405. *The Ionisation Constants of the Tartaric Acids and the Nature of the Borotartaric Acids.*

By ISLWYN JONES and F. G. SOPER.

THE ionisation constants of the active tartaric acids have been measured by a variety of methods and the more recent determinations are in good agreement with each other. No determinations of these constants of the *meso*-acid have been made by the electrometric method, and as they were required in order to compare the ratio of the first and the second ionisation constant of the *d*- and the *meso*-acid, an electrometric study of both acids has been carried out using a form of cell which eliminates any liquid–liquid junction. Measurements were made at a series of ionic strengths and the thermodynamic ionisation constants were deduced therefrom. Both have also been measured over the temperature range 25—75°.

The results obtained, together with those of previous workers, are shown in Table I.

TABLE I.

Ionisation Constants of d- *and* meso-*Tartaric Acids.*

T.	$K_1 \times 10^3$.	$K_2 \times 10^5$.	Ref.	T.	$K_1 \times 10^3$.	$K_2 \times 10^5$.	Ref.
				d-*Tartaric acid.*			
25°	0·97		O., B. & W.	25°	0·97	2·8	P2.
25		4·5	W.	25		3·94	D. & F.
25		3·43	McC.	25	0·96	2·8	K. & B.
25		6·9	D. & D.	25	1·04	4·55	J. & S.
76		3·0—3·6	P1.	50	1·14	4·06	,,
25	1·02		B.	74	0·98	3·08	,,
25	0·896	7·46	A. & S.				
				meso-*Tartaric acid.*			
25	0·6		W.	25	0·60	1·53	J. & S.
25	0·63	1·4	H.	50	0·73	1·46	,,
				74	0·52	1·26	,,

References.—O. = Ostwald, *Z. physikal. Chem.*, 1889, **3**, 372; B. & W. = Bischoff and Walden, *ibid.*, 1891, **8**, 466; W. = Wegscheider, *Monatsh.*, 1902, **23**, 635; McC. = McCoy, *Amer. Chem. J.*, 1908, **30**, 694; D. & D. = Datta and Dhar, J., 1915, **107**, 826; P1. = Paul, *Z. Elektrochem.*, 1915, **21**, 552; B. = Böeseken, *Rec. trav. chim.*, 1918, **37**, 181; A. & S. = Auerbach and Smolczyk, *Z. physikal. Chem.*, 1924, **110**, 65; P2. = Paul, *ibid.*, p. 417; D. & F. = Duboux and Frommelt, *J. Chim. physique*, 1927, **24**, 245; K. & B. = Kolthoff and Bosch, *Rec. trav. chim.*, 1928, **47**, 861; W. = Walden, *Ber.*, 1896, **29**, 1702; H. = Holmberg, *J. pr. Chem.*, 1911, **84**, 166; J. & S. = present communication.

With increasing temperature, the secondary ionisation constants of the two acids decrease, and the primary constants increase to a maximum and then decrease. The difference in the primary ionisation constants of the two acids, like that of the electric moments of the ethers (Wolf, *Trans. Faraday Soc.*, 1930, **26**, 319), indicates the absence of free rotation and is in harmony with a type of internal co-ordination suggested by Lowry and Burgess (J., 1923, **123**, 2111) and Lowry and Austin (*Nature*, 1924, **114**, 431). Two formulæ have been suggested, (I) and (II), but (II) is the more probable, since, owing to the

smallness of the hydrogen atom, 5-membered rings involving this atom would be associated with considerable strain.*

When models of the *d*- and the *meso*-acid are constructed, it is immediately apparent that structure (II) is strainless for the active acid but not for the *meso*-acid; some of the latter may therefore exist in form (III), and, in effect, will not be so highly co-ordinated
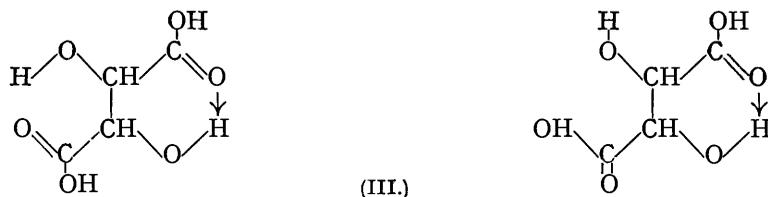
as the active acid. Since co-ordination of the carbonyl oxygen causes electron recession from the carbonyl carbon and facilitates the ionisation, the *d*-acid should have the higher primary ionisation constant, as is observed.

