Stability−Charge and Stability−Structure Relationships in the Binding of Tri- and Tetracarboxylic Ligands by Open-Chain Polyammonium Cations

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The interaction of eight polyammonium cations with citrate, 1,2,3-propanetricarboxylate, and 1,2,3,4-butanetetracarboxylate has been studied potentiometrically, by using the H^+-glass electrode, at 25 °C. The stability and the speciation of the systems investigated in this work are quite similar to those found in previous works for several polyammonium−polycarboxylic systems. The formation constants given here, together with several data already reported, have been analyzed to find reliable stability−charge and stability−structure relationships.

Introduction

Several studies on the binding of polyanions by polyammonium cations have been performed in this laboratory.[1−7] Particular attention has been paid to interactions between linear polyammonium cations and polycarboxylic anions.[2−6] We recently reported formation data for a variety of polyammonium−dicarboxylate systems[6] including a careful analysis of the stability of the species formed as a function of some parameters that characterize the different ligand and equilibrium reactions, particularly in relation to reactant charges. Further data regarding macrocyclic polyammonium cations in particular can be found in the literature.[8−11]

This paper describes a potentiometric study on the binding of tri- and tetracarboxylic anions (citrate, 1,2,3-propanetricarboxylate, and 1,2,3,4-butanetetracarboxylate) by eight polyammonium cations. All but one of the aminic ligands are linear with quite different alkyl chains. Measurements were performed at (25 ± 0.1) °C and equilibrium constants are reported at $I = 0$ mol·L^{-1}. Formulas and abbreviations for polyamines and polycarboxylic acids are reported in Table 1.

Experimental Section

Materials. Amines (A), Fluka *purum*, were purified by transformation into the corresponding hydrochlorides and were used in this form; only 1,6-diaminohexane dihydrochloride (Fluka, purity ≥ 99%) was used as purchased. NMR spectra of the amine hydrochlorides were performed to confirm their total transformation into this form. Carboxylic acids (L) citric, 1,2,3-propanetricarboxylic, and 1,2,3,4-butanetetracarboxylic (Fluka, purity ≥ 98%) were used without further purification. Solutions of NaCl (Fluka *puriss*) were prepared by mass, after drying in an oven at 110 °C. NaOH and HCl solutions were prepared from Fluka ampules and standardized against potassium hydrogenphthalate or sodium carbonate (Fluka

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puriss), respectively. All of the solutions were prepared with twice-distilled water, and grade A glassware was used.

Apparatus and Procedure. Potentiometric measurements were carried out with a Metrohm 654 potentiometer (resolution = ±0.1 mV) coupled with an Orion 8102 combination glass electrode (Ross type) and connected to a Metrohm Dosimat 665 dispenser (minimum reading = 0.001 ± 0.003 mL). The apparatus was coupled with a PC, so automatic titrations were carried out using a suitable computer program for the acquisition of data (volume of titrant, check for the stability of emf, and relative value). The measurement cell was thermostated at (25 ± 0.1) °C. A magnetic stirrer was employed, and a stream of purified nitrogen was bubbled into the solution.

Twenty-five milliliters of aqueous solution containing protonated amine and carboxylic acid under study was titrated with standard NaOH to complete neutralization (90−100 experimental points). For each system the concentration of the amine was (5, 10, 20) mmol·L^{-1}, and for each of them the carboxylic acid concentration was (5, 10, 25) mmol·L^{-1}. To obtain pH = −log [H^+] values, the electrode couple was standardized for each measurement by titrating 10 mmol·L^{-1} HCl with standard NaOH; NaCl was also added to the solution in order for it to maintain the same mean ionic strength value as the solution under study. From these data, the formal $E°$ value was calculated. Measurements were performed without adding any background salt, to minimize interferences, because the cation and anion of added salt form weak complexes with polycarboxylic anions and polyammonium cations.

Calculations. Potentiometric data were analyzed using suitable computer programs. We used the least squares computer programs ESAB2M for the calibration of the electrode system and to test the purity of the reagents and BSTAC or STACO for the refinement of formation constants of the carboxylic anion−protonated amine complexes. Both BSTAC and STACO programs are able to perform calculations in nonconstant ionic strength conditions. The ionic strength dependence of formation constants

Table 1. Amines and Carboxylic Ligands Studied in This Work

formula	name	abbreviation
$H_2N-(CH_2)_6-NH_2$	1,6-diaminohexane	A1
$H_2N-(CH_2)_{10}-NH_2$	1,10-diaminodecane	A2
$H_2N-(CH_2)_3-NH-(CH_2)_3-NH_2$	3,3′-diaminodipropylamine	A4
$H_2N-(CH_2)_6-NH-(CH_2)_6-NH_2$	6,6′-iminodihexylamine	A5
$H_2N-(CH_2)_4-CH(CH_2NH_2)-(CH_2)_3-NH_2$	4-(aminomethyl)-1,8-octanediamine	A6
$[(CH_3)NH-(CH_2)_6]_2-N(CH_3)$	*N,N′,N′*-trimethylbis(hexamethylene)triamine	A7
$H_2N-(CH_2)_3-N(CH_3)-(CH_2)_3-NH_2$	3,3′-diamino-*N*-methyldipropilamine	A8
$N(CH_2-CH_2-NH_2)_3$	tris(2-aminoethyl)amine	A10
$HO_2C-CH_2-CH(CO_2H)-CH_2-CO_2H$	1,2,3-propanetricarboxylic acid	tca
$HO_2C-CH_2-C(OH)(CO_2H)-CH_2-CO_2H$	2-hydroxy-1,2,3-propanetricarboxylic or citric acid	cit
$H_2OC-CH_2-[CH(CO_2H)]_2-CH_2-CO_2H$	1,2,3,4-butanetetracarboxylic acid	btc

