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Binding of fluoride and carbonate by open chain polyammonium cations

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Abstract

The formation of open chain polyammonium cation-fluoride and -carbonate complexes was studied by potentiometric and calorimetric techniques at $t = 25\,^{\circ}\mathrm{C}$. Several species of H_iAL (A = amine; L = F^-, $CO_3{}^{2-}$) are formed in both systems with a mean stability $\log K = 1.0\zeta$ ($\zeta = |z_{\mathrm{anion}} \times z_{\mathrm{cation}}|$) and $\log K = 2.0\zeta$ for fluoride and carbonate, respectively. The comparison with analogous systems (chloride and acetate for fluoride and hydrogenphosphate, sulfate and malonate for carbonate) showed that fluoride and carbonate form the most stable species with open chain polyammonium cations, among low molecular weight anions. The *N*-alkyl substitution does not play negligible role in the stability of these complexes, the species formed by substituted amines being more stable.

Keywords: Open chain polyammonium cations; Fluoride; Carbonate; Anion coordination chemistry; Potentiometry; Calorimetry; Complex formation; Thermodynamic parameters

1. Introduction

Amines are quite an important class of ligands, present as trace components in all biological fluids and natural waters. In particular, polyamines are found in all living organisms, and their concentration becomes quite high in tissues and biological fluids in some pathologies [1–3]. The mean concentration of amino groups in some biological fluids is 1–2, 0.1–0.05, 15–30 and 0.2–0.3 mmol l^{-1} in urine, blood, sperm and sweat, respectively [4]. Furthermore, amino compounds play an important role in reactions with sugars (or their derivates) in natural waters leading to polymerised products [5,6] containing several amino groups along a linear chain, whose composition is very similar to that of the humic water-soluble fraction. Therefore, polyamines can be considered a representative model of aminic sites binding in the humic acids. Despite the great importance of amines both as model molecules and as involved in several biological processes, few studies have been carried out on their speciation in natural waters and in biological water. In the last years [7–19] our research group developed two aspect concerning the amine speciation: (a) the protonation in natural fluids and the interactions with the major components of natural and biological fluids (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and $SO_4{}^{2-}$); (b) the interaction of open chain polyammonium cations with many ligands of biological and environmental interest such as carboxylic polyanions or nucleotides and inorganic anions (Cl^-, $SO_4{}^{2-}$, $HPO_4{}^{2-}$, $P_2O_7{}^{4-}$, $P_4O_{10}{}^{5-}$, $Fe(CN)_6{}^{4-}$). In order to complete the knowledge on the speciation of these compounds in natural and biological fluids, we have extended our studies towards two interesting inorganic ligands: fluoride and carbonate.

Fluoride and carbonate anions are among the major constituents of natural waters (0.7 and 2.7 mmol l^{-1} for fluoride and carbonate, respectively, in seawater at 35‰ in salinity). Fluoride is the smallest simple anion that can exist in aqueous solution and, unlike the other halides, has no d orbitals with sufficient energy to participate in covalent π bonding. These two factors suggest that interactions between cations and fluoride anion, more than for any other ligand, should be governed by electrostatic attraction, and therefore, fluoride ion is of considerable interest as model for electrostatic interaction in solution. It is a “well behaved” ligand: it is neither reducible nor oxidisable in aqueous solution, does not hydrolyse under normal conditions and shows little tendency to form outer sphere complexes. Moreover, fluoride forms quite strong hydrogen bonds. Carbonate is the major constituent

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Table 1
Amines considered in this work

A	Formula	Name
1	$H_2N–(CH_2)_2–NH_2$	1,2-Diaminoethane (ethylenediamine)
2	$H_2N–(CH_2)_4–NH_2$	1,4-Diaminobutane (putrescine)
3	$H_2N–(CH_2)_5–NH_2$	1,5-Diaminopentane (cadaverine)
4	$H_2N–(CH_2)_6–NH_2$	1,6-Diaminohexane
5	$H_2N–(CH_2)_8–NH_2$	1,8-Diaminooctane
6	$(CH_3)_2N–(CH_2)_2–N(CH_3)_2$	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
7	$H_2N–(CH_2)_4–CH(CH_2NH_2)–(CH_2)_3–NH_2$	4-Aminomethyl-1,8-diaminoctane
8	$H_2N–(CH_2)_3–NH–(CH_2)_4–NH_2$	*N*-(3-aminopropyl)-1,4-diaminobutane (spermidine)
9	$H_2N–(CH_2)_3–NH–(CH_2)_3–NH_2$	Bis-(3-aminopropyl)amine
10	$H_2N–(CH_2)_6–NH–(CH_2)_6–NH_2$	Bis-(6-aminoesil)amine
11	$(CH_3)_2N–(CH_2)_2–N(CH_3)–(CH_2)_2–N(CH_3)_2$	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine
12	$H_2N–(CH_2)_3–NH–(CH_2)_4–NH–(CH_2)_3–NH_2$	*N*,*N*′-bis(3-aminopropyl)-1,4-diaminobutane (spermine)
13	$(CH_3)_2N–(CH_2)_2–[N(CH_3)–(CH_2)_2]_2–N(CH_3)_2$	1,1,4,7,10,10-Esamethyltriethylenetetramine

of several natural fluids, and the $CO_3^{2-}/CO_2/HCO_3^-$ equilibrium is very important since it regulates the pH of seawater and controls the circulation of CO_2 around the biosphere, the lithosphere, the atmosphere and the oceans. Furthermore, HCO_3^- is a component of biological fluids (e.g. its concentration in human plasma ranges between 24 and 27 meq l^{-1}), and regulates many buffer systems of living organisms.

