Thermodynamics of sulfate anion binding by macrocyclic polyammonium receptors

Paloma Arranz,[a] Andrea Bencini,[b] Antonio Bianchi,*[b] Pilar Diaz,[c] Enrique García-España,*[c] Claudia Giorgi,[b] Santiago V. Luis,[d] Manuel Querol[d] and Barbara Valtancoli[b]

[a] *Department of Inorganic and Organic Chemistry, University of Jaen, Jaen, Spain*
[b] *Department of Chemistry, University of Florence, Via Maragliano 75/77, 50144 Florence, Italy*
[c] *Department of Inorganic Chemistry, University of Valencia, C/ Dottor Moliner, 46100 Burjassot (Valencia), Spain*
[d] *Department of Inorganic and Organic Chemistry, University Jaume I, E-12080 Castellón, Spain*

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The interaction of SO_4^{2-} with polyammonium cations derived from fourteen polyamines (5 polyazacycloalkanes, 2 polyazacyclophanes, 3 phenanthrolinacyclophanes, 2 dibenzenacyclophanes and 2 acyclic polyamines) in aqueous solution has been studied by means of potentiometric and microcalorimetric techniques. Only 1 : 1 receptor–anion complexes have been found in solution. Complexed species of considerable stability are formed, although the two acyclic polyamines (dimethylpentaethylenehexaamine and dimethylhexaethyleneheptaamine) and the smallest phenanthrolinacyclophane do not interact with the anion. The complexation reactions are endothermic, or almost athermic, and promoted by invariably favourable entropic contributions, indicating that these pairing processes are mostly determined by the desolvation of the interacting species that occurs upon charge neutralisation. The results are compared with those previously obtained for phosphate binding.

Introduction

The supramolecular chemistry of anions has grown rapidly in recent years to become an important area of supramolecular chemistry owing to the ubiquitous presence of negatively charged species in both inorganic and biological systems.[1] Two principal strategies have been developed in order to achieve strong and selective anion binding, consisting, respectively, of the use of i) non-covalent interactions with positively charged centres and ii) coordinative interactions with metal ions.

Regarding the first strategy, polyammonium receptors have proved particularly useful due to their ability to form very stable adducts with anions in aqueous solution.[2] In addition, as such receptors are generated upon protonation of polyamines, it is possible to adjust the strength of the anion–receptor interaction by modulating the ligand protonation, that is, by using the solution pH as a tuning control. As a matter of fact, it is well known that the strength of this interaction is mainly determined by the positive charge of the receptor, although hydrogen bonding between the interacting partners constitutes a significant contribution to the association. In this respect, we have recently shown,[3] in a paper dealing with the interaction of phosphate type anions with polyammonium receptors, that the stability trends of such complexes are not strictly determined by electrostatic forces, hydrogen bonding being of considerable importance in the complex formation, even in aqueous solution where the hydrogen bonding properties of the interacting species are quenched by water. Apparently, when protonated forms of phosphate anions are considered, increasing complex stability with decreasing charge on the two partners was observed in several cases. The enthalpy changes determined microcalorimetrically for the formation of these phosphate complexes, and the derived entropic terms, were consistent with the occurrence of different hydrogen bonding modes (which protonated forms of phosphate anions can bring about by virtue of their donor and acceptor properties) in determining such unexpected trends.[3]

In order to get further insight into the nature of the interaction of oxo-anions with polyammonium receptors in aqueous solution, we have undertaken a thermodynamic study on the formation of SO_4^{2-} complexes with the macrocyclic ligands displayed in Chart 1. Although SO_4^{2-} and PO_4^{3-} have very similar structures, the former anion displays a lower tendency than phosphate to undergo protonation, the HSO_4^- species being formed only in very acidic solutions (pH < 2). For this reason, the complexation equilibria involving sulfate are much easier to interpret than the analogous equilibria involving phosphate. For the sulfate systems there is a large pH range (pH > 2.5) in which sulfate acts exclusively as a hydrogen bond acceptor.

