

## The Dissociation Constants of Dihydroxytartaric and Tartronic Acids

KAI JULIUS PEDERSEN

*Chemical Laboratory, Royal Veterinary and Agricultural College, Copenhagen, Denmark*

The first and the second dissociation constant of dihydroxytartaric acid at 25° C, and the first and the second dissociation constant of tartronic acid at 25 and 37° C, have been determined by measuring hydrogen ion concentrations by means of the glass electrode in solutions containing various concentrations of potassium chloride. Formulae expressing the dissociation constants as functions of the ionic strength of the solutions are given. The activity dissociation constants have been estimated by extrapolation to zero ionic strength.

Dihydroxytartaric acid decomposes in aqueous solution into tartronic acid and carbon dioxide. In a kinetic study of this reaction reported in the following paper<sup>1</sup>, it was of importance to know the dissociation constants of the two organic acids. They were therefore determined by means of the glass electrode in solutions containing potassium chloride. While the two dissociation constants of tartronic acid were determined both at 25 and 37° C, those of dihydroxytartaric acid were, owing to the too rapid decarboxylation at 37°, only determined at 25° C.

The sparingly soluble di-sodium salt of dihydroxytartaric acid was prepared by the method of Filippo<sup>2</sup>. It was purified in the following way. The crude salt was dissolved in twice the equivalent amount of 2 M hydrochloric acid at about 5° C. The solution was filtered and added an excess of 2 M sodium acetate. The precipitate was isolated by suction and washed with a large amount of redistilled water. Since it has been found by Lachman<sup>3</sup> that the salt has an enormous tendency to occlude other salts, the washing was continued long after the filtrates failed to give an opalescence with silver nitrate. The crystals were dried in the air and, finally, in vacuum over concentrated sulphuric acid. When samples of the dry product were ignited in a platinum crucible, the residue dissolved in hydrochloric acid, and the solution titrated back with sodium hydroxide, a molecular weight of 263.1 was found, while 262.1 is calculated for the formula  $[C(OH)_2COONa]_2 \cdot 2H_2O$ . The purified preparation contained less than 0.05 % sodium chloride as shown by Volhard titration.

Tartrate buffers were prepared by complete decarboxylation of solutions of dihydroxytartrate. The other chemicals used were of analytical purity. Redistilled water was used to make up the solutions.

The measurements were carried out and the hydrogen ion concentrations computed by the same procedure as that followed by the author in an earlier paper<sup>4</sup>. In the following tables,  $E$  denotes the e.m.f. in volts (measured by means of the glass electrode) of the cell



where X denotes the solution under investigation, while S is always the solution: 0.00999 molar HCl, 0.0900 molar NaCl. The composition of solution X may be expressed as



where T denotes either dihydroxytartrate or tartronate.

#### THE DISSOCIATION CONSTANTS OF DIHYDROXYTARTARIC ACID

Dihydroxytartrate buffers were prepared by weighing out the sodium salt and dissolving it in a solution containing appropriate amounts of hydrochloric acid and potassium chloride. The cell was made up, and the measurements were started as quickly as possible, in general about 8 minutes after the salt was dissolved. Readings were taken with short intervals for about half an hour. Owing to decarboxylation,  $E$  increased gradually with a rate which varied with the composition of the solution examined (from 0.02 to 0.15 millivolts per minute). The values of  $E$  given in Table 1 were found by extrapolation of the readings to the time when the salt was dissolved.

Three series of solutions were measured; within each the ionic strength  $I$  was nearly constant. The results are shown in Table 1 where the hydrogen ion concentrations  $h$  obtained directly from the measurements are given in the next to the last column. The first and the second dissociation constant of dihydroxytartaric acid,  $K_1$  and  $K_2$ , respectively, were computed from the data in the following way. From the two equations

$$[\text{H}_2\text{T}] + [\text{HT}^-] + [\text{T}^{--}] = b$$

and

$$2[\text{H}_2\text{T}] + [\text{HT}^-] = a - h$$

and the usual expressions for  $K_1$  and  $K_2$ , we derive the equation

$$\frac{(2b-a+h)h^2}{a-h} = K_1K_2 + \frac{(a-b-h)h}{a-h} K_1 \quad (1)$$

As a first approximation, we neglect the small variation of  $K_1$  and  $K_2$  within a series. By means of eqn. (1) we compute graphically the constants  $K_1$  and  $K_1K_2$  for each of the three series. A correction for the influence of the small variation in ionic strength within a series was made in the following way. Eqn. (1) was written as

$$\frac{(2b-a+h)h^2}{a-h} f_1 f_2 = K_{1m} K_{2m} + \frac{(a-b-h)h}{a-h} f_2 K_{1m} \quad (2)$$

Table 1. Measurements of hydrogen ion concentrations in dihydroxytartrate buffers at 25° C.