No data are reported in literature on the interaction of open chain polyammonium cations with fluoride and carbonate. Several papers can be found concerning the interactions of some polyazacycloalkanes with F^- [20–22] and very few data are available on their interaction with CO_3^{2-} [22,23]. In this paper we report a potentiometric (ISE-F^- and ISE-H^+) and calorimetric study on the formation and stability of polyammonium cations-F^- and -CO_3^{2-} complexes, in aqueous solution, at $t = 25\,°C$. Amines considered are reported in Table 1.

2. Experimental

2.1. Reagents

Amines (Aldrich or Fluka products) were purified by transformation into the corresponding hydrochlorides and were used in this form. Their purity, checked alkalimetrically, was always >99.5%. Hydrochloric acid and sodium hydroxide solutions were prepared by diluting concentrated ampoules (Fluka) and were standardised against potassium biphthalate or sodium carbonate, respectively. Sodium fluoride and sodium carbonate were prepared by weighing pure salts (Fluka) previously dried in an oven at 110 °C. Grade A glassware and twice-distilled water were used for all solutions.

2.2. Apparatus

The free hydrogen ion concentration was measured using apparatus consisting of a Metrohm model 713 potentiometer, equipped with an Orion combination glass electrode (Ross type 8102) and a Metrohm model 765 motorised burette. The estimated accuracy was ±0.2 mV and ±0.003 ml for e.m.f. and titrant volume readings, respectively. The apparatus was connected to a personal computer, and automatic titrations were performed using a suitable computer program (titrant delivery, data acquisition, check for the stability of e.m.f.). When measuring pF, a Metrohm fluoride electrode was used coupled with an Ag/AgCl double junction Orion mod. 900200 reference electrode. The measurement cells were thermostated at 25 °C with an uncertainty of ±0.1 °C. All titrations were carried out by stirring magnetically and by bubbling purified and pre-saturated N_2 through the solution, in order to exclude O_2 and CO_2 inside. Calorimetric measurements were performed at 25±0.001 °C using a Tronac isoperibol model 450 titration calorimeter coupled with a Keithey 196 system Dmm digital multimeter. The titrant was delivered by a 2.5 ml capacity model 1002TLL Hamilton syringe. A computer program was used for the acquisition of calorimetric data. The accuracy was checked by titrating a Tris (tris-(hydroxymethyl)amino methane; $\Delta H° = -47.54\,kJ\,mol^{-1}$ [24]) buffer with HCl. The accuracy of calorimetric apparatus was $Q \pm 0.008\,J$ and $v \pm 0.001\,ml$.

2.3. Procedure

ISE-H^+ measurements were carried out by titrating 25 ml of the solution containing the amine under study (4–10 or 3–7 mmol l^{-1}, for fluoride and carbonate systems, respectively), an excess of hydrochloric acid and NaF or Na_2CO_3 ($0.02 \le I \le 0.06\,mol\,l^{-1}$) with standard NaOH solution up to ≅90% neutralisation. Separate titrations of HCl at about the same ionic strength value as the sample under study were carried out in order to calculate the standard electrode potential $E°$ of the electrodic cell. A stream of purified and pre-saturated N_2 was bubbled through all solutions in order to exclude the presence of CO_2 and O_2. ISE-F^- measurements were performed by adding the amine under study (2.5–7 mmol l^{-1}) to a solution containing NaF (0.05 mol l^{-1}); calibration was performed separately by titrating with NaF. Calorimetric measurements of amines **1**, **6**, **9**, **12** and **13** were performed by titrating 50 ml of the solution containing the amine hydrochloride (5–10 mmol l^{-1})

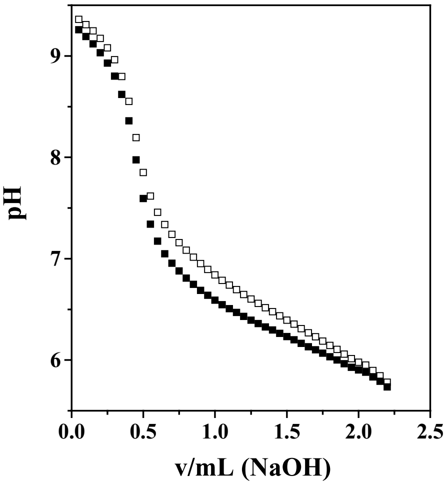

Fig. 1. Titration curve, pH vs. v (ml) (NaOH 0.1006 mol l^{-1}), for the system carbonate-ethylenediamine (**1**), at 25 °C. Analytical conditions: $C_{\mathbf{1}} = 3$ and $C_{CO_3} = 5$ mmol l^{-1}. (☐) Experimental curve; (■) calculated curve (without considering the formation of **1**-$CO_3{}^{2-}$ species).

with NaF or Na_2CO_3 (0.3 mol l^{-1}). The heat of dilution was measured before each experiment.

