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

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The stability of complexes formed by 5 dicarboxylic ligands with 11 open-chain polyammonium cations (40 systems) was studied potentiometrically, in aqueous solution, at 25 °C. In all the systems ALH_r species (A = amine, L = dicarboxylic ligand, $r = 1 \ldots n$; diamines $n = 3$, triamines $n = 4$, tetraamines $n = 4$ or 5) were found. Formation constants for the various complexes studied in this work, together with data for the analogous systems previously studied (20 systems), were examined as a function of charges involved in the formation reaction and of the structure of both the dicarboxylic ligand and the polyammonium cation. Structure generally has little effect on stability, while charges play a fundamental role. The most general relationship, valid for all the complexes (the formation constants of 249 complexes were examined), is $\log K = 0.925(\pm 0.010)\zeta^{2/3}$ ($\zeta = |z_{\mathrm{anion}} z_{\mathrm{cation}}|$). The likely role of the formation of these mixed species in the speciation of natural waters and biological fluids is also discussed.

Introduction

Carboxylic acids play an active role in many very important reactions occurring in biological fluids and in natural waters. Di- and tricarboxylic acids are involved in the Krebs cycle and other biochemical reactions. Low molecular weight polycarboxylic acids are present in natural waters and derive from the degradation of humic substances. Polyamines are also widely present in natural systems. It is well-known that their concentration in biological fluids is regulated by numerous enzymes in their metabolism and is high in the urine of patients with a variety of tumors.[1]

In the pH range of biological and natural fluids (pH ≅ 5−9) carboxylic acids are present as polyanions and amines are generally fully or partially protonated. The simultaneous presence of carboxylic anions and polyammonium cations leads to the formation of complexes whose stability is strictly dependent on anion and cation charges. Quantitative data have been reported for some species formed between carboxylic ligands and both open-chain[2−7] and polyazamacrocyclic ammonium cations.[8−10] In previous works we studied the interactions of protonated polyamines with the anions of organic and inorganic polyacids, identifying simple relationships between the reactant charges in the formation reactions and the formation constant values for homogeneous classes of ligands. In this work we turn our attention to the formation and stability of dicarboxylic ligand−open-chain polyammonium cations with the aim of identifying the effects of structure and charges. To this end we chose some quite different dicarboxylic acids (malonic, succinic, azelaic, 2,2′-oxydiacetic, 3,6,9-trioxaundecanedioic) and di-, tri-, and tetraamines (1,6-diaminohexane, 1,10-diaminodecane, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, bis(3-aminopropyl)amine, bis-(6-aminohexyl)amine, 4-aminomethyl-1,8-octanediamine, *N*,*N*′,*N*″-methylbis(hexamethylene)triamine, 3,3′-diamino-*N*-methyldipropilamine, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, tris(2-aminoethyl)amine, and 1,1,4,7,10,10-hexamethyltriethylenetetramine). Formulas and abbreviations for amines and dicarboxylic ligands are shown in Table 1.

Experimental Section

Materials. Amines [A = 1,10-diaminodecane, *N*,*N*,*N*′,*N*′-tetramethylethylendiamine, bis(3-aminopropyl)amine, bis-(6-aminohexyl)amine, 4-aminomethyl-1,8-octanediamine, *N*,*N*′,*N*″-trimethylbis(hexamethylene)triamine, tris(2-aminoethyl)amine, 3,3′-diamino-*N*-methyldipropilamine, *N*,*N*,-*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, and 1,1,4,7,10,-10-hexamethyltriethylenetetramine, Fluka purum] were purified by transformation into the corresponding hydrochlorides and were used in this form; 1,6-diaminohexane dihydrochloride (Fluka, purity ≥ 99%) was used without further purification. NMR spectra of the amine hydrochlorides were performed, to confirm their total transformation into hydrochlorides, starting from simple amines. Carboxylic acids [L = malonic, succinic, azelaic, 2,2′-oxydiacetic, 3,6,9-trioxaundecanedioic, Fluka, purity ≥ 98%] were used without further purification. Solutions of NaCl (Fluka puriss) were prepared by weight after drying in an oven at 110 °C. NaOH and HCl solutions were prepared from Fluka standard volumetric solutions and standardized against potassium hydrogen phthalate (Fluka puriss) or sodium carbonate (Fluka puriss), respectively. All the

