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THE FORMATION OF PROTON AND ALKALI-METAL COMPLEXES WITH LIGANDS OF BIOLOGICAL INTEREST IN AQUEOUS SOLUTION. PART I. POTENTIOMETRIC AND CALORIMETRIC INVESTIGATION OF H^+ AND Na^+ COMPLEXES WITH CITRATE, TARTRATE AND MALATE *

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ABSTRACT

The thermodynamic parameters for the interaction of H^+ and Na^+ with citrate, tartrate and malate are determined potentiometrically and calorimetrically in aqueous solution. The investigation is carried out at various ionic strengths and temperatures. The data obtained by direct calorimetry are reported for the first time. The species NaA and NaHA are found to exist for tartrate and malate only, whereas the species NaH_2A is found to be present for citrate also. Simultaneous analysis of the potentiometric and calorimetric data enables the temperature and ionic strength dependence of the equilibrium parameters to be obtained for the complexes.

INTRODUCTION

Although alkali-metal complexes have been known for a long time, Sidgwick and Plant [1], their thermodynamic properties in aqueous solution have been very little studied [2—4]. Recently there has been great interest in the complexes of biological interest of these metal ions [5]. Sodium and potassium are the main ionic constituents of all intra- and extra-cellular liquids and play a fundamental role in electrical communication through membranes [6,7]. For this reason, greater attention is now being paid to the study of the interaction of these ions with natural and synthetic ligands called "ion carriers". When complexed, these ions can be made soluble in non-polar solvents. Thermodynamic investigations have been, and still are, concerned mainly with the search for possible selectivity of these ligands. In consequence, the thermodynamic data have been almost exclusively ob-

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tained in non-aqueous solvents owing to the liposoluble characteristics of the complexes formed, thus neglecting the behaviour of these ions in aqueous solution [8,9]. Furthermore, although the number of works reporting the complexing capacities of cryptated and polypeptide macrocyclics [10—12] has always been substantial, there are few data (and in some cases they are in disagreement) on the interactions of alkali-metal ions with low-molecular-weight organic ligands [13]. Finally, even though the protonation constants of such ligands have been extensively studied, there is a lack of data on protonation enthalpies [14]. These enthalpies are often obtained from the p*K* temperature coefficient and sometimes this method gives unreliable results, especially when the p*K* values have not been measured with high precision over a wide range of temperatures [15].

In view of the above, we considered it useful to undertake a series of studies on the protonation and formation of alkali-metal complexes with ligands of biological interest. This paper represents the first stage in this programme.

Because of the biological interest of citrate, tartrate and malate, as well as the high sodium ion concentration in biofluids, we have made a detailed study of these ligands both with Na^+ and the proton. It is well known that the ligands form weak complexes with alkali-metal ions [16—22]. Thus, protonation constants determined in solutions containing NaCl, KCl, $NaNO_3$, KNO_3, $NaClO_4$, all of which are used to keep the usually high ionic strength constant, are subject to error; that is protonation constants, as a function of the alkali-metal concentration, are lower than the true values [16—59].

The formation constants for H^+—Na^+—A systems (where A denotes citrate, cit; tartrate, tar; malate, mal) have been determined using a glass electrode at various temperatures, 20°C (in some cases), 25°C and 37°C, and various ionic strengths, <0.05 (in some cases), 0.05, 0.1, 0.15, 0.2, 0.5, 1.0 and 3 (in some cases). The formation enthalpies have been determined at 25°C and ionic strengths of 0.05, 0.1 and 0.15 mole dm^{-3} in $NaClO_4$. The simultaneous analysis of our potentiometric and calorimetric data has enabled the temperature and ionic strength dependence of log β, ΔH, and ΔS to be obtained for the complexes studied.

EXPERIMENTAL

Materials

Trisodium citrate, disodium tartrate (both C. Erba) and disodium malate (Merck) were recrystallized from water—ethanol. Titrations with standard $HClO_4$ or HCl gave a purity $>99.5\%$. Citric acid (Merck), tartaric acid and malic acid (both C. Erba) were recrystallized from hot twice-distilled water. Titration with standard NaOH gave a purity $>99.7\%$. Sodium-perchlorate-free heavy metals were prepared according to Holmes and Williams [60]. NaOH solutions 0.05—1 mole dm^{-3} were prepared by diluting Normex C. Erba ampoules and standardized against potassium hydrogenphthalate

(Merck). The perchloric acid solutions 0.05—1 mole dm^{-3} were prepared by diluting 70% solutions (C. Erba) and standardized against THAM (Merck). All solutions were prepared with freshly twice-distilled water. Grade A glassware was used in all operations.

