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Interaction of L-tartaric acid with alkaline metals and open chain polyammonium cations in aqueous solution

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The interaction of L-tartrate with alkaline metal ions was studied by potentiometry and ultraviolet circular dichroism (UV/CD), and the formation of L-tartrate–polyammonium cation species was also studied by calorimetry. The ultraviolet circular dichroism technique was also used in order to clarify some aspects of the ion pair formation process between L-tartrate anion and alkaline (various ionic strength values were employed) or polyammonium cations. As in potentiometry, tetraethylammonium chloride has been considered as a reference ionic medium (that is, used as a non-interactive salt) for each comparison of the CD spectra recorded in different solutions. The spectropolarimetric technique was shown to be an efficient means of establishing the capacity of the ions considered for mutual conformational adaptability. Some differences clearly appear between the ion pairs formed by L-malate, studied in a previous paper, and L-tartrate anions. In the systems L-tartrate–polyammonium cations the species ALH_r are formed [L = tartrate, A = amine, $r = 1, 2, \cdots, (n + 1)$, n = maximum protonation degree of amine] with stability depending on the charges involved in the formation reaction. Comparisons are made with other carboxylic ligands previously investigated.

Introduction

Numerous general observations have been made by researchers regarding the importance of alkaline metal ions in chemical solutions.[1] Even if the thermodynamic stability of the species formed by ionic interaction between alkaline metal cations and some common inorganic or organic molecules is not very high, it must be remembered that they are practically ubiquitous in nature, that their concentration is generally quite high in all natural fluids, and that they are endowed with a good affinity towards molecules that contain oxygen donor atoms. It has been shown experimentally[1–4] that a formation constant assumes different values by changing the alkaline cation (Li^+, Na^+, K^+, *etc.*) as a background salt (in addition to varied ionic strength and temperature). This has been interpreted in terms of complex formation and has led to an evaluation of the formation constants between alkaline ions and oxygen-containing ligands assuming as a reference the formation constants determined in a tetraethylammonium ionic medium [$(C_2H_5)_4N^+$], which is used as a non interactive cation. Formation constants of alkali metal complexes obtained by the pH-metric method have been confirmed by ion selective electrode-measurements.[5,6]

Even at the low ionic strength obtained with alkaline salts, a significant percentage of an oxygenated ligand is found in the form of the ionic interaction compound with the alkaline cation. This could have important repercussions in many scientific fields (for example, in environmental, biomedical and material sciences) if one considers the numerous differences in, for example, electrical charge and conformation in solution between the free form of the generic ligand L^{n-} and the one bound to the generic alkaline cation M^+, or rather $ML^{(n-1)}$. Moreover, even the protonated forms of the ligand could interact with the alkaline cation, forming species whose stability decreases with a decrease in the number of charges involved.

Furthermore, if systems containing a negatively-charged ligand (such as a carboxylate anion) and a positively-charged ligand (such as a protonated amine) are studied in aqueous solution, it can be shown that in addition to the ion pairs formed between the protonated amine and the anion of the background salt (*e.g.* chloride or nitrate) and the oxygenated anion and the cation of the background salt (*e.g.* sodium or potassium), compounds of association also form between the two molecules.[7–11]

Generalizing, it has been widely demonstrated experimentally, principally through the use of pH-metric measurements, that the generic carboxylate anion, $RCOO^-$, can interact with different kinds of cations, including alkaline cations or protonated (poly)amines, to form compounds of association which have a noteworthy or significant thermodynamic stability.

If a chiral ligand, such as L-tartaric acid (H_2L) is used, it is possible to obtain spectropolarimetric evidence of the formation of compounds of association with non-chiral cations.[12] The peak at approximately 210 nm is due to the transition $n \longrightarrow \pi^*$ of the carbonyl chromophore of the L-tartaric acid, and in fact undergoes modifications in the presence of alkaline or alkylammonium cations, which allows us to obtain information to complement the potentiometric data available for this type of interaction.

This paper describes a potentiometric, calorimetric and spectropolarimetric (ultraviolet circular dichroism, UV/CD) study on the interaction of L-tartaric acid with alkaline (lithium, sodium and potassium) or (poly)ammonium (ethylenediamine, en; diethylenetriamine, dien; triethylenetetramine, trien; spermine, sper; tetraethylenepentamine, tetren and pentaethylenehexamine, penten) cations. To evaluate interaction with alkaline metal cations, different ionic media, namely LiCl, NaCl, KCl, Me_4NCl (tetramethylammonium chloride) and Et_4NCl (tetraethylammonium chloride), and ionic strength values, $0.1 \le I \le 0.9$ M, (T = 25 °C), were employed for both potentiometric and UV/CD studies; the L-tartaric acid signal recorded in tetramethylammonium chloride was employed as a reference and assumed as a non-interactive background salt.[12]

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In order to give a complete picture of the binding of L-tartrate anion by polyammonium cations, we also performed calorimetric measurements to obtain ΔH^0 values for these interactions.

