19. *The Determination of the Primary and Secondary Dissociation Constants of Some Aliphatic Dicarboxylic Acids.*

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A colorimetric method has been devised for the determination of the first and second thermodynamic dissociation constants of dibasic acids, thereby avoiding some of the difficulties inherent in electrometric methods, such as the uncertainties of interpretation introduced by the existence of liquid-junction potentials, or by the necessity for extrapolation of E.M.F. data from cells without liquid junctions. The pH scale is standardised by use of buffer solutions prepared from monocarboxylic acids of accurately known dissociation constants. The method has been tested by experiments on malonic, succinic, glutaric, adipic, and α-methyl-, β-methyl-, and ββ-dimethyl-glutaric acid, and has been found satisfactory.

THE determination of the dissociation constants of dibasic acids has usually been made by one of two main methods, conductimetric and electrometric, though fairly recently a spectrophotometric method [1] has been employed. The conductimetric method has been extensively used by Vogel and his co-workers [2,3,4] to determine the primary dissociation constants (K_1) of a series of dicarboxylic acids, but its disadvantages are now well known, and it may be fairly regarded as obsolete. There are also a number of distinct disadvantages inherent in the electrometric method, which have been discussed by German and Vogel,[2] and later by Speakman [5] and Bates.[6] Chief among these are the difficulties involved in overcoming the uncertainties introduced by the existence of liquid-junction potentials, and of the standardisation of the pH scale.

In the present paper we have avoided the first difficulty by adopting a colorimetric method, and the second by using as pH standards partly neutralised solutions of monobasic weak acids, whose hydrogen-ion concentrations could be calculated very accurately from known dissociation constants. The method of computing the thermodynamic dissociation constants of a dibasic acid, H_2A, is essentially that described by Speakman,[5] with such minor modifications as are rendered necessary by the fact that colorimetric and electrometric methods measure different functions of the hydrogen-ion concentration.

If, in accordance with general usage, pH is defined in terms of the hydrogen-ion *activity*, as pH $= -\log a_{\mathrm{H}^+}$, it follows that electrometrically measured pH gives a direct measure of the function $f_1[\mathrm{H}^+]$, where f_1 signifies the activity coefficient of a univalent ion, and $[\mathrm{H}^+]$ the *concentration* of hydrogen ions. However, in the case of colorimetric " pH " determination it has been shown [7] that two solutions in which the colour and concentration of an indicator are identical do not have the same pH value, as defined above, except coincidentally if they chance to have the same ionic strength (I). The function measured will depend on the nature of the indicator, and for sulphonephthalein indicators such as Bromophenol Blue and Bromocresol Green, used in the present work, the quantity $f_{\mathrm{H}^+} . f_{\mathrm{B}^{2-}} [\mathrm{H}^+]/f_{\mathrm{HB}^-}$ is the same in each, as the main colour change of the sulphonephthalein indicators is known to be associated with the ionisation of a phenolic hydrogen atom in the singly-charged yellow carboxylate ion.[7,8] The activity coefficients of the two univalent ions being taken as equal, and that of the bivalent ion B^{2-}, *i.e.*, $f_{\mathrm{B}^{2-}}$, being written as f_2, equality of colour in two solutions will indicate identity of the quantity $\mathrm{p}f_2[\mathrm{H}^+] = -\log f_2[\mathrm{H}^+]$.

Our experimental procedure was therefore to prepare a series of solutions of the

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[1] Robinson and Kiang, *Trans. Faraday Soc.*, 1956, **52**, 327.
[2] German and Vogel, *J. Amer. Chem. Soc.*, 1936, **58**, 1546.
[3] Jeffery and Vogel, *J.*, 1936, 1756.
[4] *Idem, J.*, 1939, 446.
[5] Speakman, *J.*, 1940, 855.
[6] Bates, *J. Amer. Chem. Soc.*, 1948, **70**, 1579.
[7] Stock and Davies, *J.*, 1949, 1371.
[8] Kolthoff, *J. Phys. Chem.*, 1931, **35**, 1433.

dicarboxylic acid being studied; to these were added fixed amounts of indicator solution and of potassium chloride solution, and then standard sodium hydroxide solution corresponding to various stages of neutralisation between 20% and 80%. Each solution was finally made up with the appropriate volume of water to make the final volume twice that of the original acid solution taken, so that the total acid concentration (a) was always maintained constant, at 0·005M. The $pf_2[H^+]$ values were then determined as described below, by comparison with standard buffer solutions of accurately known $pf_2[H^+]$.