Instrumentation

Potentiometric measurements were carried out with titration equipment composed of: (1) an Orion 801A pH meter, (2) an Amel timer—printer (Model 882), and (3) an Amel dispenser (Model 232). The electrode couple consisted of an EIL glass electrode and an Ingold saturated calomel electrode.

The potentiometric vessels were fitted with a thermostatic jacket connected to a Haake thermostat. The temperature was maintained constant to 0.1°C. Magnetic stirring was used. The solutions were degassed with purified nitrogen and presaturated in $NaClO_4$ solutions of the same concentration used to keep the ionic strength constant. Calorimetric measurements were carried out using an LKB precision calorimeter (Model 8700). The titrant was delivered by means of a motorized Radiometer ABU 12-b burette.

Potentiometric measurements

20—25 cm^3 of solution containing the acid or the di (or tri)-sodium salt were titrated with standard NaOH or $HClO_4$, as appropriate. The solutions contained an amount of $NaClO_4$ according to the ionic strength desired. The electrode system was calibrated before and after each run by titrating 5—75 mmole dm^{-3} THAM with standard 5—10 mmole dm^{-3} $HClO_4$ or $HClO_4$ with standard NaOH at the same ionic strength as the solution under study. The pH reproducibility was ±0.005. Other details of potentiometric measurements have been reported elsewhere [61—67].

Calorimetric measurements

80—90 cm^3 of solution containing the neutralized acid were titrated with $HClO_4$ to complete formation of H_2A or H_3A. Some trials were carried out by titrating the acids with NaOH, but the results obtained with the first method were far more reliable. The Q-value reproducibility was ±0.015 cal. Other details of calorimetric measurements have been reported elsewhere [61—65]. In Table 1 some experimental details are given.

Calculations

Calculations of (1) purity of acids and the corresponding salts, (2) determination of the E^0 value of the electrode system, and (3) determination of the protonation constants (not corrected for Na^+ complex formation) were performed with the ACBA least-squares computer program [68]. Calculations for the simultaneous determination of protonation constants and sodium complex formation constants were carried out with the SCOGSB

TABLE 1

Experimental details of potentiometric and calorimetric measurements

	$[A]_T$ [a]	I [a]	pH	No. of titrations (points)	
Citrate	0.005 —0.175	0.015—1.0 (3.0)	1.9—7.1	20 (1000)	potentiometry
Tartrate	0.01 —0.222	0.02 —1.0	1.9—5.5	15 (750)	
Malate	0.01 —0.217	0.02 —1.0	2.5—6.2	13 (650)	
Citrate	0.0015—0.01	0.004—0.175		22 (142)	calorimetry
Tartrate	0.005 —0.01	0.02 —0.17		10 (64)	
Malate	0.011 —0.026	0.02 —0.21		8 (93)	

[a] Concentrations and ionic strength in mole dm^{-3}.

[69,70] and MINIQUAD 76 [71] computer programs. The calorimetric data were analysed by the DOEC computer program [72]. All these programs use the least-squares method.

RESULTS

Potentiometric measurements were carried out at temperatures of 20°C (in some cases), 25°C and 37°C, and ionic strengths 0.05, 0.1, 0.15, 0.20, 0.50, 1.00 and 3.00 (only in the case of the citrate at 25°C). The ionic strength varied during titration by ±2% at most. The data were examined initially without taking into account the formation of sodium complexes. The protonation constant values thus obtained were fitted by means of the equation

$$\log \beta = a_1 + a_2 I^{1/2} + a_3 I + a_4 I^{2/3} \tag{1}$$

The coefficient values for eqn. (1) are reported in Table 2. The pK values of the citric, tartaric and malic acids are markedly lower than those obtained in the absence of alkali ions [16—22] as can also be seen from Fig. 1, where the pK vs. $I^{1/2}$ and pK' vs. $I^{1/2}$ curves are reported together (where the prime denotes that the constants were calculated without allowing for sodium complex formation). Firstly the values of formation constants of the ligands formed in the presence of sodium ions can be estimated by using the equation

$$\log K = \log K' + \log(1 + K^{\mathrm{Na}}[\mathrm{Na}]) \cong \log K' + \log(1 + K^{\mathrm{Na}} I) \tag{2}$$

The approximated values thus calculated for the formation constants are then used as input data for the SCOGSB and MINIQUAD 76 programs. In Table 3 the protonation constant values are reported, corrected for sodium complex formation, for 25°C and 37°C and various ionic strengths. A statistical analysis of potentiometric data [73,74] has revealed NaA and NaHA complex formation for tartrate and malate, and NaA, NaHA and NaH_2A for citrate.

