54. *The Extent of Dissociation of Salts in Water. Part V. Calcium Mandelate.*

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Calcium mandelate has been studied in dilute aqueous solution at 25°. The electrical conductivity is abnormally low, and leads to the conclusion that the intermediate ion, $C_6H_5{\cdot}CH(OH){\cdot}CO_2Ca^{\cdot}$ is present in considerable amounts; in 0·005M-solution 15% of the calcium is in this form. A value $K = 0{\cdot}035$ is derived for the dissociation constant of the intermediate ion, and this is used to calculate the ionic composition of certain solutions, containing sodium *l*-mandelate in the presence of calcium salts, which Levene and Rothen have found to exhibit abnormal optical activity. The calculations lead to a consistent value for the molecular rotation of the calcium mandelate ion differing greatly from that of the free mandelate ion, a fact which suggests that the constituents of the intermediate ion are united by a definite chemical linkage.

SOME years ago Levene and Rothen (*J. Physical Chem.*, 1930, **34**, 2567) reported the effect of a large number of salts on the optical activity of sodium *l*-mandelate in aqueous solution. Although in most cases the usual small " salt effect " was observed, yet solutions containing the alkaline-earth metals, and especially calcium, showed very much greater changes. The authors considered that their results proved the complete dissociation of calcium and barium mandelate in dilute aqueous solution, but actually the evidence was inconclusive, and, on the contrary, these anomalous salt effects seemed too great to be due to normal electrostatic influences, and to imply a more intimate interaction between the mandelate ion and the added cation. To test this, the conductivity of calcium mandelate was measured.

The calcium mandelate, prepared from calcium carbonate and mandelic acid, was obtained as anhydrous crystals on addition of alcohol to the aqueous solution. After three recrystallisations by the same method the salt was dried in a vacuum at 50° for 24 hours, and its purity was confirmed by conductimetric titration against sodium oxalate. The salt forms soft waxy crystals which are not wetted by water and for this reason dissolve extremely slowly. During the recrystallisations this inconvenience was overcome by first moistening the dry crystals with a drop of alcohol; after this treatment they sank in water and dissolved readily.

The conductivity apparatus and technique were as described in a former paper (J., 1937, 432), measurements being made at 1000 and 3150 cycles. The solutions were made up by weight, and their equivalent concentrations were calculated from the molecular weight $M = 342{\cdot}20$ and the following density figures, which were determined in these laboratories by Dr. W. H. Banks: *m* 0·0119, *d* 0·9985; *m* 0·0215, *d* 0·9997. All measurements were made at 25° ± 0·005°, and are based on the Jones and Bradshaw standard (*J. Amer. Chem. Soc.*, 1933, **55**, 1780).

The results are in Table I, where col. 1 gives the equivalent concentration, and col. 2 the equivalent conductivity obtained by applying the normal solvent correction, *i.e.*, by subtracting

TABLE I.

$C \times 10^4$.	Λ, norm.	Λ, corr.	Λ, calc.	$100 \times (1 - \alpha)$.	*I*.	*K*.
7·2235	83·08	83·30	84·50	2·1	0·001069	0·0289
10·370	81·96	82·14	83·71	2·8$_5$	0·001525	0·0294
17·786	80·05	80·17	82·15	3·8	0·002600	0·0355
24·513	78·49	78·57	81·10	4·9	0·003558	0·0361
34·715	76·52	76·56	79·81	6·68	0·004976	0·0350
39·730	75·66	75·70	79·29	7·35	0·005668	0·0353
49·798	74·11	74·14	78·33	8·80	0·007032	0·0350
57·362	73·04	73·05	77·72	9·70	0·008048	0·0353
81·109	70·20	70·21	76·01	12·4	0·01117	0·0354
121·98	66·33	66·34	73·87	16·6	0·01628	0·0346

the conductivity of the solvent from that of the solution. It has been shown in earlier papers that these results will be too low, whilst figures corrected for hydrolysis on the assumption that the sole impurity in the water is carbon dioxide will be slightly too high. The corrected figures given in col. 3 were obtained by adding to those of col. 2 two-thirds of the difference between these and the hydrolysis-corrected values (cf. Banks and Davies, this vol., p. 73); the uncertainty introduced by this procedure is very small except for the two most dilute solutions.