The thermodynamic dissociation constants of a dibasic acid, H_2A, may be defined by the equations:

$$K_1 = [H^+][HA^-]f_1^2/[H_2A]f_0 \quad \text{and} \quad K_2 = [H^+][A^{2-}]f_2/[HA^-]$$

where f_0, f_1, f_2, are the activity coefficients of uncharged species, univalent ions, and bivalent ions respectively. In a solution of total acid concentration a (molar)

$$a = [H_2A] + [HA^-] + [A^{2-}]$$

and when a strong monoacid base such as sodium hydroxide, which may be taken as completely dissociated (as may its salts), has been added to give a molar concentration b, electrical neutrality requires that

$$b + [H^+] = [HA^-] + 2[A^{2-}] + [OH^-]$$

If, following Speakman,[5] we define L, M, and N by the equations

$$L = b + [H^+] - [OH^-] \qquad (= [HA^-] + 2[A^{2-}])$$

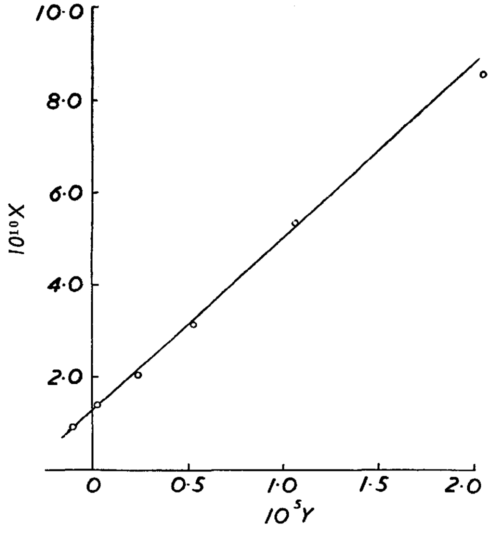
$$M = a - b - [H^+] + [OH^-] \qquad (= [H_2A] - [A^{2-}])$$

$$N = 2a - b - [H^+] + [OH^-] \qquad (= 2[H_2A] + [HA^-])$$

it can easily be shown that

$$[H^+]^2 . f_1^2 f_2 L/N f_0 = K_1([H^+]f_2 M/N f_1) + K_1K_2 \quad . \quad . \quad . \quad . \quad \text{(i)}$$

which may be written shortly $X = K_1Y + K_1K_2$. If the parameter X be plotted against Y, a straight line should be obtained, the slope of which equals K_1, and the intercept on the X-ordinate K_1K_2. In deriving X and Y from the experimental data, certain approximations must be made, but these may be shown to be such as not seriously to affect the accuracy of conclusions drawn from equation (i), which is rigorous. First, it is apparent that at pH's below 7 the hydroxyl-ion concentration can safely be neglected; further, in solutions of ionic strengths as low as those encountered (not greater than 0·036) the activity coefficient f_0 is unlikely to differ appreciably from unity. Speakman assumed that for most of his solutions f_1 was unity, so that the activity of H^+ as measured electrometrically could be used in place of the concentration in evaluating L, M, and N, and in those cases where allowance was made for the activity coefficient, the Debye–Hückel limiting law (*viz.*, $\log f_i = -0{\cdot}5z_i^2 I^{\frac{1}{2}}$) was used. The same law was used to evaluate the activity coefficients in his equation (i). In the present work, in order to minimise errors, the ionic strengths of the test solutions and of the comparison buffer solutions were made approximately the same by the addition of a fixed amount of potassium chloride to each solution. This made the ionic strength about 0·035 in each case, a value rather too high for the



Debye–Hückel equation to be used. The Davies activity equation[9] (*viz.*, $\log f_i = -0{\cdot}5z_i^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I\}$) has been shown to be applicable up to ionic strengths of 0·05, certainly well within the accuracy at which we were aiming. By assigning an approximate value to I the activity coefficients f_1 and f_2 were calculated, and hence $[H^+]$, X, and Y. From the resulting plot initial values of K_1 and K_2 could be obtained, and thence $[H_2A]$, $[HA^-]$, and $[A^{2-}]$, from which a new value of I could be calculated. After about three successive approximations constant values for K_1 and K_2 resulted. The slope and the intercept were evaluated by the method of least squares. The method is illustrated by a typical plot of X against Y for adipic acid in the Figure.

EXPERIMENTAL

The procedure was tested by measurements on malonic, succinic, glutaric, and α-methyl-, β-methyl-, and ββ-dimethyl-glutaric, and adipic acid. These, and the mandelic and benzoic acid used for preparing the standard buffer solutions, were pure specimens, and were further purified by several recrystallisations from conductivity water, and dried *in vacuo* over concentrated sulphuric acid. The purity of each acid was checked by m. p., and by titration against standard alkali. The acid solutions were freshly prepared for each run, and in no case was any solution kept for longer than three days. The potassium chloride was of " AnalaR " grade, thrice recrystallised from conductivity water. Sodium hydroxide solution was prepared from clean pieces of sodium, which were allowed to react in a platinum dish standing over carbon dioxide-free conductivity water in a vacuum-desiccator; the resulting solution was transferred, diluted, and stored with the necessary precautions in a nickel bottle, and was standardised, through hydrochloric acid, against " AnalaR " sodium carbonate. The indicators, Bromophenol Blue and Bromocresol Green, were purchased as solids from B.D.H. Ltd., and made up to a final concentration of 0·04% by the method of Clark and Lubs.[10]

As subsequent calculations call for the determination of ionic strengths and hydrogen-ion concentrations as accurately as possible, the colour standards were prepared by partially neutralising solutions of monobasic acids, of accurately known dissociation constants, with standard sodium carbonate solution. That carbonic acid does not interfere at the pH values encountered was proved both experimentally and by calculation. Mandelic and benzoic acid were selected because their dissociation constants are known with high accuracy from conductivity investigations, which have also shown ion association to be negligible in dilute solutions of the sodium salts. The test solutions and the comparison standards contained the same amount of indicator, in the proportion of 5·0 ml. of 0·04% solution in a total volume of 55·0 ml., and the benzoate (or mandelate) buffers were of concentration 0·01M (total organic radical).

