56. *The Extent of Dissociation of Salts in Water. Part VI. Some Calcium Salts of Organic Acids.*

By Cecil W. Davies.

Calcium lactate and mandelate are known to be abnormally weak electrolytes, and the purpose of the present work was to investigate the structural factors on which this anomaly depends. The dissociation constants of several calcium salts of monobasic acids have been obtained, and of these the weakest is the glycollate; in a 0·02M-solution of this salt only one-half of the calcium is in the form of free calcium ions. Amongst other calcium salts of oxy-acids, the methoxyacetate and pyruvate are weak, though not as weak as the salts of α-hydroxy-acids; the salts of β-hydroxy-acids are stronger. The aminoacetate has almost the same dissociation constant as the lactate, showing that the anomaly is not restricted to oxy-acids.

In the two preceding papers it has been shown that calcium mandelate is a relatively weak electrolyte, and Kilde (*Z. anorg. Chem.*, 1936, **229**, 321) has found the same to be true of calcium lactate. The results reported in this paper form part of an investigation into the structural factors on which the anomaly depends. The method used was to measure the solubility of calcium iodate in the presence of the sodium salt of an organic acid; the dissociation constant of the calcium salt of the acid was then calculated by the method applied to calcium mandelate in the preceding paper. In addition, Kilde's results, which are not strictly comparable with ours, have been recalculated, and some measurements of the conductivity of calcium acetate have also been considered.

The Dissociation Constant of Calcium Lactate.—The value $K = 0{\cdot}04$ was obtained by Kilde (*loc. cit.*) by methods generally similar to those used here and in the preceding paper; *i.e.*, he measured the solubility of calcium iodate in the presence of sodium or calcium lactate, and calculated the amount of the calcium lactate ion necessarily present to bring the results into harmony with those for normal salts; by plotting $\log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{Lac.}']/[\mathrm{CaLac.}^{\cdot}] - 2{\cdot}02\sqrt{I}$ against I (where I is the ionic strength) he then obtained the result $\log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{Lac.}']/[\mathrm{CaLac.}^{\cdot}] - 2{\cdot}02\sqrt{I} + 2{\cdot}8I = 0{\cdot}04$. Kilde, however, made no corrections for the presence of sodium iodate molecules and $\mathrm{CaIO_3}^{\cdot}$ ions, which he assumed to be completely dissociated. As we have evidence that this is not so, and as the corresponding corrections, though not affecting Kilde's main conclusions, are nevertheless significant when we come to compare the dissociation constant of calcium lactate with those of other salts of hydroxy-acids, we have recalculated the results on the same basis as our other figures. The results are in Table I. Cols. 1 and 2 show Kilde's values for the concentration of solvent salt and the solubility of calcium iodate, both in millimols./l. The next six columns give the results of the calculations; the figures in col. 5 are derived from $\frac{1}{3}\log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{IO_3}']^2 = \bar{3}{\cdot}9474 + 1{\cdot}01\sqrt{I}/(1 + \sqrt{I}) - 0{\cdot}19I$, an equation which follows from the results of the preceding paper; col. 7 gives the calculated concentration of the CaLac.˙ ion, and col. 8 the dissociation constant of this ion, calculated from the equation $\log K = \log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{Lac.}']/[\mathrm{CaLac.}^{\cdot}] - 2{\cdot}02\sqrt{I} + 2{\cdot}8I$. The last column shows the dissociation constant obtained by Kilde's method.

TABLE I.

Solubility of Calcium Iodate in Lactate Solutions.

m.	*s*.	$[\mathrm{NaIO_3}]$.	$[\mathrm{CaIO_3}^{\cdot}]$.	$\frac{1}{3}\log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{IO_3}']^2$.	*I*.	$[\mathrm{CaLac.}^{\cdot}]$.	*K*.	K_{Kilde}.
				Sodium lactate solutions.				
200·0	16·89	1·19	0·36	$\bar{2}{\cdot}2298$	0·2257	11·82	0·035	0·042
100·0	13·15	0·49	0·38	$\bar{2}{\cdot}1868$	0·1239	7·15	0·032	0·040
40·0	10·32	0·17	0·41	$\bar{2}{\cdot}1381$	0·06305	3·46	0·032	0·044
20·0	9·18	0·08	0·44	$\bar{2}{\cdot}1124$	0·04274	1·92	0·033	0·047
10·0	8·53	0·04	0·46	$\bar{2}{\cdot}0958$	0·03264	1·00	0·034	0·047
				Calcium lactate solutions.				
99·2	5·85	—	1·01	$\bar{2}{\cdot}2149$	0·1820	65·46	0·035	0·039
49·6	5·93	—	0·85	$\bar{2}{\cdot}1799$	0·1127	26·10	0·035	0·040
19·8	6·33	—	0·69	$\bar{2}{\cdot}1371$	0·06211	7·45	0·036	0·049
9·92	6·77	—	0·60	$\bar{2}{\cdot}1123$	0·04263	3·12	0·035	0·049
4·96	7·15	—	0·54	$\bar{2}{\cdot}0955$	0·03257	1·35	0·035	0·053

