18. *The Dissociation Constant of Mandelic Acid in Water.*

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Conductivity measurements on aqueous solutions of sodium mandelate and mandelic acid at 24·915° lead to the value $K = 3{\cdot}88 \times 10^{-4}$ for the true dissociation constant of mandelic acid. The measurements on sodium mandelate were taken to fairly high concentrations, and show it to be a normal completely dissociated salt. Preliminary measurements on barium mandelate, however, yield low conductivities, and it is suggested that the solutions contain appreciable concentrations of the intermediate ion, $C_6H_5\cdot CH(OH)\cdot CO\cdot OBa^{\bullet}$, for which a dissociation constant $K = 0{\cdot}17$ is derived. Some measurements of the adsorption of mandelic acid on a surface of paraffin wax are also described, and it is shown that conductivity measurements afford a sensitive method of studying adsorption at high dilutions.

THE measurements recorded in this paper were undertaken in 1930 with the primary object of testing the Debye–Hückel limiting activity equation, and their agreement with the requirements of this equation was reported in a preliminary note (*J. Amer. Chem. Soc.*, 1932, **54**, 1698). Since then, many investigations of a similar type (MacInnes and Shedlovsky, *ibid.*, p. 1429; Saxton and Langer, *ibid.*, 1933, **55**, 3638; Brockman and Kilpatrick, *ibid.*, 1934, **56**, 1483) have established the accuracy of the Debye–Hückel formula, so it is now unnecessary to stress this aspect of the work. In recording our results we have recalculated them to the basis of the new Jones and Bradshaw standard (*ibid.*, 1933, **55**, 1780).

The conductivity of the acid was measured in a cell of the Hartley and Barrett type. The cylindrical body of this was of transparent silica, but the cap and electrode leads were of borosilicate glass, and these were thinly coated with paraffin wax to avoid contact of the dilute acid solutions with a glass surface. Separate measurements of the adsorption of mandelic acid on paraffin wax enabled the necessary corrections to be calculated for the acid adsorbed on the leads of the cell.

EXPERIMENTAL.

Materials.—The inactive mandelic acid was obtained from a commercial product by three recrystallisations from warm ether. Titration against standard baryta showed it to be 99·9 ± 0·1% pure acid. The lævorotatory acid was a pure specimen kindly placed at our disposal by Dr. J. Kenyon, F.R.S. Some difficulty was experienced in obtaining pure sodium mandelate. Its aqueous solubility is very high, and crystallisation from aqueous alcohol gives a product containing acid salt. A pure neutral product was obtained by mixing equivalent quantities of sodium hydroxide and mandelic acid in absolute alcohol and recrystallising from the same solvent. Barium mandelate was prepared from the pure acid and a slight excess of barium carbonate. After filtering and concentrating the solution, the salt was obtained as fine crystals of the hemihydrate (cf. MacKenzie, J., 1899, **75**, 964). The stability of these was not investigated; they were dried on filter-paper and used at once. The salt was analysed by the precipitation of barium sulphate [Found: Ba, 30·8. Calc. for $Ba(C_8H_7O_3)_2,\frac{1}{2}H_2O$: Ba, 30·6%].

Conductivity water was obtained from a still of the type described by Bourdillon (J., 1913, **103**, 791) and modified by Bengough, Stuart, and Lee (J., 1927, 2156). Owing to an error in the standard thermometer, which was not discovered until the measurements had been begun, the oil thermostat was maintained at 24·915 ± 0·005°.

Conductivity Measurements on the Dilute Solutions.—The apparatus was that described in an earlier paper (J., 1937, 432), and the technique employed was similar except that all measurements were made at a frequency of 1000 cycles; small corrections for polarisation were applied where necessary on the basis of the work just quoted, it being assumed (as sufficiently accurate for the purpose of these corrections) that the polarisation for a given cell is a function of the resistance only. The cell constant was determined by measurements on a number of dilute potassium chloride solutions at 17·915° and at 18·00°, the equation of the paper just cited and the temperature coefficients of Déguisne (see Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," p. 199) being used; 17 determinations gave the mean value 0·047718, on the Jones and Bradshaw standard, with an average deviation of 0·02%.