Moreover, the ability of the anion to form hydrogen bonds of different types leads to remarkable consequences as shown by the fact that the formation of protonated forms of phosphate at physiological pH is a discriminating feature for selective recognition of phosphate, over sulfate, by proteins in living systems.[4]

Experimental

Materials

Ligands **L2–L14** were synthesised according to described procedures.[5] **L1** was purchased from commercial sources and purified as its hydrochloride salt. High purity Na_2SO_4, $NaClO_4$ and Me_4NCl employed in the potentiometric measurements were purchased from Merck.

Potentiometric measurements

All pH measurements ($pH = -\log [H^+]$) employed for the determination of protonation constants were carried out in 0.15 mol dm^{-3} $NaClO_4$ (aliphatic ligands) or 0.1 mol dm^{-3}

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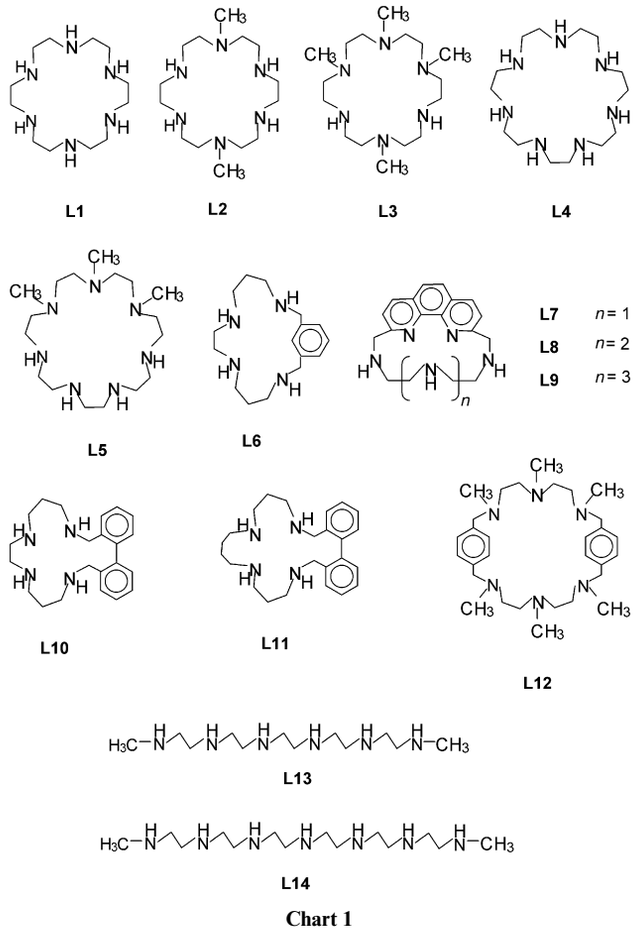

Chart 1

Me_4NCl (aromatic ligands) solutions at 298.1 ± 0.1 K, by using the equipment and the methodology that have already been described.[6] The use of different ionic media was dictated by the formation of insoluble ligand salts during the measurements. The combined Ingold 405 S7/120 electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalent point by Gran's method,[7] which allows one to determine the standard potential $E°$ and the ionic product of water ($pK_w = 13.73(1)$ and 13.83(1) in $NaClO_4$ and Me_4NCl, respectively, at 298.1 ± 0.1 K). At least three measurements (about 100 data points for each one) were performed for each system over the pH range 2.5–10.5. In all the experiments the ligand concentration [L] was about 1×10^{-3} mol dm^{-3}. In the complexation experiments the anion concentration was varied over the range $[L] \leq [SO_4^{2-}] \leq 2[L]$. The computer program HYPERQUAD[8] was used to calculate the equilibrium constants from EMF data. The protonation constants of **L1–L5**, **L7–L9** and **L12–L14** employed in the calculations were determined in earlier works.[3,5,9]

Microcalorimetric measurements

The enthalpies of ligand protonation and anion complexation were determined (in the same ionic medium as that utilised for the potentiometric measurements) by means of an automated system composed of a Thermometric AB thermal activity monitor (model 2277) equipped with a perfusion-titration device and a Hamilton Pump (model Microlab M) coupled with a 0.250 cm^3 gas-tight Hamilton syringe (model 1750 LT). The microcalorimeter was checked by determining the enthalpy of reaction of a strong base (NaOH) with a strong acid (HCl) solution. The value obtained, −13.55(5) kcal mol^{-1}, was in agreement with the literature value.[10] Further checks were performed by determining the enthalpies of protonation of ethylenediamine.