* Since this paper was submitted, Ferrell, Ridgion, and Riley (this vol., p. 1447) have measured the extent to which copper ions are removed by the *d*- and *meso*-tartrate ions. The affinity for copper ions follows the order of affinity for hydrogen ions. The authors point out that the difference cannot be explained if the internal co-ordination is of type (I), but is in harmony with formula (II).

This view also serves to explain the difference in the ratio K_1/K_2 for the two acids, which is 39·4 for the *meso-* and 22·8 for the *d*-acid. If the former exists as (III), the first ionisation stage favours the ionisation of the co-ordinated carboxyl group, leaving a greater proportion of unco-ordinated carboxyl groups for the second ionisation stage. There is therefore a greater difference between the secondary than between the primary ionisation constants of the two acids. An additional factor which may further diminish the second ionisation constant of the *meso*-acid relative to that of the *d*-acid also results from the difference in co-ordination. The smaller co-ordination in the *meso*-acid permits of greater freedom of rotation of one of the carboxyl groups, causing the mean distance of the ionising groups in this acid to be less than in the *d*-acid, with the resulting Bjerrum effect.

The Influence of Boric Acid.—The effect of boric acid on the tartaric acids is of interest with regard both to the normal configuration of these acids (Böeseken and Coops, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **29**, 368; Böeseken, *ibid.*, p. 562) and to the suppression of the anomalous rotatory dispersion of tartaric acid (Lowry and Austin, *Phil. Trans.*, 1922, **222**, *A*, 249). Böeseken and Coops claim that boric acid has a greater effect on the active acids than on the *meso*-acid, and regard this as an indication of the juxtaposition of the hydroxyl groups in the former acids (*cf.* Goldschmidt, " Stereochemie," Leipzig, 1933) :

Active.   Meso-.
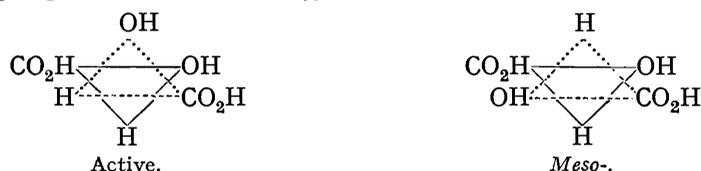
This claim is based on the increased conductivity of a solution of 0·5*M*-boric acid on addition of various concentrations of the active and *meso*-acids; *e.g.*, in presence of 0·5*M*-boric acid, κ for $M/256$-solutions of *d*- and *meso*-acid is 302 and 248 units respectively, increasing to 55,280 and 53,950 units respectively for *M*-tartaric acid. Amadori (*Gazzetta*, 1931, **61**, 215), however, points out that, although the actual increase in conductivity is greater for the *d*- than for the *meso*-acid (54,878 and 53,702 units respectively), yet the ratio of the conductivity of the former to that of the latter, which is 1·25 over a wide range of concentration, is actually decreased by the presence of 0·5*M*-boric acid and, in the *M*-tartaric acid mixtures, has fallen to 1·02; he therefore regards boric acid as having a greater effect on the *meso*-acid.

Electrometric titrations of *d*- and *meso*-tartaric acids in the presence of various amounts of boric acid have now been carried out. Increasing concentration of boric acid causes the titration curves for the two acids to approach each other for the first neutralisation stage, and for the 0·5*M*-boric acid and 1·0*M*-tartaric acid mixture, the *meso*-acid has slightly the higher hydrogen-ion concentration. In more dilute tartaric acid solutions and excess boric acid, the hydrogen-ion concentrations also approximate very closely. These observations support Amadori's conclusions that boric acid has the greater effect on the weaker *meso*-acid.

If the effect of the boric acid is to bridge the hydroxyl groups and to force these into contiguous positions in the case of the *meso*-acid, the configuration of the complex acids would be (IV) and (V), on Böeseken's quadrivalent boron conception (*Proc. K. Akad.*

(IV; active.)   (V; meso-.)