Sodium mandelate solutions. Three series of measurements were made at 24·915°, and the results are in Table I. Col. 1 shows the concentration in g.-mol./l., calculated on a molecular weight of 174·056; the specific conductivity of the solvent water is given in col. 2, and that of the solution in col. 3.

Mandelic acid solutions. One run, which gave very discordant results, has been rejected. Of the remainder, recorded in Table II, the first two were on the inactive, and the third on the *l*-acid; for these runs the electrode leads were waxed, the area of wax being **44** sq. cm. The fourth run, on the inactive acid, was designed as a check on the adsorption corrections, and for this the whole interior of the cell was waxed, giving a total wax surface of **355** sq. cm. Col. 1 of the table shows the initial concentration of acid, col. 2 the true concentration after

TABLE I.

$C \times 10^4$.	$\kappa_{soln.} \times 10^6$.	Λ_1.	Λ_2.	$C \times 10^4$.	$\kappa_{soln.} \times 10^6$.	Λ_1.	Λ_2.	$C \times 10^4$.	$\kappa_{soln.} \times 10^6$.	Λ_1.	Λ_2.
Run 1; $\kappa_{H_2O} = 0{\cdot}787 \times 10^{-6}$.				Run 2; $\kappa_{H_2O} = 0{\cdot}671 \times 10^{-6}$.				Run 3; $\kappa_{H_2O} = 0{\cdot}437 \times 10^{-6}$.			
1·0091	8·652	77·95	78·80	1·0477	8·894	78·47	79·21	2·7385	21·757	77·85	78·20
2·2773	18·497	77·76	78·41	3·7467	29·774	77·68	78·13	5·2376	40·955	77·36	77·61
3·2195	25·785	77·65	78·25	5·7152	44·774	77·17	77·55	8·7830	67·946	76·86	77·06
4·4194	35·029	77·48	78·00	7·7594	60·397	76·97	77·30	10·931	84·116	76·55	76·72
5·4816	43·120	77·23	77·69	8·7246	67·692	76·82	77·15				
7·5202	58·618	76·90	77·30	10·941	84·443	76·56	76·85				

allowance had been made for adsorption. These corrections were obtained by interpolation from a curve, based on the data given in the next section, in which the amount of acid adsorbed per sq. cm. of wax surface was plotted against the equilibrium concentration of the solution. The corrections are very important for the fourth run, and the good agreement between this and the others shows that adequate allowance has been made for adsorption. Col. 3 gives the equivalent conductivity, calculated from the specific conductivity of the solution (without solvent correction) and the true concentrations of col. 2.

TABLE II.

$C' \times 10^4$.	$C \times 10^4$.	Λ.
Run 1. Inactive acid.		
13·198	13·190	158·65
22·949	22·938	128·91
62·309	62·307	85·44
Run 2. Inactive acid.		
7·3821	7·3770	193·50
14·014	14·006	155·36
21·464	21·454	132·39
29·058	29·045	117·44
41·418	41·414	101·50
Run 3. Active acid.		
5·7064	5·7023	210·35
11·764	11·757	165·70
18·574	18·565	140·19
26·122	26·110	122·72
34·339	34·329	109·95
Run 4. Inactive acid. Waxed cell.		
1·1253	1·1149	306·69
2·2820	2·2647	268·29
3·6947	3·6703	239·09

Adsorption Measurements.—For the adsorption measurements a roll of paper was drawn through hot paraffin wax and rolled loosely round a glass rod, to which one end of the roll was secured. With one end of the glass rod held by a rubber bung, the roll hung loosely coiled inside a waxed cylinder, the total area of waxed surface being 1950 sq. cm. Between experiments, the cylinder and coil were soaked in dilute sodium hydroxide, washed with much water, conductivity water being used for the final washing, and dried, after removal of adhering droplets with filter-paper, with pure air. An acid solution was then made up in the conductivity cell in the usual way, and after its conductivity had been determined, a fixed volume (260 ml.) was transferred to the adsorption vessel and this was allowed to remain in the thermostat with gentle agitation for 2 hours, the conductivity of the solution then being redetermined. The results are in Table III, where C is the original concentration and κ_A the original specific conductivity; κ_B is the specific conductivity after adsorption, and C_e the corresponding concentration of the solution, which was read off from a large-scale curve connecting κ_A and C. From these results the amount of acid adsorbed was calculated and is shown in col. 5 of the table as the number of g.-mols. adsorbed per sq. cm.