Table 1 Thermodynamic parameters for the protonation of **L6**, **L10** and **L11** determined in 0.1 mol dm^{-3} Me_4NCl at 298.1 K

	L6	L10	L11
		log *K*	
$L + H \rightleftharpoons HL$ [a]	9.64(1) [b]	9.7(1)	10.22(1)
$HL + H \rightleftharpoons H_2L$	9.07(1)	8.73(1)	8.82(1)
$H_2L + H \rightleftharpoons H_3L$	7.38(1)	6.42(1)	6.84(1)
$H_3L + H \rightleftharpoons H_4L$	3.80(1)	4.02(1)	6.22(1)
		$-\Delta H°$/kcal mol^{-1}	
$L + H \rightleftharpoons HL$	9.6(3)	9.4(2)	12.1(1)
$HL + H \rightleftharpoons H_2L$	11.1(3)	11.9(2)	10.6(1)
$H_2L + H \rightleftharpoons H_3L$	11.2(3)	10.7(2)	11.0(1)
$H_3L + H \rightleftharpoons H_4L$	4.9(3)	10.0(2)	10.9(1)
		$T\Delta S°$/kcal mol^{-1}	
$L + H \rightleftharpoons HL$	3.5(3)	3.8(2)	1.8(1)
$HL + H \rightleftharpoons H_2L$	1.3(3)	0.0(2)	1.4(1)
$H_2L + H \rightleftharpoons H_3L$	−1.1(3)	−1.9(2)	−1.7(1)
$H_3L + H \rightleftharpoons H_4L$	0.3(3)	−4.5(2)	−2.4(1)

[a] Charges have been omitted. [b] Values in parentheses are standard deviations on the last significant figures.

In a typical experiment, an Me_4NOH solution (0.15 mol dm^{-3}, addition volumes 15 μl) was added to acidic solutions of the ligands (5×10^{-3} mol dm^{-3}, 1.5 cm^3), containing equimolar quantities of the anion in the complexation experiments. Corrections for the heats of dilution were applied. The corresponding enthalpies of reaction were determined from the calorimetric data by means of the AAAL program.[11] Protonation enthalpies for ligands **L6**, **L10**, and **L11** that were obtained in this work are listed in Table 1, while those for the other ligands were reported previously.[3,5] At least three titrations (about 120 data points) were performed for each system.

Results and discussion

Protonation of L6, L10, and L11

The thermodynamic parameters (log *K*, $\Delta H°$, $T\Delta S°$) for the proton transfer processes involving **L6**, **L10**, and **L11** are reported for the first time in this paper (Table 1). The values obtained are in good agreement with the general trends observed for this type of ligand.[3,12] Probably, the most interesting feature of such values is the different enthalpic and entropic contributions of the first protonation step of the polyazacyclophanes **L10** and **L11**; while for the first receptor, like in **L6** and in other related cyclophanes,[12] the entropy provides an important contribution, for **L11** the enthalpy term is much larger and the entropy term is less significant. The results obtained for **L11** are closer to those which are found in comparable cyclic polyazalkanes lacking the aromatic spacer,[13] suggesting the lower influence of the hydrophobic moiety in the protonation parameters of this receptor.

