208. *Physicochemical Studies of Complex Formation involving Weak Acids. Part VIII. The Optical Rotation of Solutions of Tartaric Acid, Tartaric Acid during Neutralisation, and of Neutral Tartrates, with a Note on the Effect of Sodium Chloride.*

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BEFORE embarking upon a detailed investigation of the alteration in the optical activity of tartaric acid on formation of complexes with different oxides, it was considered advisable to ascertain whether the rotation caused by the acid itself in dilute solution, and especially whilst undergoing neutralisation with alkali, could be correlated quantitatively with its two dissociation constants. Ionisation has long been known to influence the optical

activity of the salts of active bases or acids in dilute solutions, and it forms the basis of the so-called law of Oudemans and Landolt; for instance, van 't Hoff (" The Arrangement of Atoms in Space," 1898, p. 140) points out that the differences between the rotations of alkali tartrates and hydrogen-tartrates in dilute solutions are constant, indicating that the tartrate and the bitartrate ion possess each a characteristic rotation. On the contrary (*op. cit.*, p. 142), tartaric acid is regarded as an imperfect electrolyte, for, temperature being kept constant, rotation decreases with increasing concentration.

Recently, Vlès and Vellinger (*Compt. rend.*, 1925, **180**, 742; *Bull. Soc. chim.*, 1925, **371**, 841) attempted to account for the increase in rotation consequent upon the neutralisation of tartaric acid by assuming that the undissociated acid and both its ions each possessed characteristic rotations. Since these rotations, however, were obtained by " trial and error " in order to secure agreement between calculated and observed results, their conclusions cannot be considered as proven.

It is now shown that the values of the molecular rotations of undissociated tartaric acid and the bitartrate ion can be calculated from the actual rotations of tartaric acid solutions of increasing concentration and the dissociation constant governing the first stage of ionisation of the acid. The rotations were measured at 25·0° with both the Na D and the Hg 5461 line. The molecular rotation due to the tartrate ion was obtained from the observed rotations of dilute sodium tartrate solutions. In order to correlate the optical activity of tartaric acid during neutralisation with the variations in ionisation, it was necessary to confine our attention to dilute solutions : these yielded comparatively small rotations and any experimental errors were consequently magnified. Nevertheless, the results clearly reveal the additive nature of the rotations of the undissociated acid and of its two ions throughout the course of neutralisation. They also show that ionisation has a definite effect on the optical activity of the tartaric acid molecule, and that the diminishing molecular rotation of tartaric acid in solutions of increasing concentration is consistent with the classical theory of incomplete ionisation.

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

1. *Determination of Molecular Rotations of Tartaric Acid and the Hydrogen Tartrate Ion at 25°.*—In order to find these molecular rotations, advantage was taken of the fact that, except in very dilute solutions of tartaric acid, the extent of the ionisation $HT' \rightleftharpoons H^{\bullet} + T''$ is negligible, and hence the ionisation may be regarded as being entirely due to the equilibrium $H_2T \rightleftharpoons H^{\bullet} + HT'$.

From a knowledge of K_1, therefore, the degree of ionisation, α, may be calculated for any concentration. Then, if $[M_{H_2T}]$ represents the molecular rotation of the free undissociated acid, $[M_{HT'}]$ that of the hydrogen tartrate ion, and $[M_{H_2T}]_{obs.}$ the observed molecular rotation, it might be expected that $[M_{H_2T}]_{obs.} = (1 - \alpha)[M_{H_2T}] + \alpha[M_{HT'}]$. Hence, if α and $[M_{H_2T}]_{obs.}$ are found for a series of solutions of tartaric acid of different concentrations, it should be possible to calculate $[M_{H_2T}]$ and $[M_{HT'}]$. For this purpose, a series of solutions extending from 0·1M- to 1·0M-tartaric acid were investigated. The observed rotations (accuracy $\pm$ 0·01°) ($l = 4$) are recorded in Table I, cols. 3 and 6; the values of $[M_{H_2T}]_{obs.}$, cols. 4 and 7, were calculated from $[M_{H_2T}]_{obs.} = \alpha^{25°}/lc$, in which $\alpha^{25°}$ is the observed angle for $l = 4$ dm., and c represents the concentration of the tartaric acid in *g.-mols. per litre*. This departure from the usual convention was necessary in order to compare the optical activity of the solutions with their degree of ionisation. The values of $[M]$ here given may be converted into those based on the recommendations of the International Union by multiplying by 10.