Experimental

Chemicals

Amines [ethylenediamine (H_2A^{2+}), diethylenetriamine (H_3A^{3+}), triethylenetetramine (H_4A^{4+}), spermine (H_4A^{4+}), tetraethylenepentamine (H_5A^{5+}) and pentaethylenehexamine (H_6A^{6+}) (Aldrich or Sigma products)] were purified by transformation into the corresponding hydrochlorides and were used in this form. L-Tartaric acid [(H_2L, tar), Fluka purum and Merck] was used without further purification. Its purity was checked alkalimetrically and was greater than 99.5%. NaCl, LiCl, KCl, Me_4NCl and Et_4NCl were Fluka or Carlo Erba products. Solutions of Na_2tar (used in the calorimetric titrations), were prepared by adding standard NaOH to H_2tar until complete neutralization occurred. Standard solutions of NaOH, KOH, HCl and HNO_3 were prepared by diluting concentrated Fluka ampoules and were standardized against potassium hydrogenphthalate or sodium carbonate, respectively. Grade A glassware and deionized and twice distilled water were used for all solutions.

Electromotive force measurements

The free hydrogen ion concentration was measured with two different potentiometric systems. (a) Metrohm 654 potentiometer coupled with a combination 8102 Ross type electrode; (b) Metrohm E-605 potentiometer equipped with a Metrohm combined glass electrode. The two pieces of equipment were connected to a Metrohm Dosimat 665 motorized burette (minimum reading 0.001 ml) and to a PC which, with appropriate software, allows fully computerized titrations. The titration program allows the evaluation of equilibrium potential values and determines the amount of titrant based on the actual buffering properties of the titrated solution, so that there is a difference in pH values of 0.05–0.08 between two successive readings; the emf was considered to be stable when the variation was less than 0.1 mV within 5 min.

As for alkaline metal ion pairs with L-tartaric acid, 25 ml of the solution containing the ligand and the cation (chloride salt) under study were titrated with standard NaOH up to 100% neutralization. Concentrations used in the experiments were: $c_{\text{cation}} = 0.1–0.9$ M, $c_{\text{ligand}} = 6$ mM.

25 ml of the solution containing the ligand and the amine hydrochloride under study were titrated with standard NaOH up to 80–90% neutralization. Titrations were performed without adding background salt. Concentrations used in the experiments were: $c_{\text{amine}} = 5–40$ mM, $c_{\text{anion}} = 10–100$ mM. Separate titration of HCl at about the same ionic strength (adjusted with NaCl) as the sample under study, was carried out to determine the standard electrode potential E^0. A stream of purified and presaturated N_2 was bubbled through all solutions in order to exclude the presence of CO_2 and O_2. The measurement cells were thermostated at 25 ± 0.1 °C by means of liquid circulation from a thermostat (model D1-G Haake).

Calorimetric measurements

Calorimetric measurements were performed by titrating 50 ml of the solution containing the amine hydrochloride (en, dien, trien, tetren, penten) under study (5–10 mM) with Na_2tar (0.3 M) at 25.000 ± 0.001 °C using a Tronac Isoperibol Titration model 450 calorimeter, coupled with a Keithley 196 system Dmm digital multimeter. The titrant was delivered by a 2.5 ml capacity Hamilton model 1002TLL syringe. A computer program was used for the acquisition of the calorimetric data. Its accuracy was checked by titrating a TRIS [tris(hydroxymethyl)aminomethane] buffer with HCl. The heat of dilution was measured before each experiment. The accuracy of the calorimetric apparatus was $Q \pm 0.008$ J and $v \pm 0.001$ cm^3.

Circular dichroism spectra

The UV/CD determinations were carried out with a J-600 JASCO spectropolarimeter, from 200 to 250 nm (optical path 0.100 cm) under the same experimental conditions as used for the potentiometric measurements. The solution being examined was transferred from the potentiometric to the optical cell using a peristaltic pump. The compositions of the solutions were the same as those used in the potentiometric determinations.

Data analysis and calculations

The non linear least squares computer program ESAB2M was used to calculate the purity of the reagents and to refine all the parameters related to the calibration of the electrode system. The computer programs BSTAC and STACO were used to calculate formation constants. The dependence on ionic strength of the formation constants was taken into account by using a Debye–Hückel type equation

$$\log\beta = \log{}^{T}\beta - z^* \sqrt{I}/(2 + 3\sqrt{I}) + CI + DI^{3/2} \qquad (1)$$

where:

$$C = c_0 p^* + c_1 z^*;\ D = d_1 z^*;\ p^* = \Sigma p_{\text{reactants}} - \Sigma p_{\text{products}};$$
$$z^* = \Sigma z^2_{\text{reactants}} - \Sigma z^2_{\text{products}}$$

(β = formation constant; ${}^{T}\beta$ = formation constant at zero ionic strength; p and z are the stoichiometric coefficients and the charges, respectively). For the calculations performed in this work we used the values $c_0 = 0.10$, $c_1 = 0.23$ and $d_1 = -0.1$. The STACO and BSTAC computer programs are able to perform calculations in non-constant ionic strength conditions. Distribution diagrams and simulated titration curves were obtained using the computer program ES4ECI.