2.4. Calculations

The computer programs STACO and BSTAC [25] were used to calculate formation constants from potentiometric measurements. Both programs can deal with measurements at different ionic strengths and are able to simultaneously analyse pH and pF titration data. Calorimetric titration data were analysed by the computer program ES5CMI [26]. The ES4ECI [25] program was used to draw the distribution diagrams. The LIANA [25] program was used to fit linear and nonlinear equations. As an example we show in Fig. 1 a titration curve for the system carbonate-ethylenediamine (**1**) together with the curve calculated without considering the formation of **1**-$CO_3{}^{2-}$ species: differences of pH values are relevant and allow the formation constants of complexes to be calculated.

The measurements were carried out without addition of background salt, i.e. at variable ionic strength in order to minimise the interference of weak Na^+-F^- or Na^+-$CO_3{}^{2-}$ and $AH_i{}^{i+}$-Cl^- complex species. The formation of weak species was taken into account into calculations, together with the protonation of carbonate, fluoride and amines [15,24,27]. Dependence on ionic strength was taken into account by using the extended Debye-Hückel-type equation [28]:

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

where

$$C = c_0 p^* + c_1 z^*, \qquad D = d_0 p^* + d_1 z^*,$$

$$p^* = \sum(\text{moles})_{\text{reactants}} - \sum(\text{moles})_{\text{products}},$$

$$z^* = \sum(\text{charges})^2_{\text{reactants}} - \sum(\text{charges})^2_{\text{products}}$$

K is the formation constant, ${}^{T}K$ the formation constant at infinite dilution, and C and D the empirical parameters. According to previous results, when all interactions are taken into account, the values $c_0 = 0.11$, $c_1 = 0.20$, $d_0 = 0$ and $d_1 = -0.075$ can be used [28].

3. Results

3.1. Amine-fluoride interactions

Calculations on potentiometric $[H^+]$ and $[F^-]$ measurements indicate the formation of mononuclear species between protonated amine and fluoride anion, according to the reaction

$$A^0 + F^- + iH^+ = H_iAF^{(i-1)+} \qquad (2)$$

where $i = 1, 2, \ldots n$ (n = max protonation degree of the amine). Preliminary calculations showed very similar behaviour of different amines towards the formation of HAF^0 species, for which was calculated the mean values of formation constant $\log K_1 = 1.6 \pm 0.1$ (referred to the reaction $HA^+ + F^- = HAF^0$, at $I = 0$ mol l^{-1} and $t = 25$ °C), valid both for the substituted (**6**, **11**, **13**) and the unsubstituted polyammonium cations (**1**, **2**, **3**, **4**, **5**, **8**, **9**, **12**). By considering this values, we obtained the formation constants for $H_iAF^{(i-1)+}$ species reported in Table 3, together with values extrapolated at $I = 0$ mol l^{-1} by using Eq. (1). In order to better evidence the stability of these species, in Table 3 equilibrium constants for the formation of amine-fluoride species are also reported, according to the reaction

$$H_iA^{i+} + F^- = H_iAF^{(i-1)+} \qquad (2a)$$

(amine protonation constants are reported in Table 2).

A first inspection of data in Table 3 shows that stability of amine-fluoride complexes increases with the charge of polyammonium cation and the increase is more marked for substituted amines. As obtained for other amine-organic and -inorganic anion systems, we tested the simple relationship:

$$\log K = a\zeta \qquad (3)$$

where $\zeta = |z_c \times z_a|$ (z_c is the cation charge and z_a the anion charge) and a the empirical parameter (by considering that in this case, $z_a = -1$; Eq. (3) can be write also in the form: $\log K = ai$, where i is the amine protonation degree). By analysing separately stability data of unsubstituted (**1**, **2**, **3**, **4**, **5**, **8**, **9**, **12**) and substituted (**6**, **11**, **13**) polyamines, we found $a = 0.85 \pm 0.02$ and 1.13 ± 0.10, respectively. The higher value of the parameter a for N-alkyl substituted amine-fluoride interactions indicates that these are more stable than those formed by the unsubstituted ones. Note that the mean values, $a = 1.00 \pm 0.15$, for both substituted and unsubstituted amines are significantly higher than the values obtained for several polyammonium inorganic anion systems, $a = 0.61$ (see Ref. [14]). A more sophisticated

Table 2
Protonation constants of amines, carbonate and fluoride, at $I = 0\,\mathrm{mol\,l^{-1}}$ and $t = 25\,^{\circ}\mathrm{C}$

X	$\log \beta_{pq}$[a]					References
	11	12	13	14	21	
1	9.90	16.77				[15]
2	10.54	19.64				[15]
3	10.80	20.34				[15]
4	10.90	20.70				[15]
5	10.94	20.90				[15]
6	9.15	14.78				[15]
7	10.90	20.86	29.67			[15]
8	10.80	20.38	28.20			[15]
9	10.54	19.86	27.01			[15]
10	11.16	21.41	30.76			[15]
11	9.23	17.39	18.88			[15]
12	10.70	20.40	28.71	35.89		[15]
13	9.22	17.36	22.10	22.67		[15]
F^-	3.18				3.63	[27]
CO_3^{2-}	10.33	16.69				[27]