Since the rotation–neutralisation experiments were carried out in 0·1M-tartaric acid solutions, the dissociation constants, K_1 and K_2, were redetermined from p_H values set up during the neutralisation of the acid in a solution of that concentration, being calculated by means of Britton's formulæ (J., 1925, **127**, 1896) from measurements with the hydrogen electrode at 18°. The typical data given below were obtained from a titration of 50 c.c. of 0·1M-tartaric acid with 0·2771N-sodium hydroxide. The mean values are in excellent agreement with those obtained by Britton, using more dilute solutions.

NaOH, c.c.	7·5	22·5	10·0	25·0	12·5	27·5	
p_H	2·75	3·75	2·94	3·93	3·11	4·10	
$K_1 \times 10^3$		1·18		1·17		1·15	Mean 1·17
$K_2 \times 10^4$		1·03		1·01		1·05	,, 1·03

TABLE I.

Variation in $[M_{H_2T}]^{25°}_{5461}$ *and* $[M_{H_2T}]^{25°}_D$ *with concentration.*

Concn. of H₂T, mols./l.	α.	$a^{25°}_{5461}$, obs.	$[M_{H_2T}]^{25°}_{5461}$. Obs.	$[M_{H_2T}]^{25°}_{5461}$. Calc.	$a^{25°}_D$, obs.	$[M_{H_2T}]^{25°}_D$. Obs.	$[M_{H_2T}]^{25°}_D$. Calc.
0·1	0·102	+ 1·04°	2·60°	2·52°	+ 0·90°	2·25°	2·26°
0·2	0·074	+ 1·97	2·46	2·43			
0·25	0·066	+ 2·43	2·43	2·40	+ 2·19	2·19	2·17
0·3	0·060	+ 2·89	2·41	2·38			
0·4	0·053	+ 3·79	2·37	2·36			
0·5	0·047	+ 4·68	2·34	2·34	+ 4·26	2·13	2·12
0·6	0·043	+ 5·57	2·32	2·32			
0·75	0·039	+ 6·89	2·30	2·31	+ 6·17	2·06	2·10
1·00	0·034	+ 9·01	2·25	2·29	+ 7·93	1·98	2·08

The values of α (col. 2 of Table I) were calculated from $K_1 = 1·17 \times 10^{-3}$, and by solving a large number of simultaneous equations, the following mean values of the molecular rotations were obtained : $[M_{H_2T}]^{25°}_{5461} = 2·18°$; $[M_{HT}]^{25°}_{5461} = 5·51°$; $[M_{H_2T}]^{25°}_D = 2·00°$; $[M_{HT}]^{25°}_D = 4·50°$.

Cols. 5 and 8 of Table I, which give the apparent molecular rotations of tartaric acid as calculated by substituting the appropriate " rotations " and degrees of ionisation in the above equation, reveal a satisfactory agreement with the observed values. They also show that the " imperfect " rotation of tartaric acid solutions can be explained on the basis of the additive nature of the rotations of the active constituents. Further proof of the value given for $[M_{H_2T}]^{25°}_{5461}$ is to be found from the rotation of a solution of 0·1*M*-tartaric acid + *N*-hydrochloric acid, in which the ionisation of the tartaric acid would be largely repressed. The rotation ($l = 4$) was 0·88°, and therefore $[M_{H_2T}]^{25°}_{5461} = 2·20°$.

2. *Determination of Molecular Rotation of Tartrate Ion.*—Darmois (*Trans. Faraday Soc.*, 1930, **36**, 384), working with 5780 Å., and Patterson (*J.*, 1904, **85**, 1116), using the D line, have both demonstrated that the rotations of alkali tartrates vary with concentration and approach the same magnitude in very dilute solution. Table II records the rotations which we obtained

TABLE II.

Concn., g.-mols./l.	Sodium tartrate. $a^{25°}$.	Sodium tartrate. $[M]^{25°}_{5461}$.	Potassium tartrate. $a^{25°}$.	Potassium tartrate. $[M]^{25°}_{5461}$.	Ammonium tartrate. $a^{25°}$.	Ammonium tartrate. $[M]^{25°}_{5461}$.
0·05	1·40°	7·00°	1·40°	7·00°	—	—
0·1	2·81	7·02	2·82	7·05	2·81°	7·02°
0·2	5·56	6·95	5·72	7·15	5·67	7·09
0·3	8·29	6·90	8·74	7·28	8·59	7·15
0·4	10·99	6·86	11·79	7·37	11·53	7·21
0·5	13·66	6·83	14·92	7·46	14·46	7·23
0·6	16·32	6·80	18·12	7·55	17·44	7·26
0·7	18·98	6·78	21·28	7·60	20·41	7·29
0·8	21·63	6·76	24·48	7·65	23·39	7·31
0·9	24·26	6·74	27·64	7·68	26·38	7·32
1·0	26·84	6·71	30·51	7·70	29·36	7·34
1·25	33·42	6·68				
1·50	39·73	6·62				

at 25° with 5461 Å. These show that, whilst solutions of potassium and ammonium tartrate increase in optical activity with increasing concentration, those of sodium tartrate diminish. These observations are similar to those of Darmois, and, as suggested by him, are very probably due to different degrees of hydration of the three kations and their resulting effect on the electrical condition of the active anions.

