Thermodynamics of (+)-Tartaric Acid and its Sodium and Potassium Complexes

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The dissociation constants of (+)-tartaric acid at 25 °C have been determined in 0·1, 0·2, and 0·4 $(Me_4N)Cl$ media † by potentiometric titration using a glass electrode. Thermodynamic constants have been determined at 15, 25, and 35 °C and standard enthalpy and entropy changes obtained from the temperature variation of the constants. The stability constants of sodium and potassium tartrate and hydrogen tartrate complexes at 25 °C in 0·2 $(Me_4N)Cl$† have been obtained from pH measurements with a glass electrode.

LITERATURE values of the dissociation constants of tartaric acid may be in error, since no allowance has been made for the effect of complexing with the alkali-metal ions usually present in solution. We have measured the dissociation constants of tartaric acid in media with and without alkali-metal ions in order to assess the accuracy of reported constants. Alkali-metal ions were replaced by tetramethylammonium ion (Me_4N^+), which has been shown by ^1H n.m.r. spectroscopy [1] and ultrasonic absorption studies [2] not to form complexes with ligands which co-ordinate alkali-metal ions.

Britton and Jackson [3] found that the molar rotations of the tartrate salts of sodium, potassium, and ammonium were different, but convergent at low concentrations. Katzin and Gulyas,[4] also from optical rotation measurements, reported that changing the alkali-metal ion present altered their results more than would be expected from variations in activity effects. Stability constants for sodium tartrate complexing have been obtained from pH measurements with glass [5] and hydrogen [6] electrodes.

Our experiments may be grouped into three series: (I) pH studies of the dissociation of tartaric acid in constant ionic media; (II) pH studies of the dissociation of tartaric acid in dilute solution at different temperatures; (III) the stability constants of the sodium hydrogen tartrate and potassium hydrogen tartrate systems of complexes from pH measurements.

EXPERIMENTAL

Units.—Concentrations have been expressed in mol l^{-1} so that stability constants will be compatible with literature values.

Symbols.—$K_{a1} = [H^+][HA^-]/[H_2A]$; $K_{a2} = [H^+][A^{2-}]/[HA^-]$; $\beta_{MTar} = [MA^-]/[M^+][A^{2-}]$; and $\beta_{MHTar} = [MHA]/[M^+][HA^-]$.

Reagents.—Distilled water was obtained from an all-glass still. Sodium chloride, potassium chloride, potassium nitrate, potassium hydrogen phthalate, and (+)-tartaric acid (B.D.H., AnalaR) were recrystallised from distilled water. Tetramethylammonium chloride (B.D.H., Reagent Grade) was recrystallised from methanol–acetone [7] or methanol. Sodium carbonate was prepared by decomposition of sodium hydrogen carbonate (B.D.H., AnalaR). Hydrochloric acid solutions were made up by dilution of the constant-boiling acid.[8] Tetramethylammonium hydroxide solutions were prepared by treating tetramethylammonium chloride solution with freshly precipitated silver hydroxide and filtering the solution. Sodium hydroxide solutions were prepared by dilution of a saturated solution made up from pellets (B.D.H., AnalaR). Hydroxide solutions were stored in, and dispensed from, the usual syphon arrangement.

Potentiometric Measurements.—Potentials were measured on a Pye 7565 potentiometer, using an Electronic Instruments Limited Vibron 33B electrometer as a null detector. The glass electrodes were GC33, made by Electronic Instruments Limited. The reference half-cell consisted of a Wilhelm Bridge [9] containing a silver–silver chloride electrode in either a tetramethylammonium chloride solution of the same ionic strength as the test solution [Series (I) and (III)] or an equimolar solution of potassium chloride and potassium nitrate (0·15 mol l^{-1} each) [Series (II)]. The latter was chosen to reduce liquid junction potentials [10] with the dilute solutions of Series (II).