TABLE 2

Coefficients for the equation $\log \beta_j = a_1 + a_2 I^{1/2} + a_3 I + a_4 I^{3/2}$ obtained by the least-squares method for the protonation of citrate, tartrate and malate with no allowance for formation of sodium complexes

A	T (°C)	j	a_1 [a]	a_2	a_3	a_4	$R \times 10^3$ [b]
Citrate	25	1	6.418	−3.567	4.049	−1.678	2.2
		2	11.19	−5.489	6.009	−2.353	1.4
		3	14.31	−6.106	6.143	−2.155	0.8
	37	1	6.444	−3.808	4.475	−1.906	2.5
		2	11.20	−5.736	6.469	−2.638	2.5
		3	14.30	−6.474	6.859	−2.576	2.8
Tartrate	25	1	4.383	−1.557	0.962	−0.066	1.9
		2	7.44	−1.148	−1.628	1.814	5.4
	37	1	4.380	−2.482	3.414	−1.650	1.5
		2	7.414	−3.539	4.777	−2.302	3.1
Malate	25	1	5.119	−1.384	0.807	—	3.0

[a] The value at $I = 0$ (calculated taking into account the formation of sodium complexes, see Table 3) was weighted heavily in the calculation.
[b] See refs. 73, 74.

TABLE 3

Protonation constants, at various ionic strengths and temperatures (the ionic strength was adjusted by adding $NaClO_4$), for citrate, tartrate and malate

T (°C)	I (mole dm^{-3})	Citrate			Tartrate		Malate	
		Log K_1^H [a] (±0.008) [b]	Log K_2^H (±0.009)	Log K_3^H (±0.007)	Log K_1^H (±0.008)	Log K_2^H (±0.014)	Log K_1^H (±0.006)	Log K_2^H (±0.015)
25	0	6.419	4.769	3.124	4.382	3.050	5.115	3.472
	0.05	5.903	4.432	2.972	4.251	2.886	4.807	3.308
	0.10	5.771	4.352	2.949	3.968	2.850	4.755	3.271
	0.15	5.697	4.309	2.944	3.928	2.833	4.742	3.253
	0.20	5.650	4.285	2.949	3.905	2.825	4.747	3.245
	0.50	5.596	4.292	3.053	3.922	2.854	4.928	3.264
	1.00	5.780	4.487	3.319 [c]	4.133	2.993	5.412 [c]	3.402 [c]
	3.00	7.16 [c]	5.68 [c]	—				
37	0	6.445	4.758	3.098	4.379	3.033	5.126	3.456
	0.05	5.919	4.413	2.942	4.245	2.864	4.813	3.287
	0.10	5.786	4.330	2.918	3.956	2.826	4.761	3.249
	0.15	5.711	4.286	2.913	3.915	2.808	4.748	3.230
	0.20	5.665	4.261	2.917	3.892	2.799	4.754	3.221
	0.50	5.619	4.267	3.021	3.911	2.823	4.945	3.243
	1.00	5.824	4.463	3.288 [c]	4.130	2.957	5.450 [c]	3.373 [c]

[a] K_j^H for $H_{j-1}A + H \rightleftharpoons H_jA$. [b] 3σ. [c] ±0.05.

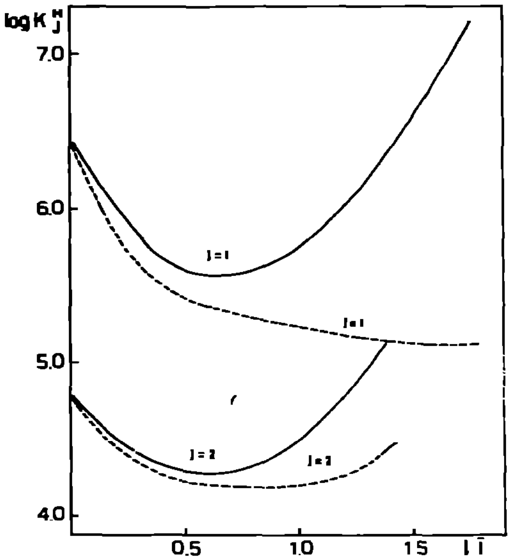


Fig. 1. Dependence of log K_1^H and log K_2^H for citric acid on ionic strength. (———) Protonation constants corrected for sodium complex formation. (- - - - -) "Apparent" protonation constants.