When plotted against the square root of the equivalent concentration, the conductivities give an almost straight line up to $C = 0{\cdot}01$, *i.e.*, far beyond the limits of validity of Onsager's equation; this behaviour is abnormal for an aqueous salt solution, but has frequently been found for incompletely dissociated salts in non-aqueous solvents. Moreover, with increasing concentration they become increasingly lower than the values to be expected for a completely dissociated salt. These values are shown in col. 4, calculated from the empirical extension of Onsager's equation derived in a previous paper (Righellato and Davies, *Trans. Faraday Soc.*, 1930, **26**, 592), which for calcium mandelate takes the form Λ, calc. $= 88{\cdot}85 - 161\ \mathrm{f}_{12}\,(C)$; here the value for zero concentration, 88·85, is the sum of the mobilities of the mandelate ion, 29·40 (Banks and Davies, *loc. cit.*), and of the calcium ion, 59·45 (Shedlovsky and Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 1066). A comparison of cols. 4 and 3 shows that the discrepancy is already large for the first three points, which are approximately within the range of validity of Onsager's limiting equation, and at 0·01N. the measured conductivity is too low by 10%. We believe that this is due to the formation of the intermediate ion according to the scheme $Ca^{\cdot\cdot} + C_6H_5{\cdot}CH(OH){\cdot}CO_2 \rightleftharpoons C_6H_5{\cdot}CH(OH){\cdot}CO_2Ca^{\cdot}$; the further association to form the neutral salt is likely to be negligible at the concentrations considered. The figures given in col. 5 of Table I show the percentages of calcium in the form of the intermediate ion, calculated by the method of the previous paper (Righellato and Davies, *loc. cit.*), and on the assumption that the mobility of the intermediate ion at zero concentration is 30. The value of this constant is necessarily uncertain; if its value had been taken as 25, the figures obtained for $(1 - \alpha)$, the fraction associated, would have been approximately 5% lower than those shown. Col. 6 of the table shows the ionic strength, calculated from the formula $I = (1 + 2\alpha)m$, where m is the molar concentration, and col. 7 gives the dissociation constant calculated from the relation $\log K = \log \{Ca^{\cdot\cdot}\}\{M'\}/\{CaM^{\cdot}\} = \log \alpha(1 + \alpha)m/(1 - \alpha) - 2{\cdot}02\sqrt{I} + BI$; the adjustable constant B was found graphically to have the value 2·7. With the exception of the most dilute measurements, for which the solvent-corrected conductivities are uncertain, the constancy of K leaves nothing to be desired; for the last six points the mean value is 0·0351 and the maximum deviation from this value corresponds to an error in the measured conductivity of 0·05 unit. On the other hand, inaccuracies in the empirical equation on which the calculations are based, and in the value taken for the mobility of the intermediate ion, may introduce errors of 5% or more, so that the value $K = 0{\cdot}035$ may be in error by 0·002. The behaviour of calcium mandelate is in marked contrast with that of the commoner calcium salts, which are usually regarded as typically strong electrolytes. It is also noteworthy that calcium mandelate is much weaker than the barium salt, for which a dissociation constant $K = 0{\cdot}17$ has been derived (Banks and Davies, *loc. cit.*).

It is now possible to calculate the ionic composition of the solutions investigated by Levene and Rothen, if we assume that the same dissociation constant will apply to the calcium salts of the active and inactive acids. Levene and Rothen made three series of measurements. In the first, varying amounts of calcium hydroxide were added to *l*-mandelic acid; four measurements of this type were available, the data being read from Fig. 1 of the authors' paper. In the second series, various amounts of calcium chloride were added to sodium mandelate; only one of these measurements could be used, since the second referred to a mixture of ionic strength greater than 1, in which the concentration of the calcium mandelate cation could not be even approximately calculated. In the third series calcium chloride was added to mandelic acid in the presence of hydrochloric acid, and these measurements were also unsuitable for our purpose since calculation showed that less than 0·5% of the mandelate radical was united to calcium. The results of the calculations are given in Table II. Col. 1 shows the stoicheiometric concentration of mandelic

TABLE II.