Wetensch. Amsterdam, 1923, **26**, 97; 1924, **27**, 174). An objection is that the interference of the carboxyl groups in the *meso*-acid complex would make this complex less readily

formed than that from the active acid. A further objection rests on the behaviour observed on addition of a second equivalent of alkali to the borotartaric acid; this addition ionises a carboxyl group and, from the spatial similarity of the carboxyl groups in the complex to those in maleic and fumaric acids, its ionisation constant should be greater for the *meso*- than for the *d*-acid complex. The titration curves (see fig.) show no evidence of this, but, instead, the opposite effect.
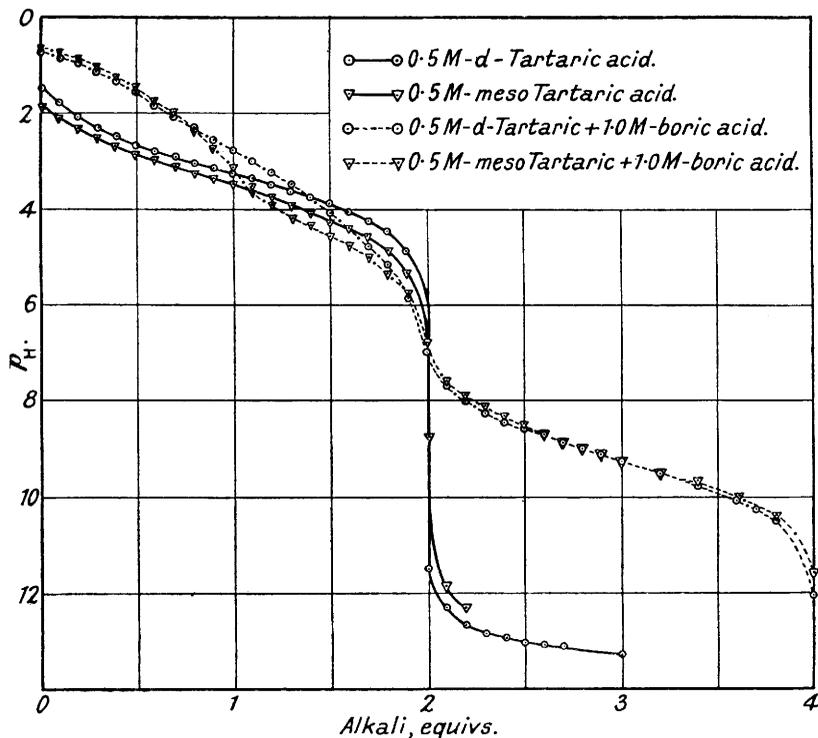
Amadori's conclusion, based on conductivity experiments, was that the borotartaric acid complex involved 2 mols. of boric acid to each mol. of tartaric acid, each boric acid molecule forming a ring with the hydroxyl and carboxyl groups attached to the same asymmetric carbon atom (VI) and so forming complexes from the *d*- and *meso*-acids of similar ionisation constants.

(VI.)   (VII.)
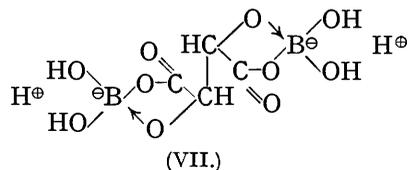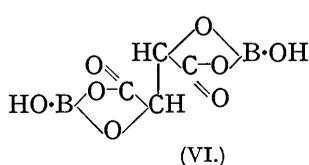
An alternative formulation is (VII), but neither explains the fact (Burgess and Hunter, J., 1929, 2838; Lowry, *ibid.*, p. 2857) that, whereas the first ionisable hydrogen in the complex is electrovalent and similar to the first ionisable hydrogen in sulphuric acid, the second hydrogen is less ionised than in tartaric acid alone. Lowry, in view of the isolation of the solid potassium borotartrate (*ibid.*, p. 2856), in which 1 mol. of boric acid is associated with 2 mols. of tartaric acid, formulates the complex as (VIII). It is possible also that this dissociates to form a dibasic one in which the tartaric and boric acids are equimolar (IX), where the strong acid nature is preserved. The weaker nature of the carboxyl group in (VIII) and (IX), compared with that in tartaric acid, is easily understood, since co-ordination with boric acid prevents the internal co-ordination of types (II) and (III) which