Stability of anion complexes

Analysis of the potentiometric data performed by means of the HYPERQUAD[8] computer program demonstrated the formation of SO_4^{2-} (A^{2-}) adducts with protonated species of ligands **L1–L6**, and **L8–L12** furnishing the corresponding overall equilibrium constants, according to the general reaction:

$$A^{2-} + L + mH^+ \rightleftharpoons (ALH_m)^{(m-2)+} \quad (1)$$

Table 2 Thermodynamic parameters for the formation of SO_4^{2-} complexes with **L1–L5** determined in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 K

	L1	L2	L3	L4	L5
			log *K*		
$H_2L + A \rightleftharpoons H_2LA$ [a]	2.79(2) [b]	2.82(5)	2.93(5)	2.2(1)	2.93(6)
$H_3L + A \rightleftharpoons H_3LA$		3.34(4)	3.38(5)	2.34(8)	3.38(4)
$H_4L + A \rightleftharpoons H_4LA$	3.84(2)	4.89(4)	4.48(5)	3.03(7)	4.09(6)
$H_5L + A \rightleftharpoons H_5LA$	4.44(3)		4.77(6)	4.05(5)	5.12(6)
$H_6L + A \rightleftharpoons H_6LA$				5.42(4)	6.94(9)
			$-\Delta H°$/kcal mol^{-1}		
$H_2L + A \rightleftharpoons H_2LA$	0.7(1)	0.1(2)	0.6(1)	0.4(1)	0.0(1)
$H_3L + A \rightleftharpoons H_3LA$		−0.3(2)	0.8(1)	0.3(1)	−0.36(9)
$H_4L + A \rightleftharpoons H_4LA$	1.6(1)	−2.6(2)	−0.1(1)	−1.15(5)	−1.70(8)
$H_5L + A \rightleftharpoons H_5LA$	−1.4(1)			−3.23(5)	−4.59(9)
$H_6L + A \rightleftharpoons H_6LA$				−4.75(5)	−7.6(1)
			$T\Delta S°$/kcal mol^{-1}		
$H_2L + A \rightleftharpoons H_2LA$	3.1(1)	3.7(2)	3.4(1)	2.6(1)	4.0(1)
$H_3L + A \rightleftharpoons H_3LA$		4.8(2)	3.8(1)	2.9(1)	5.0(1)
$H_4L + A \rightleftharpoons H_4LA$	3.6(1)	9.3(2)	6.2(1)	5.3(1)	7.3(1)
$H_5L + A \rightleftharpoons H_5LA$	7.4(1)			8.7(1)	11.6(1)
$H_6L + A \rightleftharpoons H_6LA$				12.1(1)	17.1(1)

[a] Charges have been omitted. [b] Values in parentheses are standard deviations on the last significant figures.

In the case of **L7**, **L13** and **L14** no appreciable interaction with the anion was found over the whole pH range investigated (2.5–10.5).

In general, the overall equilibrium constants do not afford any information about the location of the H^+ ions in the adducts and, in principle, there is no reason to assume that the same proton location found in the isolated reagents is maintained in the complex. This was an intriguing point when studying the interaction of polyamine ligands with phosphate and pyrophosphate, since this type of anion undergoes multiple protonation over a wide pH range, and only by taking advantage of the additional information from NMR measurements was it possible to establish the actual protonation sites in the complexes.[3] In the case of SO_4^{2-}, however, protonation takes place at very acidic pH (log $K = 1.81(3)$, 1.71(2) for $SO_4^{2-} + H^+ \rightleftharpoons HSO_4^{2-}$, in $NaClO_4$ and Me_4NCl, respectively, under our experimental conditions) and consequently all of the complexation equilibria can be referred to the interaction of the unprotonated anion, according to (2), to calculate the relevant equilibrium constants collected in Tables 2 and 3.

$$A^{2-} + H_mL^{m+} \rightleftharpoons (H_mLA)^{(m-2)+} \quad (2)$$

It should be taken into account that some association between the protonated forms of the ligands and the anions of the electrolytes used in the potentiometric measurements could occur and, hence, the studied reactions of sulfate binding would be reactions that involved, to some extent, the displacement of another anion. Similar equilibria were not considered in calculations assuming that no interaction occurs with the electrolyte species.