TABLE III.

$C \times 10^4$.	$\kappa_A \times 10^4$.	$\kappa_B \times 10^4$.	$C_e \times 10^4$.	$\Gamma \times 10^9$.	$\Gamma_{calc.} \times 10^9$.
0·7142	0·2304	0·2212	0·6720	0·563	0·552
1·800	0·4867	0·4683	1·721	1·06	1·08
2·685	0·6926	0·6704	2·590	1·27	1·35
3·440	0·8317	0·8085	3·314	1·68	1·54
4·116	0·9233	0·9095	3·913	1·71	1·65
5·522	1·1721	1·1518	5·387	1·80	1·85

Conductivity Measurements on More Concentrated Solutions.—For these, a pipette cell of the Washburn type was used, and the cell constant was determined by means of Parker and Parker's 0·01*D*-potassium chloride solution. Corrected to the Jones and Bradshaw standard, the mean of three determinations was 2·0794. The salt solutions were all made up separately by weight, and their concentrations were calculated from the densities given below, which were determined in a small pycnometer; m is here the concentration in g.-mol./l. At higher concentrations of sodium mandelate the measurements given in International Critical Tables, Vol. III, p. 84, were available.

Densities of mandelate solutions at 24·915°.

Sodium mandelate.				Barium mandelate.			
m	0·0136	0·0236	0·0382	m	0·0215	0·0309	0·0534
d	0·9880	0·9987	0·9998	d	1·0025	1·0046	1·0104

The conductivity measurements are in Table IV, where col. 1 gives the concentrations in g.-equiv./l., and col. 2 the equivalent conductivities; in calculating these, a solvent correction of 1×10^{-6} r.o. has been deducted.

TABLE IV.

(*a*) Sodium mandelate at 24·915°.						(*b*) Barium mandelate at 24·915°.				
C.	Λ.	Λ, calc.	C.	Λ.	Λ, calc.	C.	Λ.	Λ, calc.	$(1 - \alpha)$.	K.
0·009776	72·35	72·35	0·02422	69·32	69·00	0·04302	64·83	68·93	0·100	0·176
0·01465	70·98	70·95	0·04676	66·13	66·09	0·06176	61·06	66·36	0·132	0·173
0·01932	70·00	69·94	0·09337	62·05	62·17	0·10685	54·74	61·85	0·196	0·175

DISCUSSION OF RESULTS.

Adsorption Measurements.—The experiments show that mandelic acid is very readily adsorbed on a paraffin-wax surface. The results can be expressed fairly well by the equation $1/\Gamma = 0{\cdot}359 \times 10^9 + 1{\cdot}03 \times 10^5 \times 1/C_e$; values calculated from this formula are shown in the last column of Table III. From Langmuir's derivation of this equation, the reciprocal of the limiting value $0{\cdot}359 \times 10^9$, *i.e.*, $2{\cdot}78 \times 10^{-9}$, should represent the number of g.-mols. of acid per cm.^{2} necessary to form a complete unimolecular layer, and it will be seen from the table that if this is approximately true, adsorption has already reached one-half of this saturation value at a concentration of 0·0003N. The wax surface was by no means smooth, and if n represents the factor by which the measured surface must be multiplied to give the actual surface, then the area occupied by one molecule of acid in the complete unimolecular layer is $n/2{\cdot}78 \times 10^{-9} \times 6{\cdot}06 \times 10^{23} = 5{\cdot}9 \times 10^{-16} \times n$ cm.^{2}, a reasonable value.

With a slightly more elaborate technique the accuracy of the measurements could readily have been increased, and we believe that interesting results would be obtained by applying the method to study the adsorption of electrolytes on various crystalline or other surfaces of limited area.