pH Electrodes were calibrated with solutions of hydrochloric acid and by titration of hydrochloric acid solutions with standard sodium hydroxide or sodium carbonate solutions. The ionic strengths in Series (I) and (III) were maintained with tetramethylammonium chloride. In Series (I) and (III) Biedermann and Sillén's empirical liquid junction correction [11] was applied and a linear relationship was obtained between the corrected e.m.f. and $-\log [H^+]$. No linear calibration was obtained in Series (II) and no suitable liquid junction correction was available. The observed e.m.f., E, and the pH were fitted to equation (1) by the method of least squares.

$$E = a_0 + a_1(pH) + a_2(pH)^2 + a_3(pH)^3 + a_4(pH)^4 \quad (1)$$

Here we define $pH = -\log [H^+] - \log f$, where f is the univalent ion activity coefficient calculated by means of the Davies equation.[12] The validity of this calibration in

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† The nomenclature of A. E. Martell and L. G. Sillén (' Stability Constants,' *Chem. Soc. Special Publ.*, No. 17, 1964), has been adopted.

[1] L. E. Erickson and R. A. Alberty, *J. Phys. Chem.*, 1962, **66**, 1702.

[2] M. Eigen, *Pure Appl. Chem.*, 1963, **6**, 97.

[3] H. T. S. Britton and P. Jackson, *J. Chem. Soc.*, 1934, 998.

[4] L. I. Katzin and E. Gulyas, *J. Phys. Chem.*, 1960, **64**, 1739.

[5] Chin Kuang Wu and Kuang Hsien Hsü, *Acta Chim. Sinica*, 1963, **29**, 173.

[6] V. Frei, *Coll. Czech. Chem. Comm.*, 1965, **30**, 1402.

[7] B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, 1966, **62**, 2738.

[8] C. W. Foulk and M. Hollingsworth, *J. Amer. Chem. Soc.*, 1923, **45**, 1220; J. A. Shaw, *Ind. Eng. Chem.*, 1926, **18**, 1065; A. C. Titus and D. E. Smith, *J. Amer. Chem. Soc.*, 1941, **63**, 3266.

[9] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 901.

[10] K. V. Grove-Rasmussen, *Acta Chem. Scand.*, 1949, **3**, 445; 1951, **5**, 422.

[11] G. Biedermann and L. G. Sillén, *Arkiv Kemi*, 1953, **5**, 425.

[12] C. W. Davies, ' Ion Association,' Butterworth, London, 1962.

the presence of other ions was checked by repeating the calibrations with potassium chloride added. No significant difference was observed. Calibrations and experiments were normalised by reference to the e.m.f. observed with 0·05m-potassium hydrogen phthalate buffer before and after every run. The sensitivity of the electrode was checked periodically and found to be constant.

TABLE 1

Dissociation constants of (+)-tartaric acid at 25 °C

I	No. of runs	No. of points	10^3K_{a1}/ mol l^{-1}	$10^6\sigma(K_{a1})$/ mol l^{-1}	10^4K_{a2}/ mol l^{-1}	$10^7\sigma(K_{a2})$/ mol l^{-1}
0·1	3	47	1·494	12·3	1·066	6·98
0·2	11	182	1·540	4·01	1·173	24·0
0·4	2	52	1·472	2·66	1·308	6·04

Titration Procedure.—*Series* (I). Tetramethylammonium hydroxide solution was added from a burette to solutions containing tartaric acid and tetramethylammonium chloride. Tetramethylammonium chloride solution was added from a second burette to maintain the chloride concentration at the desired level (0·1, 0·2, or 0·4 mol l^{-1}).

Series (II). Tetramethylammonium hydroxide solution was added from a weight burette to solutions of tartaric acid made up by weight. All weights were corrected for the buoyancy of air.

TABLE 2

Tartaric acid data [Series (I)]

