

70. The Dissociation Constants of Some Acids in Mixed Solvents.

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Thermodynamic dissociation constants (K_1 and K_2) of some dibasic acids in aqueous alcohol and aqueous dioxan have been determined by using the glass electrode in conjunction with a cell involving liquid-liquid potentials. Similar measurements have been made with benzoic acid, and the dissociation constants of this acid have also been found from measurements on cells not involving liquid junctions. The significance of results for mixed solvents obtained by the former method is considered. The dependence of K_1/K_2 for a dibasic acid upon the structure of the molecule and the composition of the solvent is discussed.

DIFFICULTIES besetting the definition of the pH scale in general, and in particular the determination of the dissociation constant of an acid from the E.M.F. of a cell involving liquid junctions, are enhanced when an attempt is made to compare dissociation constants in different solvents (*e.g.*, Michaelis and Mizutani, *Z. physikal. Chem.*, 1925, 116, 135; Brønsted, *Chem. Reviews*, 1928, 5, 291; Wynne-Jones, *Proc. Roy. Soc.*, 1933, 140, A, 440). Nevertheless, the method possesses practical advantages and has often given useful results (for references see Dippy, *Ann. Reports*, 1941, 38, 132). Some of the theoretical difficulties can be avoided by considering the ratio of the first to the second dissociation constant of a dibasic acid (K_1/K_2). The present paper describes measurements of the thermodynamic dissociation constants of benzoic, adipic, succinic, and *cis*-tetrahydronaphthalene-2:3-dicarboxylic acids, and of methyl hydrogen succinate, in aqueous ethyl alcohol and in aqueous dioxan. The dissociation constants of benzoic acid in the same solvents have also been measured approximately by the use of cells not involving liquid junctions; this was done since dissociation constants have frequently been expressed with reference to that of benzoic acid.

EXPERIMENTAL.

Materials.—Ordinary absolute ethyl alcohol was refluxed over lime and distilled. The small water content of the distillate was estimated from the density, and the calculated weights of alcohol and carbon dioxide-free distilled water were mixed to give the required solvents. Commercially purified dioxan was refluxed over sodium and fractionally crystallised twice (Hess and Frahm, *Ber.*, 1938, 71, 2627), the setting point then being 10.8°. Aqueous dioxan was made up by weighing. The compositions, densities, and dielectric constants (the last from the data of Åkerlöf, *J. Amer. Chem. Soc.*, 1932, 54, 4130, and of Åkerlöf and Short, *ibid.*, 1936, 58, 1241) at 20.0° of the mixed solvents used are shown in Table I.

TABLE I.

Solvent.	Organic liquid, % by wt.	d .	D .	A .
H ₂ O	—	0.998	80.4	0.50
H ₂ O-C ₂ H ₅ ·OH	25	0.965	65.7	0.68
H ₂ O-C ₂ H ₅ ·OH	50	0.919	50.4	1.01
H ₂ O-C ₄ H ₈ O ₂	30	1.025	53.3	0.93

Pure commercial benzoic, adipic, and succinic acids were thrice recrystallised from water; *cis*-tetrahydronaphthalene-2:3-dicarboxylic acid (Haworth and Slinger, *J.*, 1940, 1321) was recrystallised once. Methyl hydrogen succinate, prepared by the method of Bone, Sudborough, and Sprankling (*J.*, 1904, 85, 539) and twice recrystallised from carbon tetrachloride, had *m. p.* 57°.

Method of Measurement.—Solutions of the acids (0.0005–0.002M) were potentiometrically titrated at 20.0° with approximately 0.05N-sodium hydroxide (carbonate-free), the glass electrode being used. The liquid junction between the working solution and the bridge, containing saturated aqueous potassium chloride and leading to the standard half-cell, was made in the doubly bent capillary tube at the end of the bridge. Further details, including the method of standardising the pH scale and of calculating thermodynamic dissociation constants, have already been described (*J.*, 1940, 855). (A similar method of calculation has since been given by Gale and Lynch, *J. Amer. Chem. Soc.*, 1942, 64, 1153.) The alkali solutions were made up in the same solvent as the acid, except in some of the experiments in 25% aqueous alcohol, for which aqueous sodium hydroxide was used; the error thus introduced by the slight change in the water content of the medium during titration was negligible. The activity coefficients needed were worked out from the Debye-Hückel limiting law, $-\log f = z^2 A \sqrt{I}$, z being the valency and I the ionic strength, and the values of A being those shown in Table I.

Dissociation constants, initially calculated in terms of molarities, have been converted to the molality basis by increasing pK ($= -\log_{10} K$) by $\log_{10} d$, where d is the density of the solvent. Results, including those for water (*J.*, 1940, 895; 1941, 490) and each the mean of several independent determinations, are given in Table II. The accuracy is estimated at ± 0.05 unit in pK , and rather better in ΔpK .

