324. *Physicochemical Studies of Complex Formation involving Weak Acids. Part XV. The Optical Rotation of* l-*Malic and* l-*Lactic Acids during Neutralisation with Sodium Hydroxide.*

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THIS work was undertaken as a preliminary to an investigation of complex formation involving malic and lactic acids. Britton and Jackson (J., 1934, 998) have demonstrated that the variations in optical rotation during the neutralisation of tartaric acid can be attributed to the changes in the concentrations of the undissociated acid and of the hydro-tartrate and tartrate ions, and the present work also shows that the optical rotations of both *l*-malic and *l*-lactic acid whilst undergoing neutralisation are the sums of the rotations of the undissociated acids and the various ions involved. That such is probably true of malic acid can be concluded from the calculations of Vellinger (*Compt. rend.*, 1927, **184**, 94), which, however, were vitiated by the assumption of certain numerical values for the molar rotations of the optically active components.

<div align="center">EXPERIMENTAL.</div>

The rotations were measured in a 4-dm. tube jacketed with running water at 25°, a sodium-vapour lamp being used as light source. Each measurement represents the mean of about 20 readings, and the accuracy is $\pm$ 0·01°. The molecular rotation, $[M]$, is equal to α/lc, c being the concentration of the optically active substance in g.-mols./litre.

I. l-*Malic Acid.*—*Determination of the molecular rotations of* (a) *undissociated* l-*malic acid and* (b) *the hydromalate ion at* 25°. On the assumption that, in solutions of malic acid of concentrations of 0·1M and above, the secondary ionisation becomes negligible, it follows that, if their optical rotations are additive

$$[M_{H_2M}]_{\text{obs.}} = (1 - \gamma)[M_{H_2M.\text{ undiss.}}] + \gamma[M_{HM'}]$$

in which γ is the degree of ionisation of $H_2M \rightleftharpoons H^{\cdot} + HM'$.

To test the validity of such a formula, it is necessary to ascertain the molar rotation of undissociated malic acid, $[M_{H_2M.\text{undiss.}}]$, and this was done by suppressing the ionisation of malic acid

by preparing 0·1M-solutions so as to contain hydrochloric acid in concentrations of 0·5N or 1·5N. In both cases the observed rotations were − 0·13°. If the rotation was caused entirely by undissociated malic acid, it follows that $[M_{H_2M, undiss.}] = − 0·325°$. Table I records the observed rotations of *l*-malic acid solutions ranging from 0·1 to 0·5M; γ was calculated from $K_1 = 4·24 × 10^{-4}$ (see Moss, Ph.D. Thesis, London, 1936). The values of $[M_{HM'}]$ are sufficiently constant to justify the assumption.

TABLE I.

Malic acid, g.-mols./l.	a, obs.	$[M_{H_2M}]$, obs.	γ.	$[M_{HM'}]$, calc.
0·1	−0·15°	−0·375°	0·065	−1·09°
0·2	−0·29	−0·361	0·045	−1·11
0·25	−0·355	−0·355	0·040	−1·08
0·4	−0·56	−0·350	0·032	−1·11
0·5	−0·685	−0·347	0·029	−1·07
			Mean	−1·09

Optical rotations during the neutralisation of 0·1M-1-*malic acid with sodium hydroxide at* 25°. In order to correlate the variation in optical activity in the course of neutralisation, it was considered advisable to use as dilute a solution as practicable, and consequently the concentration of the solution with respect to malic acid was maintained at 0·1M throughout. Even so, the angles of rotation were very small, and this placed a strain on the experimental accuracy, especially when the observed data were compared with those obtained by calculation.

TABLE II.

NaOH, g.-mols./l.	p_H.	a_D, obs.	$[M]_D^{25°}$. Obs.	Calc.	NaOH, g.-mols./l.	p_H.	a_D, obs.	$[M]_D^{25°}$. Obs.	Calc.
0	2·26	−0·15°	−0·375°	−0·379°	0·125	4·45	−0·48°	−1·20°	−1·20°
0·025	2·94	−0·225	−0·56	−0·54	0·150	4·83	−0·535	−1·34	−1·34
0·050	3·35	−0·29	−0·73	−0·72	0·175	5·28	−0·59	−1·48	−1·48
0·075	3·71	−0·36	−0·90	−0·89	0·180	5·40	−0·60	−1·50	−1·50
0·100	4·10	−0·415	−1·04	−1·04	0·200	8·64	−0·64	−1·60	−1·60