The different equilibria considered in this work were expressed as follows:

$$A^0 + iH^+ = H_iA^{i+}\ (\beta_i^{H}) \qquad (2a)$$

$$L^{z-} + jH^+ = H_jL^{(j-z)}\ (\beta_j^{H}) \qquad (2b)$$

$$A^0 + L^{z-} + rH^+ = ALH_r^{(r-z)}(\beta_r) \qquad (2c)$$

$$H_iA^{i+} + H_jL^{(j-z)} = ALH_r^{(r-z)}\ (K_r,\ r = i + j) \qquad (2d)$$

Calorimetric titration data were analysed by the computer program ES5CM. The dependence on ionic strength of the formation enthalpies was taken into account as previously proposed. This was also allowed for in calculations by considering the relative ΔH^0 values. The computer programs used in this work are described in ref. 13.

Circular dichroism spectra were analysed by means of the least squares computer program MOLEX,[14] which calculates molar absorption (ε_λ) or molecular ellipticity ($[\theta_\lambda]$) values for single species using experimental spectra (ellipticity, ψ/mdegrees, or absorbance, A, *vs.* wavelength, λ/nm), analytical concentrations of the reagents and the proposed chemical model (stoichiometric coefficients and known stability constant values of all complexes) as input. After the calculation of the species distribution, spectra are estimated for each complex formed in solution, assuming only the additivity of ellipticity or absorbance in the investigated concentration range. No assumptions about the shape of the curves or on the nature of the electronic transitions involved are taken into account by the program. As for CD data, the values of circular dichroism, $\Delta\varepsilon_\lambda$, are then calculated from the values of molecular ellipticities, $[\theta_\lambda]$, by means of the formula $[\theta_\lambda] = 3300\Delta\varepsilon_\lambda$.[15]

In a potentiometric and calorimetric study of the interaction between L-tartrate and polyammonium cations, protonation data must be available for all the ligands: this study has already been made[2,16] and the data are collected in Table 1. Weak interactions between Na^+ and L-tartrate or Cl^- and polyammonium cations were also taken into account.[2,16]

Results and discussion

Stability data for alkaline cations

Table 2 reports the pH-metric results obtained in this study for the protonation of L-tartaric acid in different ionic media and at two ionic strength values. By comparing the formation constant values obtained in tetraethylammonium with those obtained in each alkaline medium, it is possible to evaluate the stability of the ion pairs amongst the different forms of the ligand under study and the alkaline cation. Elaboration of the potentiometric data allowed us to accurately simulate the experimental trend of the titration curves: the chemical model suggested the formation of two ion pairs, namely MHL^0 (with the monoanion L-hydrogentartrate, HL^-) and ML^- (with the dianion L-tartrate, L^{2-}). Table 3 shows the results, at 25 °C, obtained in this study for the ion pairs of lithium, sodium, and potassium at two ionic strength values (namely 0.1 and 0.9 M). The thermodynamic results obtained can be considered to be in agreement with those of the literature for sodium[17,18] or potassium[18] ion pairs of L-tartaric acid.

Table 1 Protonation constants[a] and protonation enthalpies[b] for L-tartaric acid (eqn. (2a), $\log\beta_i^H$), and polyamines (eqn. (2b), $\log\beta_j^H$) at $I = 0$ M and $T = 25$ °C

	$\log\beta_i^H$ or $\log\beta_j^H$					
i or *j*	tar[c]	en[d]	dien[e]	trien[f]	tetren[f]	penten[g]
1	4.37	9.91	9.80	9.67	9.83	9.89
2	7.40	16.77	18.54	18.54	18.84	18.95
3			22.20	24.66	26.57	27.04
4				27.04	30.47	32.86
5					32.35	35.94
6						37.54
ΔH^0						
1	−4[c]	−51.3[g]	−49.2[g]	−42.6[g]	−42.2[g]	−45.3[g]
2	−6	−96.3	−98.7	−88.9	−87.2	−90.2
3			−130.2	−131.2	−130.5	−131.4
4				−164.5	−161.8	−166.1
5					−188.0	−190.1
6						−218.8

[a] eqn. (2a) or (2b). [b] In kJ mol^{-1}. [c] Ref. 2. [d] Ref. 20. [e] Ref. 21. [f] Ref. 22. [g] Ref. 16.