Table 2. Protonation and Cl^- or Na^+ Complex Formation Constants of Amines and Carboxylic Acids at 25 °C and $I = 0$ mol·L^{-1}

	$\log \beta_{qi}{}^a$ or $\log \beta_{pj}{}^b$ index										
ligand	0 1	0 2	0 3	0 4	1 1	1 2	1 3	1 4	2 3	2 4	ref
A1	10.90	20.68			10.74	21.47					14
A2	10.94	20.98			10.99	21.70					14
A4	10.56	19.87	27.01		10.50	20.68	28.47		28.85		15
A5	11.18	21.42	30.76		11.00	22.18	32.13		32.57		15
A6	10.90	20.88	29.69		10.92	21.67	31.13		31.46		15
A7	11.20	21.50	30.66		11.26	22.34	32.09		32.44		15
A8	10.36	19.64	26.05		10.37	20.36	27.48		27.89		15
A10	10.14	19.33	27.21	27.24	10.04	20.17	28.60	28.84	29.06	29.54	15

	$\log \beta_{qi}{}^a$ or $\log \beta_{pj}{}^b$ index										
	0 1	0 2	0 3	0 4	1 0	1 1	1 2	1 3	2 0	2 1	3 0	ref
tca	6.49	11.41	15.09		1.40	7.31	11.56		1.98	6.96		16
cit	6.42	11.17	14.30		1.54	7.29	11.27		2.34	7.01		17
btc	7.18	13.01	17.54	20.92	1.82	8.67	13.94	17.76	3.45	9.31	3.30	18

^{a} Indices refer to the reaction $A^0 + iH^+ + qCl^- = H_iACl_q{}^{(q-i)-}$. ^{b} Indices refer to the reaction $pNa^+ + L^{z-} + jH^+ = Na_pLH_j{}^{(z-p-j)-}$.

was taken into consideration by using the Debye−Hückel-type equation[12]

$$\log \beta = \log {}^T\beta - zI^{1/2}/(2 + 3I^{1/2}) + CI + DI^{3/2} \quad (1)$$

where

$$C = 0.11p^* + 0.20z^*; \quad D = -0.075z^*$$

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

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

$${}^T\beta = \text{overall formation constant at } I = 0 \text{ mol·L}^{-1}$$

The distribution of the species was calculated using the ES4EC computer program. Details of the calculation techniques used in this laboratory can be found in ref 13. Concentrations and formation constants are given in the molar scale. In calculations, it is necessary to take amine and polycarboxylic ligand protonation constants into account. Moreover, because protonated amines form weak complexes with Cl^- (amine hydrochlorides are used) and carboxylic anions form weak complexes with Na^+ (coming from titrant NaOH), all of these species must be considered too. Formation data are reported in Table 2.

Results and Discussion

Formation Constants. Overall formation constants, relative to the reaction

$$A^0 + L^{z-} + rH^+ = ALH_r{}^{(r-z)} \quad (I)$$

for all of the systems studied in this work, are shown in Table 3. The species formed are always $ALH_r{}^{(r-z)}$ with $r = 1, 2, ..., (n + z - 1)$, where n represents the maximum degree of amine protonation. To show the real stability of these species, Tables 4−6 report the equilibrium constants relative to the partial reaction

$$AH_i{}^{i+} + H_jL^{(z-j)-} = ALH_r{}^{(r-z)} \quad (r = i + j) \quad (II)$$
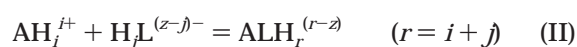
for the systems tca−, cit−, and btc−polyamine, respectively. The same tables also report literature data.[2−4,7] Data in Tables 4−6 show, as a first approximation, that (a) the stability for the species deriving from the same reaction (i.e., with the same charges) is fairly independent of polyammonium cations and polycarboxylic anions, (b) the stability is strictly dependent on charges involved in the formation reaction, and (c) the stability is fairly dependent on the length of the alkyl chain. Unfortunately, the choice of i and j is not always straightforward; when $\log K^H$ values for the amine and the carboxylic acid are close, it is difficult to assign the correct i and j values in reaction II. This is particularly true when $AH_n{}^{n+}$ species are involved. This problem was discussed in a previous paper[5] (see ahead).

Relevance of Polyammonium−Polycarboxylic Species. High yields of $ALH_r{}^{(r-z)}$ species are observed in experimental conditions. For example, Figures 1−3 show three relevant speciation diagrams for the systems A2−tca, A5−btc, and A8−btc, respectively. In the first system (Figure 1) formation percentages of A2LH$_r$ species are low, and only for the species A2LH$_3{}^0$ do we have (in the chosen conditions) yields >10%. The two speciation profiles shown in Figures 2 and 3 refer to btc systems with two triamines