Error of Glass Electrode in Mixed Aqueous Solvents.—Although the glass electrode has been used successfully in mixed aqueous solvents (*e.g.*, by Bennett, Brookes, and Glasstone, *J.*, 1935, 1821), it may become subject to errors when the proportion of water becomes low (*cf.* Goodhue and Hixon, *J. Amer. Chem. Soc.*, 1935, 57, 1688; Dole, "The Glass Electrode," p. 140). For this reason the present work was not extended to solvents containing less than 50% by weight of water. In 50% aqueous alcohol the activity of the water, $\{H_2O\}$, is 0.83; and the error of the glass electrode, if Dole's formula, $\Delta E = (RT/F) \ln \{H_2O\}$, is accepted, is -0.0046 v., or $+0.08$ pH unit. This is larger than the experimental error in the present work, but was neglected because its precise magnitude is uncertain and it seems likely to give rise

TABLE II.
Thermodynamic dissociation constants at 20·0°.

Acid.	Solvent :			25% C ₂ H ₅ ·OH.			50% C ₂ H ₅ ·OH.			30% C ₄ H ₈ O ₂ .		
	pK ₁ .	pK ₂ .	ΔpK.	pK ₁ .	pK ₂ .	ΔpK.	pK ₁ .	pK ₂ .	ΔpK.	pK ₁ .	pK ₂ .	ΔpK.
Adipic	4·43	5·42	0·99	4·93	6·00	1·07	5·83	6·98	1·15	5·45	6·55	1·10
Succinic	4·22	5·67	1·45	4·65	6·19	1·54	5·48	7·24	1·76	5·19	6·84	1·65
Methyl hydrogen succinate	4·56	—	—	5·03	—	—	5·89	—	—	5·43	—	—
cis-Tetrahydronaphthalene-2 : 3-dicarboxylic	3·98	6·47	2·49	4·48	7·59	3·11	5·27	8·85	3·58	4·99	8·33	3·34
Benzoic	4·24	—	—	4·83	—	—	5·87	—	—	5·35	—	—

to a consistent error. It was observed that, as the percentage of water in the solvent diminished, the electrode needed longer to respond to changes of pH during titration.

Measurements using Cells without Liquid Junctions.—Approximate measurements were made of the dissociation constants of benzoic acid in the same solvents by use of cells not involving liquid junctions (cf. Harned, *Chem. Reviews*, 1939, 25, 31). The cells were of the type Ag|AgCl|solution|quinhydrone|Pt, the solution being 0·1-molal hydrogen chloride or a benzoic acid-benzoate buffer containing sodium chloride and of total ionic strength about 0·006. The E.M.F., along with the activities of hydrogen chloride in the respective solvents obtained by interpolation from the data of Butler and Robertson (*Proc. Roy. Soc.*, 1929, 125, A, 694) for aqueous alcohol and of Harned and Morrison (*J. Amer. Chem. Soc.*, 1936, 58, 1908) for aqueous dioxan, enabled the thermodynamic dissociation constants of the benzoic acid to be calculated by an unequivocal method. The usual procedure of extrapolation to zero ionic strength was omitted, since the above interpolation was not very certain, and the E.M.F. measurements had in consequence been made only approximately. Results are given in Table III, the estimated accuracy being ± 0·1 unit. These values differ but little

TABLE III.
Thermodynamic dissociation constants of benzoic acid at 20·0°.

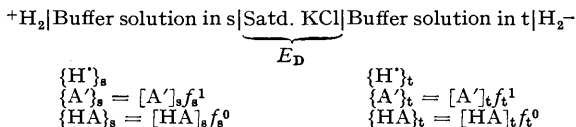
Solvent.	(Cells without liquid junctions.)			
	H ₂ O.	25% C ₂ H ₅ ·OH.	50% C ₂ H ₅ ·OH.	30% C ₄ H ₈ O ₂ .
pK	4·2 ₂	4·7	5·6 ₅	5·2

from those found by the other method (Table II), and the differences would be even smaller had allowance been made for the error of the glass electrode in the mixed solvents. In this particular instance, at least, the uncertainties involved in the use of cells with liquid junctions have not led to any very considerable errors.