Table 2 Overall protonation constants of L-tartaric acid in various ionic media and at two ionic strengths ($T = 25$ °C)

	$I = 0.1$ M		$I = 0.9$ M	
Cation	$\log\beta_1^H$	$\log\beta_2^H$	$\log\beta_1^H$	$\log\beta_2^H$
Li^+	3.901(3)[a]	6.715(3)	3.625(9)	6.262(8)
Na^+	3.910(3)	6.707(3)	3.687(9)	6.405(9)
K^+	3.926(6)	6.757(6)	3.732(9)	6.467(9)
Me_4N^+	3.974(6)	6.816(6)	3.900(8)	6.764(8)
Et_4N^+	3.992(3)	6.841(3)	4.170(9)	7.140(9)

[a] Uncertainty is reported in parentheses as ±3*s* (*s* = standard deviation) on the last significant figure.

Circular dichroism data for alkaline cations

The degree of protonation of the ligand (varied through alkalimetric titration) affects circular dichroism intensity and the position of the absorption maximum (Fig. 1); UV/CD data are different for the three forms, namely H_2L, HL^- and L^{2-} (see Fig. 2 and Table 4), as previously seen for the protonation of the L-malate ion.[19]

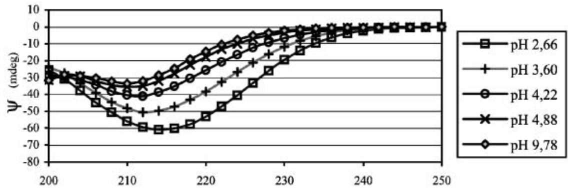

Fig. 1 Experimental UV/CD spectra recorded on an aqueous solution of L-tartaric acid 5 mM (ionic medium = $Et_4N^+Cl^-$, $I = 0.1$ M and $T = 25$ °C).

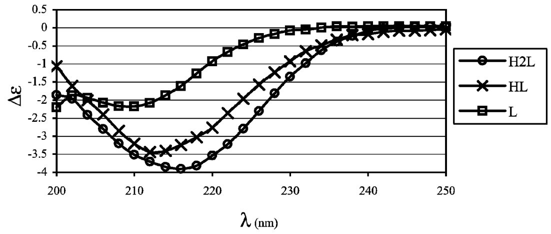

Fig. 2 Calculated UV/CD spectra of each complex with proton (or with hydrogen ion) for L-tartaric acid (ionic medium = $Et_4N^+Cl^-$, $I = 0.1$ M and $T = 25$ °C).

The UV/CD spectrum of the completely deprotonated ligand (L^{2-}, $\lambda_{max} = 210$ nm), due to the $n \longrightarrow \pi^*$ transition of the carbonyl chromophore, shows significant differences when the ionic medium is varied (Table 5). This behaviour can be interpreted as direct spectroscopic evidence of the interaction between the L-tartrate ion and the alkaline cations.

Table 5 shows that the UV/CD signals of the L-tartrate ion obtained in the two tetralkylammonium solutions at different ionic strengths are almost identical, as are those obtained in Na^+ and K^+. Nevertheless, the signals due to Na^+ and K^+ or to Li^+ can be significantly different from those recorded in Et_4N^+ (or Me_4N^+). Therefore, we can say that this spectroscopic tech-

Table 3 Formation constants of the ion pairs of the L-hydrogentartrate (MHL^0) or L-tartrate (ML^-) ions with alkaline cations (M^+) at two ionic strengths ($T = 25$ °C)

	$I = 0.1$ M			$I = 0.9$ M		
Cation M^+	$\log\beta_{MHL^0}$[a]	$\log K_{M(LH)}$[b]	$\log K_{ML^-}$	$\log\beta_{MHL^0}$[a]	$\log K_{M(LH)}$[b]	$\log K_{ML^-}$
Li^+	4.10(4)[c]	0.11	0.73(5)	4.25(6)	0.08	0.86(6)
Na^+	4.08(6)	0.09	0.56(5)	4.10(8)	−0.07	0.70(7)
K^+	3.78(5)	−0.21	0.41(5)	4.06(7)	−0.11	0.63(6)

[a] The values of $\log\beta_{MHL^0}$ refers to the reaction: M + L + H = MLH. [b] The values of $\log K_{M(LH)}$ refers to the reaction: M + HL = MLH (see Table 2 for protonation constant values). [c] Uncertainty is reported in parentheses as ±3*s* (*s* = standard deviation) on the last significant figure.