As far as the stability of the complexes is considered, it should be noted first that in spite of the different sizes, molecular architectures, and number of binding groups in the ligands, only complexes with 1 : 1 anion–receptor stoichiometry were found in solution.[14] For all the ligands, the equilibrium constants for the binding of SO_4^{2-} increase with increasing positive charge (number of protons) on the receptors indicating that electrostatic attraction is the principal force that determines the stability of these anion complexes, as previously observed for similar species with other inorganic anions like

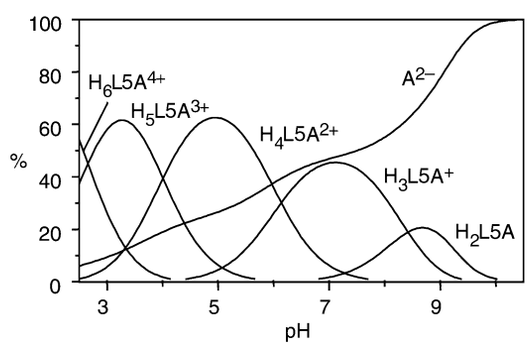

Fig. 1 Distribution curves of SO_4^{2-} (A^{2-}) complexes with **L5**. Curves of the free ligand species are not shown.

$Fe(CN)_6^{4-}$, $Co(CN)_6^{3-}$, and $Pt(CN)_4^{2-}$,[15] although hydrogen bonding between the anions and the polyammonium receptors is expected to give a favourable contribution. Hence, the amount of bound anion increases with decreasing pH, as depicted in Fig. 1 for the heptaaza ligand **L5**.

Concerning the complexes with the aliphatic polyamines **L1–L5**, it is noteworthy that ligand methylation increases the stability of the anion complexes. This result can be explained by considering that the substitution of methyl groups on the nitrogen atoms reduces the basicity of the corresponding amine groups in aqueous solution, shifting the protonation to the secondary (non-methylated) groups. This causes a greater localisation of positive charge in the receptors, leading to stronger interactions with the anions. Furthermore, nitrogen methylation lowers the hydration of the amine groups. This effect, which also contributes to reduce the basicity of the methylated amines, favours anion binding by attenuating the competitive interaction with solvent molecules.

Depending on the location and the number of methyl groups, particular trends in the stability of the anion complexes can be obtained. As a matter of fact, for a given charge on the receptor, the complex stability is higher for **L1** than for the larger **L4**, in agreement with the electrostatic nature of the interaction, but when methylated ligands are considered, different trends can be found. For instance, the equilibrium constants for SO_4^{2-} binding with **L2**, **L3**, and **L5** are equal, within experimental

Table 3 Thermodynamic parameters for the formation of SO_4^{2-} complexes with **L6** and **L8–L12** determined in 0.1 mol dm^{-3} Me_4NCl at 298.1 K

	L6	L8	L9	L10	L11	L12
			log *K*			
$HL + A \rightleftharpoons HLA$ [a]	3.06(1) [b]			4.02(1)	3.81(1)	
$H_2L + A \rightleftharpoons H_2LA$	3.28(1)		2.6(1)	4.55(1)	4.06(1)	1.9(1)
$H_3L + A \rightleftharpoons H_3LA$	3.48(1)	2.47(8)	3.1(1)	5.08(1)	4.21(1)	2.26(8)
$H_4L + A \rightleftharpoons H_4LA$	3.73(1)		3.8(1)	5.49(1)	4.29(1)	2.53(6)
$H_5L + A \rightleftharpoons H_5LA$			4.8(1)			3.66(3)
			$-\Delta H°$/kcal mol^{-1}			
$HL + A \rightleftharpoons HLA$	−1.9(2)			−1.6(2)	−2.0(2)	
$H_2L + A \rightleftharpoons H_2LA$	−0.3(2)		1.2(6)	−1.9(2)	−1.5(2)	−0.6(1)
$H_3L + A \rightleftharpoons H_3LA$	−1.0(2)	−0.5(3)	0.9(5)	−2.2(2)	−2.0(2)	0.71(9)
$H_4L + A \rightleftharpoons H_4LA$	0.7(2)		−0.2(4)	−3.7(2)	−1.8(2)	−0.45(7)
$H_5L + A \rightleftharpoons H_5LA$			−5.0(5)			
			$T\Delta S°$/kcal mol^{-1}			
$HL + A \rightleftharpoons HLA$	6.1(2)			7.1(2)	7.2(2)	
$H_2L + A \rightleftharpoons H_2LA$	4.8(2)		2.3(3)	8.1(2)	7.0(2)	3.2(1)
$H_3L + A \rightleftharpoons H_3LA$	5.7(2)	3.9(3)	3.3(3)	9.1(2)	7.7(2)	2.4(1)
$H_4L + A \rightleftharpoons H_4LA$	4.4(2)		5.4(3)	11.2(2)	7.6(2)	3.9(1)
$H_5L + A \rightleftharpoons H_5LA$			11.5(3)			