Table 3. Overall Formation Constants[a] of ALH_r Complexes, at 25 °C and $I = 0$ mol·L^{-1}

amine	r[b]	log β_r tca	cit	btc	amine	r[b]	log β_r tca	cit	btc
A1	1	12.4 (2)	12.5 (2)	13.0 (1)	A6	1	12.7 (1)	12.6 (1)	13.0 (1)
	2	23.40 (2)	23.55 (2)	24.33 (2)		2	23.79 (2)	23.80 (2)	24.58 (2)
	3	28.95 (5)	28.85 (5)	30.55 (3)		3	33.83 (2)	33.91 (2)	34.95 (2)
	4	33.1 (1)	33.1 (1)	35.35 (8)		4	39.24 (2)	39.07 (2)	40.96 (1)
	5			39.1 (2)		5	43.15 (3)	42.72 (8)	45.63 (2)
						6			49.07 (8)
A2	1	12.7 (1)	12.8 (1)	13.1 (1)	A7	1	12.8 (1)	12.7 (1)	13.0 (1)
	2	23.55 (2)	23.61 (2)	24.24 (2)		2	24.02 (2)	24.14 (4)	24.56 (5)
	3	29.35 (4)	28.88 (8)	30.49 (4)		3	34.42 (2)	34.49 (2)	35.43 (2)
	4	33.77 (4)	33.1 (1)	35.28 (9)		4	39.87 (2)	39.76 (2)	41.49 (2)
	5			39.0 (2)		5	43.92 (3)	43.56 (5)	46.12 (4)
						6			49.4 (2)
A4	1	11.9 (2)	12.1 (1)	12.6 (1)	A8	1	12.1 (2)	12.5 (1)	12.7 (1)
	2	22.44 (5)	22.53 (3)	23.33 (2)		2	22.65 (2)	22.88 (2)	23.55 (2)
	3	31.27 (2)	31.44 (2)	32.52 (2)		3	30.49 (2)	30.71 (2)	31.83 (1)
	4	36.38 (3)	36.30 (3)	38.35 (2)		4	35.64 (2)	35.70 (2)	37.66 (2)
	5	37.7 (2)	39.11 (2)	42.66 (3)		5	39.53 (3)	39.28 (3)	42.15 (3)
	6			45.90 (9)		6			45.60 (9)
A5	1	12.6 (2)	13.2 (1)	13.7 (1)	A10	1	11.8 (1)	11.9 (1)	12.4 (1)
	2	23.42 (9)	24.13 (6)	25.28 (8)		2	22.30 (2)	22.29 (4)	23.23 (2)
	3	34.36 (2)	34.61 (2)	35.80 (2)		3	31.71 (2)	31.95 (2)	33.11 (2)
	4	39.78 (2)	39.79 (2)	41.82 (4)		4	36.80 (1)	36.80 (2)	38.86 (2)
	5	43.41 (7)	43.62 (8)	46.58 (4)		5	40.49 (6)	40.03 (8)	43.27 (3)
	6			50.1 (1)		6			46.5 (1)

[a] ±3 SD in parentheses. [b] Indices refer to the reaction $A^0 + L^{z-} + rH^+ = ALH_r^{(z-r)-}$.

Table 4. Equilibrium Constants of tca–Polyamine Complexes According to Reaction II, at 25 °C and $I = 0$ mol·L^{-1}

reaction (diamines)	ζ	log K A1	A2	en[a]	ptr[a]	cdv[a]	total[b]
$AH^+ + L^{3-}$	3	1.5	1.8	1.8	2.0	3.0	2.0 ± 0.3[c]
$AH_2^{2+} + L^{3-}$	6	2.7	2.6	3.3	3.2	3.3	3.0 ± 0.2
$AH_2^{2+} + HL^{2-}$	4	1.8	1.9	2.4	2.3	2.2	2.1 ± 0.1
$AH_2^{2+} + H_2L^-$	2	1.0	1.4	1.6	1.6	1.5	1.4 ± 0.1

reaction (triamines)	ζ	log K A4	A5	A6	A7	A8	A10	dien[a]	spd[a]	total
$AH^+ + L^{3-}$	3	1.3	1.4	1.8	1.6	1.7	1.7	1.7	1.0	1.5 ± 0.1
$AH_2^{2+} + L^{3-}$	6	2.6	2.0	2.9	2.5	3.0	3.0	3.1	2.4	2.4 ± 0.3
$AH_3^{3+} + L^{3-}$	9	4.3	3.6	4.1	3.8	4.4	4.5	5.6[d]	4.0	4.1 ± 0.1
$AH_3^{3+} + HL^{2-}$	6	2.9	2.5	3.1	2.7	3.1	3.1	3.8	2.6	3.0 ± 0.2
$AH_3^{3+} + H_2L^-$	3	1.3	1.2	2.1	1.9	2.1	1.9	2.5	1.1	1.8 ± 0.2

[a] en = ethylenediamine; ptr = putrescine; cdv = cadaverine; dien = diethylenetriamine; spd = spermidine, refs 2–4. [b] Values calculated from the weighted least-squares fit. [c] ±SD. [d] Improbable reaction (see text).

Table 5. Equilibrium Constants of cit–Polyamine Complexes, According to Reaction II, at 25 °C and $I = 0$ mol·L^{-1}

reaction (diamines)	ζ	log K A1	A2	en[a]	ptr[a]	cdv[a]	total[b]
$AH^+ + L^{3-}$	3	1.6	1.8	1.5	2.5	1.9	1.9 ± 0.2[c]
$AH_2^{2+} + L^{3-}$	6	2.9	2.6	3.6	3.7	3.2	3.2 ± 0.2
$AH_2^{2+} + HL^{2-}$	4	1.8	1.5	2.5	2.6	2.2	2.1 ± 0.2
$AH_2^{2+} + H_2L^-$	2	1.2	0.9	1.6	1.8	1.5	1.4 ± 0.2

reaction (triamines)	ζ	log K A4	A5	A6	A7	A8	A10	dien[a]	spd[a]	total
$AH^+ + L^{3-}$	3	1.5	2.0	1.7	1.5	2.1	1.8	2.0	1.3	1.7 ± 0.1
$AH_2^{2+} + L^{3-}$	6	2.7	2.7	2.9	2.6	3.2	3.0	3.3	2.6	2.9 ± 0.1
$AH_3^{3+} + L^{3-}$	9	4.4	3.9	4.2	3.8	4.6	4.7	5.6[d]	4.1	4.2 ± 0.1
$AH_3^{3+} + HL^{2-}$	6	2.9	2.6	3.0	2.7	3.2	3.2	3.8	2.7	3.0 ± 0.2
$AH_3^{3+} + H_2L^-$	3	0.9	1.7	1.9	1.7	2.0	1.6	2.2	1.2	1.7 ± 0.2

[a–c] See Table 4. [d] Improbable reaction.

