

**18.** *The Extent of Dissociation of Salts in Water. Part IX.  
Calcium and Barium Salts of Dicarboxylic Acids.*

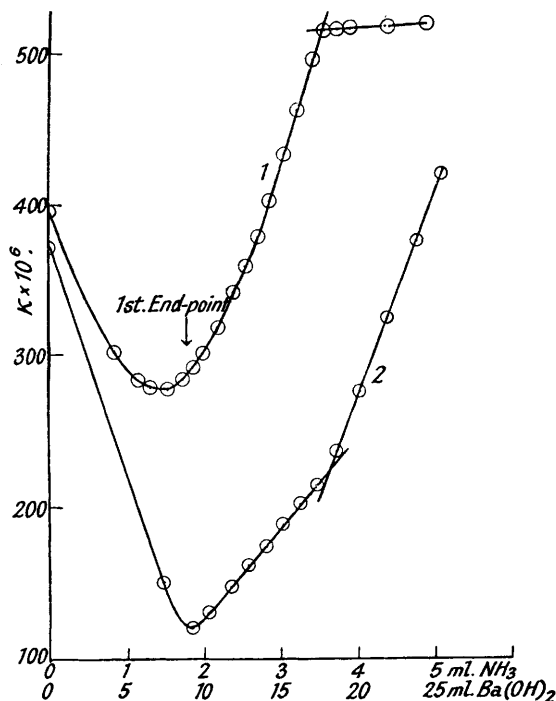
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The dissociation constants of the calcium and barium salts of eight dicarboxylic acids have been determined by conductivity measurements in water at 25°. A wide diversity of behaviour is shown; in 0.001M-solution, for instance, barium succinate and *isophthalate* are almost completely dissociated, whereas the weakest salt, calcium tartrate, is only 75% dissociated. The barium salts are all stronger than the corresponding calcium salts. If the salts of the above cations are arranged in order of decreasing dissociation constant, the disposition of the anions is not the same in the two series, showing that the order is not governed solely by the diameter of the anion. The *o*-phthalates are very much weaker than the *isophthalates*, and the maleates than the fumarates. The hydroxy-acids malic and tartaric give salts far weaker than the succinates. It is noteworthy that the ratio of the mobility of the intermediate ion HA' to that of the bivalent ion A'' is high for all those acids with weak calcium and barium salts.

PREVIOUS investigations have shown that ionic association is extensive in aqueous solutions of bi-bivalent salts. Dissociation constants of the order  $K = 5 \times 10^{-3}$  have been derived

for metal sulphates and selenates (Davies, *Trans. Faraday Soc.*, 1927, **23**, 354; Money and Davies, *ibid.*, 1932, **28**, 609; Banks, J., 1934, 1010; Owen and Gurry, *J. Amer. Chem. Soc.*, 1938, **60**, 3074), and the oxalates and malonates of several bivalent metals have been found to be very much weaker (Ives and Riley, J., 1931, 1998; Money and Davies, *loc. cit.*; Clayton and Vosburgh, *J. Amer. Chem. Soc.*, 1937, **59**, 2414). The object of the present work was to extend the investigation to salts of other organic acids, and, to cover as much ground as possible in a limited time, measurements were made by the conductimetric technique described in the preceding paper. For each acid the mobility of the anion was first obtained by a titration with ammonia, and the strengths of the calcium and barium salts were then estimated by titrating the acid with standard calcium and barium hydroxide solutions.

"AnalaR" Tartaric and maleic acids and Kahlbaum's purest malic acid were used



Curve 1: Titration of 0.004137N-fumaric acid with ammonia.

Curve 2: Titration of 0.002148N-maleic acid with barium hydroxide.

without further purification; the other acids were recrystallised several times from conductivity water. All were dried in a vacuum at appropriate temperatures. The standard solutions of base were prepared with rigorous precautions against contamination by carbon dioxide, the baryta from "AnalaR" barium hydroxide, the calcium hydroxide from freshly precipitated calcium carbonate heated for 8 hours at 1000°, and the ammonia from a sample freshly distilled from alkali into conductivity water. The conductivity water used throughout had a specific conductivity of 0.2—0.8 gemmho.

