182. *The Determination of Dissociation Constants of Monobasic Acids.*

By D. J. G. Ives.

A knowledge of the equivalent conductivity at zero concentration is required for the determination of dissociation constants by the conductivity method, and is usually obtained by application of the law of independent mobilities of ions. For monobasic acids, sodium salt conductivity data are extrapolated to zero concentration, and accepted values of the mobilities of the sodium and the hydrogen ion are used. That dissociation constants of reasonable accuracy can be obtained without this independent information is shown by the present work.

Methods based on the dilution law alone, when applied to weak acids, give misleading results. The errors due to neglect of mobility and activity changes, whilst not intrinsically large, are greatly magnified, as the length of the extrapolation is necessarily much greater than that of the experimental range. The only other method available for weak acids is that of deriving the equivalent conductivity at zero concentration (Λ_0) on the basis of the number of carbon atoms in the molecule, and is only approximate.

A method has now been devised suggested by an equation proposed by Onsager (*Physikal. Z.*, 1927, **28**, 277), *viz.*,

$$\Lambda + aC_i^{\frac{1}{2}} = \Lambda_0 - \Lambda_0 C/K$$

which is only applicable to highly dissociated electrolytes, since it involves the assumption that Λ/Λ_0 may be taken as unity. Values of Λ_0 and K are found by plotting $\Lambda + aC_i^{\frac{1}{2}}$ against C, C_i being the concentration of each ionic species, Λ the equivalent conductivity at total concentration C, Λ_0 that at infinite dilution, and a a constant depending on the solvent and the value of Λ_0.

The new method is based on the following principles. The true dissociation constant of a binary electrolyte in dilute aqueous solution is equal to the product of the activities of the ions divided by the activity of the undissociated molecules; hence

$$K = C_i^2 f^2 / C_u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

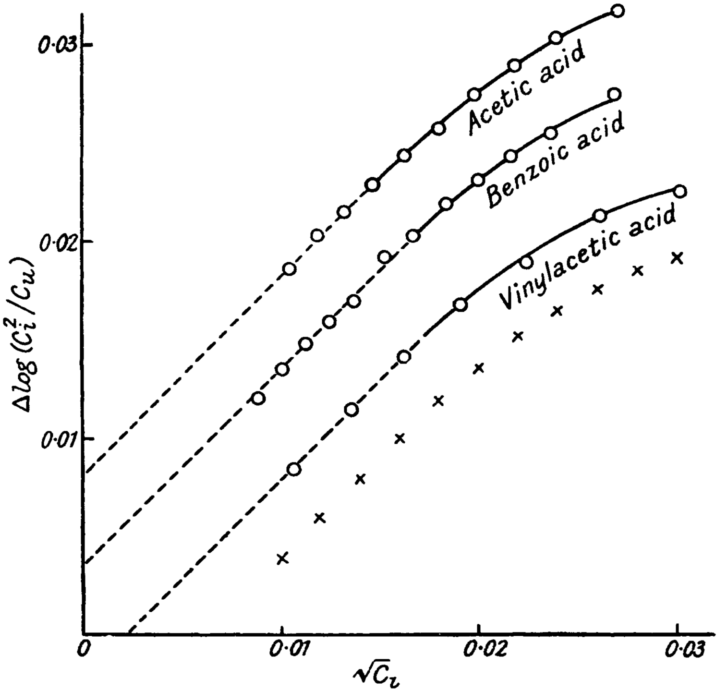
where C_u is the concentration of undissociated molecules, and f the mean ion activity coefficient referred to that of the undissociated molecules as unity. This equation may be expanded in the following way.