[a] Charges have been omitted. [b] Values in parentheses are standard deviations on the last significant figures.

error, for all the diprotonated forms, and the same applies for the triprotonated ones. On the other hand, the tetraprotonated forms of **L2** and **L3** interact with SO_4^{2-} more strongly than the tetraprotonated form of **L5**, while an opposite trend is observed when considering the pentaprotonated species formed by **L3** and **L5**.

As far as the polyamines containing aromatic groups are concerned, it is interesting to note that some of these ligands display a larger tendency, than **L1–L5**, to form SO_4^{2-} complexes in which the ligands bear a small positive charge, as denoted by the formation of monoprotonated complexes by **L6**, **L10** and **L11**, which display considerable stability, and by the high values of the equilibrium constants for the formation of diprotonated complexes with the same ligands. These properties can be ascribed to a lower hydration of the molecules that contain hydrophobic aromatic groups. In fact, the pairing process that occurs between the oppositely charged partners gives rise to an important charge neutralisation accompanied by a large desolvation of the interacting species, which is an expensive process from an energetic point of view. Hence, for less solvated receptors, we expect a less important (less expensive) desolvation process, upon complexation, thus enhancing the complex stability.

Nevertheless, it seems that, in spite of the favourable contribution derived from desolvation, the presence of very large aromatic groups does not favour the formation of SO_4^{2-} complexes, as shown by the phenanthroline derivatives **L7–L9**, probably because of a significant repulsive interaction between the anion and the large electronic π cloud of the aromatic moiety. In fact, the smaller ligand **L7** is not able to interact appreciably with SO_4^{2-}, while **L8** forms just a triprotonated complex and only the larger **L9** can form complexes of significant stability in which the anion should be located sufficiently far away from the aromatic group.

As was already observed for PO_4^{3-} and its protonated forms,[3] and also in the case of SO_4^{2-}, **L12** displays a low tendency for formation of anion complexes, although this ligand is able to form highly protonated species. Ligand **L12** can bind up to five protons in the pH range studied (2.5–10.5) but, due to its ditopic nature, the positive charges are shared between the two separated polyamine units of the ligand, leading to poor complementarity with anions such as SO_4^{2-} and PO_4^{3-} which do not have a ditopic structure.

Indeed, the receptor structure is quite important for achieving a tight association with anions as shown by the fact that SO_4^{2-} does not interact appreciably with the acyclic ligands **L13** and **L14**. Protonated forms of these ligands assume a rod-like conformation, as a result of intramolecular repulsion between the positive charges, thus preventing multiple interactions with SO_4^{2-}. A similar situation was also found for the isostructural anion PO_4^{3-}, while in the case of the longer $P_2O_7^{4-}$ a significant interaction with the two acyclic receptors was observed.[3] In contrast, multiple interactions with spherical, or almost spherical, anions, such as SO_4^{2-} and PO_4^{3-}, are facilitated by the cyclic structure of the other receptors.

