CCVII.—*Electrometric Titration Curves of Dibasic Acids. Part I. Normal Acids.*

By Richard Gane and Christopher Kelk Ingold.

The hypothesis that the angles between the valencies of a carbon atom are modified by the space requirements of the attached groups has been attested by chemical evidence of various kinds during the past 13 years, and it therefore seemed desirable to examine the possibility of obtaining confirmation by physical methods. The most hopeful line of inquiry appeared to be to endeavour to establish a connexion between molecular configuration, as determined by the valency-deflexion hypothesis, and the external molecular electrical field, utilising physical properties which are known to depend mainly on this field. Two properties suggested themselves for this purpose, namely, the dielectric constants of dipolar substances and the dissociation constants of acids containing a free pole (*e.g.*, the second dissociation constant of dibasic acids). This paper constitutes a preliminary inquiry into the suitability of the second method of attack.

Bjerrum (*Z. physikal. Chem.*, 1923, **106**, 219) has considered the effect of the external field of a free pole on the active mass of the hydrogen ions in the neighbourhood of a dissociating carboxyl group, and, for the case of a symmetrical dibasic acid, he has calculated from Boltzmann's potential energy–concentration relationship that $\log K_1/K_2 - 0{\cdot}6 = 3{\cdot}1 \times 10^{-8}/r$, where K_1 and K_2 are the first and second dissociation constants of the acid, and r is the distance between the ionising groups. This formula gives values of r which are of the correct order of magnitude (a few Ångstrom units for acids of simple constitution), but the theory is obviously far too simple to warrant the expectation of quantitative accuracy, and even for dilute solutions a complete theory would have to take account *inter alia* of the following factors : (1) The effect of the external field of the pole on hydrogen-ion concentration (Bjerrum), (2) the effect of the external field (the " direct " effect, *D*, see Ingold and Vass, this vol., p. 417) of the pole on the hydrogen-ion affinity of the carboxylate ion, (3) the effect of the internally propagated field (" inductive " and " tautomeric " effects, *I* and *T*) of the pole on the hydrogen-ion affinity of the anion, (4) the influence of electrostriction by the pole of kations and the positive ends of dipolar molecules in diminishing the effects of the pole, as specified under (1), (2), and (3). The neglect of factors (2) and (3) will diminish the apparent distance, r, between the carboxyl groups, and the error arising from the second of these causes will be greater the shorter the intervening carbon chain. On the other hand, the neglect of (4) will render r too large, and for a given degree of electrostriction this effect will be independent of the length of the chain.* In short, it is to be expected that when internally propagated polar factors are negligible, the application of the Bjerrum formula will place a series of substances in the correct order, although the calculated distances between their carboxyl groups will not be physically accurate; when, however, internal factors cannot be neglected, this result will be achieved only for series so chosen that the internal effects are closely comparable. Therefore, as a preliminary to the utilisation of Bjerrum's principle for the purpose referred to at the outset, it seemed desirable to endeavour to determine the region of applicability of the method by the examination of a number of homologues, each of which might conceivably constitute the parent of a series suitable for the investigation of valency deflexion. The parent acids which have been examined are those represented by the general formula $CO_2H{\cdot}(CH_2)_n{\cdot}CO_2H$.

It is well known that the dissociation constant of an acid depends upon the method by which it is measured, that is, on the manner in which concentrations and activities enter into the expression from which it is calculated. Thus the "conductivity" dissociation constant of acetic acid at 18° is $1{\cdot}85 \times 10^{-5}$, whilst values above $2{\cdot}0 \times 10^{-5}$ have been obtained electrometrically. This difference becomes of importance in the application of recorded data to the Bjerrum expression; for whereas K_1 has usually been determined by measurements of the conductivity of the acid, K_2 is exceedingly difficult to evaluate in this way, and has more often been determined by such methods as partition or sugar inversion. Which sort of dissociation constant should theoretically be employed is a remote question, but it seemed to us of greater importance that both K_1 and K_2 should be measured by the *same* method, if possible in the same experiment, and we have therefore employed the mixed activity-concentration constants calculated from electrometric measurements made during neutralisation with a strong base. The theory of the method has been given by Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 65) and is represented by the equation

$$\frac{x}{v} = \frac{K_1C([\mathrm{H}^{\cdot}]^2 + 2K_2[\mathrm{H}^{\cdot}]) - ([\mathrm{H}^{\cdot}]^2 - K_w)([\mathrm{H}^{\cdot}]^2 + K_1[\mathrm{H}^{\cdot}] + K_1K_2)}{([\mathrm{H}^{\cdot}]^2 + K_1[\mathrm{H}^{\cdot}] + K_1K_2)([\mathrm{H}^{\cdot}]^2 + N[\mathrm{H}^{\cdot}] - K_w)}$$

where C and v are respectively the initial concentration and volume

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* This follows because in the Bjerrum expression the assumed effective ionic charge e and distance r occur only in the form of the ratio e^2/r.