Table II gives the p_H values of the 0·1M-malic acid in the various stages of neutralisation, together with the observed angles of rotation and the observed molecular rotations derived directly therefrom. The values recorded in the last column were calculated from the molecular rotations of undissociated acid, of hydromalate ion (both given above), and of the malate ion by the method used by Britton and Jackson for tartaric acid; K_1 was taken as 4·24 × 10^{-4} and K_2 as 1·70 × 10^{-5}, these values referring to malic acid at 0·1M-concentration. The molecular rotation of the malate ion was taken as equal to that of 0·1M-sodium malate given in the last row of Table II, *i.e.*, $[M_{M''}] = − 1·60°$. The agreement of the values in the last two columns is good.

II. 1-*Lactic Acid.*—Purdie and Walker (J., 1895, **67**, 616) have investigated the optical rotation of solutions of *l*-lactic acid and its salts. In concentrations greater than 0·2M, the acid is dextrorotatory, but the rotation diminishes with decreasing concentration, becoming zero at 0·1M, and then lævorotatory. The dextrorotation of the more concentrated solutions is probably caused by lactide formation (see, *e.g.*, Bancroft and Davis, *J. Physical Chem.*, 1931, **35**, 2506), but the following work shows that, on reaching a dilution of 0·2M, any lactide becomes completely hydrolysed. Salts of *l*-lactic acid are, however, lævorotatory in aqueous solution, and the optical rotation found by Purdie and Walker for 0·1M-sodium lactate agrees with the value now obtained.

Optical rotations during the neutralisation of 0·2M-1-*lactic acid with sodium hydroxide at* 25°. Table III gives the observed optical rotations of 0·2M-lactic acid to which sodium hydroxide had been added in the concentrations recorded in col. 1. The p_H values (determined with the hydrogen electrode) are also given, and from these the p_K values corresponding with the concentration of 0·2M have been calculated (col. 5): 0·1M-solutions gave extremely small angles of rotation (see, however, col. 2).

A somewhat different procedure was adopted to test the additivity of the optical rotations. The molecular rotation of the lactate ion was calculated from observed rotation of 0·1M-sodium lactate, *viz.*, $a_D = − 0·60°$, whence $[M_{L'}] = − 1·50°$. If the rotation at any point of the neutralisation is equal to the sum of the rotations due to the lactate ion and the undissociated acid, it should be possible to calculate the molecular rotation of the undissociated lactic acid, $[M_{HL, undiss.}]$. By assuming that C_{HL} (the total concentration of the lactic acid) = [HL, un-

diss.] + [L′], the concentration of any undissociated sodium lactate being considered negligibly small, then [M], obs. should be equal to

$$[\text{HL, undiss.}][M_{\text{HL, undiss.}}]/C_{\text{HL}} + [\text{L′}][M_{\text{L′}}]/C_{\text{HL}}$$

and since [H][L′] = K[HL, undiss.], it follows that [M], obs. should be equal to

$$[\text{H }][M_{\text{HL, undiss.}}]/([\text{H˙}] + K) + K[M_{\text{L′}}]/([\text{H }] + K)$$

from which [$M_{\text{HL, undiss.}}$] may be calculated. The last column of Table III gives the results obtained.

TABLE III.

NaOH, g.-mols./l.	a, obs.	$[M]_{\text{D}}^{25°}$, obs.	p_{H}.	p_K.	$[M_{\text{HL, undiss.}}]_{\text{D}}^{25°}$, calc.
0·000	+0·05°	+0·0625°	2·19	3·67	+0·11°
0·025	−0·10	−0·125	2·85	3·66	+0·09
0·050	−0·25	−0·312	3·18	3·64	+0·09
0·075	−0·40	−0·50	3·42	3·64	+0·10
0·100	−0·58	−0·725	3·66	3·66	+0·10
0·125	−0·72	−0·90	3·90	3·68	+0·10
0·150	−0·86	−1·075	4·14	3·66	+0·20
0·175	−1·00	−1·25	4·48	3·64	+0·39
0·200	−1·14	−1·42	6·89		

It will be observed that, except the last two values in Table III, the calculated values seem to point to the additive character of the optical activities of the active components. The anomaly in the last two values may be caused by the incomplete ionisation of the sodium lactate which is then present in large concentrations compared with unneutralised acid. This would account for the difference between the rotations of 0·1M- and 0·2M-sodium lactate solutions.

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