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Table 1. Amines and Carboxylic Ligands Studied in This Work

formula	name	abbreviation
$H_2N(CH_2)_6NH_2$	1,6-diaminohexane	A1
$H_2N(CH_2)_{10}NH_2$	1,10-diaminodecane	A2
$(CH_3)_2N(CH_2)_2N(CH_3)_2$	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine	A3
$H_2N(CH_2)_3NH(CH_2)_3NH_2$	bis(3-aminopropyl)amine	A4
$H_2N(CH_2)_6NH(CH_2)_6NH_2$	bis(6-aminohexyl)amine	A5
$H_2N(CH_2)_4CH(CH_2NH_2)(CH_2)_3NH_2$	4-(aminomethyl)-1,8-octanediamine	A6
$[(CH_3)NH(CH_2)_6]_2N(CH_3)$	*N*,*N*′,*N*″-trimethylbis(hexamethylene)triamine	A7
$H_2N(CH_2)_3N(CH_3)(CH_2)_3NH_2$	3,3′-diamino-*N*-methyldipropilamine	A8
$(CH_3)_2N(CH_2)_2N(CH_3)(CH_2)_2N(CH_3)_2$	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine	A9
$N(CH_2CH_2NH_2)_3$	tris(2-aminoethyl)amine	A10
$(CH_3)_2N(CH_2)_2\text{-}[N(CH_3)(CH_2)_2]_2N(CH_3)_2$	1,1,4,7,10,10-hexamethyltriethylenetetramine	A11
$COOHCH_2COOH$	malonic acid	mal
$COOH(CH_2)_2COOH$	succinic acid	succ
$COOH(CH_2)_7COOH$	azelaic acid	aza
$O(CH_2COOH)_2$	2,2′-oxydiacetic acid	oda
$[COOHCH_2O(CH_2)_2]_2O$	3,6,9-trioxaundecanedioic acid	toda

solutions were prepared with twice distilled water, and grade A glassware was used.

Apparatus. Potentiometric measurements were carried out with a Metrohm 654 potentiometer (resolution ±0.1 mV) coupled with an Orion combination pH electrode, model 8102 (Ross type); the titrant was delivered by a Metrohm Dosimat 665 dispenser (minimum reading ±0.001 cm^3). 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 (25 cm^3) was thermostated at 25 ± 0.1 °C, a magnetic stirrer was employed, and a stream of purified nitrogen was bubbled into the solution.

Procedure. A volume of 25 cm^3 of aqueous solution containing protonated amine and carboxylic acid was titrated with standard NaOH up to 90% neutralization (80−100 experimental points). For each system under study the concentration of the amine was 5, 10, and 20 $mmol \cdot dm^{-3}$ and the carboxylic acid concentration was 5, 10, and 25 $mmol \cdot dm^{-3}$. The electrode couple was standardized for each measurement in order to obtain $pH = -\log [H^+]$ values by titrating HCl 10 $mmol \cdot dm^{-3}$ with standard NaOH; NaCl was also added to the solution in order to reach the mean ionic strength value of the corresponding solution under examination. From these data, the formal $E°$ value was calculated. No background salt was used in the experiments to minimize interferences since cations and anions form weak complexes with dicarboxylic anions and polyammonium cations, respectively.[3]

Calculations. Potentiometric data were analyzed by using suitable computer programs. We used the least-squares computer programs ESAB2M[11] for the calibration of the electrode system and for testing the purity of the reagents and BSTAC[12] or/and STACO[13] for the refinement of complex formation constants. Both BSTAC and STACO programs are able to perform calculations in nonconstant ionic strength conditions. For the ionic strength dependence of formation constants we used the Debye−Hückel type equation[14]

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

where ${}^{T}\beta$ is the overall formation constant at $I = 0$ $mol \cdot dm^{-3}$ and

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

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

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

The distribution of the species was calculated by the computer program ES4ECI.[12] Concentrations and formation constants are given in the molar scale. In the calculations it is necessary to take the protonation constants of the amines and the dicarboxylic ligands into account. Moreover, protonated amines form weak complexes with Cl^- (amine−hydrochlorides are used) and carboxylic anions form weak complexes with Na^+ (deriving from the NaOH titrant), and all these species must be considered too.

Results and Discussion

Protonation and Weak Complex Formation. The protonation constants of amines and dicarboxylic ligands, studied in other works,[15−17] are shown in Table 2. All the amines form H_iA protonated species with $i = 1 \ldots n$ (n = maximum degree of protonation) and the dicarboxylates form H_jL species with $j = 1, 2$. Moreover, protonated amines form weak AH_iCl_q type complexes with $i = 1 \ldots n$ and $q = 1 \ldots n-2$ and dicarboxylates form weak NaHL and NaL type complexes. Formation constants for weak complexes are shown in Table 2.

Diamine−Dicarboxylate Complexes. In these systems ALH_r ($r = 1, 2, 3$) three species are formed. Overall stability constants are shown in Table 3, and partial formation constants K_{ij}, according to the reaction

$$H_iA^{i+} + H_jL^{(j-2)} = ALH_r^{(r-2)} \quad (r = i + j) \qquad (I)$$

are shown in Table 4. As can be seen, the species with charge ±2 in the cation and in the anion is, as expected, the most stable. Moreover its partial formation constant is quite similar for all the systems: $\log K_{20} = 2.1 \pm 0.2$ (only for toda complexes can we note a significant difference, which will be discussed later). As concerns ALH^- and ALH_3^+ species there is a higher dispersion in the values of formation constants. This dispersion can be attributed to two factors: (i) higher errors for smaller constants; (ii) structure effects.