<i>a</i>	<i>b</i>	<i>s</i>	<i>I</i>	<i>E</i>	—log <i>h</i> (found)	—log <i>h</i> (calc.)
0.02999	0.01502	0.0700	0.1106	—0.0002	1.985	1.986
0.02744	0.01499	0.0700	0.1089	0.0048	2.070	2.070
0.02000	0.01000	0.0800	0.1079	0.0077	2.118	2.117
0.01499	0.01002	0.0800	0.1046	0.0243	2.400	2.397
0.00999	0.00498	0.0900	0.1047	0.02175	2.356	2.354
0.00747	0.00505	0.0900	0.1030	0.0368	2.609	2.613
0.00499	0.00497	0.0900	0.1021	0.0605	3.011	3.011
0.03001	0.01502	0.1700	0.2110	—0.0005	1.972	1.972
0.02747	0.01505	0.1700	0.2093	0.0042	2.052	2.055
0.01998	0.01000	0.1800	0.2082	0.0075	2.107	2.105
0.01499	0.01000	0.1800	0.2049	0.0233	2.375	2.375
0.00999	0.00498	0.1900	0.2048	0.02155	2.344	2.342
0.00747	0.00502	0.1900	0.2031	0.03595	2.589	2.591
0.00499	0.00498	0.1900	0.2023	0.05875	2.976	2.972
0.03002	0.01504	0.2700	0.3112	—0.00095	1.966	1.964
0.02744	0.01500	0.2700	0.3094	0.00395	2.049	2.045
0.02498	0.01501	0.2700	0.3080	0.0090	2.134	2.137
0.01999	0.01003	0.2800	0.3084	0.0067	2.094	2.098
0.01748	0.01003	0.2800	0.3066	0.0140	2.218	2.216
0.01499	0.01003	0.2800	0.3051	0.02265	2.364	2.364
0.01200	0.00998	0.2800	0.3038	0.03675	2.603	2.599
0.00999	0.00504	0.2900	0.3050	0.02095	2.334	2.340
0.00747	0.00508	0.2900	0.3033	0.03535	2.578	2.584
0.00499	0.00503	0.2900	0.3024	0.0576	2.957	2.950

where  $K_{1m}$  and  $K_{2m}$  denote the values of  $K_1$  and  $K_2$  corresponding to the average value of the ionic strength in the series ( $I$  given in Table 2), while  $f_1$  denotes the ratio  $K_{1m}/K_1$  and  $f_2$  the ratio  $K_{2m}/K_2$ . The ratios  $f_1$  and  $f_2$ , which are both very close to unity, were computed by means of the expressions (3) and (4) (or, actually, from preliminary expressions practically identical with these). Finally, the constants  $K_{1m}$  and  $K_{1m}K_{2m}$  were computed graphically by means of eqn. (2). The dissociation constants thus obtained are shown in the third and fifth column of Table 2, while the corresponding ionic strengths are given in the second column. For simplicity, the subscripts  $m$  have been omitted. In order to demonstrate the agreement with the experimental data, the values found for  $K_1$  and  $K_2$  were introduced into eqn. (2), and  $h$  was calculated for all the solutions examined. The results obtained are given in the last column of Table 1.

Table 2. The first and the second dissociation constant of dihydroxytartaric acid at 25° C

Series	<i>I</i>	—log $K_1$	—log $K_1$ (calc.)	—log $K_2$	—log $K_2$ (calc.)
1	0.1060	1.694	1.696	3.513	3.518
2	0.2062	1.642	1.640	3.435	3.422
3	0.3063	1.612	1.613	3.378	3.385

Table 3. The first dissociation constant of tartronic acid at 25° C.