Table 4 UV/CD (λ_{max} and $\Delta\varepsilon_{max}$) data in tetraethylammonium calculated for H_2L, HL^- and L^{2-} at two ionic strengths in aqueous solution (T = 25 °C)

	I = 0.1 M		I = 0.9 M	
Species	λ_{max}/nm	$\Delta\varepsilon_{max}$/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	$\Delta\varepsilon_{max}$/dm^3 mol^{-1} cm^{-1}
L^{2-}	210	−2.17	210	−2.26
HL^-	213	−3.44	215	−3.76
H_2L	215	−3.90	216	−4.13

Table 5 Experimental signal [ellipticity, ψ (mdegrees)] of circular dichroism recorded at 210 nm on 5 mM L-tartrate solutions in various ionic media and at two ionic strengths. Ellipticity differences at 210 nm ($\Delta\psi_{210}$ (mdegrees)) for 5 mM L-tartrate between the signal in tetraethylammonium and that in alkaline salt [$\Delta\psi = \psi(Et_4N^+) - \psi(M^+)$] at two ionic strengths (T = 25 °C)

Cation	ψ_{210} (I = 0.1)	$\Delta\psi_{210}$ (I = 0.1)	ψ_{210} (I = 0.9)	$\Delta\psi_{210}$ (I = 0.9)
Li^+	−36.4	0.2	−38.4	0.8
Na^+	−37.8	1.6	−40.9	3.3
K^+	−37.5	1.3	−41.0	3.4
Me_4N^+	−35.8	–	−37.2	–
Et_4N^+	−36.2	–	−37.6	–

Table 6 Value of circular dichroism ($\Delta\varepsilon$ (dm^3 mol^{-1} cm^{-1})) calculated at 210 nm for the ion pairs (ML^-) between alkaline cations and the L-tartrate ion and at two ionic strengths in aqueous solution (T = 25 °C)

Ion pair	$\Delta\varepsilon_{210}$ (I = 0.1)	$\Delta\varepsilon_{210}$ (I = 0.9)
LiL^-	−2.28	−2.35
NaL^-	−2.63	−2.54
KL^-	−2.70	−2.55

nique is a little less sensitive than the pH-metric technique, which allows us to significantly differentiate the stabilities of all the species examined, though it still constitutes an important independent method of verification of the hypotheses of the chemical model formulated on the basis of pH-metric evidence.

The differences between the signals (ellipticity, ψ (mdegrees)) recorded in tetraethylammonium and those observed in the various alkaline media are reported in Table 5. With the model proposed, such differences grow consistently with increased ionic strength. In fact, by increasing I, the percentage of formation of the ion pair ML^- in solution increases. The experimental differences in ellipticity are almost equal for Na^+ and K^+, but lower for Li^+. The results that emerge from Tables 5 and 6 are in clear agreement with the thermodynamic data relative to Na^+ and K^+, if one takes into consideration that $\log K_{ML}$ values for these two cations are quite similar (Table 3). Therefore, the results obtained for lithium are surprising. Owing to its high charge density, lithium is the alkaline cation which interacts with the maximum stability (Table 3); on the other hand, lithium exhibits the minor capacity of differentiating the spectropolarimetric behaviour of L^{2-} with respect to ML^- (Table 6). Nevertheless, one must consider that in UV/CD the information obtained is qualitatively different from that obtained using the pH-metric technique; in particular, the differences in spectral intensity that we have reported relate to the different conformational situations of the L^{2-} species in various ionic environments.

Moreover, a difference in the position of the experimental absorption maximum of approximately 2 nm (Fig. 3) is observed for L^{2-} in Et_4N^+ and in Li^+ (in fact even the calculated data are in agreement since $\lambda_{max\ LiL}$ = 208 nm). Such a difference is not observed for Na^+ and K^+, consistent with the findings for L-malic acid.[12] Even though this difference is small, it provides precious information about the nature of the compounds we are examining. Table 6 reports circular dichroism values at 210 nm ($\Delta\varepsilon_{210}$) for the various ion pairs calculated by means of a simple procedure based on the application of the Lambert–Beer law whose validity ranges, in this specific case, have already been studied.[12]

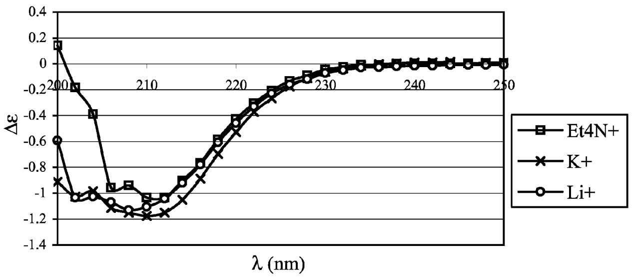

Fig. 3 Experimental UV/CD spectra recorded on an aqueous solution of L-tartaric acid 5 mM in various ionic medium at I = 0.9 M and T = 25 °C.

Stability data for polyammonium cations

L-Tartrate forms ALH_r species with polyammonium cations with $r = 1, 2, \cdots, (n + 1)$ (n = maximum number of protons in the polyammonium cation). Stability, in terms of $\log K$ [reaction (2d)], ranges between 0.2 and 4.8 (Table 7), and is strictly dependent on the charges involved in the formation reaction. If we consider the fully protonated amine and the dianion of L-tartrate, *i.e.* $H_nA^{n+} + L^{2-} = ALH_n^{(n-2)}$ ($\log K_n$, ΔG^0_n) we have a straight line whose equation is (ΔG^0 in kJ mol^{-1}):