	I	$10^3[H_2Tar]$/ mol l^{-1}	$10^3[Me_4NOH]$/ mol l^{-1}	pH
Run 1	0·1	3·831	0·775	2·841
		3·765	1·369	2·961
		3·710	1·872	3·066
		3·671	2·222	3·147
		3·596	2·899	3·322
		3·524	3·550	3·516
		3·455	4·173	3·726
		3·389	4·775	3·961
		3·325	5·355	4·239
		3·263	5·910	4·645
Run 2	0·1	2·875	0·770	2·959
		2·814	1·508	3·140
		2·784	1·864	3·239
		2·755	2·212	3·355
		2·699	2·892	3·600
		2·629	3·734	3·987
		2·603	4·045	4·166
		2·568	4·471	4·485
Run 3	0·1	3·832	0·771	2·851
		3·750	1·508	2·996
		3·634	2·563	3·237
		3·490	3·866	3·620
		3·389	4·777	3·960
		3·325	5·353	4·241
		3·263	5·911	4·639
Run 4	0·2	4·791	1·848	2·920
		4·745	2·340	3·004
		4·709	2·728	3·076
		4·407	5·984	3·853
		4·376	6·321	3·962
		4·345	6·651	4·079
Run 5	0·2	11·20	5·189	2·856
		10·66	7·497	3·096
		9·817	11·13	3·565
Run 6	0·2	8·659	3·719	2·861
		7·596	9·826	3·756
		7·158	12·35	4·382
Run 7	0·2	11·14	5·409	2·876
		10·55	7·968	3·151
		9·183	13·87	4·029
Run 8	0·2	6·029	1·435	2·768
		5·779	3·030	3·003
		5·624	4·019	3·176
		5·159	6·985	3·849
		5·034	7·779	4·100
Run 9	0·2	2·717	0·873	2·997
		2·659	1·706	3·218
		2·525	3·629	3·982
		2·470	4·417	4·563
Run 10	0·2	10·00	2·679	2·695
		9·546	4·381	2·875
		9·265	5·426	2·997
		8·069	9·874	3·676
		7·658	11·40	4·008
		7·286	12·79	4·452
Run 11	0·2	4·859	1·168	2·814
		4·694	2·483	3·034
		4·591	3·307	3·197
		4·276	5·813	3·857
		4·170	6·661	4·178
Run 12	0·2	1·164	0·771	3·399
		1·138	1·646	4·064
Run 13	0·2	1·162	0·835	3·435
		1·141	1·550	3·967
		1·127	2·000	4·604
Run 14	0·2	1·875	1·073	3·236
		1·815	2·314	3·825
		1·772	3·215	4·775
Run 15	0·4	8·020	1·254	2·652
		7·923	1·653	2·694
		7·830	2·042	2·739
		7·649	2·793	2·827
		7·477	3·508	2·918
		7·313	4·192	3·011
		7·156	4·845	3·106
		6·932	5·775	3·256
		6·790	6·365	3·359
		6·641	6·984	3·487
		6·523	7·472	3·575
		6·398	7·992	3·689
		6·277	8·494	3·809
		6·161	8·978	3·937
		6·049	9·443	4·076
Run 16	0·4	3·825	0·800	2·852
		3·739	1·561	2·995
		3·698	1·929	3·069
		3·657	2·288	3·149
		3·594	2·845	3·285
		3·540	3·318	3·413
		3·467	3·969	3·611
		3·410	4·470	3·786
		3·375	4·776	3·904
		3·328	5·194	4·094
		3·262	5·771	4·454

Series (III). Sodium hydroxide solution was added to solutions containing tartaric acid, sodium chloride, and tetramethylammonium chloride. Alternatively, tetramethylammonium hydroxide solution was added to solutions of the acid, tetramethylammonium chloride, and either sodium or potassium chloride. The chloride concentration was maintained (at 0·2 mol l^{-1}) as in Series (I). Nitrogen from a cylinder (B.O.C. Ltd.) was passed successively through solutions of hydrochloric acid, sodium hydroxide, and tetramethylammonium chloride (twice) before being bubbled through the test solutions in order to mix them and to prevent the absorption of carbon dioxide. The saturators were at the temperature and ionic strength of the test solutions, except in Series (II), where distilled water replaced the tetramethylammonium chloride solutions.

The titration cell and Wilhelm Bridge were immersed in a water bath whose temperature was controlled to ±0·01 °C by a mercury–toluene regulator operating a heating element through a Sunvic relay (A.E.I. Ltd.). A Frigidaire refrigerator unit with its coil in the water enabled measurements to be made at temperatures below ambient. All operations were carried out in a room maintained at 25 ± 1 °C.

Volumetric glassware was of grade A standard and its calibration had been checked.