The nature of these uncertainties has been indicated by Guggenheim (*e.g.*, *J. Physical Chem.*, 1929, 33, 842; 1930, 34, 1758; *Phil. Mag.*, 1936, 7, 983). The thermodynamic dissociation constants of an acid (HA) in two solvents (s and t) are defined by the equations.

$$K_s = \{H^+\}_s \{A^-\}_s / \{HA\}_s \dots \dots (1) \quad \text{and} \quad K_t = \{H^+\}_t \{A^-\}_t / \{HA\}_t \dots \dots (2)$$

{ } indicating activities, and the subscripts indicating that these are referred, as usual, to infinite dilution in the respective solvents. The experimental arrangement used in attempting to compare K_s and K_t by use of cells with liquid junctions consists in principle of a cell of the type :



The E.M.F. of this cell can be expressed by the equation

$$E = (RT/F) \ln \{H^+\}_s / \{H^+\}_t + E_D \dots \dots \dots (3)$$

The double subscript t/s is now added to the activity appearing in the denominator since {H⁺}_t and {H⁺}_s are expressed on different scales, and the quantity obtained by the use of equation (3) is related to the former by the relationship {H⁺}_{t/s}/{H⁺}_t = l, in which l is the distribution ratio for hydrogen ions between s and t—a quantity which, like E_D, is not accessible to measurement. Substituting in (3), we have :

$$E - \left(E_D - \frac{RT}{F} \ln l \right) = \frac{RT}{F} \ln \frac{K_s}{K_t} + \frac{RT}{F} \ln \frac{[HA]_s [A^-]_t}{[HA]_t [A^-]_s} + \frac{RT}{F} \ln \frac{f_s^0 f_t^{-1}}{f_t^0 f_s^{-1}} \dots \dots \dots (4)$$

In general, we cannot find the ratio K_s/K_t because we do not know the terms in parentheses on the left-hand side of (4). These terms being neglected, and the activity coefficients being estimated in the conventional manner (by use of the Debye-Hückel limiting law for the ions), let the ratio actually found be K_s/K'_t [K'_t will in general differ from K_t: Michaelis and Mizutani call it the "reduced dissociation constant" (cf. the "acidity function" of Brönsted)]. The dissociation constants given in Table II (and the results of many previous workers in this field) really correspond to K'_t. The fact that for benzoic acid K'_t (Table II) and K_t (Table III) do not differ substantially suggests that the terms neglected are together small. Indeed, it seems possible that they might individually act in opposite directions: s being water and t (for example) aqueous alcohol, it seems reasonable to suppose that l should be greater than unity; whilst E_D would be expected to be positive since the dielectric constant of s is the greater. In any case it seems that E_D - (RT/F) ln l could be determined for any pair of solvents by comparing the dissociation constants of a given acid as found by the two methods; l would be constant, and, if E_D were reproducible and independent of the nature of the acid (as is likely), true thermodynamic dissociation constants of other acids in the two solvents could then be compared by the use of cells with liquid junctions.

DISCUSSION.

Bjerrum (*Z. physikal. Chem.*, 1923, 106, 219) derived a simple relationship (5) between the first and the second dissociation constant of a symmetrically dibasic acid; e is the electronic charge, k the Boltzmann

constant, D the dielectric constant of the solvent, and R the distance between the negative poles in the double anion. The formula implies that the anion can be replaced by a model consisting of two point charges a

$$\Delta pK - \log 4 = e^2 / (2 \cdot 3 k T D R) \quad (5)$$

distance R apart and having extension in one dimension only. This is an obvious over-simplification, but gives reasonable values of R provided it be not too small. When R is small, its value calculated from (5) is improbably low (e.g., 3.7 Å. for succinic acid).

It is convenient, following Eucken (*Z. angew. Chem.*, 1932, 45, 203), to replace (5) by (6), in which D_E is the effective dielectric constant of the region between the negative poles. Attempts can then be made to

$$\Delta pK - \log 4 = e^2 / (2 \cdot 3 k T D_E R) \quad (6)$$

calculate D_E . Ingold (J., 1931, 2179; see also Jones and Soper, J., 1936, 133) has considered the effect of the field near the ion in modifying the properties of the solvent (water) locally; the ion was still regarded as of negligible bulk. Kirkwood and Westheimer (*J. Chem. Physics*, 1938, 6, 506, 513; note errata, *ibid.*, 1939, 7, 437, and others) have taken account of the fact that the region around and between the poles is occupied, not by solvent but by the body of the acid molecule, which for most organic acids may be regarded as having a low dielectric constant. They made calculations on the bases of two models which were convenient for mathematical treatment. The first represented the molecule by a sphere of dielectric constant 2 immersed in water ($D = 78$), with two point charges embedded in it; by the methods of spherical harmonics D_E was calculated as a function of the positions of the charges. The second (more suited for elongated molecules) represented the molecule by an ellipsoid of revolution with the charges at the foci; D_E was calculated as a function of the eccentricity of the ellipsoid. These calculations led to the surprising result that D_E can exceed the value of D for the solvent, and that it does so for positions of the charges corresponding to probable physical conditions [*viz.*, with the spherical model, when the charges are at, or near, the surface of the sphere; with the ellipsoidal, when the eccentricity exceeds a value of about 0.77 (*i.e.*, when λ_0 is less than 1.3) which corresponds to a molecule of quite moderate elongation]. This result is opposed to empirical requirements in most cases where the simple Bjerrum relationship breaks down.