The colour comparisons were made by means of a Unicam SP.600 spectrophotometer, with 1 cm. glass cells. Absorption curves for solutions of varying pH, containing the standard concentration of indicator, were obtained and from these the wavelength ($\lambda_{max.}$) corresponding to maximum absorption was determined. At this wavelength the sensitivity of the indicator to pH change is also at its maximum, and the subsequent measurements were all made at this wavelength. The transmission was measured on the spectrophotometer (to an accuracy of 0·2%) in a room maintained at 25°, all solutions being kept in a thermostat at 25° ± 0·01° until used to make up the test solutions.

The method adopted for the determination of the hydrogen-ion concentration of the test solutions was as follows: a series of solutions of the monobasic acid was made up, neutralised to known extents by the addition of 0·04N-sodium carbonate, and containing the standard amounts of indicator and potassium chloride. The percentage transmission of each solution was measured, at the appropriate $\lambda_{max.}$ for the particular indicator, and a graph constructed of the percentage transmission at $\lambda_{max.}$ against the volume of carbonate solution. From this graph the range of pH over which the plot was linear was found. In the subsequent experiments conditions were arranged so that the transmission of the test solution was always in the range 25—60%. A graph relating $f_2[H^+]$ to percentage transmission was also constructed, from the known composition of the solutions (the Davies equation being used to calculate the activity coefficients) and the dissociation constants of the acids (mandelic, $K = 3{\cdot}88 \times 10^{-4}$, Banks and

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[9] Davies, *J.*, 1938, 2093.

[10] Clark, " The Determination of Hydrogen Ions," London, 1928, p. 94.

Davies;[11] benzoic, $K = 6{\cdot}320 \times 10^{-5}$, Brockman and Kilpatrick[12]). By interpolating on this curve it is possible to determine directly the value of $f_2[H^+]$ in the dicarboxylate buffer, equality of colour being taken to indicate equality of $f_2[H^+]$.[4]

Thermodynamic dissociation constants at 25°, *in aqueous solution.*

Acid	Malonic		Succinic		Glutaric		Adipic	
Ref.	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
13	2·85	—	4·18	—	4·34	—	4·43	—
2	2·84	5·66	4·20	5·60	4·34	5·42	—	—
14	2·75	5·36	4·13	5·35	4·34	5·27	4·41	5·28
15	2·83	5·69	4·19	5·48	4·34	5·42	4·42	5·41
16	—	—	4·16	5·61	4·34	5·41	4·43	5·41
Present work	2·87	5·70	4·22	5·70	4·35	5·40	4·44	5·44

Acid	α-Methylglutaric		β-Methylglutaric		ββ-Dimethylglutaric	
Ref.	pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
4	—	—	4·24	—	3·72	—
17	—	—	4·24	6·20	3·69	6·26
15	—	—	4·33	6·22	3·70	6·29
16	—	—	4·25	5·41	3·70	6·34
Present work	4·36	5·37	4·27	5·37	3·73	6·71

The results of a series of measurements on the seven dicarboxylic acids studied are collected in the Table, together with the pK's obtained, at the same temperature, by previous workers: the values of α-methylglutaric acid do not appear to have been previously determined.

DISCUSSION

The values obtained for the dissociation constants of the acids are generally in good agreement with those previously reported by other workers using other methods. It is perhaps not unreasonable to infer that the various assumptions made are justified, and that the colorimetric method may offer a considerable advantage over electrometric methods. In the present work the reproducibility of ±0·2% in transmission corresponds to a p$f_2[H^+]$ accuracy of $\pm 0{\cdot}002_5$. While it is true that the reproducibility in E.M.F. of a particular cell may correspond to perhaps as little as ±0·001 pH unit, the uncertainties in the final (absolute) pK's obtained, resulting from the existence of liquid-junction potentials, or from the necessity for the extrapolation of data to infinite dilution, may largely offset this greater reproducibility. It is realised that the used of such thermodynamically unsatisfactory quantities as individual ion activities may militate to some extent against the present treatment, but in solutions of as low ionic strength as these the consequent uncertainties are unlikely to be very great. We estimate that the final pK values quoted are probably accurate to ±0·01.

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[11] Banks and Davies, *J.*, 1938, 73.
[12] Brockman and Kilpatrick, *J. Amer. Chem. Soc.*, 1934, **56**, 1485.
[13] Jeffery and Vogel, *J.*, 1935, 21.
[14] Gane and Ingold, *J.*, 1928, 1594.
[15] *Idem*, *J.*, 1931, 2153.
[16] Jones and Soper, *J.*, 1936, 133.
[17] Gane and Ingold, *J.*, 1928, 2267.