RESULTS

Series (I).—The acid dissociation constants were calculated by Speakman's method,[13] the equation of the line defining the constants being determined by the method of least squares. The results in 0·1, 0·2, and 0·4 $(Me_4N)Cl$ media are given in Table 1. A representative sample of the data is given in Table 2 (alternate points for Runs 1—4, 15, and 16, every fifth point for runs 5—14). The constants were extrapolated to infinite dilution by plotting $F(K,I)$, from equation (2), against I, the ionic strength.

$$F(K,I) = -\log K + r\,.\,A\,.\,I^{\frac{1}{2}}/(1 + B\,.\,a\,.\,I^{\frac{1}{2}}) = -\log K^{\circ} + r\,.\,A\,.\,b\,.\,I \qquad (2)$$

K and K° Represent the dissociation constant at a particular ionic strength and at infinite dilution respectively, r is an integer characteristic of the equilibrium constant concerned and equals 2 for K_{a1} and 6 for $K_{a1}\,.\,K_{a2}$, A and B are the parameters of the Debye–Hückel equation, and a and b are adjustable parameters. This procedure is equivalent to finding the best values of a and b for calculating the activity coefficients from equation (3). As a was

$$-\log f_z = A\,.\,z^2[I^{\frac{1}{2}}/(1 + B\,.\,a\,.\,I^{\frac{1}{2}}) - b\,.\,I] \qquad (3)$$

varied systematically, $F(K,I)$ and I were fitted to equation (4) by the method of least squares and that value, $a_{\text{min.}}$,

$$F(K,I) = p\,.\,I + q \qquad (4)$$

found which produced the best fit of the data, with the coefficients $p_{\text{min.}}$ and $q_{\text{min.}}$. We then obtained $-\log K^{\circ} = q_{\text{min.}}$ and the 'best' $b = p_{\text{min.}}/(r\,.\,A)$. In this way we calculated $pK_{a1}^{\circ} = 3{\cdot}00$ ($a_{\text{min.}} = 5{\cdot}25$, $b = 0{\cdot}34$) and $p(K_{a1}\,.\,K_{a2})^{\circ} = 7{\cdot}37$ ($a_{\text{min.}} = 10{\cdot}15$, $b = 0{\cdot}07$).

Series (II).—The dissociation constants were calculated by Speakman's method,[13] with activity coefficients calculated from equation (3). Initially an approximation was made to the ionic strength corresponding to each data point and the calculations performed iteratively until successive cycles reproduced the dissociation constants to within 0·1%.

The values of a and b chosen for equation (3) had little effect on the calculated values of the dissociation constants. At constant b (=0·1), varying a from 1·0 to 8·0 produced a 0·3% change in K_{a1} and a 0·6% change in its standard deviation. At constant a (=2·6), a variation in b from −2·0 to 0·5 changed K_{a1} by 0·5% and the standard deviation by 0·6%. There was less than 1% difference in K_{a1} over any combination of a and b tried. As a compromise with the extrapolated results of Series (I), a was set equal to 7·0 and b to 0·2. The dissociation constants obtained with these figures are given in Table 3. The experimental data (alternate points only) are given in Table 4.

TABLE 3

Thermodynamic dissociation constants of (+)-tartaric acid

T/°C	No. of runs	No. of points	10^4K_{a1}/ mol kg^{-1}	$10^6\sigma(K_{a1})$/ mol kg^{-1}	10^5K_{a2}/ mol kg^{-1}	$10^7\sigma(K_{a2})$/ mol kg^{-1}
15	2	32	9·043	17·4	4·228	19·8
25	2	22	8·640	5·41	5·447	6·22
35	1	13	8·284	5·76	4·319	34·9

TABLE 4

Tartaric acid data [Series (II)]