In the case of the polyamine macrocycles **L1–L5**, stability constants are available for both sulfate (Table 2) and phosphate complexes, and hence it is possible to analyse the selectivity of these receptors in the binding of the two anions. This can be accomplished by calculating the percentage of each anion bound to the ligand, as a function of pH, in a solution containing equimolar concentrations of sulfate, phosphate, and receptor.[16] The results obtained by means of similar calculations do not show particular selectivity trends for this set of ligands. For instance, preferential binding of phosphate is found for **L2** over the entire pH range (2.5–10.5), while the opposite situation is observed for **L3**. Nevertheless, an interesting example of a selectivity pattern is found for **L1**. As shown in Fig. 2, in alkaline solution (pH > 8.55), sulfate is selectively recognised in preference to phosphate, but a selectivity inversion occurs on lowering the solution pH, when the phosphate complexes become largely predominant. Hence, selective recognition of phosphate over sulfate takes place along with increasing phosphate protonation, thus mimicking the function accomplished in living systems by phosphate binding proteins.[4]

Enthalpic and entropic contributions

In order to get more insight into the nature of the interaction between the polyammonium receptors and SO_4^{2-}, we measured the enthalpy changes associated with the formation of these anion complexes. The values obtained are listed in Tables 2 and 3 along with the derived entropy changes.

According to the simple electrostatic model, the formation of ion pairs between rigid cations and anions (hard sphere with

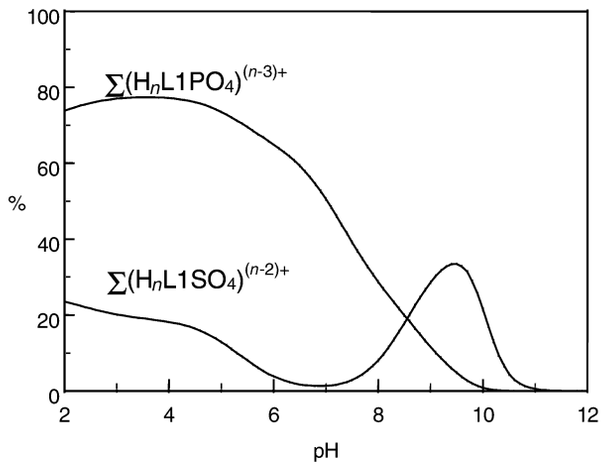

Fig. 2 Overall percentages of sulfate and phosphate respectively bound to protonated forms of **L1**.

embedded point charges) in an ideal, structureless homogeneous solvent is expected to be accompanied by slightly unfavourable ΔH° contributions and largely favourable entropic terms, principally deriving from the desolvation of the interacting species caused by the charge neutralisation that occurs in the pairing process.[17]

As can be seen from Tables 2 and 3 the reactions of SO_4^{2-} binding are endothermic, or almost athermic, and promoted by invariably favourable entropic contributions ($T\Delta S^\circ > 0$), in agreement with the ideal electrostatic model.

In contrast, as reported in an earlier paper dealing with the binding of protonated phosphate anions, a considerable number of association reactions promoted by large favourable enthalpy changes and accompanied by evident entropy losses were also observed.[3] In order to explain such behaviour, the formation of different types of hydrogen bonds, and the relevant, expected enthalpic and entropic contributions, were considered. There are five possible modes (1)–(5) of hydrogen bonding involving amine or ammonium groups and phosphate, or protonated phosphate anions.

$$\text{–N–H}^+\cdots{}^-\text{O–} \quad \Delta H^\circ > 0,\ T\Delta S^\circ > 0 \qquad (1)$$

$$\text{–N–H}^+\cdots\text{OH–} \quad \Delta H^\circ > 0,\ T\Delta S^\circ \approx 0 \qquad (2)$$

$$\text{–N–H}\cdots{}^-\text{O–} \quad \Delta H^\circ > 0,\ T\Delta S^\circ \approx 0 \qquad (3)$$

$$\text{–N–H}\cdots\text{OH–} \quad \Delta H^\circ > 0,\ T\Delta S^\circ < 0 \qquad (4)$$

$$\text{–N:}\cdots\text{H–O–} \quad \Delta H^\circ < 0,\ T\Delta S^\circ < 0 \qquad (5)$$