<i>a</i>	<i>b</i>	<i>s</i>	<i>I</i>	<i>E</i>	$-\log h$	$-\log K_1$	$-\log K_1$ (calc.)
0.02999	0.01502	0.0700	0.1076	0.0077	2.120	2.114	2.116
0.02744	0.01500	0.0700	0.1060	0.01395	2.226	2.123	2.117
0.02000	0.01000	0.0800	0.1058	0.0148	2.239	2.118	2.116
0.01499	0.01002	0.0800	0.1028	0.0349	2.579	2.107	2.119
0.00999	0.00498	0.0900	0.1036	0.02755	2.454	2.113	2.119
0.00747	0.00506	0.0900	0.1018	0.0466	2.775	2.106	2.120
0.03002	0.01505	0.1700	0.2080	0.00715	2.102	2.061	2.062
0.02747	0.01505	0.1700	0.2063	0.01345	2.209	2.076	2.063
0.01998	0.01000	0.1800	0.2060	0.0145	2.226	2.072	2.063
0.01499	0.01000	0.1800	0.2030	0.0339	2.556	2.065	2.064
0.00999	0.00498	0.1900	0.2037	0.0274	2.444	2.079	2.064
0.00747	0.00502	0.1900	0.2019	0.0456	2.753	2.073	2.064
0.03002	0.01504	0.2700	0.3082	0.00655	2.093	2.034	2.038
0.02744	0.01500	0.2700	0.3064	0.0128	2.198	2.052	2.038
0.02498	0.01501	0.2700	0.3051	0.01915	2.306	2.033	2.038
0.01999	0.01003	0.2800	0.3061	0.0140	2.218	2.041	2.039
0.01748	0.01003	0.2800	0.3045	0.0223	2.358	2.033	2.038
0.01499	0.01003	0.2800	0.3031	0.0332	2.543	2.027	2.038
0.01200	0.00998	0.2800	0.3018	0.05295	2.879	2.031	2.038
0.00999	0.00504	0.2900	0.3037	0.0269	2.436	2.011	2.039
0.00747	0.00508	0.2900	0.3019	0.04555	2.752	2.041	2.038

As a result of the measurements we obtain the following formulae for the two dissociation constants of dihydroxytartaric acid at 25° C (the square-root terms have been calculated according to Debye and Hückel)

$$-\log K_1 = 1.947 - 1.013 \sqrt{I} + 0.74 I \quad (3)$$

$$-\log K_2 = 4.004 - 2.026 \sqrt{I} + 1.64 I \quad (4)$$

Values calculated by means of these formulae are, for comparison, given in the fourth and sixth column of Table 2. If we extrapolate to zero ionic strength by means of the formulae, we find the activity constants  $K_1 = 1.13 \times 10^{-2}$

Table 4. The first dissociation constant of tartronic acid at 37° C.

<i>a</i>	<i>b</i>	<i>s</i>	<i>I</i>	<i>E</i>	$-\log h$	$-\log K_1$	$-\log K_1$ (calc.)
0.02995	0.01500	0.0700	0.1076	0.00805	2.120	2.114	2.124
0.01995	0.00999	0.0800	0.1058	0.0155	2.243	2.125	2.125
0.00998	0.00500	0.0900	0.1035	0.02885	2.460	2.127	2.127
0.02995	0.01500	0.1700	0.2079	0.00745	2.104	2.067	2.069
0.01995	0.00999	0.1800	0.2060	0.01515	2.229	2.081	2.070
0.00998	0.00500	0.1900	0.2036	0.02865	2.449	2.085	2.071
0.02995	0.01500	0.2700	0.3082	0.00675	2.092	2.032	2.044
0.01995	0.00999	0.2800	0.3061	0.0146	2.220	2.052	2.045
0.00998	0.00500	0.2900	0.3037	0.02815	2.438	2.043	2.045

Table 5. The second dissociation constant of tartronic acid at 25° C.

<i>a</i>	<i>b</i>	<i>s</i>	<i>I</i>	<i>E</i>	$-\log h$	$-\log K_2$	$-\log K_2$ (calc.)
0.00748	0.01499	0.0700	0.1077	0.13445	4.264	4.247	4.247
0.004985	0.00999	0.0800	0.1051	0.1348	4.268	4.248	4.250
0.002492	0.004993	0.0900	0.1026	0.1357	4.282	4.254	4.252
0.00748	0.01499	0.1700	0.2077	0.1294	4.172	4.152	4.153
0.004985	0.00999	0.1800	0.2052	0.1298	4.178	4.155	4.154
0.002492	0.004993	0.1900	0.2026	0.1312	4.200	4.167	4.155
0.00748	0.01499	0.2700	0.3077	0.1261	4.117	4.096	4.116
0.004985	0.00999	0.2800	0.3052	0.1268	4.128	4.103	4.117
0.002492	0.004993	0.2900	0.3027	0.12855	4.156	4.121	4.116

and  $K_2 = 9.9 \times 10^{-5}$ . The only value reported in the earlier literature is  $K_1 = 1.24 \times 10^{-2}$  found in the year 1898 by Skinner<sup>5</sup> by conductance at 25° C.