$$-\Delta G^0_n = (7.0 \pm 0.3)n$$

Fig. 4 shows the diagram ΔG^0_n *vs.* n. The linear dependence is quite good and, in addition, a single function can fit the data of L-tartrate, malonate and L-malate (see refs. 8 and 12). By considering ΔG^0 formation for the three anions altogether, we have:

$$-\Delta G^0_n = (6.9 \pm 0.2)n$$

Calorimetric data for polyammonium cations

Calorimetric measurements allowed us to obtain enthalpy changes for the formation of ALH_n and ALH_{n+1} species. ΔG^0_n, ΔH^0_n and $T\Delta S^0_n$ values are reported in Table 8. ΔH^0_n values are always positive and increase with increasing polyammonium cation charge. In Fig. 5 we plotted $T\Delta S^0_n$ *vs.* n. As can be seen, the data are fitted by straight lines ($T\Delta S^0_n$ in kJ mol^{-1}):

$$T\Delta S^0_n = (8.8 \pm 0.2)n$$

The dependence of $T\Delta S^0_n$ for L-tartrate species is significantly different from that of L-malate [$T\Delta S^0_n = (11.1 \pm 0.3)n$] or malonate [$T\Delta S^0_n = (12.4 \pm 0.3)n$]. This different trend is shown in Fig. 5.

Table 7 Formation constants of L-tartrate–polyammonium cation complexes, at $I = 0$ M and $T = 25$ °C. logβ_r is related to the overall formation reaction [reaction (2c)] of the ion pair ALH_r given in the Data analysis and calculations section; logK_r [reaction (2d)] is calculated taking into account the reaction here reported (an hypothesis, based on protonation constant values, on the position of the proton is made)

logβ_r ± 3s[a]	Reaction	logK_r
A = en		
10.80 ± 0.14	$HA^+ + L^{2-} = ALH^-$	0.9
19.01 ± 0.03	$H_2A^{2+} + L^{2-} = ALH_2^0$	2.2
22.13 ± 0.05	$H_2A^{2+} + HL^- = ALH_3^+$	0.9
A = dien		
12.2 ± 0.2	$HA^+ + L^{2-} = ALH^-$	2.4
21.64 ± 0.03	$H_2A^{2+} + L^{2-} = ALH_2^0$	3.1
26.29 ± 0.05	$H_2A^{2+} + HL^- = ALH_3^+$	3.3
26.29 ± 0.05	$H_3A^{3+} + L^{2-} = ALH_3^+$	4.1
29.2 ± 0.2	$H_3A^{3+} + HL^- = ALH_4^{2+}$	2.6
A = trien		
11.4 ± 0.2	$HA^+ + L^{2-} = ALH^-$	1.7
21.04 ± 0.05	$H_2A^{2+} + L^{2-} = ALH_2^0$	2.5
28.03 ± 0.04	$H_3A^{3+} + L^{2-} = ALH_3^+$	3.4
31.94 ± 0.04	$H_3A^{3+} + HL^- = ALH_4^{2+}$	2.85
34.52 ± 0.05	$H_4A^{4+} + HL^- = ALH_5^{3+}$	3.05
34.0 ± 0.2	$ALH_3^+ + HL^- = AL_2H_4^0$	1.5
34.0 ± 0.2	$ALH_4^{2+} + L^{2-} = AL_2H_4^0$	2.1
A = sper[b]		
12.60 ± 0.09	$HA^+ + L^{2-} = ALH^-$	1.9
23.24 ± 0.04	$H_2A^{2+} + L^{2-} = ALH_2^0$	2.8
32.29 ± 0.05	$H_3A^{3+} + L^{2-} = ALH_3^+$	3.6
40.28 ± 0.05	$H_4A^{4+} + L^{2-} = ALH_4^{2+}$	4.3
43.29 ± 0.12	$H_4A^{4+} + HL^- = ALH_5^{3+}$	2.9
42.5 ± 0.2	$ALH_4^{2+} + L^{2-} = AL_2H_4^0$	2.2
A = tetren		
10.0 ± 0.4	$HA^+ + L^{2-} = ALH^-$	0.2
20.82 ± 0.05	$H_2A^{2+} + L^{2-} = ALH_2^0$	2.0
29.44 ± 0.03	$H_3A^{3+} + L^{2-} = ALH_3^+$	2.9
34.74 ± 0.03	$H_4A^{4+} + L^{2-} = ALH_4^{2+}$	4.3
38.08 ± 0.05	$H_4A^{4+} + HL^- = ALH_5^{3+}$	3.2
40.02 ± 0.07	$H_5A^{5+} + HL^- = ALH_6^{4+}$	3.2
40.86 ± 0.06	$ALH_4^{2+} + HL^- = AL_2H_5^+$	1.7
A = penten		
12.4 ± 0.2	$HA^+ + L^{2-} = ALH^-$	2.5
21.95 ± 0.15	$H_2A^{2+} + L^{2-} = ALH_2^0$	3.0
30.86 ± 0.10	$H_3A^{3+} + L^{2-} = ALH_3^+$	3.8
37.67 ± 0.08	$H_4A^{4+} + L^{2-} = ALH_4^{2+}$	4.8
41.87 ± 0.09	$H_4A^{4+} + HL^- = ALH_5^{3+}$	4.6
44.65 ± 0.10	$H_5A^{5+} + HL^- = ALH_6^{4+}$	4.3
45.9 ± 0.2	$H_6A^{6+} + HL^- = ALH_7^{5+}$	3.9
48.3 ± 0.3	$ALH_5^{3+} + HL^- = AL_2H_6^{2+}$	2.0

[a] s = standard deviation. [b] Ref. 23.