X	ΔH_{pq}[a]					References
	11	12	13	14	21	
1	−51.3	−96.3				[14]
6	−29.2	−55.2				[16]
9	−51.4	−105.3	−151.0			[16]
12	−48.5	−96.9	−142.6	−186.5		[14]
13	−27.8	−57.7	−83.1	−98.1		[16]
F^-	13.2				17.3	[24]
CO_3^{2-}	−14.6	−23.40				[b]

[a] Refer to the reaction: $pX + qH = X_pH_q$ (charges omitted for simplicity).

[b] Unpublished data from this laboratory.

equation which makes allowance for the difference in the polyamine structure can be used; after some trials we found the empirical relationship

$$\log K = a(\zeta + R_{\mathrm{C/N}}^{-1/2}) \tag{4}$$

where $R_{\mathrm{C/N}}$ is the ratio of C atoms of alkyl chain and N atoms in the polyammonium cation (see Table 3), and $a =$ 0.68±0.01 and 0.83±0.11 for unsubstituted and substituted amines, respectively.

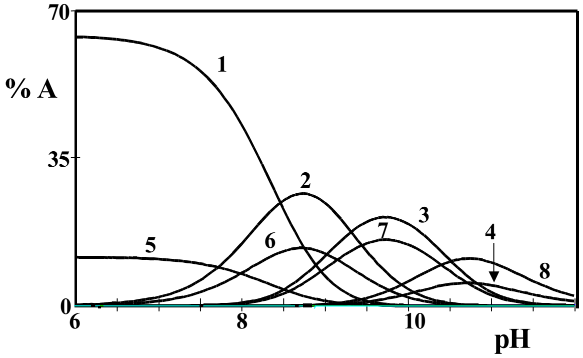

Fig. 2. Distribution diagram of A^0-F^- species (A = **12**) vs. pH, at $t = 25\,^{\circ}\mathrm{C}$. Conditions: $C_A = 10$, $C_F = 20\,\mathrm{mmol\,l^{-1}}$, $C_{Cl} = 500\,\mathrm{mmol\,l^{-1}}$, $I \sim 0.5\,\mathrm{mol\,l^{-1}}$. Species: (1) H_4ACl^{3+}; (2) H_3ACl^{2+}; (3) H_2ACl^{+}; (4) $HACl^0$, (5) H_4AF^{3+}; (6) H_3AF^{2+}; (7) H_2AF^{+}; (8) HAF^0.

The importance of amine-fluoride species in the speciation of natural fluids is showed in Fig. 2, where, as an example, the distribution diagram of spermine (**12**)-F^- system in the seawater chloride concentration is reported. As can be seen, formation percentage of $H_iAF^{(i-1)+}$ species is not negligible. In particular, at marine water pH value (pH = 8.1) ~ 25% of spermine is present as H_3AF^{2+} and H_4AF^{3+} species.

3.2. *Amine-carbonate interactions*

Potentiometric measurements on H^+-amine-CO_3^{2-} systems showed the formation of $H_iACO_3^{(i-2)+}$ species, according to the reaction

$$A^0 + CO_3^{2-} + iH^+ = H_iACO_3^{(i-2)+} \tag{5}$$

where i = 1, 2 for diamines **1**, **2**, **4**, **6**; n = 2, 3 for triamines **7**, **8**, **9**, **10**; n = 3, 4 for tetramines **12**, **13**. Formation constants of $H_iACO_3^{(i-2)+}$ species referred to the overall

Table 3
Equilibrium constants for the formation of amine-F^- complexes at $I = 0\,\mathrm{mol\,l^{-1}}$ and $t = 25\,^{\circ}\mathrm{C}$

A	$R_{\mathrm{C/N}}$[a]	$\log \beta_2$[b]	$\log K_2$[c]	$\log \beta_3$[b]	$\log K_3$[c]	$\log \beta_4$[b]	$\log K_4$[c]
1	1.0	18.73 ± 0.02[d]	2.0				
2	2.0	21.66 ± 0.02	2.0				
3	2.5	22.09 ± 0.01	1.75				
4	3.0	22.26 ± 0.03	1.6				
5	4.0	21.97 ± 0.09	1.1				
6	1.0	16.99 ± 0.04	2.2				
8	2.33	22.19 ± 0.02	1.8	30.66 ± 0.06[d]	2.5		
9	2.0	21.93 ± 0.04	2.1	29.88 ± 0.04	2.9		
11	1.33	19.19 ± 0.12	1.8	23.37 ± 0.06	4.5		
12	2.5	22.47 ± 0.02	2.1	31.21 ± 0.01	2.5	38.61 ± 0.02[d]	2.7
13	1.5	18.96 ± 0.09	1.6	24.35 ± 0.08	2.25	28.02 ± 0.04	5.35

[a] Ratio between C atoms in the alkylchain and amino groups.