	T/°C	$10^4[H_2Tar]$/ mol kg^{-1}	$10^4[Me_4NOH]$/ mol kg^{-1}	pH	$10^4[Me_4NCl]$/ mol kg^{-1}
Run 1	15	19·74	0·873	3·030	0·735
		19·59	4·960	3·150	4·177
		19·45	8·859	3·284	7·461
		19·33	12·20	3·436	10·27
		19·24	14·82	3·561	12·48
		19·11	18·30	3·750	15·41
		19·01	21·16	3·906	17·82
		18·87	25·01	4·148	21·06
		18·77	27·92	4·344	23·52
Run 2	15	9·829	1·441	3·280	1·214
		9·791	3·593	3·381	3·026
		9·747	6·051	3·548	5·096
		9·703	8·489	3·755	7·149
		9·662	10·76	3·980	9·063
		9·626	12·82	4·208	10·79
		9·595	14·54	4·419	12·25
Run 3	25	14·14	3·679	3·233	0·056
		14·10	5·722	3·320	0·087
		14·06	7·610	3·412	0·117
		14·04	9·040	3·486	0·139
		14·01	10·15	3·548	0·156
		13·99	11·40	3·622	0·175
Run 4	25	23·26	6·272	3·124	0·096
		23·16	9·460	3·220	0·145
		23·03	13·35	3·352	0·205
		22·92	16·51	3·460	0·253
		22·82	19·63	3·590	0·301
		22·71	23·01	3·742	0·353
Run 5	35	14·01	2·585	3·210	2·177
		13·91	6·380	3·381	5·372
		13·84	9·438	3·552	7·947
		13·73	13·65	3·825	11·49
		13·68	15·64	3·968	13·17
		13·63	17·49	4·104	14·72

The constants in Table 3 were fitted to equation (5)

$$pK = A/T + B + C\,.\,T \qquad (5)$$

where T is the temperature (in K), by solving simultaneous equations. The coefficients for each dissociation are given below.

	A	B	C
pK_{a1}	0·0	2·50	0·002
pK_{a2}	3014	−198	0·34

The standard Gibbs energy, enthalpy and entropy changes for each dissociation can be expressed in terms of the above coefficients: $\Delta G^{\circ} = -2{\cdot}3026RT\log K$, $\Delta H^{\circ} = 2{\cdot}3026R(A - C\,.\,T^2)$, and $\Delta S^{\circ} = 2{\cdot}3026R(-B - 2C\,.\,T)$. The values of these thermodynamic quantities at 25 °C are set out in Table 5. With results at only three temperatures, the figures must be treated with

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[13] J. C. Speakman, *J. Chem. Soc.*, 1940, 855.

caution; McAuley,[14] however, has found the procedure adequate with metal–dicarboxylic acid complexes.

Series (III).—(a) *Sodium complexes.* The data were treated as a system (Na^+, $NaTar^-$, $NaTar_2^{3-}$, H_2Tar, $HTar^-$, Tar^{2-}) by Gelles and Nancollas's method.[15] The resulting plots passed through the origin and became more curved as the pH was lowered. The former feature shows that $NaTar_2^{3-}$ formation is negligible in the experimental conditions and the latter that protonated complexes are formed. It was assumed that only $NaTar^-$ and NaHTar complexes were formed and, assuming a value for β_{NaHTar}, β_{NaTar} was calculated.[16] β_{NaHTar} was varied systematically and that value accepted as best which produced a minimum in the standard deviation in β_{NaTar}. This was done for each of four runs (66 points in all). The mean stability constants were $\beta_{NaTar} = 1·9$ l mol^{-1} and $\beta_{NaHTar} = 9 \times 10^{-1}$ l mol^{-1} with standard deviations of 0·03 and 0·3 l mol^{-1} respectively. Selected data (alternate points) are given in Tables 6 and 7.

TABLE 5

Thermodynamic data for (+)-tartaric acid in water at 25 °C

	$10^{-4}\Delta G°$/ J mol^{-1}	$10^{-3}\Delta H°$/ J mol^{-1}	$\Delta S°$/ J deg^{-1} mol^{-1}
First dissociation	1·75	−3·2	−70
Second dissociation	2·43	0·6	−79