The Dissociation Constant of Calcium Hydroxide.—This has also been determined by Kilde, and, as with calcium lactate, it seemed desirable to make the recalculations. The results are in Table II, where col. 1 gives the added electrolyte and its concentration in millimols./l. The K values are calculated from the equation $\log K = \log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{OH}']/[\mathrm{CaOH}^{\cdot}] - 2{\cdot}02\sqrt{I} + 2I$.

TABLE II.

Solubility of Calcium Iodate in Alkaline Solutions.

m.		*s*.	$[\mathrm{NaIO_3}]$.	$[\mathrm{CaIO_3}^{\cdot}]$.	$\frac{1}{3}\log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{IO_3}']^2$.	*I*.	$[\mathrm{CaOH}^{\cdot}]$.	*K*.	K_{Kilde}.
10·0	NaOH	8·4	0·04	0·47	$\bar{2}{\cdot}0965$	0·0331	0·59	(0·058)	(0·20)
25·0	NaOH	9·4	0·10	0·44	$\bar{2}{\cdot}1199$	0·0480	2·09	0·034	0·048
25·0 100·0	NaOH NaCl	11·4	0·52	0·47	$\bar{2}{\cdot}2019$	0·1523	2·45	0·026	0·047
50·0	NaOH	10·5	0·21	0·42	$\bar{2}{\cdot}1491$	0·0738	4·23	0·029	0·053
50·0 50·0	NaOH NaCl	11·4	0·43	0·44	$\bar{2}{\cdot}1883$	0·1263	3·32	0·037	0·056
10·8	$\mathrm{Ca(OH)_2}$	6·4	—	0·65	$\bar{2}{\cdot}1202$	0·0483	1·00	(0·14)	(0·26)
10·8 100·0	$\mathrm{Ca(OH)_2}$ NaCl	8·5	0·31	0·63	$\bar{2}{\cdot}2009$	0·1501	3·13	0·030	0·056
							Mean	0·031	

The Dissociation Constant of Calcium Acetate.—At low concentrations MacGregory's conductivity data (Landolt–Börnstein Tabellen, 5te Aufl., 1081) for calcium acetate at 18° are in fair agreement with Onsager's equation. At the higher concentrations the experimental values are somewhat lower than values calculated from the empirical extension of Onsager's equation for a completely dissociated salt (*Trans. Faraday Soc.*, 1930, **26**, 592), and the method of calculation used by Righellato and Davies (*ibid.*) leads to the following values for the dissociation constant: $C = 0{\cdot}03$, $K = 1{\cdot}0$; $C = 0{\cdot}05$, $K = 0{\cdot}9$; $C = 0{\cdot}1$, $K = 1{\cdot}0$; mean: $K = 1{\cdot}0$. The accuracy of this value is not great, but the consistency of the results is sufficiently good to show that calcium acetate is a stronger electrolyte than calcium nitrate, and that at the concentrations considered in this series of papers its dissociation into free ions is almost complete.

New Solubility Measurements.—These were made as described in the previous paper, except that the saturated solutions were estimated, with little apparent sacrifice of accuracy, by the ordinary volumetric methods. Each measurement reported is the mean of two titrations, agreeing within at least 0·2%, between which the saturated solution was passed for a second time through the saturating column. The solubility in pure water was checked before and after each series with a given salt. The results are at 25° ± 0·01°.