Conductivity Measurements.—The measurements on very dilute sodium mandelate solutions were undertaken to provide a value for the mobility of the mandelate ion, and they were also designed to test the combined solvent and hydrolysis correction put forward and used in previous papers (*Trans. Faraday Soc.*, 1932, **28**, 607; *Nature*, 1933, **131**, 328). The idea underlying this correction is that when the salt of a weak acid is dissolved in any but the purest water, the main interaction in dilute solutions is that expressed by the equation $A' + H_2CO_3 \rightleftharpoons HA + HCO'_3$, resulting in an increase in the concentration of bicarbonate ion, and consequently, a decrease in the concentration of hydrogen ion and a decrease in the correction to be deducted from the conductivity of the solution. There is no difficulty in calculating the concentrations of the various ionic and molecular species and so obtaining this correction with ample accuracy; but the method involves the assumption that carbonic acid is the only impurity present in appreciable amounts. The simplest way to test this assumption was to carry out measurements on a single salt in samples of water of appreciable, and widely differing, conductivities. The results for sodium mandelate are given in Table I and in the figure: Λ_1 is the equivalent conductivity calculated from the "normal" solvent correction, *i.e.*, after subtracting the conductivity of the solvent from that of the solution; Λ_2 is the equivalent conductivity obtained by applying the combined solvent and hydrolysis correction on the assumption that the conductivity of the solvent is wholly due to carbon dioxide. In the figure, the Λ_1 values form the lower series of points, the Λ_2 the upper series, and it is clear that the Λ_2 values are slightly over-corrected, since the triangulated points of Run 1 have become the highest, instead of being the lowest, values, and the average slope is slightly greater, instead of being less, than the theoretical Onsager slope. For this reason we think that the continuous line of the figure, which is drawn with the theoretical slope, best represents the true conductivity of sodium mandelate, and we accordingly take Λ_0 = 79·35 as the equivalent conductivity at infinite dilution. We do not think that this is in error by more than 0·10 unit. Assuming a temperature coefficient of 0·024 per degree, Λ_0 = 79·51 at 25°, and taking the mobility of the sodium ion as 50·11 (Robinson and Davies, *loc. cit.*), the mobility of the mandelate ion becomes 29·40 at 25°, or 29·34 at 24·915°. From Shedlovsky's results we obtain Λ_0 = 426·27 for hydrochloric acid, and 76·39 for the mobility of the chloride ion at 25° (Robinson and Davies, *loc. cit.*). Subtraction gives 349·88 for the mobility of the hydrogen ion at 25°, which, with the temperature coefficient 0·015 (Landolt–Börnstein Tabellen, 5te Aufl., p. 1104), becomes 349·43 at 24·915°, and hence for mandelic acid Λ_0 = 378·77. Using this value, we have calculated K, the true dissociation constant of mandelic acid, by means of the Debye–Hückel and Onsager limiting equations. The results are in Table V.

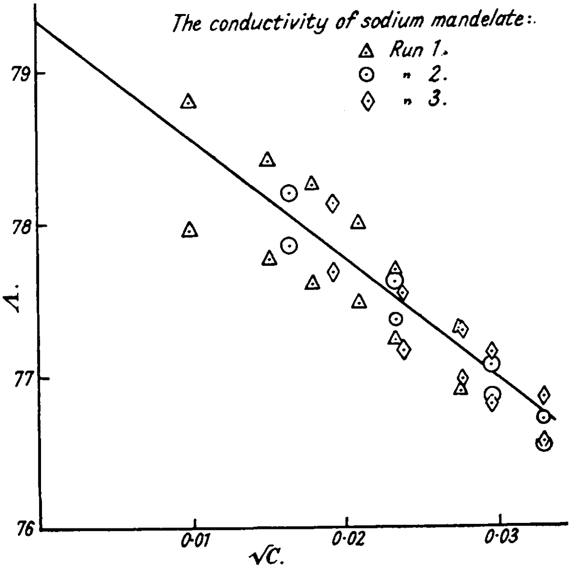

TABLE V.