For the formation constants of sodium complexes with citrate, tartrate and malate, it can be seen that allowing for the equilibrium (for simplicity, charges have been omitted)

$$H_jA + Na \rightleftharpoons NaH_{j-1}A + H \qquad (3)$$

a value of the equilibrium constant is obtained which is independent (within experimental errors) of temperature and ionic strength. In Table 4 these equilibrium constant values are reported for the acids studied here.

The ΔH protonation values are given in Table 5 and those for sodium complex formation in Table 6. The pK values obtained at various temperatures have been fitted together with the ΔH values by

$$pK = \frac{A}{T} + B + CT \qquad (4)$$

TABLE 4

Log values for the constant of the equilibrium $H_jA + Na \rightleftharpoons NaH_{j-1}A + H$ [a]

	—Log K_1 (±0.06) [b]	—Log K_2 (±0.1)	—Log K_3 (±0.1)
Citrate	4.99	4.2	2.9
Tartrate	3.56	2.8	—
Malate	4.46	3.3	—

[a] These values are practically independent of temperature and ionic strength (within experimental error).

[b] 3σ.

TABLE 5

Thermodynamic parameters for the protonation of citrate, tartrate and malate in $NaClO_4$ at 25°C [a,b]

I (mole dm^{-3})	$-\Delta G_1$ (±0.01) [c]	ΔH_1 (±0.03)	ΔS_1 (±0.07)	$-\Delta G_2$	ΔH_2 (±0.03)	ΔS_2 (±0.1)	$-\Delta G_3$ (±0.01)	ΔH_3 (±0.03)	ΔS_3 (±0.1)
Citrate				(±0.01)					
0	8.75	0.80	32.03	6.50	−0.48	20.2	4.26	−0.95	11.1
0.05	8.05	0.53	28.78	6.04	−0.72	17.8	4.05	−1.06	10.0
0.10	7.84	0.46	27.84	5.93	−0.75	17.4	4.02	−1.08	9.9
0.15	7.77	0.41	27.44	5.87	−0.78	17.1	4.01	−1.13	9.7
Tartrate				(±0.02)					
0	5.97	−0.16	19.49	4.16	−0.66	11.7			
0.05	5.79	−0.40	18.08	3.93	−0.80	10.5			
0.10	5.41	−0.45	16.64	3.88	−0.86	10.1			
0.15	5.35	−0.48	16.33	3.86	−0.90	9.9			
Malate				(±0.02)					
0	6.97	0.33	24.48	4.73	−0.64	13.7			
0.05	6.55	0.18	22.57	4.51	−0.77	12.5			
0.10	6.48	0.14	22.20	4.46	−0.82	12.2			
0.15	6.46	0.13	22.10	4.43	−0.85	12.0			

[a] ΔG, ΔH and ΔS subscripts refer to the reaction $H_{j-1}A + H \leftrightharpoons H_jA$.

[b] ΔG and ΔH are expressed in kcal mole^{-1}; ΔS is expressed in cal deg^{-1} mole^{-1}.

[c] 3σ.

TABLE 6

Thermodynamic parameters for complexes of citrate, tartrate and malate with sodium in $NaClO_4$ at 25°C [a,b]

I (mole dm^{-3})	$-\Delta G_1$ (±0.1) [c]	ΔH_1	ΔS_1	$-\Delta G_2$ (±0.1)	ΔH_2	ΔS_2	$-\Delta G_3$ (±0.1)	ΔH_3 (±0.3)	ΔS_3 (±1.1)
Citrate		(±0.09)	(±0.5)		(±0.2)	(±0.8)			
0.05	1.2	0.53	5.8	0.3	1.4	5.7	0.1	−0.3	−0.7
0.10	1.1	0.40	5.0	0.2	0.2	1.3	0.1	−0.5	−1.3
0.15	1.0	0.06	3.6	0.1	−0.7	−2.0	0.0	−1.4	−4.7
Tartrate		(±0.08)	(±0.4)		(±0.1)	(±0.5)			
0.05	0.9	−0.12	2.6	0.1	−0.5	−1.3			
0.10	0.6	−0.18	1.4	0.1	−0.5	−1.3			
0.15	0.6	−0.23	1.2	0.0	−0.5	−1.7			
Malate		(±0.09)	(±0.5)		(±0.1)	(±0.5)			
0.05	0.5	−0.07	1.4	0.0	−1.3	−4.4			
0.10	0.4	−0.11	1.0	−0.1	−1.3	−4.7			
0.15	0.4	−0.11	1.0	−0.1	−1.3	−4.7			