These data also show that in 0·1*M*-alkali tartrate solutions the molecular rotation is, within experimental error, almost independent of the kation, the effects of possible hydration then having been largely minimised by the enhanced dilution. Table II shows that the molecular rotations are 7·02—7·05°. If it be assumed that the alkali tartrates are so dilute that the specific electrical effects of the kations are reduced to small magnitudes, it follows that $[M_{T''}]^{25°}_{5461} = 7·0°$ approx. It might be held that the actual degree of ionisation of these salts should have been introduced into the foregoing calculation, but in the subsequent calculations, referring to neutralisation of tartaric acid, ionisation has been assumed complete, so it is highly probable that any errors thereby introduced will be compensated. The value of $[M_{T''}]^{25°}_D$ as deduced from the rotation of 0·1*M*-sodium tartrate solution was 6·0°. In consequence of the

above observations, it was considered that any relationship which might exist between optical activity and the degree of ionisation would best be observed with 0·1M-tartaric acid solutions, despite the relatively large inaccuracies in the optical measurements.

3. *Neutralisation of* 0·1M-*Tartaric Acid with Sodium Hydroxide at* 25°.—A series of tartaric acid solutions were prepared such that they corresponded to 0·1M-tartaric acid in increasing degrees of neutralisation. Their p_H values and rotations were determined and are recorded in Table III; col. 4 gives the molecular rotation calculated from the data in respect of the total concentration of tartaric acid, free and neutralised, and col. 5 gives the rotations which were

TABLE III.

Solutions 0·1M-*tartaric acid and* xM-*sodium hydroxide.*

(A) $[M_{H_2T, undiss.}]^{25°}_{5461} = 2·18°$; $[M_{HT'}]^{25°}_{5461} = 5·51°$; $[M_{T''}]^{25°}_{5461} = 7·0°$.

NaOH, xM.	p_H.	a_{5461}, obs.	$[M]^{25°}_{5461}$. Obs.	Calc.	NaOH, xM.	p_H.	a_{5461}, obs.	$[M]^{25°}_{5461}$. Obs.	Calc.
0	1·90	1·04°	2·60°	2·48°	0·12	3·68	2·17°	5·43°	5·60°
0·02	2·37	1·30	3·25	2·93	0·14	3·94	2·31	5·78	6·10
0·04	2·73	1·51	3·77	3·55	0·16	4·20	2·45	6·13	6·35
0·06	2·99	1·70	4·25	4·13	0·18	4·52	2·62	6·55	6·63
0·08	3·24	1·88	4·70	4·70	0·20	9·22	2·80	7·00	7·00
0·10	3·48	2·04	5·10	5·20	0·25	12·40	2·80	7·00	7·00

(B) $[M_{H_2T,undiss.}]^{25°}_D = 2·00°$; $[M_{HT'}]^{25°}_D = 4·50°$; $[M_{T''}]^{25°}_D = 6·0°$.

NaOH, xM.	p_H.	a_D, obs.	$[M]^{25°}_D$. Obs.	Calc.	NaOH, xM.	p_H	a_D, obs.	$[M]^{25°}_D$. Obs.	Calc.
0	1·90	0·90°	2·25°	2·23°	0·15	4·06	2·08°	5·20°	5·20°
0·0514	2·87	1·28	3·20	3·25	0·20	9·22	2·40	6·00	6·00
0·101	3·48	1·73	4·33	4·35					

computed by assuming the additivity of the molecular rotations of the two tartrate ions and of the undissociated acid. The following is an outline of the mode of calculation. The principle of additivity is expressed in the equation

$$[M] = \frac{[H_2T]}{C_{H_2T}} [M_{H_2T}] + \frac{[HT']}{C_{H_2T}} [M_{HT'}] + \frac{[T'']}{C_{H_2T}} [M_{T'}]$$

in which $[M]$ is the apparent molecular rotation, and $[H_2T]$, $[HT']$, and $[T'']$ refer to the concentrations of the respective molecular and ionic species, C_{H_2T} being the total concentration of tartaric acid. The following equations hold for the ionisation of tartaric acid :

$$K_1 = [H^·][HT']/[H_2T]; \quad K_2 = [H^·][T'']/[HT']$$
$$C_{H_2T} = [H_2T] + [HT'] + [T''],$$

and from these are derived equations for the proportions of the total acid existing in various forms, from which it is clear that the latter can be calculated from K_1, K_2, and $[H^·]$:

$$[H_2T]/C_{H_2T} = 1/(1 + K_1/[H^·] + K_1K_2/[H^·]^2)$$
$$[HT']/C_{H_2T} = 1/(1 + [H^·]/K_1 + K_2/[H^·]^2)$$
$$[T'']/C_{H_2T} = 1/(1 + [H^·]/K_2 + [H^·]^2/K_1K_2)$$