Since $C_i = \alpha C = \Lambda C/\Lambda_x$ and $C_u = (1 - \alpha)C = (\Lambda_x - \Lambda)C/\Lambda_x$, where α is the degree of dissociation and Λ_x the sum of the mobilities of the ions at concentration C, then

$$K = \Lambda^2 C f^2/\Lambda_x(\Lambda_x - \Lambda) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Λ_x is related to Λ_0 by means of Onsager's ionic mobility equation (*Trans. Faraday Soc.*, 1927, **23**, 341) and is obtained by application of the equation to the ionised part of the solute (Davies, *ibid.*, p. 351), thus : $\Lambda_x = \Lambda_0 - a(\Lambda C/\Lambda_x)^{\frac{1}{2}} = \Lambda_0 - aC_i^{\frac{1}{2}}$. Equation (2) may therefore be rewritten

$$K = \Lambda^2 C f^2/(\Lambda_0 - aC_i^{\frac{1}{2}})(\Lambda_0 - aC_i^{\frac{1}{2}} - \Lambda) \quad . \quad . \quad . \quad . \quad . \quad (3)$$



According to the Debye–Hückel theory relating the activity of ions to their concentration (Noyes, *J. Amer. Chem. Soc.*, 1924, **46**, 1080), the mean ion activity coefficient is given by $\log f = - A\sqrt{C_i}$, where A is a constant, which should have the value 0·5065 for uni-univalent electrolytes in water at 25°.

The expression for the true dissociation constant can therefore finally be written

$$K = \Lambda^2 C \times 10^{-2A\sqrt{C_i}}/(\Lambda_0 - aC_i^{\frac{1}{2}})(\Lambda_0 - aC_i^{\frac{1}{2}} - \Lambda) \quad . \quad . \quad . \quad . \quad (4)$$

which may be rearranged thus

$$\Lambda + aC_i^{\frac{1}{2}} = \Lambda_0 - \Lambda^2 C \times 10^{-2A\sqrt{C_i}}/(\Lambda_0 - aC_i^{\frac{1}{2}})K \quad . \quad . \quad . \quad . \quad (5)$$

By plotting $\Lambda + aC_i^{\frac{1}{2}}$ against $\Lambda^2 C \times 10^{-2A\sqrt{C_i}}/(\Lambda_0 - aC_i^{\frac{1}{2}})$ a straight line should be obtained of gradient $1/K$ and intercept at $C = 0$ of Λ_0.

Unfortunately, the Debye–Hückel ionic activity equation applies only to very dilute solutions (MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1429; Davies, *ibid.*, p. 1698); with increasing concentration " medium effects " due to un-ionised molecules of the solute cause a divergence.

Some accurate measurements have been carried out at 25° with the view of providing additional data as to the range of applicability of the Debye–Hückel equation. It is shown in a later section that equation (5) can be used successfully as a method of extrapolation over this range, and approximations are suggested whereby it may be applied to more concentrated solutions.

EXPERIMENTAL.

The apparatus, which has already been described (Ives and Riley, J., **1931**, 1998), was not altogether satisfactory according to modern views (cf. Jones and Josephs, *J. Amer. Chem. Soc.*, 1928, **50**, 1049; Shedlovsky, *ibid.*, 1930, **52**, 1739) and considerable error occurred in resistance measurements owing to indiscriminate earthing and screening. Such errors, however, can be represented by a constant factor over the entire resistance range and are expressed in the cell constant (cf. Shedlovsky, *loc. cit.*).

Errors of a variable nature are more significant and must be considered in detail.

(1) Polarisation. A very small oscillating current of frequency 1200 was used, necessitating the use of a two-stage amplifier. Resistances below 250 ohms were not measured, and a cell with large, grey, platinised electrodes was used (const. = 0·07623).

(2) The Parker effect (Jones and Bollinger, *J. Amer. Chem. Soc.*, 1931, **53**, 411). The symmetrical design of the cell was such as to minimise this effect, relegating the resistance capacity shunt, of which it is a function, to that between the contact tubes of the cell. The resistance of the thermostat water between these tubes was found to be very low, a condition tending to reduce the effect.

(3) The use of water as a thermostat liquid is alleged by Jones and Josephs (*loc. cit.*) to be undesirable owing to " capacity by-path " and eddy-current effects. The errors so produced would appear to be of opposite sign, and no error whatever could be detected in comparative experiments using (*a*) C_6H_6, (*b*) conc. KCl aq. directly earthed as bath liquids.

There seems some justification, therefore, in assuming that the apparatus was capable of measurements of considerable relative accuracy over a wide resistance range, although no claim to any great absolute accuracy can be made.