Measurements were made in a thermostat maintained at 25°. The conductivity apparatus was similar to that previously described (Righellato and Davies, *Trans. Faraday Soc.*, 1933, **29**, 429). The hard-glass cell was standardised several times during the course of the work by means of Jones and Bradshaw's 0.01M-potassium chloride solution (*J. Amer. Chem. Soc.*, 1933, **55**, 1780). During titrations the standard solution of base was added from a calibrated burette or micro-burette connected to a reservoir, while pure air passed through the cell. All conductivities were corrected for dilution (Righellato and Davies, *loc. cit.*).

Curve 1 of the figure illustrates a typical ammonia titration. Apart from a very slight rounding off at the end-point, the titration diagram in the neighbourhood of complete neutralisation consists of two straight lines, the intersection of which gives the experimental end-point. This does not coincide exactly with the theoretical end-point, and as a check on our interpretation of the data a number of "theoretical" titration diagrams were constructed. In the neutralisation of an acid  $H_2A$  the following solute species are present:  $H^+$ ,  $NH_3$ ,  $NH_4^+$ ,  $OH^-$ ,  $HA'$ ,  $A''$ ,  $HCO_3^-$ ,  $H_2A$  and  $H_2CO_3$ , and, from the mass-action equations and the condition of electrical neutrality, the concentration of each can be calculated for any given stage of neutralisation, the last two being neglected in the first approximation (Topp, Thesis, London, 1937); from known or approximate mobilities the conductivity diagram can then be constructed. Diagrams for acids of various strengths show, as might be expected, that at the experimental end-point the carbon dioxide present in the solution is practically completely converted into ammonium hydrogen carbonate; and that the rounding off at the end-point, and the discrepancy between experimental and theoretical end-point, are the more important the lower the second dissociation constant of the acid investigated.

These theoretical diagrams were used in correcting the end-point conductivities of our actual titrations. In most cases the true specific conductivity of the ammonium salt could be obtained by deducting from the end-point conductivity the ammonium hydrogen carbonate equivalent of the carbon dioxide originally present in the solvent; this corrected value, when divided by the known concentration in equivalents per c.c., gave the equivalent conductivity of the salt. In a few runs the initial concentration of the acid was not measured, and in these cases the *uncorrected* conductivity was divided by the apparent concentration as given by the end-point of the titration; the justification for this is that the carbon dioxide neutralised in the titration increases both the conductivity and the apparent acid concentration. With the weakest acids studied a further small correction was necessary for "hydrolysis", *i.e.*, for the incomplete reaction between acid and base. From our theoretical diagrams we estimate that the maximum error that could arise from the approximations made was 0.7 unit in the equivalent conductivity.

Curve 2 of the figure shows a typical titration with calcium or barium hydroxide. In these runs corrections for carbon dioxide and for hydrolysis were estimated in a similar way to that just described. The possible errors involved in the corrections are smaller than in the titrations with ammonia, but the error in reading the end-point conductivity is greater, and the uncertainty in the equivalent conductivities reported is about the same.

*The Mobilities of the Bivalent Anions.*—In the calculation of mobilities, the equivalent conductivities found for the ammonium salts must be converted into their infinite dilution values. Many of the runs were at concentrations somewhat beyond the range in which Onsager's equation can be expected to hold, and we therefore used an equation containing an additional term:  $\Lambda_0 = \Lambda + b\sqrt{C} - 175C$ , where  $C$  is the equivalent concentration and  $b$  is the Onsager slope. The third term on the right-hand side is empirical, but as its contribution does not exceed 0.8 unit in any of our runs, and as the equation fits Shedlovsky and Brown's data for the alkaline-earth chlorides (*J. Amer. Chem. Soc.*, 1934, 56, 1066) up to  $C = 0.005$  with a maximum deviation of 0.2 unit, it is undoubtedly sufficiently accurate for our purpose. Subtraction of 73.5, the mobility of the ammonium ion (Longworth, *ibid.*, 1935, 57, 1185) from  $\Lambda_0$  for the ammonium salt then gave the mobility of the anion. The results are in Table I, in which col. 1 gives the equivalent concentration, col. 2 the corrected equivalent conductivity, and col. 3 the mobility of the anion. The accuracy of the results is not great, for reasons already given, and in calculating dissociation constants it has been assumed that the error in the mobility value may amount to one unit. The value for the adipate ion agrees well with Jeffery and Vogel's value (*J.*, 1935, 21), but their value for the succinate is much higher than ours.