of the solution of acid, and N and x are respectively the concentration and volume of alkali after addition of which the hydrogen-ion concentration is $[H^{\cdot}]$; K_1 and K_2 are the first and second dissociation constants of the acid, and K_w that of water. The expression assumes that the acid is a weak electrolyte and that the base is completely dissociated; it is therefore not applicable to oxalic acid, which does not obey the laws of weak electrolytes in respect of its first dissociation constant.

For the acids $CO_2H \cdot (CH_2)_n \cdot CO_2H$ from malonic acid to azelaic acid, the values of r calculated from the data recorded in the experimental portion are given in the following table. The bottom line shows the deviations from the straight line $r = 4{\cdot}4 + 1{\cdot}73n$ to which the observed values for all the acids from glutaric to azelaic closely approximate.

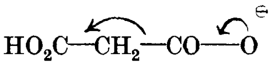
$n =$	1	2	3	4	5	6	7
r (found), Å.U.	1·5	5·0	9·2	11·5	13·2	14·5	16·8
Deviation	−4·6	−2·9	−0·4	+0·2	+0·2	−0·3	+0·3

[The value of r for succinic acid calculated from Auerbach and Smolczyk's electrometric data (*loc. cit.*) is 4·9 Å.U.]

It will be seen that there is no indication of 5-carbon periodicity; this suggests that the polymethylene chain tends to a straight (zigzags) and not a coiled configuration. Further, for these acids the apparent increase in the distance between ionic centres for an increase by one methylene group in the length of the carbon chain is 1·73 Å.U., *i.e.*, it is greater than the distance between the carbon atoms in the diamond (1·52 Å.U.). We are of the opinion that this effect is due largely to the influence of electrostriction which should increase the apparent increment per methylene group by an approximately constant amount throughout the series.

The small deviations shown by the acids from glutaric to azelaic acid may be accounted for as experimental error. Azelaic acid represents the limit of applicability of the method as used by us, partly on account of the sparing solubility of sebacic and the higher acids, and partly because the form of the Bjerrum expression renders the calculated values of r more sensitive to experimental error as the series is ascended. Succinic acid, however, shows a negative deviation which far exceeds experimental error, and malonic acid shows a still larger deviation in the same direction. These we attribute to internally propagated polar effects, which naturally become of greater significance the shorter the chain between the carboxyl groups. In malonic acid, moreover, the effect of inductively propagated electronic strain is probably enhanced by incipient tautomeric disturbances of the type which has been held responsible

(Baker, Cooper, and Ingold, this vol., p. 426) for the characteristic thermal decomposition of malonic acids :



$$HO_2C—CH_2—CO—O^{\ominus}$$

As indicated above, it is proposed to make further studies of this kind along the lines prescribed by the foregoing results.

EXPERIMENTAL.

The dibasic acids were either purchased or prepared by known methods, and in all cases carefully purified by repeated crystallisation before use.

The hydrogen-potential measurements were made with accurately calibrated apparatus kindly lent by Messrs. W. R. Atkin and F. C. Thompson of the Leather Industries Department, whose valuable help throughout this work we gratefully acknowledge.

The hydrogen, derived from a cylinder, was purified by passing successively through alkaline permanganate, alkaline pyrogallol, silver nitrate, lead acetate, alkaline permanganate, alkaline pyrogallol, cotton wool, and distilled water. The pole of the hydrogen electrode was re-platinised before each experiment, the direction of the current being reversed every half-minute. A saturated calomel electrode was employed as the second electrode, the two half-cells being connected, through a vessel containing water saturated with potassium chloride and mercurous chloride, by a bridge of saturated potassium chloride containing 1·5% of agar. The potentials were measured on a bridge wire one scale division of which corresponded to 0·1 millivolt, the potential gradient being checked repeatedly by a standard cadmium cell having 1·0183 volts at 20°. All hydrogen-potential measurements were made at 25°. The alkali used was carbonate-free sodium hydroxide, and the solutions of the acids were made up with air-free distilled water immediately before use. All duplicate determinations agreed very closely.