The weight dilution method was employed in making up the solutions, and since the original weighing of the solute was the least accurate operation, the results quoted are dependent in every case on a single series of dilutions. All weighings were corrected to vac., and a separate series of dilutions was used for density determinations. H_2O of $\kappa < 0{\cdot}3 \times 10^{-6}$ mho was used, and the solutions were exposed as little as possible.

In all the measurements, the following method of filling the cell was used. After being rinsed with the solution, the cell was filled and placed in the thermostat until a const. reading was obtained. It was then emptied, rinsed again, refilled, and a second reading obtained. In every case the difference between the two readings was exceedingly small, and the second was taken as correct. The cell was then filled with conductivity water and kept in the thermostat for ½ hr. before the next dilution was effected. The entire series of dilutions was carried out without any break, in as regular a manner as possible.

Pure AcOH, $Ph{\cdot}CO_2H$, and vinylacetic acid were examined in this manner. To prepare the first, B.D.H. " A.R." acid was frozen out and redistilled several times from small amounts of $KMnO_4$, and then from small quantities of P_2O_5; the acid, m. p. 16·40°, was finally distilled with a trace of added H_2O in an all-glass apparatus, and the excess of H_2O in the distillate was calculated from the f. p. $Ph{\cdot}CO_2H$ was recryst. several times from conductivity H_2O and finally sublimed. The last acid was kindly provided by Dr. R. P. Linstead.

Values of Λ_0 were determined by application of the Onsager ionic mobility equation (*Trans. Faraday Soc.*, 1927, **23**, 341) to data from the Na salt. Dissociation consts. were calculated, correction for mobility changes being applied by means of the Onsager equation (Davies, *loc. cit.*). Logarithms of the dissociation consts. were plotted against $\sqrt{C_i}$; the curves obtained are shown in the fig., the broken lines indicating the theo. slope according to the Debye–Hückel activity equation. The agreement between the exptl. and the theo. slope in the more dil. solutions is apparent from these curves, and also from the true dissociation consts. calculated on the basis of the theo. slope ($2A = 1{\cdot}0130$) shown in Table I, and provides confirmation of the theo. value of the const. A in the equation. The possible errors in Λ_0 and the cell constant (see above) do not invalidate the results as a test of the Debye–Hückel theory. In order to show this, the constants for AcOH and $Ph{\cdot}CO_2H$ have been calculated with slightly different values of Λ_0 (cols. 4 and 5); these consts. differ numerically, but still show the same range of constancy, the condition required by the test.

TABLE I.

Acetic acid.					*Benzoic acid.*				
$C\times10^3$.	Λ.	$K\times10^5$. (Λ_0 = 390·35.)	$K'\times10^5$. (Λ_0 = 389.)	$K''\times10^5$. (Λ_0 = 391.)	$C\times10^3$.	Λ.	$K\times10^5$. (Λ_0 = 380·15.)	$K'\times10^5$. (Λ_0 = 379.)	$K''\times10^5$. (Λ_0 = 381.)
29·398	9·6207	1·755	1·768	1·749	8·2268	32·865	6·462	6·503	6·432
18·177	12·187	1·762	1·774	1·756	5·1571	40·973	6·481	6·520	6·448
12·735	14·504	1·765	1·778	1·759	3·7007	47·845	6·491	6·534	6·460
8·6879	17·475	1·768	1·780	1·762	2·7464	54·905	6·499	6·542	6·468
6·0331	20·848	1·768	1·781	1·762	1·9875	63·623	6·507	6·550	6·475
4·0724	25·199	1·769	1·782	1·763	1·4295	73·711	6·506	6·550	6·473
2·7450	30·441	1·770	1·783	1·764	1·0335	85·017	6·512	6·559	6·479
1·8814	36·424	1·770	1·783	1·764	0·72014	99·171	6·502	6·549	6·468
1·2454	44·229	1·771	1·784	1·765	0·52110	113·48	6·505	6·553	6·470
0·76141	55·556	1:770	1·784	1·764	0·36504	130·95	6·508	6·558	6·471
					0·25091	151·23	6·508	6·561	6·470
					0·17195	173·36	6·502	6·559	6·476

Vinylacetic acid.