[b] β_i refer to the reaction: $A^0 + iH^+ + F^- = H_iAF^{i-1}$.

[c] K_i refer to the reaction: $H_iA^{i+} + F^- = H_iAF^{i-1}$.

[d] ±S.D.

Table 4
Equilibrium constants of amine-CO_3^{2-} complexes at $I = 0\,mol\,l^{-1}$ and $t = 25\,°C$

A	$R_{C/N}$[a]	$\log \beta_1$[b]	$\log K_1$[c]	$\log \beta_2$[b]	$\log K_2$[d]	$\log \beta_3$[b]	$\log K_3$[d]	$\log \beta_4$[b]	$\log K_4$[d]
1	1.0	13.51 ± 0.05[e]	3.6	22.89 ± 0.02[e]	2.7				
2	2.0	14.42 ± 0.03	3.9	23.75 ± 0.03	2.9				
4	3.0	14.18 ± 0.05	3.3	24.50 ± 0.04	3.3				
6	1.0	12.96 ± 0.06	3.8	21.51 ± 0.04	2.0				
7	3.0	–	–	25.02 ± 0.06	3.8	34.78 ± 0.03[e]	3.6		
8	2.33	–	–	24.88 ± 0.09	3.75	33.96 ± 0.07	3.25		
9	2.0	–	–	26.67 ± 0.06	5.8	34.58 ± 0.03	4.4		
10	4.0	–	–	25.39 ± 0.02	3.9	35.09 ± 0.03	3.35		
12	2.5	–	–	–	–	34.49 ± 0.03	3.8	42.52 ± 0.03[e]	3.5
13	1.5	–	–	–	–	32.90 ± 0.12	5.2	38.39 ± 0.08	6.0

[a] Ratio between C atoms in the alkylchain and amino groups.
[b] β_i refer to the reaction $A^0 + iH^+ + CO_3^2 = H_iA(CO_3)^{i-2}$.
[c] K_1 refer to the reaction: $HA^+ + CO_3^{2-} = HACO_3^-$.
[d] K_i refer to the reaction: $H_{i-1}A^{(i-1)+} + HCO_3^- = H_iACO_3^{(i-2)}$.
[e] ±S.D.

reaction (5) at $I = 0\,mol\,l^{-1}$ and $t = 25\,°C$ are reported in Table 4, together with equilibrium constants according to the most probable reaction. Analogously to fluoride systems, using all the stability data of the polyamine-CO_3^{2-} complexes (Table 4), we test the simple relationship (3), for which we obtain $a = 1.99 \pm 0.04$. By taking also into account the contribution of the structure and the length of the alkylic chain in the polyamine cations (Eq. (4)), we obtain $a = 1.46 \pm 0.05$. For these systems too, the *N*-alkyl substitution plays also an important role, increasing the stability. If we compare, for example, formation constant of $H_3ACO_3^+$ species, we found $\log K = 3.8$ and 5.2 for amines **12** and **13**, respectively. Nevertheless, it was not possible consider separately substituted amines, because only two substituted amine systems (**6** and **12**) were studied.

In Figs. 3 and 4 the distribution diagrams for the system spermine-CO_3^{2-} are shown, in our experimental condition and in seawater chloride concentrations (at 35‰ in salinity), respectively. As can be seen, in both diagrams the most important species at pH ∼ 8 is $H_3ACO_3^+$, which reaches formation percentages of ∼70–80%, also in presence of high chloride concentrations.

3.3. *Enthalpy and entropy changes of polyamine-fluoride and polyamine-carbonate complexes*

By calorimetric measurements, enthalpy and entropy change for **1**- and **12**-F^- complexes, and for **1**-, **6**-, **9**-, **12**- and **13**-CO_3^{2-} complexes, were determined. Values referred to the partial reaction are reported in Table 5. Calculations were performed considering literature values for $\Delta H°$ protonation of amine [14] and fluoride [24]; for CO_3^{2-}, we used $\Delta H_1 = -14.60$ for reaction $H^+ + CO_3^{2-} = HCO_3^-$ and $\Delta H_2 = -8.80$ for reaction $H^+ + HCO_3^- = CO_2 + H_2O$ ($t = 25\,°C$ and $I = 0\,mol\,l^{-1}$; unpublished data from this laboratory). As obtained for other amine-inorganic ligand species [14,17–19], we can do some considerations. The formation of all species is endothermic or slightly exothermic with $\Delta H°$ values quite low, and $T\Delta S°$ values positive and high. This confirms the electrostatic nature of these species ($-\Delta G° > \Delta H°$). $-\Delta G°$ and $T\Delta S$ values of substituted amines are always higher respect to those of unsubstituted values: if we compare for example $H_4ACO_3^{2+}$ species, we obtain $-\Delta G° = 20.0$ and 34.2, and $T\Delta S = 14.2$ and 56.5, for unsubstituted and *N*-alkyl-substituted tetramines