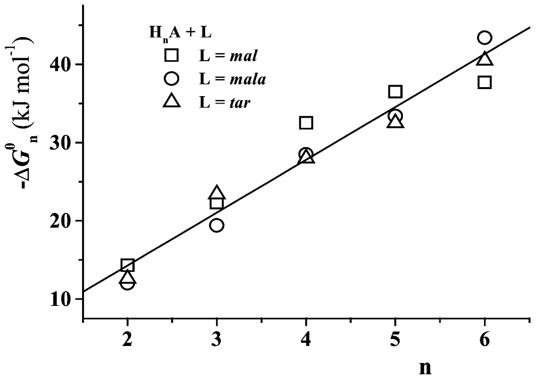

Fig. 4 ΔG^0_n for the interaction of malate (mala), malonate (mal) and tartrate (tar), at $I = 0$ M and $T = 25$ °C (n = maximum protonation degree of amine).

Table 8 Thermodynamic parameters (kJ mol^{-1}; ±3s)[a] for L-tartrate–polyammonium cation (ALH_n) complexes at $I = 0$ M and $T = 25$ °C

Amine	n[b]	$-\Delta G^0_n$	ΔH^0_n (H_nA^{n+} + tar^{2-})	$T\Delta S^0_n$
en	2	12.6 ± 0.3	1.5 ± 0.7	14.1 ± 0.8
dien	3	23.4 ± 0.4	2.3 ± 0.8	25.7 ± 0.9
trien	4	28.0 ± 0.3	7.1 ± 1.1	35.1 ± 1.1
tetren	5	32.5 ± 0.4	12.0 ± 1.4	44.5 ± 1.5
penten	6	40.5 ± 0.7	13.8 ± 1.7	54.3 ± 1.8

[a] s = standard deviation. [b] n = maximum protonation degree of amine.

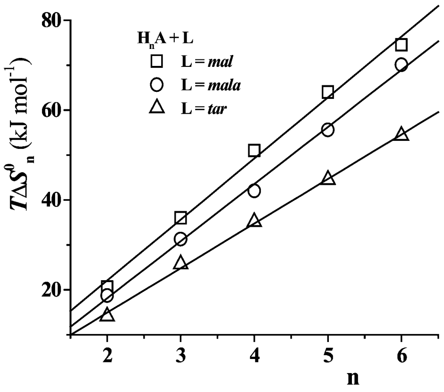

Fig. 5 $T\Delta S^0_n$ for the interaction of malate (mala), malonate (mal) and tartrate (tar), at $I = 0$ M and $T = 25$ °C (n = maximum protonation degree of amine).

Circular dichroism data for polyammonium cations

In order to calculate UV/CD spectra for each ion pair between L-tartrate ion and polyammonium cations, we start from spectra calculated for each species of the H^+–L-tartaric acid system in Et_4N^+ under the same experimental ionic strength conditions (for $I = 0.6$ M the values are: L^{2-} $\Delta\varepsilon_{210} = -2.16$, HL^- $\Delta\varepsilon_{213} = -3.54$, H_2L $\Delta\varepsilon_{215} = -4.00$). Thus, spectra were calculated for the dominating complexes (see Table 9) using a chemical model (even the formation constants were calculated at the ionic strength value actually used in order to record the UV/CD spectra) that is very close to experimental reality (ionic strength was determined from the excess of polyammonium cations used in the solutions studied). Even the interaction of the polyammonium cations with the chloride ion was taken into account in the calculations. Spectropolarimetric results for ion pairs of the L-tartrate ion with polyammonium cations are reported in Table 9.

As already seen with alkaline cations, the values of $\Delta\varepsilon_{210}$ for the ion pairs, even at equal cation charge (H_4A^{4+} for spermine and tetraethylenepentamine), can differ, presumably because of the different charge density. Furthermore, spermine contains four amino groups, all protonated in the ALH_4^{2+} ion pair, while in the same complex, the tetraethylenepentamine also contains a deprotonated amino group that could cause steric hindrance, which does not favour the global conformation of the complex in solution. Therefore, if one considers the trend in $\Delta\varepsilon_{210}$ values for ion pairs with increasing charges, excluding the tetraethylenepentamine pair for reasons previously explained, one can note a regular decrease in the value of $\Delta\varepsilon_{210}$ with increasing cation charge. It therefore increases the tendency of the spectrum of these ion pairs to resemble the HL^-spectrum (Table 4). These results support the hypothesis of a priority electrostatic component in this species.