$C\times10^3$	18·577	10·470	5·8346	3·1872	1·7564	0·93394	0·40274
Λ	18·530	24·483	32·390	43·094	56·746	75·401	108·23
$K\times10^5$ (Λ_0 = 382·05)	4·384	4·414	4·429	4·441	4·443	4·443	4·443

An attempt to obtain similar results with $H{\cdot}CO_2H$ was not successful. Solutions of $H{\cdot}CO_2Na$ showed a prolonged increase of conductivity whilst in the cell, and solutions of $H{\cdot}CO_2H$ showed a decrease. This variation was not observed in a cell with small electrodes and seems to indicate catalytic decomposition of the formate ion at the surface of the Pt electrodes (cf. Müller and Schwabe, *Z. Elektrochem.*, 1928, **34**, 170).

DISCUSSION.

The above results conform to the Debye–Hückel ionic activity equation over a considerable range, and equation (5) has been used to calculate dissociation constants within this range, the value of A being taken as 0·5. The results are shown in Table II.

TABLE II.

Acetic acid.		*Benzoic acid.*		*Vinylacetic acid.*	
Λ_0 = 391·6.		Λ_0 = 379·7.		Λ_0 = 382·0.	
$C \times 10^3$.	$K \times 10^5$.	$C \times 10^3$.	$K \times 10^5$.	$C \times 10^3$.	$K \times 10^5$.
4·0724	1·758	1·9875	6·527	3·1872	4·445
2·7450	1·759	1·4295	6·526	1·7564	4·445
1·8814	1·759	1·0335	6·533	0·93394	4·445
1·2454	1·759	0·72014	6·522	0·40274	4·445
0·76141	1·759	0·52110	6·526		
		0·36504	6·529		
		0·25091	6·530		
		0·17195	6·525		

In comparing these results with those in Table I, it must be borne in mind that the latter are also subject to error in both the mobility determinations and the cell constant. The values in Table II, however, are independent of any reference to recorded mobility data, and the absolute accuracy of the experimental conductivity data is therefore of no importance. Multiplication of the experimental Λ values by a constant factor produces only a slight change in the value of the constant, although, of course, a considerable change in the value of Λ_0 which is deduced by means of equation (5); *e.g.*, if Λ is multiplied by 1·2 in the acetic acid data, the constant changes from $1{\cdot}759 \times 10^{-5}$ to $1{\cdot}748 \times 10^{-5}$, the Λ_0 value being changed from 391·6 to 471·2. The values of Λ_0 obtained by means of equation (5) therefore cannot be compared with those directly determined as a criterion of the successful application of the equation in determining dissociation constants.

The fundamental quantity in the calculation of dissociation constants by this method is the rate of change of equivalent conductivity with concentration; an accurate knowledge of the cell constant is not required, since errors in the absolute values of the conductivities are only significant in so far as they affect the constant in the Onsager equation. There is reason to suppose, in fact, that the results in Table II may be more accurate than those in

Table I; for instance, the value for acetic acid in Table II agrees more closely with recent very accurate determinations, *viz.*, 1·752 × 10^{-5} (MacInnes and Shedlovsky, *loc. cit.*) and 1·754 × 10^{-5} (Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350).

Extension to Wider Concentration Range.

In routine conductivity work, where dissociation constants are required to an accuracy of ± 1%, the precision of the measurements is usually not sufficient to show the curvature apparent in the figure. The experimental points over a normal working range are represented within experimental error by a straight line of gradient 2 × 0·39 to 2 × 0·40, which provides constants of the required order of accuracy (cf. Ives, Linstead, and Riley, this vol., p. 561). The question arises, therefore, as to whether the method can be extended to apply over a wider concentration range by assuming a value for the constant A of this order.

In Table III results are given for a number of acids covering a wide range of strengths which have been obtained by assuming for A the value 0·39. K_1 is the " true " constant obtained in an orthodox manner, and K_2 is that obtained by use of equation (5).