*The Mobilities of the Intermediate Acid Anions.*—From the titration diagram it was possible to read off the conductivity of the half-neutralised solution and hence to calculate, by the method described in a previous paper (*J.*, 1939, 1850), the mobility of the intermediate ion; no solvent correction was made since the solution was acid. The values used for the dissociation constants of the acids are in Table II, and the results of the calculations are

in Table III, where col. 1 shows the equivalent concentration, col. 2 the total specific conductivity, col. 3 the corrected conductivity of the ammonium acid salt, and col. 4 the mobility.

TABLE I.

$C \times 10^3$ .	$\Lambda$ .	$l_0A''$ .	$C \times 10^3$ .	$\Lambda$ .	$l_0A''$ .	$C \times 10^3$ .	$\Lambda$ .	$l_0A''$ .
Ammonium succinate.			Ammonium adipate.			Ammonium fumarate.		
1.189	124.2	56.6	1.336	119.8	52.4	1.702	128.4	61.9
1.548	124.7	57.9	2.031	117.8	51.7	1.733	127.4	61.0
2.730	122.6	57.8	2.293	119.2	53.6	1.872	129.2	63.0
4.989	118.6	56.7			Mean 52.6	2.045	127.2	61.4
	Mean 57.3					4.137	124.6	61.9
			Ammonium tartrate.					Mean 61.8
Ammonium maleate.			2.035	125.6	59.7	Ammonium malate.		
1.851	128.4	62.4	2.043	125.5	59.7	2.286	124.4	58.9
3.395	125.7	62.1	2.786	123.9	59.2	3.023	123.1	58.8
3.606	125.1	61.8	3.041	125.1	60.8	3.121	123.1	58.9
3.739	125.3	62.1	3.427	122.4	58.6	3.974	121.8	58.7
4.160	124.3	61.7			Mean 59.6	4.499	121.1	58.6
4.364	124.0	61.6				4.602	121.0	58.7
	Mean 61.9		Ammonium isophthalate.					Mean 58.8
Ammonium o-phthalate.			1.766	120.9	54.4			
1.863	119.6	53.2	1.864	120.8	54.5			
3.004	116.8	52.2	2.601	120.3	55.3			
3.638	115.3	51.6			Mean 54.7			
6.178	113.3	52.3						
	Mean 52.3							

TABLE II.

Acid.	$K_1$ .	$K_2$ .	Reference.
Succinic .....	$6.4 \times 10^{-5}$	$3.3 \times 10^{-8}$	Gane and Ingold, J., 1931, 2153.
Adipic .....	$3.8 \times 10^{-5}$	$3.9 \times 10^{-8}$	
Fumaric .....	$9.6 \times 10^{-4}$	$4.1 \times 10^{-5}$	German, Jeffery, and Vogel, <i>Phil. Mag.</i> , 1936, 22, 790.
Maleic .....	$1.2 \times 10^{-2}$	$6.0 \times 10^{-7}$	
Tartaric .....	$3.0 \times 10^{-3}$	$6.9 \times 10^{-5}$	Clark, "Hydrogen Ions," 3rd Edn., p. 678.
Malic .....	$3.5 \times 10^{-4}$	$9.0 \times 10^{-8}$	
o-Phthalic .....	$7.9 \times 10^{-4}$	$4.0 \times 10^{-8}$	Maxwell and Partington, <i>Trans. Faraday Soc.</i> , 1935, 31, 922.
isoPhthalic .....	$2.0 \times 10^{-4}$	$2.2 \times 10^{-5}$	

TABLE III.

