculated.

¹ Ber. D. chem. Ges., **32**, 3084 (1899).

² Zs. physik. Chem., **32**, 189 (1900).