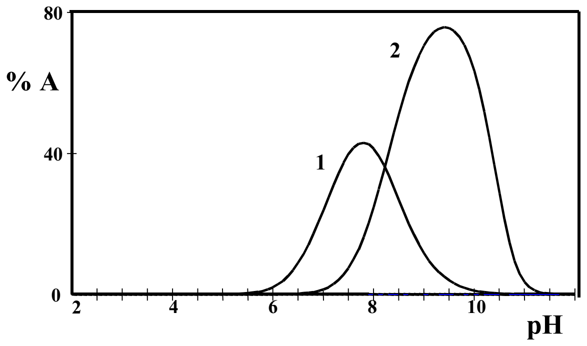

Fig. 3. Distribution diagram of A^0-CO_3^{2-} species (A = **12**) vs. pH, at $t = 25\,°C$. Conditions: $C_A = 7$, $C_{CO_3} = 10\,mmol\,l^{-1}$, $I \sim 0.1\,mol\,l^{-1}$. Species: (1) $H_4ACO_3^{2+}$; (2) $H_3ACO_3^+$.

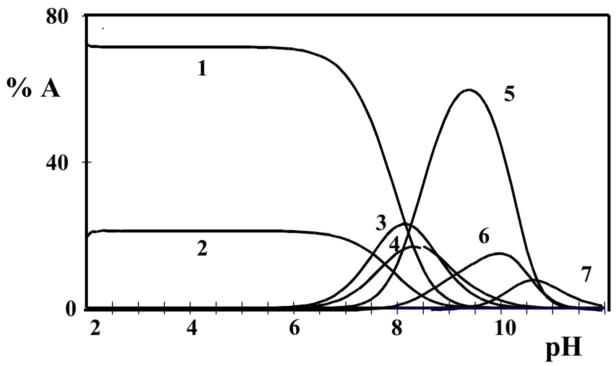

Fig. 4. Distribution diagram of H^+-A^0-CO_3^2-Cl^- (A = **12**) vs. pH, at $t = 25\,°C$. Conditions: $C_A = 7$, $C_{CO_3} = 10$, $C_{Cl} = 500\,mmol\,l^{-1}$, $I \sim 0.5\,mol\,l^{-1}$. Species: (1) H_4ACl^{3+}; (2) $H_4ACl_2^{2+}$; (3) $H_4ACO_3^{2+}$; (4) H_3ACl^{2+}; (5) $H_3ACO_3^+$; (6) H_2ACl^+; (8) $HACl^0$.

Table 5
Thermodynamic parameters[a] for the formation of H^+-amine-F^- and H^+-amine-CO_3^{2-} species at $I = 0\,mol\,l^{-1}$ and $t = 25\,°C$

A	Reaction	$-\Delta G°$	$\Delta H° \pm 1$[b]	$T\Delta S° \pm 2$[b]
1	$H_2A^{2+} + F^-$	11	3	14
	$HA^+ + CO_3^{2-}$	21	16	37
	$HA^+ + HCO_3^-$	15	12	27
6	$HA^+ + CO_3^{2-}$	21	19	40
	$HA^+ + HCO_3^-$	11	17	28
9	$HA^+ + HCO_3^-$	33	−7	26
	$H_2A^{2+} + HCO_3^-$	25	−8	17
12	$H_4A^{4+} + F^-$	15	4	19
	$H_2A^{2+} + HCO_3^-$	22	−3	19
	$H_3A^{3+} + HCO_3^-$	20	−6	14
13	$H_2A^{2+} + HCO_3^-$	30	3	33
	$H_3A^{3+} + HCO_3^-$	34	22	56

[a] In $kJ\,mol^{-1}$.
[b] ±S.D.

(**12** and **13**), respectively. Enthalpy or entropy values for fluoride- and carbonate-polyamine systems are higher than those of other inorganic ligands having the same charge, such as chloride and sulfate or hydrogenphosphate, respectively (e.g. for the formation of $H_2(\mathbf{1})L^0$ species ($L = F^-$ and Cl^-) we have $\Delta H° = 3.1$ and -1.3, and for $H_4(\mathbf{12})L^0$ $\Delta H° = 3.6$ and 2.7, for fluoride and chloride respectively).

4. Discussion

Data reported in this work show that in solution containing polyammonium cations and inorganic ligands such as fluoride or carbonate, formation of mixed species $H_iAL^{(i-z)+}$ ($L^{z-} = F^-$ or CO_3^{2-}) is significant, in particular in the pH range of natural waters. As pointed out in the results section, stability is strictly related to the charges involved in the formation reaction, and an empirical relationship was obtained (Eq. (3)). The structure of polyammonium cations plays a less important role (Eq. (4)). Considering $n = \xi/2$ as a crude approximation of the number of possible salt bridges [14,17–19], we can give the free energy contribution per bond, ΔG_b°. Using the equilibrium constants reported in Tables 3 and 6, we obtain the mean values:

$$\Delta G_b^\circ = 10.0 \pm 0.2\,kJ\,mol^{-1}\,n^{-1} \qquad (6)$$

$$\Delta G_b^\circ = 12.2 \pm 0.6\,kJ\,mol^{-1}\,n^{-1} \qquad (7)$$

for unsubstituted and *N*-alkyl-substituted amine-fluoride species, respectively, and

$$\Delta G_b^\circ = 28.8 \pm 1.4\,kJ\,mol^{-1}\,n^{-1} \qquad (8)$$

for amine-carbonate species. Error is reported as $\sigma/N^{1/2}$, with σ = standard deviation and N = number of species taken into account. The high dispersion of ΔG_b° values, in particular for amine-carbonate systems, is probably due to secondary factors which influence stability such as structure, charge/radius ratio and amine basicity. Values obtained in this work can be compared with that of other polyamine-inorganic polyanion (phosphate, pyrophosphate and hexacyanoferrate) systems for which recently [19] we reported the mean values $\Delta G_b^\circ = 7.8\,kJ\,mol^{-1}$. The differences evidence that fluoride and carbonate ligands must be considered separately.