In view of the fact that there is no universally accepted standard of reference for hydrogen potential measurements, we deemed it desirable to correlate our standards with those used by Walpole (J., 1914, **105**, 2501) in his investigation of acetic acid–sodium acetate solutions. Walpole worked at 18° and adopted the Sörensen standard for the decinormal calomel electrode. Our saturated calomel electrode *A*, which was selected from among several for use throughout these experiments, when used with a half-cell consisting of diluted standard acetate buffer (molecular dilution of free acetic acid, 173 l.) prepared from carefully purified acetic acid, gave a potential of 0·5200 volt at 18° and 0·5223 volt at

25°. For the same diluted standard acetate used in conjunction with a decinormal calomel electrode at 18°, Walpole observed 0·6089 volt. It follows that, according to the standards used by Walpole, our electrode *A* has a potential of 0·2449 volt at 25°, and that this figure includes the difference of potential at the liquid junction, since a correction for this is contained in Walpole's data. The titres recorded in the tables are in c.c. and the *E.M.F.*'s in volts. The remaining data necessary for the application of the Auerbach–Smolczyk equation are recorded in the second, third, and fourth columns of the following table. The calculated values of K_1 and K_2 are in the fifth and sixth columns.

Acid.	Original conc., *M*.	Conc. of NaOH (g. Na/c.c.).	Equivalent titre (c.c.).	$K_1 \times 10^5$.	$K_2 \times 10^6$.
Oxalic	0·05850	0·03671	11·00	—	—
Malonic	0·04991	0·02567	13·42	177	4·37
Succinic	0·04880	0·02567	13·12	7·36	4·50
Glutaric	0·00673	0·002567	18·10	4·60	5·34
Adipic	0·00673	0·002567	18·05	3·90	5·29
Pimelic	0·004835	0·002567	13·00	3·33	4·87
Suberic	0·003295	0·002567	8·86	3·07	4·71
Azelaic	0·0006715	0·0003671	13·00	2·82	4·64

Oxalic Acid.—E.M.F. = 0·3341 at titre 0·00 and 0·8590 at titre 11·06.

Titre	0·00	0·51	0·98	1·70	2·41	2·97	3·37	3·79	4·21
p_H ...	1·510	1·560	1·609	1·692	1·787	1·879	1·961	2·056	2·171
Titre	4·62	5·04	5·40	5·80	6·18	6·60	7·00	7·48	8·00
p_H ...	2·315	2·501	2·712	2·970	3·181	3·373	3·536	3·689	3·849
Titre	8·51	8·99	9·49	9·90	10·10	10·29	10·38	10·47	10·52
p_H ...	4·002	4·149	4·331	4·511	4·614	4·736	4·802	4·881	4·927
Titre	10·57	10·61	10·65	10·70	10·75	10·80	10·84	10·89	10·93
p_H ...	5·014	5·025	5·085	5·156	5·239	5·332	5·444	5·610	5·869
Titre	10·97	11·02	11·06						
p_H ...	6·504	9·376	10·390						

These values lie on a smooth curve having two points of inflexion, but, for the reason given on p. 1596, they cannot be represented by an equation of the Auerbach–Smolczyk type.

Malonic Acid.—E.M.F = 0·3668 at titre 0·00 and 0·8466 at titre 13·49.

Titre	0·00	0·50	0·96	1·97	2·98	4·08	5·03	5·72	6·33
p_H ...	2·064	2·158	2·265	2·499	2·719	2·973	3·2405	3·494	3·816
Titre	6·74	7·14	7·72	8·50	9·50	10·98	12·00	12·52	12·67
p_H ...	4·090	4·377	4·712	4·957	5·229	5·607	5·925	6·146	6·252
Titre	12·82	12·90	12·98	13·06	13·13	13·20	13·26	13·29	13·33
p_H ...	6·352	6·419	6·507	6·597	6·714	6·858	6·967	7·066	7·245
Titre	13·36	13·39	13·43	13·45	13·49				
p_H ...	7·503	7·951	8·675	9·746	10·180				

Succinic Acid.—*E.M.F.* = 0·3980 at titre 0·00 and 0·8970 at titre 13·48.