[a] ΔG, ΔH and ΔS subscripts refer to the reaction $Na + H_{j-1}A \rightleftharpoons NaH_{j-1}A$.

[b] ΔG and ΔH are expressed in kcal mole^{-1}; ΔS is expressed in cal deg^{-1} mole^{-1}.

[c] 3σ.

TABLE 7

Dependence of the protonation constants of citrate, tartrate and malate on temperature and ionic strength [a]

		$A \times 10^{-2}$	B	$C \times 10^{3}$ [b]	$\frac{\partial C}{\partial T} \times 10^{3}$ (±0.2)	C' (±0.05) [c]
Citrate	Log K_1	4.8749	2.5574	7.467	4.5	0.95
	Log K_2	4.8012	1.8970	4.2324	1.0	0.75
	Log K_3	3.8118	1.2619	1.9565	0.5	0.7 [d]
Tartrate	Log K_1	4.1354	1.7351	4.227	2.0	0.80
	Log K_2	3.4677	1.2056	2.286	−0.6	0.48
Malate	Log K_1	4.2491	2.0258	5.580	4.2	1.3 [d]
	Log K_2	3.3348	1.3836	2.692	0.7	0.45 [d]

[a] Log $K^0 = A/T + B - CT$ with T expressed in K. Log K_j = Log $K_j^0 - Z^*A'\{I^{1/2}/(1 + I^{1/2})\} + C_j'I$ at 25°C. $Z^* = 3 - J + 1$ for citrate; $Z^* = 2 - J + 1$ for tartrate and malate; A' = Debye—Hückel coefficient.

[b] With data at only three temperatures this parameter must be treated with caution, and a value for ΔCp cannot be found.

[c] 3σ.

[d] ±0.2.

(T = temperature in K) the parameters of which are shown in Table 7.

Finally the dependence of the sodium complex formation constants on ionic strength was calculated; the parameters for this dependence are shown in Table 8. In Figs. 2—4 the distribution diagrams of the systems Na-cit, Na-tar and Na-mal are reported.

The extrapolated values of protonation constants to zero ionic strength are in good agreement with those reported previously by other authors and obtained by measurements in cells without liquid junctions [24]. However it should be noted that their values are systematically lower than ours, which might be because no allowance was made for potassium complex formations

TABLE 8

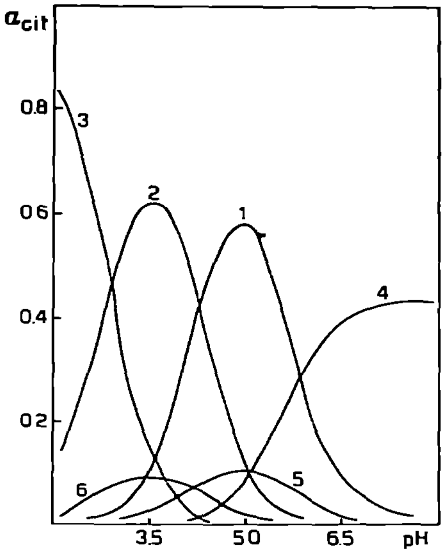
Ionic strength dependence for complexes of citrate, tartrate and malate with sodium [a]

	Log K_1^0 [b] (±0.05) [c]	Log K_2^0 (±0.1)	Log K_3^0 (±0.1)	C_1'' (±0.1)	C_2'' (±0.1)	C_3'' (±0.1)
Citrate	1.35	0.6	0.25	0.4	0.4	0.5
Tartrate	0.95	0.2	—	0.4	0.4	—
Malate	0.63	0.15	—	0.6	0.5	—

[a] Log K_j = Log $K_j^0 - Z_j^*A'(\frac{I^{1/2}}{1 + I^{1/2}} - C_j''I)$. $Z^* = 3 - J + 1$ for citrate; $Z^* = 2 - J + 1$ for tartrate and malate; A' = Debye—Hückel coefficient.