An approximately 1N-sodium hydroxide solution was prepared from washed " AnalaR " sticks, and stored in a nickel reservoir; it was standardised by titration against weighed samples of " AnalaR " potassium hydrogen tartrate and potassium hydrogen phthalate. With one exception the sodium salt solutions were made up from this solution and solutions of the purified acids, an added drop of phenolphthalein being just decolourised. The salicylic, glycollic, and cyanoacetic acids were commercial samples; their acid equivalents agreed within 0·1% with the theoretical values. The glycine, an " AnalaR " sample, was also used without further purification. The pyruvic acid (b. p. 73°/11 mm.) was redistilled just before use; its acid equivalent was 87·5 (Calc.: 88·0). The methoxyacetic acid was prepared in these laboratories, b. p. 102°/18 mm.; its acid equivalent was 90·2 (Calc.: 90·05). The sodium β-hydroxybutyrate solutions were made up by weight from a sample of the salt which had been recrystallised from absolute alcohol and dried in a vacuum.

Before each salt solution was taken into use, a portion was mixed with 25 ml. of an almost saturated solution of calcium iodate, and the whole titrated, under standard conditions, after standing for one hour. Only with the β-hydroxybutyrate was there any evidence of interaction; for this salt a small correction (+ 0·3%) was derived, and was applied to the subsequent results.

The results are given in Table III in the same manner as before; col. 7 shows the calculated concentration of the product of association of the calcium ion with the organic anion present, and col. 8 shows the dissociation constant of this ion, calculated from the equation $\log K = \log [\mathrm{Ca}^{\cdot\cdot}][\mathrm{X}']/[\mathrm{CaX}^{\cdot}] - 2{\cdot}02\sqrt{I} + 2{\cdot}8I$. The adjustable constant in this equation has been given the value 2·8 in view of the values previously found for similarly constituted ions: calcium mandelate, 2·7 (cf. preceding papers); barium mandelate, 2·83 (Banks and Davies, this vol., p. 73); calcium lactate, 2·8 (Kilde, *loc. cit.*). It will undoubtedly apply with the required accuracy to the data of Table III.

The results for sodium aminoacetate are probably less accurate than the others, as no special precautions were taken to protect the alkaline solutions from the atmosphere. The calculations, also, for this salt were complicated by the necessity of allowing for the $\mathrm{CaOH}^{\cdot}$ ion formed in these alkaline solutions, and for hydrolysis; in obtaining the figures shown in the table (HX represents glycine) the acid dissociation constant of glycine was taken to be $3{\cdot}4 \times 10^{-10}$, and it was assumed that the glycine molecules do not contribute to the ionic strength.

The calculations for calcium lactate in Table I reveal some points of interest. A comparison of the last two columns shows that the chief effect of the recalculations is to reduce the dissociation constant. The constancy of the new values is very satisfactory, the mean of the measurements being 0·034, with an average deviation of ± 0·001. Kilde's results, on the other hand, show variations at the lower concentrations, which are more pronounced in the calcium lactate than in the sodium lactate series. Kilde neglected these, no doubt correctly, in deriving his mean value, $0{\cdot}04_0$, but it is satisfactory to find that the discrepancies are entirely removed by the new method of calculation; the fact provides additional evidence for the substantial accuracy of the dissociation constants assigned to sodium and calcium iodates. In Table II, where the same considerations are involved, the recalculation greatly reduces, though it does not entirely remove, the anomalies in the most dilute solutions.

Another striking feature of the figures in Table I is the constancy of K in the two most concentrated solutions, in which two-thirds or more of the total calcium is in the form of calcium lactate ion. With the glycollates, oxalates, and other relatively weak salts of the transitional metals it is found (Ferrell, Ridgion, and Riley, J., 1934, 1440; Money and Davies, *ibid.*, p. 400) that as the concentration rises the cation shows a marked tendency

TABLE III.