Table 6
Equilibrium constants for the formation of amine-mono-charged anion complexes at $I = 0\,mol\,l^{-1}$ and $t = 25\,°C$

A	Reaction	log *K*		
		F[a]	Cl[b]	ac[c]
1	$HA^+ + L^-$	1.6	−0.2	−0.1
	$H_2A^{2+} + L^-$	2.0	0.6	0.7
2	$HA^+ + L^-$	1.6	−0.4	1.4
	$H_2A^{2+} + L^-$	2.0	0.6	1.8
3	$HA^+ + L^-$	1.6	−0.1	
	$H_2A^{2+} + L^-$	1.75	0.8	
8	$HA^+ + L^-$	1.6	−0.3	1.0
	$H_2A^{2+} + L^-$	1.8	0.6	1.2
	$H_3A^{3+} + L^-$	2.5	1.3	1.6
12	$HA^+ + L^-$	1.6	−0.2	
	$H_2A^{2+} + L^-$	2.1	0.7	
	$H_3A^{3+} + L^-$	2.5	1.3	
	$H_4A^{2+} + L^-$	2.7	2.0	
[16]aneN$_4$	$H_4A^{4+} + L^-$	1.9[d]		
[18]aneN$_4$	$H_4A^{4+} + L^-$	2.0[d]		
[20]aneN$_4$	$H_4A^{4+} + L^-$	2.8[d]		

[a] This work.
[b] Ref. [15].
[c] Refs. [7–9].
[d] $I = 0.1\,mol\,l^{-1}$ (KNO_3), $t = 20\,°C$ (Ref. [22]).

Stability of amine-fluoride complexes can be compared to that of other monocharged ligands, both inorganic and organic, such as chloride and acetate (Table 6). Between inorganic ligands, very high differences can be found, and stability follows always the trend $F^- \gg Cl^-$. Towards acetate ligand too, interacting ability of fluoride is higher, but differences are in some case smaller than those with chloride. For example, for $H(\mathbf{2})L^0$ species ($L = F^-$, ac^- or Cl^-), we found log K = 1.6, 1.4 and −0.4 for fluoride, acetate and chloride, respectively. If we explain the interaction between polyamine and polyanion in terms of hydrogen bonding we may justify the differences. Fluoride anion acts as hydrogen bonding acceptor and the proton transfer from polyamine to fluoride anion is strongly endothermic. The higher strength of hydrogen bond in fluoride systems with respect to chloride is also evidenced from the mean distance in $N^+H_3 \cdots L^-$ values (we have 1.67 and 2.247 for $L = F^-$ and Cl^-, respectively [29]). Moreover, *N*-alkyl substitution increases the stability of the anion complexes (see Eqs. (6) and (7)), because it causes a greater localisation of positive charge, due to the lowering of the hydration of amine groups, leading to stronger interaction with the anion.

Table 7
Equilibrium constants for the formation of amine-bicharged anion complexes at $I = 0\,\mathrm{mol\,l^{-1}}$ and $t = 25\,^\circ\mathrm{C}$

A	Reaction	CO_3^{2-}[a]	HCO_3^{-}[a]	SO_4^{2-}[b]	HPO_4^{2-}[c]	tar^{2-}[d]	HPO_4^{-}[c]	$Htar^{-}$[d]
1	$HA^{+} + L$	3.6	2.7	0.9	1.5	0.7		
	$H_2A^{2+} + L$			2.4	3.0	2.1	1.6	0.9
2	$HA^{+} + L$	3.9	2.9	1.3	1.5	2.0		
	$H_2A^{2+} + L$			2.6	2.6	2.9	1.7	2.4
3	$HA^{+} + L$			0.7	1.4	1.3		
	$H_2A^{2+} + L$			2.05	2.3	2.2	1.4	1.0
8	$HA^{+} + L$		3.8	0.8	2.3	1.35		
	$H_2A^{2+} + L$		3.25	1.4	2.4	2.1		
	$H_3A^{3+} + L$			2.8	3.3	2.9	1.3	1.3
12	$HA^{+} + L$			0.9	2.0	1.9		
	$H_2A^{2+} + L$		3.8	2.1	2.8	2.8		
	$H_3A^{3+} + L$		3.5	3.2	3.6	3.6		
	$H_4A^{4+} + L$			3.9	4.5	4.3	2.7	2.9
[16]aneN_5	$H_3A^{3+} + L$	4.44[e]			2.04[e]			
[17]aneN_5	$H_3A^{3+} + L$	4.28[e]						
[18]aneN_6	$H_3A^{3+} + L$	2.76[e]		1.64[e]	1.14[e]			

[a] This work.
[b] Ref. [17].
[c] Refs. [8,14].
[d] Refs. [9,14].
[e] Ionic strength not specified (Ref. [22]).