TABLE 6

Data for sodium tartrate complexing

	$10^3[H_2Tar]$/ mol l^{-1}	$10^2[NaCl]$/ mol l^{-1}	pH	$10^3[NaOH]$/ mol l^{-1}
Run 1	5·158	2·066	3·009	2·691
	5·053	2·024	3·138	3·393
	4·953	1·984	3·274	4·064
	4·765	1·909	3·575	5·326
	4·675	1·873	3·739	5·924
	4·590	1·839	3·916	6·499
	4·507	1·806	4·117	7·052
Run 2	10·63	10·64	2·560	1·586
	10·09	10·10	2·730	3·399
	9·704	9·712	2·870	4·703
	9·519	9·528	2·944	5·322
	9·340	9·348	3·017	5·924
	9·166	9·174	3·091	6·505
	9·001	9·009	3·167	7·059
	8·614	8·622	3·359	8·357
	8·060	8·067	3·689	10·22
	7·868	7·875	3·823	10·86
	7·746	7·753	3·918	11·27
	7·628	7·635	4·019	11·66

TABLE 7

Data for sodium tartrate complexing

	$10^3[H_2Tar]$/ mol l^{-1}	$10^2[NaCl]$/ mol l^{-1}	pH	$10^3[Me_4NOH]$/ mol l^{-1}
Run 3	5·006	2·080	2·983	2·494
	4·955	2·059	3·048	2·852
	4·875	2·026	3·157	3·413
	4·732	1·966	3·378	4·422
	4·552	1·892	3·708	5·682
	4·468	1·856	3·892	6·277
	4·427	1·839	3·992	6·564
	4·347	1·806	4·223	7·124
Run 4	3·543	2·127	2·986	1·477
	3·469	2·083	3·142	2·169
	3·398	2·040	3·315	2·832
	3·330	1·999	3·506	3·467
	3·265	1·960	3·715	4·078
	3·202	1·922	3·947	4·663

(b) *Potassium complexes.* The data were treated in the same way as for sodium complexes, and the same trends were observed. The results, from a single run (23 points), are $\beta_{KTar} = 1$ l mol^{-1} with a standard deviation of 0·15 l mol^{-1} and $\beta_{KHTar} = 0·3$ l mol^{-1}. The data for alternate points are given in Table 8.

TABLE 8

Data for potassium tartrate complexing

$10^3[H_2Tar]$/ mol l^{-1}	$10^2[KCl]$ mol l^{-1}	pH	$10^3[Me_4NOH]$/ mol l^{-1}
5·244	2·179	2·732	0·821
5·131	2·132	2·849	1·618
5·057	2·101	2·929	2·136
4·995	2·075	3·005	2·572
4·954	2·059	3·057	2·860
4·874	2·025	3·166	3·423
4·729	1·965	3·390	4·441
4·550	1·891	3·719	5·695
4·466	1·856	3·905	6·290
4·425	1·839	4·006	6·577
4·385	1·822	4·114	6·859
4·307	1·790	4·378	7·404

All the stability constants above were calculated by means of ALGOL programs run on the English Electric KDF.9 computer in the Department of Computing of this University.

LITERATURE DATA

Tartaric Acid.—The best and most extensive measurements of the second dissociation constant of tartaric acid have been made by Bates and Canham.[17] They neglected sodium tartrate complexing, even though sodium is present at concentrations up to 0·416 g-ion kg^{-1}. We have recalculated their data at 25 °C, allowing for the existence of a 1 : 1 sodium tartrate complex, but, in view of the high pH values, neglecting protonated complexes. We followed Bates and Canham's procedure of plotting a function F [equation (6)] against I. The intercept is equal to $pK_{a2}°$

$$F = \text{pwH} - \log \frac{[A]}{[HA]} + \frac{2A \, . \, I^{\frac{1}{2}}}{1 + B \, . \, a \, . \, I^{\frac{1}{2}}} \qquad (6)$$

and from the slope is derived the coefficient b of equation (3). We took $a = 6·0$ in conformity with Bates and Canham. pwH is $-\log [H] f_H f_{Cl}$. Bates and Canham's [A] is high by a factor $(1 + \beta_{NaTar}°[Na]f_A)$ and our allowance for this introduces a further iterative step into the calculation.