TABLE III.

trans-*β-Methyl-αβ-pentenoic acid.**

$C \times 10^3$.	$10^5 K_1$.	$10^5 K_2$.
23·5159	0·73	0·71
12·9198	0·73	0·72
4·4848	0·74	0·72
1·5219	0·73	0·72
0·4864	0·74	0·73
0·0791	0·73	0·72

*βγ-Pentenoic acid.**

$C \times 10^3$.	$10^5 K_1$.	$10^5 K_2$.
13·4464	3·12	3·13
7·7378	3·12	3·13
2·1063	3·12	3·14
0·6712	3·12	3·13
0·3343	3·12	3·13

*Benzoic acid.**

$C \times 10^3$.	$10^5 K_1$.	$10^5 K_2$.
5·0315	6·44	6·47
2·6692	6·46	6·48
1·5147	6·46	6·48
0·8245	6·46	6·48
0·4500	6·46	6·47

*αβ-Hexenoic acid.**

$C \times 10^3$.	$10^5 K_1$.	$10^5 K_2$.
8·1482	1·97	1·94
6·3478	1·98	1·94
3·3387	1·98	1·95
3·2789	1·98	1·95
1·7130	1·98	1·95
1·4410	1·98	1·95
0·9354	1·98	1·95
0·6090	1·98	1·95
0·5110	1·97	1·94

*Vinylacetic acid.**

$C \times 10^3$.	$10^5 K_1$.	$10^5 K_2$.
18·5765	4·46	4·40
10·4697	4·48	4·42
7·2557	4·49	4·42
5·8346	4·49	4·43
3·4544	4·49	4·43
3·1872	4·49	4·43
1·7564	4·48	4·42
0·9339	4·48	4·41
0·8804	4·48	4·41
0·4800	4·49	4·42

o-*Chlorobenzoic acid.*‡

$C \times 10^3$.	$10^3 K_1$.	$10^3 K_2$.
6·662	1·20	1·20
3·331	1·21	1·21
1·666	1·22	1·21
0·8327	1·22	1·21
0·4163	1·22	1·19

3 : 5-*Dinitrobenzoic acid.*‡

$C \times 10^3$.	$10^3 K_1$.	$10^3 K_2$.
3·929	1·50	1·53
1·965	1·51	1·53
0·9823	1·50	1·54
0·4012	1·51	1·54
0·2456	—	1·54

Formic acid.†

$C \times 10^3$.	$10^4 K_1$.	$10^4 K_2$.
32·08	1·86	1·87
15·95	1·85	1·87
8·809	1·86	1·88
4·161	1·86	1·88
3·855	1·86	1·87
1·923	1·86	1·88
1·052	1·85	1·87

* Ives, Linstead, and Riley, *loc. cit.*

† Auerbach and Zeglin, *Z. physikal. Chem.*, 1922, **103**, 191; calculations by Davies, " Conductivity of Solutions," 1930, p. 91.

‡ Kendall, J., 1912, **101**, 1275; calculations by MacInnes, *J. Amer. Chem. Soc.*, 1926, **48**, 2068.

The comparisons shown in this table are not entirely satisfactory, since the data available are scarcely of sufficient precision for the successful application of the method, and results showing least apparent experimental error have therefore been arbitrarily selected for the calculations. That such precision can be obtained with no special complication of apparatus is apparent from the data recorded in Table I, to which this method of approximation has also been applied. Different assumed values of the constant A have been taken in order to show the latitude of error. The results of these calculations are shown in Table IV.

A second method of approximation is based on the shape of the curve shown in the figure. It will be noticed that these curves are almost parallel, *i.e.*, medium effects become apparent at roughly the same ionic concentrations, irrespective of the strength of the acid. There is no theoretical justification for assuming that this is always the case, but any divergence from such a type of curve is likely to be small. The shape of the curves after the deviation first becomes apparent is expressed fairly well by the simple equation

$$2A = 1{\cdot}00 - 50(\sqrt{C_i} - 0{\cdot}016),$$

where $2A$ is the gradient. The separate points in the figure indicate this equation. Dissociation constants have also been calculated on this basis and are shown in Table IV.

TABLE IV.