Taking into account that deprotonation of an amino group is a strongly endothermic reaction, while protonation of phosphate anions is almost athermic, the partial amine-to-anion proton transfer processes involved in the four hydrogen bonding modes (1)–(4) are expected to give unfavourable enthalpic contributions ($\Delta H^\circ > 0$), while the partial proton transfer process of the bonding mode (5), occurring from the anion to the amine group, is the only mode that furnishes favourable enthalpy changes ($\Delta H^\circ < 0$). The formation of the last type of hydrogen bond (5), which is favoured by anion protonation, was invoked to explain the $\Delta H^\circ < 0$, and $T\Delta S^\circ < 0$ values found for the interaction of many protonated phosphate anions with polyammonium receptors.[3]

As noted above in this paper, we performed the present study over a pH region (2.5–10.5) in which protonated forms of SO_4^{2-} are not present and, consequently, only hydrogen bonds of the types (1) and (3) may occur in the formation of the sulfate complexes analysed in this work and, accordingly, the relevant association reactions are mostly endothermic, or almost athermic. Binding mode (1), leading to the formation of hydrogen bonded ion pairs, is of principal importance since it furnishes synergic hydrogen bonding and electrostatic attraction, and represents the preferred association scheme, especially in acidic solution where most of the ligand amine groups are protonated. On the other hand, binding mode (3) is favoured in alkaline solutions, where the receptors are extensively deprotonated; for this reason it seems not to be very important since under similar pH conditions anion complexes are rarely formed. In any case, taking into account that the protonation of SO_4^{2-} is an endothermic reaction by about 5 kcal mol^{-1}, we must expect that in the formation of sulfate complexes hydrogen bonding modes (1) and (3) give a more unfavourable enthalpic contribution than in the formation of phosphate complexes. Accordingly, the pairing processes considered herein (Tables 2, 3) are endothermic or almost athermic. Hence, the stability of the present sulfate complexes is mostly determined by largely favourable entropic terms produced by the desolvation of the interacting species, which occurs as a consequence of the charge neutralisation that accompanies the pairing process. From this point of view, the binding of SO_4^{2-} with polyamines containing aromatic groups should be less entropically favoured, than with aliphatic ones, by such desolvation processes, since the former ligands are generally less solvated in water. On the other hand, these aromatic molecules are more rigid and, hence, they undergo lower structural modifications, or stiffening, upon complexation, producing a more favourable entropic contribution. The last effect is expected to be more evident for the ligands in low protonation states, since upon extensive protonation the aliphatic polyamines also acquire significant rigidity. As a matter of fact, the entropic terms obtained for the formation of SO_4^{2-} complexes with the less charged forms of the aromatic ligands (Table 3) are generally more favourable than the corresponding terms obtained for aliphatic ones.

Conclusions

As shown by the thermodynamic data obtained in this work for the association of SO_4^{2-} with polyammonium receptors ($\Delta H^\circ \geq 0$, $T\Delta S^\circ > 0$), the driving force for these pairing processes is electrostatic attraction, according to one of the most fundamental natural principles which holds together species of opposite charges. Nevertheless, as demonstrated by the different behaviours of SO_4^{2-} and PO_4^{3-}, the formation of hydrogen bonds between anion and receptor can be of considerable importance, in particular when protonated forms of the anion are involved. The binding properties of the receptors considered are determined by the number and localisation of the positive charges in the receptors, as well as by the overall ligand structure and the presence of hydrophobic aromatic ligand sectors. Accordingly, selectivity in the recognition of SO_4^{2-} and PO_4^{3-} is a peculiar characteristic of each receptor. Interestingly, in the case of **L1**, recognition of phosphate over sulfate takes place in line with increasing phosphate protonation, thus mimicking the function accomplished in living systems by phosphate binding proteins.

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