facilitates ionisation. In addition, there may exist a Bjerrum effect, since the planar configuration of the boric acid portion of the complex increases the free rotation and causes
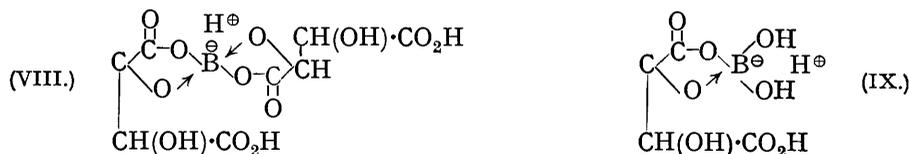
the average distance of the ionising carboxyl group from the negative centre to be less than in the second ionisation stage of tartaric acid itself. The greater effect of boric acid on the *meso*-acid is noteworthy (see fig.). It is to be attributed to the greater ease of formation of the boro-*meso*-acid complex, owing to the lesser degree of internal co-ordination which obtains in the *meso*-acid. This internal co-ordination competes against the formation of the boro-complex, and has already provided an explanation of the difference in the ionisation constants of the active and the *meso*-acid.

It is probable that (VII), (VIII), and (IX) all exist in solution. Predominance of type (IX) under certain conditions is in agreement with the observations of Burgess and Hunter, who found that the maximum rotatory power per mol. of solutions containing both boric and tartaric acids occurred in the equimolar solution; (VII) appears to exist in solutions containing excess of boric acid, where it is found that the second ionisation stage of the complex is associated with a higher hydrogen-ion concentration than that of tartaric acid itself. This change in behaviour when passing to solutions containing excess of boric acid is shown in Table III.

On neutralisation of tartaric acid, negative charge accumulates in the carbonyl group and results in an increased tendency to internal co-ordination. This militates against the formation of boric acid complexes and accounts for its decomposition in weak alkaline solution. The same explanation applies to the smaller amount of complex formation in dilute tartaric acid solutions, where the tartaric acid is ionised.

EXPERIMENTAL.

The cell used was of the type, $H_2(Pt)|$tartaric acid + tartrate, cM-NaCl$|$AgCl,Ag, all solutions, including the standard alkali used for titration, containing chloride at some fixed concentration, c. A similar type of cell has been used by Harned and Robinson (*J. Amer. Chem. Soc.*, 1928, **50**, 3157) and Harned and Owen (*ibid.*, 1930, **52**, 5079) for the determination of ionisation constants of weak acids and bases. The hydrogen electrode was prepared according to the directions of Ellis (*ibid.*, 1916, **38**, 737), and the silver chloride electrode according to Carmody (*ibid.*, 1929, **51**, 2901). The capacity of the titration cell was 200—300 c.c.

The results obtained for the e.m.f., $E_{0.001}$, of the reference cell, $H_2(Pt)|N/1000$-HCl$|$Ag,AgCl, from 25° to 75° are given below; they are not corrected for the partial pressure of the water vapour, but refer to a total pressure of 760 mm. :

E.m.f. of the hydrogen–silver chloride cell.

Temp.	25·0°	35·0°	46·8°	57·0°	64·8°	74·8°
E.m.f., volts	0·5793	0·5847	0·5897	0·5920	0·5931	0·5929

The hydrogen-ion concentration of the tartaric mixtures was determined from the e.m.f. of cells in which the chloride concentration was 0·001M. If the e.m.f. observed (corrected to a total pressure of 760 mm.) is E_1, the concentration of hydrogen-ion in the solution is given by :

$$- \log[\text{H}^\cdot] = (E_1 - E_{0.001})/0\cdot0001983T + 3\cdot00 + 2\log f_1/f_{0.001}$$

where f_1 is the mean activity coefficient of the hydrogen and the chlorine ions in the tartaric acid solution, and $f_{0.001}$ (= 0·965) is that in the hydrochloric acid solution. The activity coefficients, calculated from the Debye–Hückel theory,* for the ionic strengths obtaining in

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* By means of the formula $-\log f = A z^2 \sqrt{\mu}/(1 + aB\sqrt{\mu})$, where A and B have the values 0·504 and 0·328 at 25°, 0·548 and 0·338 at 50°, 0·620 and 0·348 at 74°, respectively, and a, the mean effective diameter of the ions, has the value 4 Å.

the solutions examined, are shown with other data in Table II ([H₂T] representing the tartaric acid concentration); those for bivalent ions, required for the evaluation of the secondary ionisation constants, are also included. The primary thermodynamic ionisation constant, K_1^a, is evaluated as $[H\cdot][HT']f_1^2/[H_2T]$, and the secondary ionisation constant, K_2^a, as $[H\cdot][T'']f_2/[HT']$, where f_2 is the activity coefficient of a bivalent ion.