	Acetic acid.		*Benzoic acid.*		*Vinylacetic acid.*	
A.	Λ_0.	$K \times 10^5$.	Λ_0.	$K \times 10^5$.	Λ_0.	$K \times 10^5$.
0·39	384·5	1·84	—	—	—	—
0·40	386·4	1·82	—	—	383·2	4·44
0·41	388·2	1·80	378·6	6·61	384·1	4·42
0·42	390·15	1·78	379·1	6·59	385·0	4·39
0·43	392·0	1·76	379·5	6·57	—	—
$\propto C_i$	393·6	1·74	380·0	6·51	382·9	4·42

It is evident that if a mean value for the gradient is used, it is dependent on the conductivity range studied (which in the case of acids is roughly equivalent to a range of ionic concentrations) and also on the distribution of the experimental points within this range.

The essential process of the method is the same as that suggested by Davies (*Trans. Faraday Soc.*, **1927**, **23**, 351), *viz.*, the selection of a value of Λ_0 such that the log (C_i^2/C_u)–$\sqrt{C_i}$ curve shall fulfil a given condition. This condition is that it shall be a straight line of gradient conforming to the Debye–Hückel theory, and these approximations, involving an assumption that any acid shall diverge from the theory in a perfectly standard manner, cannot be considered satisfactory, since there is no theoretical justification for such an assumption. They may, however, provide a method of obtaining fairly reliable dissociation constants in cases where other methods are not available. The fact remains, however, that provided precise measurements be available below the range where medium effects enter, the suggested equation is capable of providing accurate dissociation constants without any previous knowledge of mobilities. The equation should be applicable to any electrolytes which are free from complex formation or secondary dissociation, such a class being limited to acids and bases in water and also, possibly, some salts in non-aqueous solvents.

Method of Computation.

In order to avoid confusion, the method of application of equation (5) has not yet been described. Any value of Λ_0 may be assumed as the starting point in the calculation, and the corresponding value of a in the Onsager equation obtained. Mobility corrections are now applied to the ionised part of the solute (see Davies, *Trans. Faraday Soc.*, **1927**, **23**, 351; Banks, J., **1931**, 3341), and for each experimental value of Λ the corresponding values of C_i (based on the *assumed* value of Λ_0) and of $\Lambda + aC_i^{\frac{1}{2}}$ and $\Lambda^2 C \times 10^{-2A\sqrt{C_i}}/(\Lambda_0 - aC_i^{\frac{1}{2}})$ deduced. An extrapolation is now carried out. Graphical methods are not sufficiently accurate or reproducible for this purpose, and the methods of " least squares " or " zero sum " may be employed. The former method has been used in these calculations, and is applied as follows. If $y = \Lambda + aC_i^{\frac{1}{2}}$, $x = \Lambda^2 C \times 10^{-2A\sqrt{C_i}}/(\Lambda_0 - aC_i^{\frac{1}{2}})$, $m = 1/K$, and $c = \Lambda_0$, by solving the simultaneous equations

$$m\Sigma x + nc - \Sigma y = 0,$$
$$m\Sigma(x)^2 + c\Sigma x - \Sigma(xy) = 0,$$

where n is the number of experimental quantities, a new value of Λ_0 is obtained. Starting with this new value, the entire calculation is repeated until a constant value is obtained, whereupon K may be calculated.

The type of approximation is shown below, successive values of Λ_0, obtained from series of calculations starting with three different assumed values of Λ_0, *viz.*, (1) 360, (2) 380, (3) 400, being used for benzoic acid.

(1) 360, 380·24, 379·86, 379·88. (2) 380, 379·86, 379·88. (3) 400, 379·48, 379·88, 379·88.

Λ_0 from mobility data = 380·15.

SUMMARY.

(1) Precise comparative measurements of the conductivities of aqueous solutions of acetic, benzoic, and vinylacetic acids have been carried out with the view of providing additional data as to the range of applicability of the Debye–Hückel theory, and it is shown that these acids conform closely to the theory over a considerable concentration range.

(2) An equation based on the Ostwald dilution law, the Onsager equation, and the Debye–Hückel equation has been devised whereby Λ_0 values and dissociation constants may be calculated from conductivity data over this range.

(3) The equation has been applied to the accurate data on the above three acids, and it is shown that accurate dissociation constants may be determined without any reference to recorded mobility data and independently of the absolute accuracy of the conductivity measurements.

(4) Methods of approximation have been suggested whereby the method may be extended to a wider conductivity range, and have been tested by application to acids already studied.

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