$\beta_{NaTar}°$ Was estimated by applying activity corrections calculated by the Davies [12] equation to the value we found in 0·2 $(Me_4N)Cl$ medium. The value so obtained was 6·45 kg mol^{-1}, and values of 0·0 and 13·0 kg mol^{-1} were also tried. Both Bates and Canham's and our results for pK_{a1} were used. The results from these various trials are summarised in Table 9.

The negative slope found when sodium complexing is

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[14] A. McAuley, Ph.D. Thesis, Glasgow, 1961.

[15] E. Gelles and G. H. Nancollas, *Trans. Faraday Soc.*, 1956, **52**, 98.

[16] G. H. Nancollas, 'Interactions in Electrolyte Solutions,' Elsevier, Amsterdam–New York–London, 1966.

[17] R. G. Bates and R. G. Canham, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 343.

neglected is, by analogy with Guggenheim's[18] specific interaction coefficients, indicative of a tendency to ion association. On the other hand, our estimated value of 6·45 kg mol^{-1} for $\beta_{NaTar}{}^{\circ}$ yields a result in good agreement with Davies's figure of 0·3 for strong electrolytes.

TABLE 9

Recalculation of Bates and Canham's data

10^4K_{a1} (mol kg^{-1})	8·64	8·64	8·64	9·01	9·01
$\beta_{NaTar}{}^{\circ}$ (kg mol^{-1})	0·0	6·45	13·0	0·0	6·45
pK_{a2}	4·362	4·405	4·445	4·363	4·406
b	−0·03	0·28	0·52	−0·03	0·28

Recalculation of Bates and Canham's data by Speakman's method gave a curve, not a straight line. A set of parallel straight lines could be obtained by joining points of equal sodium concentration.

Sodium Tartrate.—(a) Frei[6] has reported $\beta_{NaTar}{}^{\circ}$ = 96 l mol^{-1} and $\beta_{NaHTar}{}^{\circ}$ = 29 l mol^{-1} at 20 °C at infinite dilution. In obtaining these results, Frei used his own method[19] of calculating activity coefficients, which produces values markedly different from those observed by experiment.[20] We have recalculated Frei's data using Bates and Canham's dissociation constants for tartaric acid and equation (3) for the activity coefficients ($a = 7{\cdot}0$, $b = 0{\cdot}2$).

As in our Series (III), the data were interpreted in terms of $NaTar^-$ and NaHTar formation, but the need for activity coefficients involved a further iterative step in the calculation. For each of Frei's two series of measurements (half- and three-quarters neutralised solutions), the calculated $\beta_{NaTar}{}^{\circ}$ was found to be a linear function of the trial value of $\beta_{NaTar}{}^{\circ}$. The 'best' values of the stability constants were taken from the intersection of the two functions, $\beta_{NaTar}{}^{\circ}$ = 8·4 l mol^{-1} and $\beta_{NaHTar}{}^{\circ}$ = 1·7 l mol^{-1}. For comparison our results at 25 °C give, on correction to infinite dilution, $\beta_{NaTar}{}^{\circ}$ = 6·45 l mol^{-1} and $\beta_{NaHTar}{}^{\circ}$ = 1·6 l mol^{-1}.

(b) Chin Kuang Wu and Kuang Hsien Hsü[5] have reported stability constants for the tartrate and hydrogen-tartrate complexes of the alkali metals and ammonium at 25 °C. The constants are obtained from single titrations of tartaric acid in 0·2 mol l^{-1} solutions of each of the metal chlorides. The accuracy of the constants depends on the accuracy of the acid dissociation constants, which were derived from one titration in 0·2 Me_4N^+ medium and contain an unusual activity correction.

DISCUSSION

Stability constants as small as those for sodium–tartrate complexes must be regarded with caution, but we have found good agreement between the results of two different methods, covering a five-fold range of sodium concentration and a three-fold range of tartrate concentration, with metal : ligand ratios varying from 2 : 1 to 15 : 1. The agreement between our results and those of Wu and Hsü is moderately good, considering the magnitude of the constants, and the difference between the values obtained by recalculating Frei's data and by correcting our own for activity effects is small. It is also encouraging that the use of our corrected β_{NaTar} with Bates and Canham's data shifts the value of the b-coefficient in equation (3) from one typical of associated electrolytes to one typical of strong electrolytes.