The second ionisation constant was first evaluated by the method of Auerbach and Smolczyk (*loc. cit.*). This constant and the equations $[H_2T] + [HT'] + [T''] = c$ and $[Na\cdot] + [H\cdot] = [HT'] + 2[T'']$, then allow of the evaluation of K_1 which is insensitive to a small error in K_2. The accurate evaluation of K_2 then follows from K_1, the two equations above, and the hydrogen-ion concentrations in the more alkaline solutions. This method is similar to that used by Kolthoff and Bosch (*loc. cit.*).

TABLE II.

$[H_2T]$ × 10³	$[NaOH]$ × 10³	Ionic strength.	$T.$	E.m.f.	$\log f_1$.	$\log f_2$.	K_1^a × 10³	K_2^a × 10⁵.
				d-Tartaric acid + 0·001*M*-NaCl.				
10·0	5·0	0·006	25·0°	0·5818	$\bar{1}$·965		1·025	
5·0	2·5	0·0035	25·0	0·5871	$\bar{1}$·972		1·030	
2·5	1·25	0·00225	25·0	0·5941	$\bar{1}$·977		1·044	
1·25	0·625	0·00162	25·0	0·6036	$\bar{1}$·980		1·045	
10·0	15·0	0·0160	25·0	0·6498	$\bar{1}$·944	$\bar{1}$·776		4·51
5·0	7·5	0·0085	25·0	0·6526	$\bar{1}$·958	$\bar{1}$·832		4·56
2·5	3·75	0·00475	25·0	0·6550	$\bar{1}$·969	$\bar{1}$·876		4·58
1·25	1·875	0·00287	25·0	0·6576	$\bar{1}$·975	$\bar{1}$·900		4·54
10·0	5·0	0·006	50·0	0·5911	$\bar{1}$·961		1·122	
5·0	2·5	0·0035	50·0	0·5958	$\bar{1}$·970		1·130	
2·5	1·25	0·00225	50·0	0·6027	$\bar{1}$·975		1·139	
1·25	0·625	0·00162	50·0	0·6126	$\bar{1}$·978		1·155	
10·0	15·0	0·0160	50·0	0·6693	$\bar{1}$·939	$\bar{1}$·756		4·02
5·0	7·5	0·0085	50·0	0·6715	$\bar{1}$·955	$\bar{1}$·820		4·12
2·5	3·75	0·00475	50·0	0·6736	$\bar{1}$·966	$\bar{1}$·864		4·12
1·25	1·875	0·00287	50·0	0·6762	$\bar{1}$·973	$\bar{1}$·892		4·01
10·0	5·0	0·006	74·0	0·5968	$\bar{1}$·957		0·970	
5·0	2·5	0·0035	74·0	0·6011	$\bar{1}$·966		0·985	
2·5	1·25	0·00225	74·0	0·6095	$\bar{1}$·972		0·983	
1·25	0·625	0·00162	74·0	0·6221	$\bar{1}$·975		0·988	
10·0	15·0	0·0160	74·0	0·6840	$\bar{1}$·931	$\bar{1}$·724		3·03
5·0	7·5	0·0085	74·0	0·6868	$\bar{1}$·949	$\bar{1}$·796		3·14
2·5	3·75	0·00475	74·0	0·6904	$\bar{1}$·961	$\bar{1}$·864		3·15
1·25	1·875	0·00287	74·0	0·6936	$\bar{1}$·970	$\bar{1}$·880		3·00
				meso-Tartaric acid + 0·001*M*-NaCl.				
10·0	5·0	0·0060	25·0	0·5933	$\bar{1}$·965		0·596	
5·0	2·5	0·0035	25·0	0·5952	$\bar{1}$·972		0·621	
2·5	1·25	0·00225	25·0	0·6014	$\bar{1}$·977		0·608	
1·25	0·625	0·00162	25·0	0·6101	$\bar{1}$·980		0·598	
10·0	15·0	0·0160	25·0	0·6777	$\bar{1}$·944	$\bar{1}$·776		1·51
5·0	7·5	0·0085	25·0	0·6789	$\bar{1}$·958	$\bar{1}$·832		1·58
2·5	3·75	0·00475	25·0	0·6819	$\bar{1}$·969	$\bar{1}$·876		1·56
1·25	1·875	0·00287	25·0	0·6848	$\bar{1}$·975	$\bar{1}$·900		1·49
10·0	5·0	0·0060	50·0	0·6011	$\bar{1}$·961		0·734	
5·0	2·5	0·0035	50·0	0·6072	$\bar{1}$·970		0·730	
2·5	1·25	0·00225	50·0	0·6134	$\bar{1}$·975		0·730	
1·25	0·625	0·00162	50·0	0·6229	$\bar{1}$·978		0·742	
10·0	15·0	0·0160	50·0	0·6967	$\bar{1}$·939	$\bar{1}$·756		1·42
5·0	7·5	0·0085	50·0	0·6998	$\bar{1}$·955	$\bar{1}$·820		1·48
2·5	3·75	0·00475	50·0	0·7015	$\bar{1}$·966	$\bar{1}$·864		1·49
1·25	1·875	0·00287	50·0	0·7047	$\bar{1}$·973	$\bar{1}$·892		1·43
10·0	5·0	0·0060	74·0	0·6108	$\bar{1}$·957		0·519	
5·0	2·5	0·0035	74·0	0·6153	$\bar{1}$·966		0·525	
2·5	1·25	0·00225	74·0	0·6219	$\bar{1}$·972		0·519	
1·25	0·625	0·00162	74·0	0·6316	$\bar{1}$·975		0·519	
10·0	15·0	0·0160	74·0	0·7093	$\bar{1}$·931	$\bar{1}$·724		1·22
5·0	7·5	0·0085	74·0	0·7126	$\bar{1}$·949	$\bar{1}$·796		1·27
2·5	3·75	0·00475	74·0	0·7158	$\bar{1}$·961	$\bar{1}$·864		1·28
1·25	1·875	0·00287	74·0	0·7187	$\bar{1}$·970	$\bar{1}$·880		1·25