Mandelic acid + calcium hydroxide.

C_1.	C_2.	$[M]_D^{25^\circ}$.	$[Ca^{\cdot\cdot}]$.	$[M']$.	$[CaM^{\cdot}]$.	$[OH']$.	$[CaOH^{\cdot}]$.	$[M_{CaM^{\cdot}}]_D^{25^\circ}$
0·0098	0·0049	183·6°	0·0042	0·0091	0·0007	—	—	274°
0·0098	0·0190	194·2	0·0132	0·0082	0·0016	0·0240	0·0042	286
0·0174	0·0174	192·8	0·0123	0·0148	0·0026	0·0149	0·0025	284
0·0260	0·0130	189·0	0·0097	0·0227	0·0033	—	—	273
Sodium mandelate + calcium chloride.								
0·04983	0·0292	193·14	0·0196	0·04023	0·0096	—	—	263

acid or sodium mandelate, col. 2 that of calcium hydroxide or calcium chloride, col. 3 the molecular rotation for the solution. The next five columns show the concentrations of the individual species, that of the calcium mandelate ion being calculated from the equation given above, and that of the calcium hydroxide ion in the alkaline solutions from the equation $\log [Ca^{\cdot\cdot}][OH']/[CaOH^{\cdot}] = \log 0{\cdot}031 + 2{\cdot}02\sqrt{I} - 2I$ (Kilde, *Z. anorg. Chem.*, 1934, **218**, 113; and see following papers). The last column shows the molecular rotation of the calcium mandelate ion calculated from the formula of the simple mixture rule, $2[M] = (1 + \alpha)[M_{\text{mand.}}] + (1 - \alpha)[M_{\text{CaM}}]$, where $[M_{\text{mand.}}]$, the molecular rotation of the free mandelate ion, is given the value determined by Levene and Rothen, *viz.*, 176·7. This treatment assumes that the whole change in rotation is due to the appearance of the new ionic species with its own characteristic optical activity; it neglects the "normal" salt effect, due to the influence exerted by the neighbouring free ions, a procedure justified, as a close approximation, by the very small effects found by Levene and Rothen for normal salts.

The dissociation constant of barium mandelate is also known (Banks and Davies, *loc. cit.*), and the same treatment has been applied to the two most dilute of Levene and Rothen's solutions containing barium ion. The results are as follows:

C_1.	C_2.	$[M]_D^{25^\circ}$.	$[Ba^{\cdot\cdot}]$.	$[M']$.	$[BaM^{\cdot}]$.	$[M_{BaM^{\cdot}}]_D^{25^\circ}$.
Mandelic acid + barium hydroxide.						
0·05	0·0256	179·95°	0·0227	0·0471	0·0029	233°
Sodium mandelate + barium chloride.						
0·04983	0·044	181·92	0·0393	0·04513	0·0047	232

For both the calcium mandelate and the barium mandelate ion the calculated molecular rotations are constant within the error of experiment and calculation. Here, then, as with the other properties of salt solutions so far investigated, the incomplete dissociation theory provides a consistent explanation of apparently anomalous results.

The molecular rotations now known for mandelic acid and its derivatives are: acid, 237·3°; free ion, 176·7°; barium mandelate ion, 233°; calcium mandelate ion, 276°. The association of a mandelate ion with a calcium ion is therefore accompanied by a considerably greater change in optical activity than is the formation of the un-ionised acid. This fact, like the abnormally low dissociation constant, is evidence that the process cannot be described in terms of a purely electrostatic linkage. The structure of the calcium mandelate ion is further discussed in the following papers.

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