[b] $Na + H_{j-1}A \rightleftharpoons NaH_{j-1}A$.

[c] 3σ.



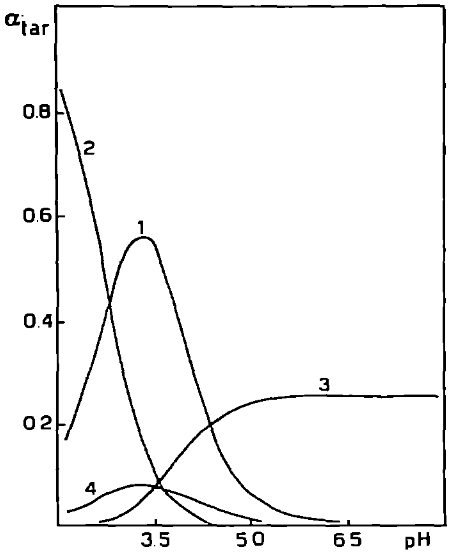


Fig. 2. Distribution diagram for the Na—H—cit system at 37°C. $[Na]_T$ = 0.15 mole dm^{-3}; $[cit]_T$ = 5.0 mmole dm^{-3}. 1. H(cit); 2. H_2(cit); 3. H_3(cit); 4. Na(cit); 5. NaH(cit); 6. NaH_2(cit).

Fig. 3. Distribution diagram for the Na—H—tar system at 37°C. $[Na]_T$ = 0.15 mole dm^{-3}; $[tar]_T$ = 5 mmole dm^{-3}. 1. H(tar); 2. H_2(tar); 3. Na(tar); 4. NaH(tar).

in their studies, and the subsequent lowering of the constants might have affected the extrapolation of the protonation data to zero ionic strength. Our formation constants for Na-cit, Na-tar and Na-mal complexes are also in good agreement with those in the literature. The formation of protonated

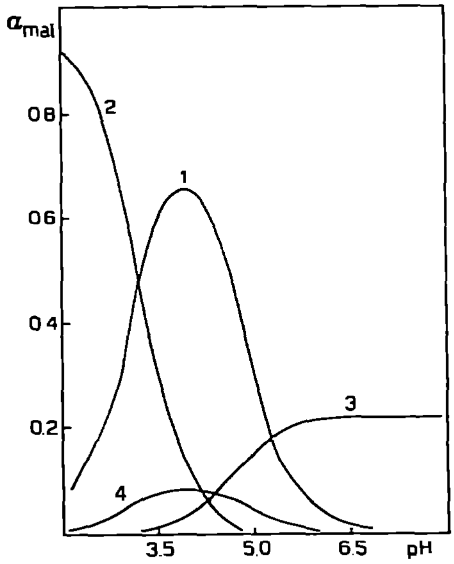


Fig. 4. Distribution diagram for the Na—H—mal system at 37°C. $[Na]_T$ = 0.15 mole dm^{-3}; $[mal]_T$ = 5 mmole dm^{-3}. 1. H(mal); 2. H_2(mal); 3. Na(mal); 4. NaH(mal).

complexes has been found previously only in the case of Na-tar [20,21], whereas we have found that these complexes are formed in all three systems studied.

Till now the protonation enthalpies of citrate, tartrate and malate have been studied using the method of temperature dependence of potentiometric data. An exception to this is the recent calorimetric determination of protonation enthalpies of tartrate [75] ($\Delta H_1 = -1.5$ kJ mole^{-1} and $\Delta H_2 = -3.3$ kJ mole^{-1}, values obtained without allowing for potassium complex formations). The values reported here are the first obtained by direct calorimetry. However, the values obtained using the two methods are not very different.

In the literature there are no data of any kind for sodium complex formation enthalpies for the ligands under study. As has already been observed previously [13], the order of stability for sodium complexes is citrate > tartrate > malate. This order of stability is also followed for protonated complexes. It can further be observed from Table 6 that whereas this order remains the same for entropic stabilization, there is an inversion for enthalpic changes.

The role of thermodynamic parameters in the formation of sodium complexes with citrate, tartrate and malate can only be discussed further in the light of additional thermodynamic data for other alkali-metal ions (in particular K^+ and Li^+) and other ligands that form weak complexes with these metals. This will follow from subsequent papers in this series.

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