Titration of Mixtures of Boric and Tartaric Acids.—Titration of the tartaric acids at concentrations of 0·02*M*, 0·2*M*, and 0·5*M* in the presence of various concentrations of boric acid was carried out, the sodium hydroxide solution used containing chloride ions at the same con-

centration as in the solution of acids in the cell. The marked intersection of the titration curves which occurs when 0·5M-tartaric acid is titrated alone and in the presence of 1·0M-boric acid (see fig.) is absent when a greater molecular excess of boric acid is used; *e.g.*, with 0·02M-tartaric acids intersection still occurs when the boric acid is 0·04M, but is absent when its concentration is 0·08—0·8M. In the presence of this excess of boric acid, there is no evidence of a weaker secondary ionisation (in comparison with tartaric acid) of the borotartaric acid complex, a fact which indicates the formation of Amadori's complex (VII). The results of the titrations of 0·8M-boric acid + 0·02M-tartaric acid are given in Table III.

TABLE III.

Titration of 0·02M-*tartaric acid* + 0·8M-*boric acid.*

	p_H of			
NaOH, equivs.	*d*-Acid.	*d*-Acid + H_3BO_3.	*meso*Acid.	*meso*Acid + H_3BO_3.
0·0	2·301	1·890	2·507	1·972
0·2	2·515	2·040	2·731	2·137
0·5	2·844	2·273	3·100	2·416
1·0	3·380	2·770	3·737	2·969
1·3	3·719	3·111	4·158	3·354
1·6	4·101	3·523	4·588	3·789
2·0	5·231	4·622	4·809	4·815

The enhanced hydrogen-ion concentration in the presence of boric acid during the secondary neutralisation stage is not appreciably affected by the ionisation of the boric acid itself ($K_1 = 5·8 \times 10^{-10}$; Owen, *J. Amer. Chem. Soc.*, 1934, **56**, 1697), until nearly the full 2 equivs. of alkali have been added. The results obtained with 0·2M-tartaric acids are similar to those with 0·5M-tartaric acids.