Not enough data has been collected in this work for much significance to be attached to the figures for potassium tartrate, which can best be regarded as an indication that complexing occurs. Stability constants of the citrate and malate complexes[21] of sodium and potassium in much the same conditions as ours ($I \simeq 0{\cdot}17$) are of the same order of magnitude and show the expected trend: citrate > tartrate > malate.

The various results for sodium and potassium tartrate complexing are given in Table 10.

TABLE 10

Stability constants of sodium–tartrate complexes

T/°C	Medium	β_{NaHTar}/ l mol^{-1}	β_{NaTar}/ l mol^{-1}	Method	Ref.
20	*a*	29·2	96·2	*c*	6
20	*a*	1·7	8·4	*c*	6 and this work
25	*a*	1·6	6·5	*d*	This work
25	0·2 $(Me_4N)Cl$	0·9	1·9	*d*	This work
25	0·2 $(Me_4N)Cl$		2·6	*e*	*b*
25	0·2 NaCl	1·6	3·6	*d*	5

[a] Corrected to infinite dilution. [b] H. S. Dunsmore and D. Midgley, *J. Chem. Soc.* (*A*), 1971, 3238. [c] Hydrogen electrode. [d] Glass electrode. [e] Sodium glass electrode.

The use of tetramethylammonium salts as background media in studies of ligands that form complexes with alkali metal ions is justified by the good agreement between the thermodynamic pK values of tartaric acid obtained in dilute solution, with correction for activity effects, and those produced by extrapolating the results at a number of different ionic strengths. The fact that extrapolation gives a b-coefficient in equation (3) close to Davies's value for strong electrolytes is further evidence for the absence of association with tetramethylammonium ion. We infer from our recalculation of Bates and Canham's results that extrapolation to zero ionic strength does not, in the presence of high concentrations of alkali metal ions, compensate for the effects of complexing, and an inert electrolyte, such as tetramethylammonium chloride, must be used if accurate constants are to be obtained.

The error introduced when alkali-metal complexes are neglected in calculating the dissociation constants of a weak acid are shown in the following example. A monoprotic weak acid, HA, in a constant ionic medium made up with sodium chloride, is titrated with a strong base, and the pH is measured. It is assumed that the medium succeeds in its purpose of keeping the activity coefficients constant and they will be neglected in the calculations. The concentrations of acid, base,

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[18] E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, 1955, **51**, 747; E. A. Guggenheim, *ibid.*, 1966, **62**, 3446.

[19] V. Frei, *Monatsh.*, 1965, **96**, 1811.

[20] R. A. Robinson and R. A. Stokes, 'Electrolyte Solutions, 2nd edition, Butterworth, London, 1965.

[21] G. A. Rechnitz and S. B. Zamochnick, *Talanta*, 1964, **11**, 1061.

and sodium chloride in the solution are T_a, T_b and T_s respectively. Without allowing for the complex, NaA^-, with a stability constant β, the mass and charge balance equations are, indicating apparent values by primes:

$$T_a = [HA]' + [A^-]'$$

and $$T_b + [H^+] = [OH^-] + [A^-]',$$

whence $$[A^-] = [H^+] + T_b - [OH^-]$$

and $$K' = [H^+]([H^+] + T_b - [OH^-])/(T_a - [H^+] - T_b + [OH^-]).$$

If we now take account of the complex, we obtain:

$$T_a = [HA] + [A^-] + [NaA]$$

and $$T_b + T_s - [NaA] + [H^+] = [A^-] + T_s - [OH^-],$$

whence $$\begin{aligned}[A^-] + [NaA] &= [H^+] + T_b - [OH^-] \\ &= [A^-](1 + \beta[Na^+]) \\ &= [A^-]'.\end{aligned}$$

It is now apparent that $[HA] = [HA]'$ and that $K' = K(1 + \beta[Na^+])$.

If $T_s \gg T_a$, $[Na^+]$ is virtually constant and calculations of K' will not have particularly large standard deviations. If we make the reasonable assumptions that $[Na^+] \simeq \beta \simeq 1$, K' is twice the true constant.

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