$C \times 10^4$ .	$\kappa \times 10^6$ .	$\kappa \times 10^6$ ( $\text{NH}_4\text{HA}$ ).	$l_0\text{HA}'$ .	$C \times 10^4$ .	$\kappa \times 10^6$ .	$\kappa \times 10^6$ ( $\text{NH}_4\text{HA}$ ).	$l_0\text{HA}'$ .
Ammonium hydrogen succinate.				Ammonium hydrogen adipate.			
5.95	70.5	41.2	30.8	6.71	78.0	40.6	29.3
7.73	90.0	53.9	29.9	10.19	114.0	61.5	27.7
13.68	157.0	99.7	34.7	11.51	129.0	72.5	29.7
			Mean 31.8				Mean 28.9
Ammonium hydrogen fumarate.				Ammonium hydrogen maleate.			
8.51	142.5	54.8	29.3	9.23	115.0	103.0	43.5
8.67	144.3	56.0	29.6	16.97	220.5	185.0	41.8
9.36	154.3	65.1	31.1	18.03	202.0	202.8	45.0
10.22	163.5	70.0	29.7	18.67	228.0	203.1	44.8
20.69	288.0	147.6	32.1	21.79	267.0	248.1	46.6
			Mean 30.4				Mean 44.3
Ammonium hydrogen tartrate.				Ammonium hydrogen malate.			
10.24	166.5	85.9	45.9	11.43	140.0	115.3	41.0
13.93	213.7	119.3	45.4	15.12	184.5	147.1	41.2
15.20	231.0	129.3	47.2	15.61	186.0	145.5	38.0
17.14	249.5	143.6	43.0	19.87	233.0	181.3	38.3
			Mean 45.4	22.50	259.0	199.7	37.5
				23.01	266.0	207.4	37.8
							Mean 39.0
Ammonium hydrogen o-phthalate.							
8.22	105.7	84.6	40.0				
9.31	117.0	99.2	37.1				
18.19	209.7	184.2	35.0				
			Mean 37.4				

Measurements were not made with *isophthalic acid*, which dissolved extremely slowly during the early stages of the titration. It will be seen that the discrepancies between individual runs are large. In one or two cases (*e.g.*, ammonium hydrogen malate) there is a definite trend in the mobility with increase of concentration, and here the error may be mainly due to errors in the acid dissociation constants. In the other cases only random variations occur and are probably due to normal experimental error; the conductivity at the first end-point cannot be read with accuracy on account of the marked curvature in this region, and an error of  $1 \times 10^{-6}$  in the total specific conductivity could cause an error of as much as 2.5 units in the mobility.

A striking result of the calculations is the consistently high mobilities found for the intermediate ions of tartaric, malic, maleic, and *o*-phthalic acids, those acids which show very low dissociation constants for their calcium and barium salts (see later); the hydrogen maleate has a far higher mobility than the isomeric hydrogen fumarate, the tartrate and malate than the succinate; and the hydrogen *o*-phthalate, though its actual value may be doubtful, has almost certainly a higher mobility than the benzoate ion ( $l_0 = 32.3$ ). We incline to the view that it is the simple carboxylate ions of low mobility, in the present comparison the hydrogen succinate, adipate, and fumarate ions, that should be considered abnormal. The anomaly might be due to a special facility with which the carboxylate group undergoes hydration; the consequent restriction on the migration of the ion may be reduced or removed when the co-ordination of the carboxylate group with adjacent hydroxylic, carboxylic, or other groups becomes possible.

The mobilities are collected in Table IV, the last column of which shows the ratio of the mobility of the intermediate ion to that of the bivalent ion. According to Chandler's rule (*J. Amer. Chem. Soc.*, 1908, **30**, 694; see J., 1939, 1850),  $l_0\text{HA}' = 0.6l_0\text{A}''$ .

TABLE IV.

Acid.	$l_0\text{A}''$ .	$l_0\text{HA}'$ .	$l_0\text{HA}'/l_0\text{A}''$ .	Acid.	$l_0\text{A}''$ .	$l_0\text{HA}'$ .	$l_0\text{HA}'/l_0\text{A}''$ .
Succinic .....	57.4	31.9	0.56	Tartaric .....	59.7	45.5	0.75
Adipic .....	52.7	29.0	0.55	Malic .....	58.9	39.1	0.66
Fumaric .....	61.9	30.5	0.49	<i>o</i> -Phthalic ...	52.4	37.5	0.72
Maleic .....	62.0	44.4	0.72	<i>iso</i> Phthalic ...	54.8	—	—