Table 6. Equilibrium Constants of btc–Polyamine Complexes, According to Reaction II, at 25 °C and $I = 0$ mol·L^{-1}

reaction (diamines)	ζ	log K A1	A2	en[a]	ptr[a]	cdv[a]	total[b]
$AH^+ + L^{4-}$	4	2.1	2.2	2.2	3.2	3.6	2.7 ± 0.3[c]
$AH_2^{2+} + L^{4-}$	8	3.6	3.2	4.2	4.1	4.2	3.9 ± 0.2
$AH_2^{2+} + HL^{3-}$	6	2.7	2.3	3.1	3.1	3.0	2.8 ± 0.2
$AH_2^{2+} + H_2L^{2-}$	4	1.7	1.3	2.0	2.2	1.8	1.8 ± 0.2
$AH_2^{2+} + H_3L^-$	2	0.9	0.5	1.1	1.4	1.0	1.0 ± 0.2

reaction (diamines)	ζ	log K A4	A5	A6	A7	A8	A10	dien[a]	spd[a]	total
$AH^+ + L^{4-}$	4	2.0	2.5	2.1	1.8	2.4	2.3	2.7	2.0	2.2 ± 0.1
$AH_2^{2+} + L^{4-}$	8	3.5	3.9	3.7	3.1	3.9	3.9	4.2	3.5	3.7 ± 0.1
$AH_3^{3+} + L^{4-}$	12	5.5	5.0	5.3	4.8	5.8	5.9	7.0[d]	5.4	5.4 ± 0.2
$AH_3^{3+} + HL^{3-}$	9	4.2	3.9	4.1	3.7	4.4	4.5	5.3[d]	4.1	4.1 ± 0.1
$AH_3^{3+} + H_2L^{2-}$	6	2.6	2.8	2.9	2.5	3.1	3.0	3.5	2.7	2.9 ± 0.1
$AH_3^{3+} + H_3L^-$	3	1.4	1.8	1.8	1.2	2.0	1.7	2.3	1.5	1.7 ± 0.1

[a–c] See Table 4. [d] Improbable reaction.

with different alkyl chains. In both systems yields ≥50% are observed for ALH_r complexes, with a maximum for ALH_4^0. It should be noted that the different amine structures produce two main effects: (i) the formation of polyammonium–polyanion species is shifted to higher pH values for longer alkyl chains (because of their higher basicity), and (ii) formation percentages are significantly higher for the cation with shorter alkyl chains separating amino groups. It is also important to consider some other factors that affect the speciation profiles for these systems: formation percentages are strongly dependent on concentrations of both components, on the C_{amine}/C_{carbox} ratio, on ionic strength, and on ionic medium. The speciation diagrams shown in Figures 1–3 refer to $I = 0.1$(NaCl) mol·L^{-1}. If we consider lower or higher ionic strengths, very different speciation profiles should be observed. In fact, both Na^+ and Cl^- interact with carboxylic anions and with polyammonium cations, respectively. Moreover, when the amine or anion concentration is too low, the formation of ALH_r species can be negligible. These effects are all shown