$C\times10^4$.	Λ.	$K\times10^4$.	$C\times10^4$.	Λ.	$K\times10^4$.	$C\times10^4$.	Λ.	$K\times10^4$.	$C\times10^4$.	Λ.	$K\times10^4$
1·1149	306·69	3·844	7·3771	193·50	3·850	*18·565	140·19	3·899	29·045	117·44	3·880
2·2647	268·29	3·866	*11·757	165·70	3·889	21·454	132·39	3·883	*34·329	109·95	3·899
3·6703	239·09	3·914	13·190	158·65	3·863	22·938	128·91	3·866	41·414	101·50	3·874
*5·7023	210·35	3·879	14·006	155·36	3·873	*26·110	122·72	3·895	62·307	85·44	3·877

The degree of dissociation varies between approximately 20 and 80%, a greater range, we believe, than has hitherto been studied for any weak electrolyte, and the mean value of the dissociation constant is 3·878 × 10^{-4}. The values for the *l*-acid (marked in Table V by asterisks) are consistently high, giving a mean value K = 3·891 × 10^{-4}; a possible explanation of this would be the presence of approximately 0·1% of non-conducting impurity in the inactive acid, but as only one run was carried out on the active acid, we take K = (3·88 ± 0·01) × 10^{-4} as the best value for both forms of the acid.

The conductivities of the more concentrated solutions of sodium and barium mandelates were measured for comparison with the extended forms of the Onsager equation previously proposed (Davies, *Trans. Faraday Soc.*, 1927, **23**, 351; Righellato and Davies, *ibid.*, 1930, **26**, 592). In Table IV (*a*), col. 2 shows the measured conductivities for sodium mandelate, and col. 3 gives the values calculated from the extended equation (cf. Robinson and Davies, *loc. cit.*). The good agreement shows that the whole change of conductivity with concentration is to be attributed to changes in the mobilities of the ions, and that sodium mandelate is completely dissociated at concentrations up to 0·1N.

The measurements on barium mandelate shown in Table IV (*b*) lead to quite a different result. The calculated conductivities shown in col. 3 are obtained from the equation $\Lambda = 92{\cdot}79 - 162{\cdot}4\, f_{12}(C)$; here the figure $\Lambda_0 = 92{\cdot}79$ has been obtained from Shedlovsky and Brown's value, 63·59, for the mobility of the barium ion (*J. Amer. Chem. Soc.*, 1934, **56**, 1066), which, with a temperature coefficient of 0·024 per degree (Landolt–Börnstein, *loc. cit.*), becomes 63·45 at 24·915°; 162·4 is the theoretical Onsager slope, and the values of $f_{12}(C)$ are taken from Righellato and Davies's paper. It will be seen that these calculated conductivities are considerably higher than the measured conductivities of col. 2. We have assumed that the discrepancy is due to the presence of the intermediate ion formed by the process : $Ba^{\cdot\cdot} + C_6H_5{\cdot}CH(OH){\cdot}CO'_2 \longrightarrow C_6H_5{\cdot}CH(OH){\cdot}CO_2Ba^{\cdot}$, and have calculated the extent to which this association occurs, assuming the value 30 for the mobility of the intermediate ion and using the method previously described (Righellato and Davies, *loc. cit.*). The results are in Table IV (*b*), where $(1 - \alpha)$ represents the fraction of barium in the form of intermediate ion; an error of 20% in the value assumed for the mobility of the intermediate ion would lead to an error of 5% in $(1 - \alpha)$. Col. 5 of the table shows the dissociation constant, $K = \frac{\{Ba^{\cdot\cdot}\}\{M'\}}{\{BaM^{\cdot}\}} = \frac{F.\,\alpha(1 + \alpha)m}{1 - \alpha}$, where M represents the mandelate radical, *m* is the molar concentration, and *F* is an activity factor. *F* was calculated from the Brönsted extension of the Debye–Hückel equation, $-\log F = 2\sqrt{I} - BI$, in which *I* is the ionic strength, given by $I = (1 + 2\alpha)m$, and *B* is an adjustable constant which was assigned the value 2·83. The values found for *K* are extremely constant, but as only three measurements were made, we regard the constant $K = 0{\cdot}17$ as provisional, and intend to check it by an independent method. With it may be compared the values for barium salts previously determined : chloride, > 1; nitrate, 0·12; chlorate, 0·20; bromate, 0·14; iodate, 0·08.

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