*Dissociation Constants of the Calcium and Barium Salts.*—The data are in Table V. Most of the runs were at concentrations somewhat beyond the range in which the limiting equations of Debye and Hückel and Onsager can be expected to hold good. In calculating dissociation constants, therefore, empirical extensions of these equations were used. The mean ionic activity coefficient was calculated from the equation previously proposed (J., 1938, 2093), which here takes the form:  $f_{\pm} = -4\sqrt{\alpha m}/(1 + 2\sqrt{\alpha m}) + 0.20(4\alpha m)$ , where  $m$  is the molar concentration and  $\alpha$  the degree of dissociation. The sum of the mobilities of cation and anion was calculated from the equation  $\Lambda_x = \Lambda_0 - b\sqrt{2\alpha m} + 800(2\alpha m)$ , where  $\Lambda_0$  was obtained from the mobilities of Table IV and the values of Shedlovsky and Brown (*loc. cit.*) for calcium and barium, and where  $b$  is the Onsager slope. The third term of the equation was obtained as follows. Closely concordant dissociation constants have been obtained for zinc and cadmium sulphates by two independent methods: from the conductivities of highly dilute solutions and from activity measurements (J., 1938, 2093). The activity measurements extend into concentrations far greater than those at which Onsager's equation is valid, and enable degrees of dissociation, and hence values of  $\Lambda_x$ , to be determined at these concentrations. Up to  $C = 0.005$  these values are fitted well by the equation just given, and its application to other bi-valent salts is unlikely to introduce errors as great as the experimental error of our results. Col. 3 of the table gives the degree of dissociation, calculated in the usual way from the relation  $\alpha = \Lambda/\Lambda_x$ , and the dissociation constants in the fourth column were obtained by means of the equation  $K = f_{\pm}^2\alpha^2m/(1 - \alpha)$ .

One or two of the stronger salts, *e.g.*, barium *isophthalate*, are almost completely dissociated in the range of concentration studied, and not much quantitative significance can be attached to the dissociation constants quoted for them. There can be no doubt, however, of the relative correctness of the values given.



For every acid studied the barium salt is stronger than the calcium salt. This is also true of the oxalates (Money and Davies, *loc. cit.*), the mandelates (J., 1938, 271), and the hydroxides (J., 1939, 349); the nitrates, iodates, and possibly sulphates, where earlier results had shown the calcium salt to be the stronger, now appear exceptional.

The barium salts show dissociation constants decreasing in the following order: *iso*-phthalic, succinic, fumaric > adipic > malic > maleic > *o*-phthalic > tartaric. For the calcium salts the order, though similar, is not identical, the malate now being weaker than either maleate or *o*-phthalate. This contradicts, at any rate for the weaker salts, the hypothesis that the dissociation constants are a simple function of two independent factors, the size of the cation and of the anion. Some conductivity data of Walden (*Z. physikal. Chem.*, 1887, 1, 529) for magnesium salts are of interest in this connection. These, while not lending themselves to quantitative treatment, indicate that the tartrate and maleate are appreciably stronger than the malate, so that the position seems to be as shown below, where the strongest salt is at the top of the column:

Mg.	Ca.	Ba.
Maleate	Maleate	Malate
Tartrate	Malate	Maleate
Malate	Tartrate	Tartrate

The presence of hydroxyl groups is clearly shown to be a factor reducing the dissociation constant, both for calcium and barium salts. A similar effect of  $\alpha$ -hydroxyl groups has already been found for the calcium salts of monocarboxylic acids (J., 1938, 277). Another point confirmed by the data is the anticipated steric effect in the phthalates, and in the fumarates and maleates; to what extent, in these and other cases, the undissociated molecule or ion-pair should be assigned a dipolar formulation,  $M^+CO_2 \cdot R \cdot CO_2^-$ , is an interesting question which our measurements alone cannot answer.

One other noteworthy fact is the relative weakness of the adipates when compared with the succinates. When the field opened by this preliminary investigation has been more extensively studied, we believe that this and other similar comparisons may prove a fruitful source of information concerning both the structure of organic acids and the nature of the undissociated part of dissolved salts.

Recently Cannan and Kibrick (*J. Amer. Chem. Soc.*, 1938, 60, 2314) have published mass-action constants for a considerable number of bivalent metal salts of carboxylic acids. These are not directly comparable with ours, since they refer to ionic strengths of approximately 0.2, but in a general way the two series of measurements are in agreement. Cannan and Kibrick find that the barium salt is invariably stronger than the calcium salt, and for these two cations both series of measurements lead to dissociation constants decreasing in the order succinate > malate > tartrate. Their results also confirm the reversal of order we have noted with magnesium salts, where the tartrate has a higher constant than the malate.