in Figure 4. In the system A4–btc–H (pH = 8.0) for $I = 0.5$ (NaCl) mol·L^{-1} there is no formation of ALH_2 species when $C_{btc} < 10^{-2}$ mol·L^{-1}, whereas at $I \sim 0$ mol·L^{-1} there
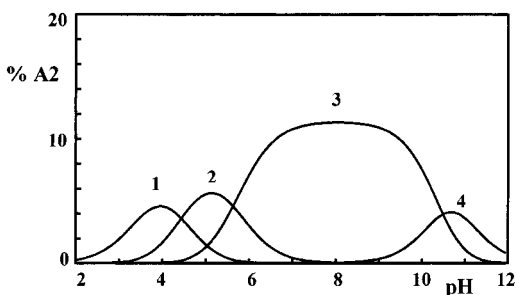
Figure 1. Distribution diagram of the species in the system A2−tca−H (1) $A2LH_2^{2-}$; (2) $A2LH_2^-$; (3) $A2LH_3^0$; (4) $A2LH_4^+$. Analytical concentrations: $C_{A2} = 1.0$ mmol·L^{-1}; $C_{tca} = 10.0$ mmol·L^{-1}; $C_{NaCl} = 100$ mmol·L^{-1}.
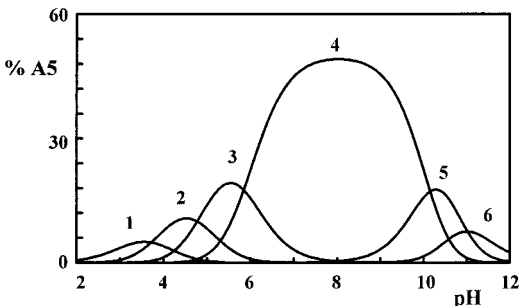
Figure 2. Distribution diagram of the species in the system A5−btc−H: (1) $A5LH^{3-}$; (2) $A5LH_2^{2-}$; (3) $A5LH_3^-$; (4) $A5LH_4^0$; (5) $A5LH_5^+$; (6) $A8LH_6^{2+}$. Analytical concentrations: $C_{A5} = 1.0$ mmol·L^{-1}; $C_{btc} = 10.0$ mmol·L^{-1}; $C_{NaCl} = 100$ mmol·L^{-1}.
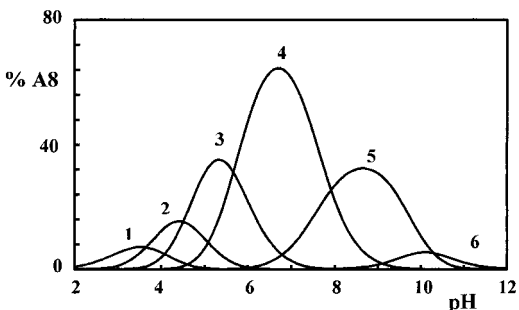
Figure 3. Distribution diagram of the species in the system A8−btc−H: (1) $A8LH^{3-}$; (2) $A8LH_2^{2-}$; (3) $A8LH_3^-$; (4) $A8LH_4^0$; (5) $A8LH_5^+$; (6) $A8LH_6^{2+}$. Analytical concentrations: $C_{A8} = 1.0$ mmol·L^{-1}; $C_{btc} = 10.0$ mmol·L^{-1}; $C_{NaCl} = 100$ mmol·L^{-1}.
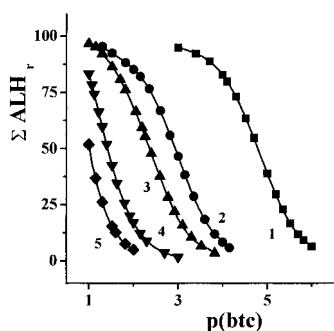
Figure 4. System A4−btc−H: Σ of ALH_r concentration, as a function of p(btc) at different NaCl concentrations (pH = 8.0): (1) 0, (2) 0.05, (3) 0.10, (4) 0.30, and (5) 0.50 mol L^{-1}.

is still formation of these species when $C_{btc} < 10^{-5}$ mol·L^{-1}. Stronger effects would be expected for electrolyte solutions containing divalent cation (e.g., Ca^{2+} and Mg^{2+}) and divalent anions (e.g., SO$_4^{2-}$) such as seawaters.

Table 7. Mean Values of log K_{ij} for the Binding of Di-, Tri-, and Tetracarboxylic Anions by Polyammonium Cations, at 25 °C and $I = 0$ mol·L^{-1}

	log K_{ij}				
ζ	di-[a]	di-[b]	tri-	tetra-	total[c]
2	1.40 ± 0.05[d]	1.33 ± 0.07[d]	1.41 ± 0.09[d]	0.98 ± 0.05[d]	1.41 ± 0.04[e]
3	1.99 ± 0.12	2.14 ± 0.16	1.73 ± 0.07	1.71 ± 0.12	1.80 ± 0.03
4	2.30 ± 0.09	2.38 ± 0.08	2.12 ± 0.11	2.12 ± 0.17	2.20 ± 0.03
6	3.02 ± 0.05	3.20 ± 0.07	2.94 ± 0.06	2.72 ± 0.19	2.99 ± 0.03
8		3.70 ± 0.05		3.77 ± 0.10	3.78 ± 0.04
9			4.17 ± 0.09	4.13 ± 0.10	4.17 ± 0.05
12				5.39 ± 0.15	5.36 ± 0.08

[a] Dicarboxylic anions (data of ref 6). [b] Dicarboxylic anions (other previous data, reported in ref 6). [c] Values calculated from the weighted least-squares fit. [d] ± $s/\sqrt{N}$ (s = SD; N = number of constants considered). [e] ± estimated SD.
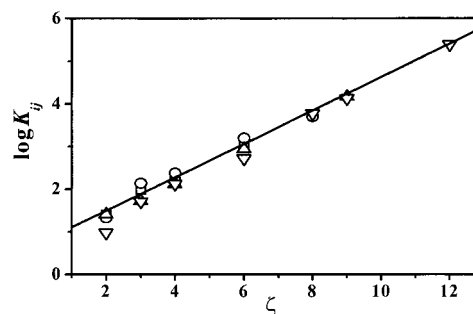

Figure 5. Dependence of log K_{ij} on ζ (eq 3): (□) dicarboxylic anions (data of ref 6); (○) dicarboxylic anions (other previous data, reported in ref 6); (△) tricarboxylic anions; (▽) tetracarboxylic anions.