Restricting ourselves to the ellipsoidal model, which more closely represents the structures of the acids dealt with here, the ellipsoid is described by the interfocal distance, R , and by the equation $\lambda = \lambda_0$, where λ is the confocal co-ordinate defined by $\lambda = (r_1 + r_2)/R$, r_1 and r_2 being the distances of any point from the foci. Closer agreement with experiment is reached if Westheimer and Kirkwood's expression for D_E is replaced by the simplified, empirical equation (7). D is the dielectric constant of the solvent in bulk, D_1 that of the molecule of the acid and assumed to be 2 (as for a paraffin), and P_n and Q_n are the Legendre polynomials of the first and the second kind.

$$\frac{1}{D_E} = \frac{1}{D_1} - \left(\frac{1}{D_1} - \frac{1}{D} \right) \left\{ \sum_{n=0}^{\infty} 2(2n+1) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} (-1)^n \right\} \quad (7)$$

Equation (7) can be deduced from the model by postulating an appropriate contact potential at the surface between the ellipsoid and the surrounding medium—a procedure of questionable validity—but it has the advantage of giving values of D_E which rise to, but do not exceed, D as λ_0 diminishes to unity. Values of the quantity in brackets (Σ) and of D_E for water and aqueous alcohol at 20° are shown in Table IV.

TABLE IV.

λ_0	1.0	1.1	1.2	1.3	1.4	1.6
Σ	(1.000)	0.99995	0.9988	0.9929	0.981	0.941
D_E { $D = 80.4$ (water)	80.4	80.2	76.6	62.9	46.0	24.4
{ $D = 50.4$ (50% alcohol)	50.4	50.3	48.9	43.0	34.5	20.8

Combination of (7) with the Eucken equation (6) suggests that ΔpK should be a linear function of $1/D$, and that the limiting value of ΔpK obtained by extrapolation to $1/D = 0$ should be larger than $\log 4$, the value to be expected from the Bjerrum formula (5). The results quoted in Table II are in general agreement with these expectations. ΔpK values in aqueous dioxan, however, fall rather below the line for those in aqueous alcohol. The composition of a mixed solvent in the neighbourhood of a dissolved ion will generally differ from that of the solvent in bulk owing to the operation of the salting-out effect (cf. Elliott and Kilpatrick, *J. Physical Chem.*, 1941, 45, 485), and the extent of this effect may differ as between alcohol and dioxan. Aqueous dioxan acts here as if it had a higher effective dielectric constant than an aqueous alcohol of the same bulk dielectric constant. This situation is also reflected in the pK values themselves.

The volume (V) of an ellipsoid of revolution is given by $(\lambda_0^3 - \lambda_0) = 6V/\pi R^3$. For succinic and adipic acids R has been calculated by assuming the polymethylene chain to be an extended zigzag, with the C-C distance 1.54 Å. and the C-C-C angle 111½° (cf. Gane and Ingold, J., 1931, 2165; also *Ann. Reports*, 1940, 37, 176; J., 1941, 940). The negative charges on the carboxylate groups were taken to be 1.0 Å. beyond the terminal carbon atoms. V has been estimated from Traube's rule of the additivity of molecular volumes in solution (*Annalen*, 1895, 290, 44). Details are shown in Table V, whence it appears that the calculated values of ΔpK are in agreement with experiment.

TABLE V.

	Succinic acid.	Adipic acid.
Volume of ion { (c.c./mole)	76.2	108.4
{ (A. ³ /molecule = <i>v</i>)	127	180
Distance between charges (<i>R</i>)	5.9	8.3
λ_0	1.38	1.20
Solvent : water { D_E	49.5	76.5
{ ΔpK (calc.)	1.46	0.99
{ ΔpK (obs.)	1.45	0.99
Solvent : 50% alcohol { D_E	36.5	49.0
{ ΔpK (calc.)	1.77	1.20
{ ΔpK (obs.)	1.76	1.15

Simple considerations lead to the expectation that the dissociation constant of methyl hydrogen succinate (*K*) should be half as great as the primary dissociation constant of succinic acid (*K*₁); *i.e.*, $pK - pK_1 = 0.30$. This expectation is fulfilled in water, and approximately in aqueous dioxan; but in aqueous alcohol ($pK - pK_1$) exceeds 0.30 by more than the experimental error.

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[Received, March 20th, 1943.]