#### THE DISSOCIATION CONSTANTS OF TARTRONIC ACID

Tartronate buffers for the glass electrode measurements were made up from solutions prepared as follows. Ten millimoles of sodium dihydroxytartrate were added to about 100 ml water containing 5 millimoles hydrochloric acid. The mixture was heated to 80° C, and was, under gentle agitation, kept at that temperature until all the sodium salt had gone into solution under evolution of carbon dioxide (about 15 minutes). The solution was left at room temperature for one or two days to secure complete decarboxylation. The remaining carbon dioxide was removed by a current of pure air, and the solution was diluted to 200 ml in a graduated flask.

The results of the measurements of the two dissociation constants at the temperatures 25 and 37° C are shown in Tables 3—6. In the computation of  $K_1$  from the experimental data given in Tables 3—4, a correction was made for the amount of divalent tartronate ion present by means of  $K_2$  calculated from formulae (7) — (8). Similarly, in the computation of  $K_2$  from the experimental data given in Tables 5—6, a correction was made for the amount of

Table 6. The second dissociation constant of tartronic acid at 37° C.

<i>a</i>	<i>b</i>	<i>s</i>	<i>I</i>	<i>E</i>	$-\log h$	$-\log K_2$	$-\log K_2$ (calc.)
0.00749	0.01499	0.0700	0.1077	0.1396	4.266	4.250	4.249
0.004985	0.00999	0.0800	0.1051	0.1402	4.274	4.254	4.253
0.002493	0.004996	0.0900	0.1026	0.14095	4.284	4.256	4.257
0.00749	0.01499	0.1700	0.2077	0.13425	4.169	4.150	4.144
0.004985	0.00999	0.1800	0.2052	0.13475	4.176	4.153	4.146
0.002493	0.004996	0.1900	0.2026	0.1351	4.180	4.146	4.148
0.00749	0.01499	0.2700	0.3077	0.1307	4.110	4.090	4.098
0.004985	0.00999	0.2800	0.3052	0.1313	4.119	4.094	4.099
0.002493	0.004996	0.2900	0.3027	0.3121	4.131	4.093	4.100

undissociated tartronic acid present by means of  $K_1$  calculated from formulae (5) — (6). The results of the computation of  $K_1$  and  $K_2$  are shown in the next to the last column of Tables 3—6. When Debye-Hückel's limiting law, extended by a linear term, is applied, it is found that the results may best be expressed by the formulae

$$\text{(at } 25^\circ \text{ C)} \quad -\log K_1 = 2.366 - 1.013\sqrt{I} + 0.76 I \quad (5)$$

$$\text{(at } 37^\circ \text{ C)} \quad -\log K_1 = 2.380 - 1.038\sqrt{I} + 0.78 I \quad (6)$$

$$\text{(at } 25^\circ \text{ C)} \quad -\log K_2 = 4.735 - 2.026\sqrt{I} + 1.64 I \quad (7)$$

$$\text{(at } 37^\circ \text{ C)} \quad -\log K_2 = 4.758 - 2.076\sqrt{I} + 1.60 I \quad (8)$$

Values calculated by means of these formulae are given in the last column of Tables 3—6. A close inspection of the data reveals a small systematic deviation from the equations. Thus the values of  $-\log K_1$  calculated from formula (5) and shown in Table 3 are on an average 0.004 too high when  $I$  is about 0.1, 0.008 too low when  $I$  is about 0.2, and 0.004 too high when  $I$  is about 0.3. The data in the three other tables show a similar departure. There may, therefore, be some doubt of the accuracy of the activity constants obtained by extrapolation to zero ionic strength by means of formulae (5) — (8), namely,  $K_1 = 4.31 \times 10^{-3}$  and  $K_2 = 1.84 \times 10^{-5}$  at  $25^\circ \text{ C}$ , and  $K_1 = 4.17 \times 10^{-3}$  and  $K_2 = 1.75 \times 10^{-5}$  at  $37^\circ \text{ C}$ . The only value reported in the earlier literature is  $K_1 = 5 \times 10^{-3}$  found by Skinner<sup>5</sup> by conductance at  $25^\circ \text{ C}$ .

## REFERENCES

1. Pedersen, K. J. *Acta Chem. Scand.* **9** (1955) 1640.
2. Filippo, H. *Rec. trav. chim.* **29** (1910) 113.
3. Lachman, A. J. *Am. Chem. Soc.* **43** (1921) 2091.
4. Pedersen, K. J. *Acta Chem. Scand.* **6** (1952) 243.
5. Skinner, S. J. *Chem. Soc.* **73** (1898) 483.

Received September 14, 1955.