Stability−Charge and Stability−Structure Relationships. As already pointed out for several systems previously studied,[1−7] the stability of polyammonium cation−polycarboxylic anion species strongly depends on charges in reaction II. The empirical relationships proposed are

$$\log K_{ij} = a + b\zeta \qquad (2)$$

$$\log K_{ij} = b\zeta^{\alpha} \qquad (2a)$$

$$\log K_{ij} = a + b|z_{anion}| + cz_{cation} \qquad (2b)$$

where a, b, c and α are empirical parameters and $\zeta = |z_{anion}z_{cation}|$ (z = charge), with $\alpha \leq 1$. To show the behavior of log K_{ij} as a function of ζ we report in Table 7 mean equilibrium constant values for each ζ value (including all of the polyammonium cations considered), for the different classes of carboxylic anions (dicarboxylic anions are also shown, ref 14, and references cited therein). The confidence intervals (expressed as standard errors, $s/\sqrt{N}$; s = standard deviation, N = number of equilibrium constants) are quite low, ranging from 0.05 to 0.19. This clearly indicates that the charge product ζ is by far the most important factor in the stability of open chain polyammonium cation−polycarboxylic anion complexes. No significant difference is observed among di-, tri-, and tetracarboxylic anions as evidenced in the last column of Table 7, where the mean is reported. Moreover, the trend of log K_{ij} versus ζ is linear, as shown in Figure 5, where the equilibrium constants for di-, tri-, and tetracarboxylic anion−polyammonium cation systems are reported together. These data are fitted by the equation

$$\log K_{ij} = (0.617 \pm 0.058) + (0.395 \pm 0.010)\zeta \qquad (3)$$

with a linear correlation coefficient $r = 0.9934$ and a mean

Table 8. $a \pm$ Standard Deviation Values for Equation 4

	diamines	ϵ^a	triamines	ϵ	diamines + triamines	ϵ
tca	0.424 ± 0.018	0.17	0.426 ± 0.011	0.34	0.425 ± 0.009	0.29
cit	0.442 ± 0.018	0.25	0.439 ± 0.011	0.30	0.439 ± 0.009	0.28
btc	0.396 ± 0.012	0.29	0.415 ± 0.008	0.30	0.411 ± 0.007	0.26
tca + cit + btc	0.415 ± 0.009	0.25	0.424 ± 0.006	0.29	0.422 ± 0.005	0.28

^{a} ϵ = mean deviation.

deviation $\epsilon = \Sigma\, |\log K - \log K_{\text{calcd}}|/N = 0.11$. By fitting the same data to eq 2a we obtain

$$\log K_{ij} = (0.923 \pm 0.032)\zeta^{2/3} \qquad (3a)$$

with a slightly higher error ($\epsilon = 0.17$). Finally, we can fit the data in Tables 4–6 (last column) to eq 2b to separate the effect of positive and negative charges on the stability. This leads to the relationship

$$\log K_{ij} = (-2.29 \pm 0.24) + (1.174 \pm 0.068)z_c +$$
$$(0.927 \pm 0.054)z_a \quad (3b)$$

($\epsilon = 0.22$). Relationship 3b accounts for the higher effect of positive charges.

Although the main contribution to the stability of $\text{ALH}_r^{(r-2)}$ species derives from the product of reactant charges in reaction II, the effect of polyanion and polyammonium cation structure has nevertheless been observed to be of some significance. In previous papers we found some relationships between the stability of ALH_r species and the distance between amino groups in the amine,[6,19,20] or between the stability and basicity.[5,6] The structure effects that can be taken into account are (a) the length of the alkyl chain in diamines, $H_2N-(CH_2)_x-NH_2$, and in triamines, $H_2N-(CH_2)_x-NH-(CH_2)_y-NH_2$, or in dicarboxylic acids, $(COOH)-(CH_2)_x-(COOH)$ [or the R_{NC} (N_{atoms}/C_{atoms}) ratio in different polyamines]; (b) the presence of $-OH$ or $-O-$ groups in the carboxylic ligands; (c) N-alkyl substitution in the amine; and (d) amine basicity. With regard to the length of alkyl chain(s) in diamines and in triamines, we found that the equilibrium constants depend slightly on $1/\sqrt{d}$ (where $d = x$ for diamines and $d = x + y$ for triamines), according to the simple equation

$$\log K_{ij} = a\zeta + 1/\sqrt{d} \qquad (4)$$

The values of parameter a of eq 4 (reported in Table 8) are very similar, and the general equation ($\pm$ SD)

$$\log K_{ij} = (0.423 \pm 0.013)\zeta + 1/\sqrt{d} \qquad (4a)$$

can be obtained and is valid for a great number of systems. Similar considerations may be made for the length of alkyl chains in carboxylic ligands, in particular for dicarboxylic ones, but no systematic studies of very different carboxylic ligands have been made. Recently, Hossain and Schneider[11] reported association ΔG for several complexes of open chain dications and dianions of quite different lengths and found little difference between the strongest and the weakest (<4 kJ·mol^{-1}). The presence of $-OH$ or $-O-$ groups in the carboxylic ligands generally has a positive effect on the stability of mixed complexes, but this effect never significantly exceeds experimental error. The main effect of amine basicity on the formation of ALH_r species is to shift the formation pH (see also Figures 2 and 3). The N-alkyl substitution in the amine produces a lowering of basicity and, therefore, complexes are formed at lower pH values. The stabilities of substituted and unsubstituted polyam-

monium cation–polyanion species are not very different, and it was found that, by taking the differing basicities into account, a single relationship may be defined for log K_{ij} values of both amines types.[5]

Correct Choice of Equilibrium II. The validity of equilibrium constants for reaction II is strictly related to the choice of stoichiometric coefficients i and j, which, in turn, depends on the basicity of both amine and carboxylic ligands. There is not always only one possible choice, because in some cases the protonation constant values of both reactants may be similar. Moreover, it is often the case that different equilibria II must be considered for different systems with similar amines. An example will clarify this matter. For triamines, the equilibrium for the formation of $A(btc)H_3^-$ species can be written as

$$AH_3^{3+} + btc^{4-} = A(btc)H_3^{-} \qquad (IIa)$$

or

$$AH_2^{2+} + H(btc)^{3-} = A(btc)H_3^{-} \qquad (IIb)$$
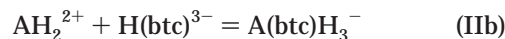
The first protonation constant of btc is log $K^H_1 = 7.18$ and the third protonation constants of diethylenetriamine (dien), A4, A5, and A8 (chosen arbitrarily for the purpose of this example), are 3.66, 7.14, 9.34, and 6.44, respectively. The use of equilibria II is fully appropriate only for A5, whereas for dien it is certainly inappropriate. A4 and A8 constitute intermediate cases, for which both equilibria IIa and IIb should probably be considered. Unfortunately, choices such as those made for the A4–btc and A8–btc systems, which are far from clear-cut, often characterize studies on polyammonium cation–polyanion complexes, and this implies the need for a further error to be taken into account when different systems are compared.