Titre	p_{H} ...
0·00	2·591
0·52	3·035
1·02	3·336
1·56	3·617
2·00	3·751
2·55	3·899
3·54	4·120
4·53	4·339
5·20	4·472
6·00	4·629
6·80	4·789
7·63	4·947
8·56	5·139
10·04	5·447
11·52	5·837
13·00	7·165
13·10	8·513
13·20	10·364
13·48	11·034

Glutaric Acid.—*E.M.F.* = 0·4365 at titre 0·00 and 0·7930 at titre 18·14.

Titre	p_{H} ...
0·00	3·240
0·30	3·340
0·70	3·472
1·13	3·593
1·59	3·709
2·23	3·858
2·81	3·972
3·40	4·074
3·99	4·164
4·62	4·257
5·21	4·342
5·80	4·419
6·49	4·505
7·17	4·587
7·91	4·676
8·70	4·768
9·38	4·853
10·09	4·937
10·78	5·021
11·52	5·112
12·21	5·202
12·90	5·293
13·60	5·389
14·30	5·499
15·00	5·616
15·69	5·753
16·44	5·946
16·92	6·122
17·27	6·297
17·52	6·468
17·76	6·729
17·91	7·000
17·95	7·144
18·00	7·361
18·05	7·749
18·10	8·809
18·14	9·274

Adipic Acid.—*E.M.F.* = 0·4390 at titre 0·00 and 0·8030 at titre 18·16.

Titre	p_{H} ...
0·00	3·285
0·21	3·372
0·55	3·469
0·90	3·598
1·26	3·700
1·61	3·795
1·99	3·880
2·45	3·976
2·98	4·071
3·62	4·175
3·99	4·237
4·60	4·318
5·18	4·399
5·70	4·464
6·30	4·536
6·89	4·602
7·58	4·687
8·16	4·751
8·80	4·823
9·79	4·932
10·64	5·029
11·38	5·115
12·25	5·214
12·98	5·309
13·96	5·447
15·00	5·618
15·56	5·726
16·22	5·887
16·76	6·066
17·29	6·303
17·70	6·642
17·89	6·963
17·94	7·081
17·99	7·293
18·03	7·579
18·08	8·590
18·12	9·105
18·16	9·445

Pimelic Acid.—*E.M.F.* = 0·4464 at titre 0·00 and 0·7910 at titre 13·06.

Titre	p_{H} ...
0·00	3·408
0·31	3·536
0·68	3·686
1·18	3·858
1·69	4·016
2·25	4·156
2·89	4·298
3·42	4·404
4·12	4·526
4·81	4·638
5·50	4·750
6·21	4·858
6·93	4·963
7·60	5·070
8·30	5·178
9·02	5·301
9·70	5·422
10·39	5·566
10·98	5·713
11·61	5·902
12·15	6·146
12·60	6·483
12·79	6·754
12·92	7·208
12·97	7·530
13·02	8·453
13·06	9·240

Suberic Acid.—*E.M.F.* = 0·4519 at titre 0·00 and 0·7805 at titre 8·91.

Titre	p_{H} ...
0·00	3·500
0·30	3·763
0·60	3·844
0·96	4·005
1·49	4·192
2·01	4·354
2·53	4·491
3·00	4·609
3·52	4·729
3·99	4·837
4·59	4·970
5·20	5·107
5·78	5·240
6·42	5·403
7·02	5·572
7·60	5·785
7·97	5·961
8·33	6·218
8·59	6·514
8·76	6·999
8·81	7·243
8·86	7·834
8·91	9·061

Azelaic Acid.—*E.M.F.* = 0·4765 at titre 0·00 and 0·7710 at titre 13·20.

Titre	0·00	0·28	0·58	0·99	1·50	1·96	2·48	3·01	3·50
p_H ...	3·920	3·979	4·030	4·120	4·221	4·307	4·399	4·484	4·567
Titre	3·97	4·50	4·98	5·55	5·98	6·50	7·09	7·52	8·25
p_H ...	4·638	4·721	4·797	4·873	4·941	5·019	5·103	5·174	5·283
Titre	8·90	9·62	10·30	10·83	11·23	11·64	12·00	12·35	12·71
p_H ...	5·394	5·519	5·655	5·782	5·900	6·053	6·206	6·418	6·763
Titre	12·91	13·01	13·10	13·20					
p_H ...	7·225	7·987	8·599	8·903					

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