m.	*s.*	$[\mathrm{NaIO_3}]$.	$[\mathrm{CaIO_3^{\cdot}}]$.	$\frac{1}{3}\log[\mathrm{Ca^{\cdot\cdot}}][\mathrm{IO_3'}]^2$.	*I.*	$[\mathrm{CaX^{\cdot}}]$.	*K.*
			Sodium glycollate.				
40·0	10·56	0·176	0·404	$\bar{2}$·1378	0·06267	4·017	0·0257
20·0	9·315	0·082	0·429	$\bar{2}$·1118	0·04242	2·294	0·0257
			Sodium methoxyacetate.				
40·0	9·664	0·160	0·446	$\bar{2}$·1396	0·06447	1·733	0·077
20·0	8·850	0·078	0·455	$\bar{2}$·1138	0·04367	0·948	0·075
			Sodium pyruvate.				
40·0	9·609	0·159	0·449	$\bar{2}$·1399	0·06463	1·568	0·086
20·0	8·837	0·077	0·456	$\bar{2}$·1139	0·04371	0·904	0·079
			Sodium β-hydroxybutyrate.				
43·04	9·470	0·166	0·461	$\bar{2}$·1439	0·06850	0·953	0·16
21·48	8·791	0·088	0·462	$\bar{2}$·1164	0·04561	0·620	0·13
			Sodium salicylate.				
40·0	9·241	0·152	0·468	$\bar{2}$·1409	0·06567	0·480	0·31
20·0	8·652	0·076	0·468	$\bar{2}$·1146	0·04429	0·328	0·24
			Sodium aminoacetate.				
40·0	10·01	0·166	0·429	$\bar{2}$·1388	0·06373	2·571	0·045
	(The solution also contained : $[\mathrm{CaOH^{\cdot}}]$, 0·082; [HX], 1·086; $[\mathrm{OH'}]$, 1·00.)						
20·0	9·113	0·080	0·439	$\bar{2}$·1127	0·04292	1·665	0·038
	(The solution also contained : $[\mathrm{CaOH^{\cdot}}]$, 0·064; [HX], 0·756; $[\mathrm{OH'}]$, 0·69.)						
			Sodium cyanoacetate.				
40·0	9·241	0·152	0·468	$\bar{2}$·1409	0·06567	0·480	0·31
20·0	8·652	0·076	0·468	$\bar{2}$·1146	0·04429	0·328	0·24

to associate with an increasing number of anions, to form first neutral molecules and then complex anions. If calcium lactate exhibited similar behaviour it would be shown in a change of *K* at the higher concentrations. It is true that this might possibly be masked by a compensation of errors, since the ionic strength of the most concentrated solutions of Table I is beyond the range in which our equations have been tested; but it appears more probable that the calcium lactate ion has no great tendency to undergo further association even in the presence of a large excess of lactate ions.

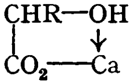
The values now available for the dissociation constants of calcium salts of univalent organic acids are as follows :

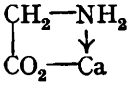
Glycollate	0·026	Methoxyacetate	0·076	Salicylate	0·28
Lactate	0·034	Pyruvate	0·083	Cyanoacetate	0·28
Mandelate	0·035	β-Hydroxybutyrate	0·15	Acetate	1·0
Aminoacetate	0·042				

It is hardly necessary to point out that these figures show no relation to the dissociation constants of the corresponding acids.

The weakest of the salts is the glycollate. A 0·02M-solution of this will contain only one-half of its calcium in the form of free calcium ions, whilst at higher concentrations the salt will probably exist mainly in the uni-univalent ionised form $(\mathrm{CaX})^{\cdot}\mathrm{X'}$. The other α-hydroxy-acid salts are almost as weak, and it is natural to suggest that a possible chelate structure, (I), contributes in all three cases to the stability of the intermediate ion. The effect is not confined to the salts of α-hydroxy-acids; it is still present, though much diminished, in the methoxyacetate and pyruvate. In the β-hydroxybutyrate, salicylate, and cyanoacetate, where chelation would result in a six-membered ring, it is interesting to find that the effect is much more feeble, if it exists at all; these three salts have higher dissociation constants than has calcium iodate. Finally, the result for the aminoacetate shows that the influence of an α-nitrogen atom is comparable with that of an α-oxygen atom in causing an abnormally low dissociation constant. The measurements cannot be interpreted with quite as much confidence in this case, since in addition to the $\mathrm{CaOH^{\cdot}}$ ion and the undissociated glycine, for which approximate allowance was made, there are conceivably present the species $Ca(OH){\cdot}CO_2{\cdot}CH_2{\cdot}NH_2$ and $[Ca(OH){\cdot}CO_2{\cdot}CH_2{\cdot}NH_3]^{\cdot}$. Probably, however, association will lead primarily to (II), and in alkaline solutions at moderate concentrations the calcium salts of the common amino-acids will exist mainly in such a form.

(I.)





(II.)

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