Error Analysis. Errors associated with the fits of log K_{ij} to different empirical equations must be compared with experimental errors, and conclusions must be drawn from the model bias. The variance of log K_{ij} can be expressed as a sum of different terms

$$\sigma_{\text{total}}^2 = \sigma_{\text{calcd}}^2 + \sigma_{\text{syst}}^2 + \sigma_{\text{prot}}^2 + \sigma_{\text{eq}}^2 \qquad (5)$$

where σ_{tot}^2 is the real (total) variance associated with log K_{ij}, σ_{calcd}^2 is the variance calculated by the computer program in refining overall formation constants, σ_{syst}^2 is related to the systematic experimental errors (reactant purity, titrant concentration, electrode couple calibration, etc.), σ_{prot}^2 is the variance in protonation constants (log K_{ij} = log β_{overall} − log β^H_i − log β^H_j), and σ_{eq}^2 is the additional variance due to the uncertainty in choosing the correct equilibrium II. If σ_{total}^2 is known, the bias in the model (represented by the different empirical equations) is given by

$$\sigma_{\text{model}}^2 = \sigma_{\text{fit}}^2 - \sigma_{\text{total}}^2 \qquad (5a)$$

For the different variances we estimated the following mean values: $\sigma_{\text{calcd}}^2 = (0.15)^2$, $\sigma_{\text{syst}}^2 = (0.15)^2$, + $\sigma_{\text{prot}}^2 =$

$(0.10)^2$, and $\sigma_{eq}^2 = (0.22)^2$; therefore, $\sigma_{total}^2 = (0.34)^2$. [These estimates were calculated by taking several factors into account and must be regarded as rough values. Systematic errors were calculated on the basis of $\sim$1% error in all concentrations in the experiments. Errors in protonation constants were estimated by considering a mean proton contribution in the various complexes considered in this work (mean protonation $\sim$4).] By considering log K_{ij} values for the polyammonium cation−polycarboxylic anion complexes described in this and in previous works[1-6] together, we have for eq 2a

$$\log K_{ij} = (0.615 \pm 0.045) + (0.430 \pm 0.010)\zeta \quad (3c)$$

with a standard deviation for the fit $\sigma_{fit} = 0.58$ and a mean deviation $\epsilon = 0.43$. (Note that the errors for eq 3c are much higher than for eqs 3−3b. This comes from the fact that in this case we did not use grouped data as we did for eqs 3−3b. Nevertheless, the values of empirical parameters for eqs 3 and 3c are quite similar.) Therefore, $\sigma_{model}^2 = (0.58)^2 - (0.34)^2 = (0.47)^2$. This indicates that the two main sources of variance are the uncertainties involved in choosing the correct formation reaction and the use of simplified models. The use of slightly more sophisticated models that take into account (i) the different contributions of positive and negative charge, (ii) the length of alkyl chains, and (iii) the effect of basicity reduces the model variance to $\sigma_{model}^2 \sim (0.3)^2$, and this can be attributed to the specificity of each system.

Final Remarks. The results reported in this work, together with some previously published data, confirm that the charges involved in the formation reaction are by far the most important factor in determining the stability of open chain polyammonium cation−polycarboxylic anion complexes. Different equations can be used to take the dependence of log K_{ij} on product charges ζ into account, that is eqs 2−3a and 3b account for the different contributions of positive and negative charges. The length of alkyl chain has been observed to have a small effect: the difference in log K_{ij} for diamine systems is $|1/\sqrt{10} - 1/\sqrt{2}| = 0.4$ when ethylenediamine and 1,10-diaminodecane are considered. Error analysis leads to the conclusion that errors mainly derive from the choice of model and, consequently, that the specificity of each system accounts for $\sim$0.3 logarithmic units in the formation constants. By using eq 3 or 3a we can calculate the stability increase per single bond or the average stability contribution per bond. In the first case we have a free energy increase per bond

$$-\Delta G^0/kJ \cdot mol^{-1} = 3.5 + 4.5n$$

(n = single salt bridge = $\zeta/2$, as a rough approximation) and

$$-\Delta G^0/kJ \cdot mol^{-1} = (5.3 \pm 0.2)n$$

when n is approximated to $\zeta/2$. Similar relationships for the stability of ion pairs have been discussed previously by us[1-7] and by Schneider[11,22,23] (and references cited therein).

Literature Cited

(1) Daniele, P. G.; Prenesti, E.; De Robertis, A.; De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Binding of Inorganic and Organic Polyanions by Protonated Open Chain Polyamines in Aqueous Solution. *Ann Chim.* (*Rome*) **1997**, *87*, 415−447; errata corrige **1998**, *88*, 447−448.

(2) De Robertis, A.; De Stefano, C.; Giuffrè, O.; Sammartano, S. Binding of Carboxylic Ligands by Protonated Amines. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4219−4226.