For a solution of tartaric acid, C_{H_2T}, undergoing neutralisation with sodium hydroxide,

$$C_{H_2T} = [H_2T] + [HT'] + [NaHT] + [T''] + [Na_2T],$$

[NaHT] and [Na$_2$T] representing the concentrations of the undissociated salts present. Provided that the solution be sufficiently dilute, the ionisation of the salts formed may be assumed to be complete. Hence the foregoing relationships may be expected to hold throughout the neutralisation of the tartaric acid.

Taking into consideration the relative magnitude of the errors involved in measuring the rotation of these dilute solutions, it is considered that the agreement between experimental and calculated rotations is satisfactory and certainly justifies the assumptions made regarding the additive property of the three active constituents present during the neutralisation of tartaric acid.

It is interesting to compare the values here obtained with the D line (5890—5894 Å.) for the molecular rotations of tartaric acid and the hydrogen tartrate and tartrate ions with those " obtenu par tâtonnement " for 5770—5791 Å. by Vlès and Vellinger. Whereas we find (by experiment) 2·00°, 4·50°, and 6·0° respectively, the corresponding values found by these workers to fit the observed rotations during the neutralisation of tartaric acid solutions at the concentrations 0·5, 0·25, and 0·10M (temperature not given) were 2·00°, 5·9°, and 6·11°.

Effect of Sodium Chloride.—As neutral salts, particularly sodium chloride, will be present in some of the complex tartaric acid and tartrate solutions to be described later, some observations have been made on the effect of various proportions of this salt on the optical activity of 0·1M-tartaric acid and 0·1M-sodium tartrate solutions, and our results on the former are given below :

NaCl, xM	0	0·1	1·0	2·0
a_{5461}, obs.	1·05°	1·04°	0·86°	0·65°
$[M_{H_2T}]^{25°}_{5461}$	2·63°	2·60°	2·15°	1·63°

The reduction in the molecular rotation might be due to two causes : (*a*) repression of ionisation of the acid and (*b*) the hydration of the sodium chloride molecules. The latter is more probable, especially if the tartaric acid is unable to dissolve in the " solvated " water.

Darmois (*Ann. Physique*, 1928, **10**, 70; *Compt. rend.*, 1927, **184**, 1239, 1438) found that calcium chloride affected tartaric acid, and also that with the mercury yellow line neutral alkali salts influence the rotation of alkali tartrates, the effect of potassium chloride being to increase, and that of sodium chloride to decrease, the rotation. Our data for 0·1M-sodium tartrate and xM-sodium chloride are given below :

NaCl, xM.	$a^{25°}_{5461}$, obs.	$[M_{Na_2T}]^{25°}_{5461}$.	$a^{25°}_D$, obs.	$[M_{Na_2T}]^{25°}_D$.	NaCl, xM.	$a^{25°}_{5461}$, obs.	$[M_{Na_2T}]^{25°}_{5461}$.	$a^{25°}_D$, obs.	$[M_{Na_2T}]^{25°}_D$
0	2·81°	7·02°	2·40°	6·00°	1·0	2·73°	6·83°	2·35°	5·87°
0·5	2·76°	6·90°	2·39°	5·97°	2·0	2·67°	6·67°	2·32°	5·80°

Cols. 3 and 5 indicate that sodium chloride reduces the molecular rotation of sodium tartrate in a fashion similar to that shown in Table II. The diminutions are undoubtedly due to the same cause, *viz.*, the common sodium kation and the fact that it is heavily hydrated. This explanation is supported, at least qualitatively, by comparing the concentrations of the solutions which give the same molecular rotations in the above table and in Table II; *e.g.*, both 0·1M-sodium tartrate plus 0·5M-sodium chloride and 0·3M-sodium tartrate give + 6·90° for $[M_{Na_2T}]^{25°}_{5461}$, and these solutions contain respectively 0·7 and 0·6 equiv. of sodium. In view of the probability that factors other than the hydration of the sodium ions, *e.g.*, activity or ionisation, come into play in the rotatory power of the above solutions, the data show that the like rotations of the two pairs of solutions are to be ascribed in a large measure to the sodium concentration.

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