Even the position of the absorption maximum is indicative of the interaction that has occurred between the L-tartrate ion and the polyammonium cation (Table 9): as already seen for lithium, a slight hypsochromic shift is observed in the absorption maximum of the ion pair when compared to that of the L-tartrate ion (Table 4).

L-Malate–L-tartrate comparison and conclusions

As regards interaction with Na^+, no particularly significant differences were observed (see Table 10) between L-malate and

Table 9 λ_{max} and $\Delta\varepsilon_{210}$ values calculated for the dominant complexes between the polyammonium cation (H_nA^{n+}) and the L-tartrate (L^{2-}) ion in aqueous solution (T = 25 °C)

Amine	Ion pair	Cation	Anion	$\Delta\varepsilon_{210}$ (ion pair)/dm^3 mol^{-1} cm^{-1}	$\Delta\varepsilon_{210}$ (L^{2-})/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm
en	ALH_2^0	H_2A^{2+}	L^{2-}	−2.23	−2.16	209
trien	ALH_3^+	H_3A^{3+}	L^{2-}	−2.32	−2.17	207
sper	ALH_4^{2+}	H_4A^{4+}	L^{2-}	−2.61	−2.16	209
tetren	ALH_4^{2+}	H_4A^{4+}	L^{2-}	−2.27	−2.17	207

Table 10 Differences in the experimental UV/CD signal for the ion pairs L-malate–alkaline and L-tartrate–alkaline, at two ionic strengths (T = 25 °C)

	L-Malate		L-Tartrate	
Cation	$\Delta\psi_{207}$/mdegrees (I = 0.1)	$\Delta\psi_{207}$/mdegrees (I = 0.9)	$\Delta\psi_{210}$/mdegrees (I = 0.1)	$\Delta\psi_{210}$/mdegrees (I = 0.9)
Li^+	1.1	4.7	0.2	0.8
Na^+	0.9	3.0	1.6	3.3

Table 11 Differences in circular dichroism values [$\Delta\Delta\varepsilon_{210} = \Delta\varepsilon_{210}(L^{2-}) - \Delta\varepsilon_{210}$(ion pair)] for L-malate ion[12] or L-tartrate ion and respective ion pairs with polyammonium cations (at equal ionic strength) (T = 25 °C)

	$\Delta\Delta\varepsilon_{210}$/dm^3 mol^{-1} cm^{-1}	
Amine	L-Malate	L-Tartrate
en	0.50	0.07
trien	0.58	0.15
sper	0.53	0.45
tetren	0.84	0.10

L-tartrate ion pairs at equal ionic strength, even taking into consideration the uncertainty of the spectropolarimeter. The situation is quite different for Li^+, which demonstrates the ability to induce clearly more significant conformational modifications to the L-malate ion: this is probably due to the steric hindrance caused by the two alcoholic groups of the L-tartrate ion. Generally, because of its high charge density, Li^+ forms more stable ion pairs than Na^+ or K^+.[1] In particular, the stability of the ion pairs with L-tartrate ion is higher than the stability of those with L-malate, even if, conformationally, the UV/CD data seem to confirm the great difficulty of the L-tartrate ion to undergo the influence of Li^+.

In order to compare the results obtained for the various ion pairs with polyammonium cations the parameter $\Delta\Delta\varepsilon = \Delta\varepsilon(L^{2-}) - \Delta\varepsilon$(ion pair) was calculated. The $\Delta\Delta\varepsilon$ parameters (at a fixed wavelength) presented in Table 11 for L-malic acid ($\Delta\varepsilon$ values for L-malic acid at I = 0.1 M are from ref. 12) and L-tartaric acid can be used as indicators of spectropolarimetric response for the interaction of the anion (L-malate or L-tartrate) with each polyammonium cation. It can be seen that for all the polyamines studied, interaction with L-malic acid produced a much more significant modification of $\Delta\Delta\varepsilon$ than with L-tartaric acid. It can therefore be hypothesized that the second alcoholic group present on the L-tartrate ion produces enough steric hindrance to make the conformational variation of the anion less significant than that of the L-malate ion interaction. Only for spermine, which forms a dominant complex in which all four of its aminic groups are protonated, do the two anions show comparable behaviour.

Thermodynamic parameters for the formation of L-tartrate–polyammonium complexes show that these species are fairly stable and that their stability is mainly entropic in nature. Free formation energy is comparable to that of other polycarboxylic anions, and the entropic contribution, though of the same order of magnitude, shows a fair discriminating capacity among different carboxylic anions. If we compare malonate, malate and tartrate we find (Fig. 5) significant differences, and the mal > mala > tar trend may indicate the contribution of –OH groups in the coordination.

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