(3) De Stefano, C.; Gianguzza, A.; Maniaci, R.; Piazzese, D.; Sammartano, S. Binding of Polyanions by Biogenic Amines. II Formation and Stability of Protonated Putrescine and Cadaverine Complexes with Carboxylic Ligands. *Talanta* **1998**, *46*, 1079−1084.

(4) De Robertis, A.; De Stefano, C.; Gianguzza A.; Sammartano, S. Binding of Polyanions by Biogenic Amines. III Formation and Stability of Protonated Spermidine and Spermine Complexes with Carboxylic Ligands. *Talanta* **1999**, *48*, 119−126.

(5) Cascio, S.; De Robertis, A.; De Stefano, C.; Sammartano, S. The Effect of N-alkyl Substitution on the Binding of Polycarboxylic Ligands by Open-Chain Polyammonium Cations. *J. Solution Chem.* **2000**, *29*, 1101−1114.

(6) Cascio, S.; De Robertis, A.; De Stefano, C.; Foti, C.; Gianguzza, A.; Sammartano, S. Stability−Charge and Stability−Structure Relationships in the Binding of Dicarboxylic Ligands by Open-Chain Polyammonium Cations, *J. Chem. Eng. Data* **2000**, *45*, 717−723.

(7) De Robertis, A.; De Stefano, C.; Foti, C.; Giuffrè, O.; Sammartano, S. Thermodynamic Parameters for the Binding of Inorganic and Organic Anions by Biogenic Polyammonium Cations. *Talanta* **2001**, *54*, 1135−1152.

(8) Bianchi, A.; Micheloni, M.; Paoletti, P. Thermodynamic Aspects of the Polyazacycloalkane Complexes with Cations and Anions. *Coord. Chem. Rev.* **1991**, *110*, 17−113.

(9) Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. Macromonocyclic Polyamines as Specific Receptors for Tricarboxylate-Cycle Anions. *J. Am. Chem. Soc.* **1981**, *103*, 3041−3045.

(10) Hosseini, M. W.; Lehn, J. M. Anion Coreceptor Molecules. Linear Molecular Recognition in the Selective Binding of Dicarboxylate Substrates by Ditopic Polyammonium Macrocycles. *Helv. Chim. Acta* **1986**, *69*, 587−603.

(11) Hossain, M. A.; Schneider, H. J. Flexibility, Association Constants, and Salt Effects in Organic Ion Pairs: How Single Bonds Affect Molecular Recognition. *Chem. Eur. J.* **1999**, *5*, 1284−1290.

(12) Daniele, P. G.; De Stefano, C.; Foti, C.; Sammartano, S. The Effect of Ionic Strength and Ionic Medium on the Thermodynamic Parameters of Protonation and Complex Formation. *Curr. Top. Solution Chem.* **1997**, *2*, 253−274.

(13) De Stefano, C.; Sammartano, S.; Mineo, P.; Rigano, C. Computer Tools for the Speciation of Natural Fluids. In *Marine Chemistry− An Environmental Analytical Chemistry Approach*; Gianguzza, A., Pelizzetti, E., Sammartano, S., Eds.; Kluwer Academic Publishers: Amsterdam, The Netherlands, 1997; pp 71−83.

(14) Cascio, S.; De Robertis, A.; Foti, C. Protonation of Diamines H₂N−(CH₂)ₙ−NH₂ ($n = 2−10$) in NaCl Aqueous Solution at Different Ionic Strengths. *J. Chem. Eng. Data* **1999**, *44*, 735−738.

(15) Cascio, S.; De Robertis, A.; Foti, C. Protonation of Polyamines in NaCl Aqueous Solution and Binding of Cl⁻ by Polyammonium Cations. *Fluid Phase Equilib.* **2000**, *170*, 167−181.

(16) De Stefano, C.; Foti, C.; Gianguzza, A. Salt Effects on the Protonation and on Alkali and Alkaline Earth Metal Complex Formation of 1,2,3-propanetricarboxylate in Aqueous Solution. *Talanta* **1994**, *41*, 1715−1722.

(17) Daniele, P. G.; De Robertis, A.; De Stefano, C.; Gianguzza, A.; Sammartano, S. Studies on Polyfunctional *O*-Ligands. Formation Thermodynamics of Simple and Mixed Alkali Metal Complexes with Citrate at Different Ionic Strengths in Aqueous Solution. *J. Chem. Res.* **1990** (S) 300−301, (M) 2316−2350.

(18) De Robertis, A.; Foti, C.; Gianguzza, A. Studies on Polyfunctional *O*-Ligands. Alkali and Alkaline Earth Metal Complexes of Butanetetracarboxylate in Aqueous Solution. *Ann Chim.* (*Rome*) **1993**, *83*, 485−497.

(19) De Stefano, C.; Foti, C.; Gianguzza, A.; Giuffrè, O.; Sammartano, S. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1511−1518.

(20) De Stefano, C.; Giuffrè, O.; Sammartano, S. Thermodynamic Parameters for the Binding of ATP by Protonated Open-Chain Polyanions. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1091−1095.

(21) De Stefano, C.; Giuffrè, O.; Sammartano, S. ΔG°- and $T\Delta S^\circ$-Charge Relationships for the Binding of Carboxylic Anions by Open-Chain Polyammonium Cations. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2395−2398.

(22) Schneider, H. J. Linear Free Energy Relationships and Pairwise Interactions in Supramolecular Chemistry. *Chem. Soc. Rev.* **1994**, 227−234.

(23) Schneider, H. J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.