Stability of amine-CO_3^{2-} species can be compared to those of other discharged anions, both organic (tartrate, tar^{2-}) and inorganic (HPO_4^{2-}, SO_4^{2-}). Comparison is reported in Table 7. As can be seen, amine-carbonate complexes are always more stable to those of other ligands, and follow the trend $CO_3^{2-} > HPO_4^{2-} > SO_4^{2-} \cong \mathrm{mal}^{2-}$. The same behaviour is noticeable for cyclic amines, as showed from stability values of [18]aneN_6 reported in Table 7. Probably, the high charge concentration in the carbonate anion plays an important role in the stability of these complexes.

It is worth to consider again, by analysing simultaneously ΔG, ΔH and $T\Delta S$ contribution to the stability, the influence of hydrogen bonding in the formation of these complexes. The formation of -N–H$^{+}\cdots^{-}$O hydrogen bonds leads to partial deprotonation of amine and to partial protonation of carbonate. For amine deprotonation we have $\Delta H \gg 0$ (and $T\Delta S \sim 0$), and for protonation of carbonate $\Delta H < 0$ (and $T\Delta S > 0$). Therefore the resultant enthalpic effect must be endothermic, with an entropic contribution $T\Delta S > 0$. The formation of -N–H$^{+}\cdots^{-}$F hydrogen bonds determines partial protonation of fluoride ($\Delta H > 0$) and partial deprotonation of amine ($\Delta H \gg 0$), with a resultant endothermic effect. We may compare data for CO_3^{2-} and F^{-} with the analogous results for SO_4^{2-} [17] that can act only as hydrogen bond acceptor, as shown in Table 8. For fluoride species the difference in stability is due to the increment on $T\Delta S$ term, with the same enthalpic contribution, whilst for carbonate the endothermic effect is quite significant with a resultant boosting effect in the $T\Delta S$ term. These considerations, though semiqualitative, show the importance of hydrogen bonding in the formation of F^{-} and CO_3^{2-} polyammonium cation species. Nevertheless, more systems have to be investigated to draw general conclusions.

Table 8
Mean ΔG°, ΔH° and $T\Delta S^\circ$ contributions in the formation of polyammonium cation–anion species at $t = 25\,^\circ\mathrm{C}$ and $I = 0\,\mathrm{mol\,l^{-1}}$

Anion	$-\Delta G^\circ/\zeta$	$\Delta H^\circ/\zeta$	$T\Delta S^\circ/\zeta$
SO_4^{2-}[a]	3.4	0.4	3.8
F^{-}	5.7	0.1	5.8
CO_3^{2-}	11.4	7.6	19

[a] Ref. [17].

No data are reported in literature on both open chain polyamine-fluoride and -carbonate systems. Comparison is only possible with cyclic polyamines [20–23] for which we have stability constants fairly close to the relative values of open chain polyamine. For example, for H_4FA^{3+} species we found $\log K = 1.9$, 2.0, and 2.8 for [16]aneN_4, [18]aneN_4 and [20]aneN_4, respectively (at $20\,^\circ\mathrm{C}$ and $0.1\,\mathrm{mol\,l^{-1}}$ in KNO_3), and for $H_3CO_3A^{+}$ $\log K = 4.44$ and 4.28, for [16]aneN_5 and [17]aneN_5, respectively.

5. Final remarks

The main conclusion of this work can be summarised as follows:

- Open chain polyammonium cations significantly interact with fluoride and carbonate anions, and $H_iAL^{(i-z)+}$ species are found ($L^{z-} = F^-$ or ${CO_3}^{2-}$).
- Enthalpy changes for the formation of some of these complexes are calculated and resulted generally low and positive; the main contribution to stability arising from the $T\Delta S^\circ$ term.
- Polyamine-F^- and -${CO_3}^{2-}$ complexes are more stable respect polyamine-monocharged anion (Cl^-, ac^-) and -dicharged anion (${HPO_4}^{2-}$, ${SO_4}^{2-}$, mal^{2-}) complexes, respectively. The mean values of the free energy contribution per bound, ΔG_b°, calculated for both systems, are higher to that previously reported for polyamine-inorganic polyanion systems.
- Differences were justified explaining the polyamine-polyanion interactions in terms of hydrogen bonding.
- Stability depends on the charges of reactants (Eq. (3)) and it is less influenced by the structure of polyammonium cation (Eq. (4)). *N*-alkyl substitution plays also an important role increasing stability of both amine-fluoride and amine-carbonate species.
- Even if the stability of fluoride and carbonate species with open chain polyammonium cations cannot be compared with that of similar species of other inorganic anions, it is confirmed the additivity of ΔG and $T\Delta S$ contributions as reported by us in previous contribution to this topic and by Schneider in several investigations (see Ref. [30], and references therein).

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