Triamine−Dicarboxylate Complexes. The formation constants of complexes formed in these systems (ALH_r; $r = 1 \ldots 4$, always) are shown in Table 3 (overall) and Table 4 (partial, reaction I). The amine A10, because of the very low value of its last protonation constant ($\log K_4^H = 0.04$), is considered as a triamine. For diamine complexes the partial reactions, i.e. the most probable reaction pathway, are always the same, while for triamine species ALH_3^+ two different reactions must be considered, as a function of different protonation constants. When $\log K_3^H(\text{amine}) \geq \log K_1^H(\text{carboxy})$ the

Table 2. Protonation and Cl^- and Na^+ Complex Formation Constants of Amines and Carboxylic Ligands, at $T = 25$ °C and $I = 0$ mol·dm^{-3}

	log β_{qi} or log β_{pj}[a] Indexes											
ligand	0 1	0 2	0 3	0 4	1 0	1 1	1 2	1 3	1 4	2 3	2 4	refs
A1	10.90	20.68				10.74	21.47					15
A2	10.94	20.98				10.99	21.70					15
A3	9.15	14.78				9.12	15.73					18
A4	10.56	19.87	27.01			10.50	20.68	28.47		28.85		18
A5	11.18	21.42	30.76			11.00	22.18	32.13		32.57		18
A6	10.90	20.88	29.69			10.92	21.67	31.13		31.46		18
A7	11.20	21.50	30.66			11.26	22.34	32.09		32.44		18
A8	10.36	19.64	26.05			10.37	20.36	27.48		27.89		18
A9	9.23	17.39	18.89			9.22	18.39	20.61		21.01		18
A10	10.14	19.33	27.21	27.24		10.04	20.17	28.60	28.84	29.06	29.54	18
A11	9.22	17.36	22.07	22.63		9.40	18.35	23.58	24.61	24.31	26.03	18
mal	5.70	8.56			0.91	5.66						16
succ	5.64	9.85			0.85	5.79						16
aza	5.49	10.04			0.86	5.76						17
oda	4.36	7.33			0.71	4.04						16
toda	4.25	7.56			1.02	4.67						17

[a] Indexes refer to the reaction $A^0 + iH^+ + qCl^- = H_iACl_q^{(q-i)-}$ for amines and to the reaction $pNa^+ + L^{2-} + jH^+ = Na_pLH_j^{(2-p-j)-}$ for carboxylic ligands.

formation reaction is

$$H_3A^{3+} + L^{2-} = ALH_3^{\ +} \qquad \text{(II)}$$

and when log K_3^H(amine) < log K_1^H(carboxy) we must consider the reaction

$$H_2A^{2+} + HL^- = ALH_3^{\ +} \qquad \text{(III)}$$

While in this case the choice of the reaction is easy, in some cases the choice is arbitrary owing to the superimposition of protonation constant values. This may imply very different partial formation constant values, as for example in the case of A9(aza)H_4^{2+} species, for which log K_{31} = 4.0 and log K_{22} = 1.0. The reaction H_2A9^{2+} + $H_2(aza)^0$ = A9(aza)H_4^{2+} on the basis of protonation constant values is the most probable. However, it is hard to accept a reaction involving a zero-charge species for a complex in which electrostatic interactions predominate. Therefore Tables 4 and 5 always show partial formation constants relative to the reactions of charged species, with a warning about their real significance.

Tetraamine−Dicarboxylate Complexes. The species formed in this system are ALH_r (r = 1 ... 5) for A11. Overall and partial formation constants are reported in Tables 3 and 4, respectively. In some tetraamine−dianion systems reported in previous works we also found weak species with a stoichiometric coefficient for dianion ≠ 1; for the tetraamine systems in this work, these species were always rejected in computer refinement. For tetraamine too there is, for higher protonated complexes, uncertainty about the reaction path.

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

		log β_r				
amines	r[b]	mal	succ	aza	oda	toda
A1	1	11.8(1)	12.0(2)		11.6(6)	11.9(6)
	2	22.66(1)	22.64(3)		22.77(6)	22.9(1)
	3	27.33(6)	27.49(6)		26.2(3)	26.2(6)
A2	1	12.1(1)	12.0(2)		12.40(8)	12.7(1)
	2	22.89(3)	22.83(5)		23.14(5)	23.55(3)
	3	27.98(5)	28.00(6)		26.5(1)	27.20(7)
A3	1	10.1[c]			10.1(1)	10.5(1)
	2	17.11			16.85(6)	17.03(6)
	3	21.9			20.4(2)	20.8(1)
A4	1	11.3(2)		12.3(1)	11.8(1)	11.6(1)
	2	21.69(6)		22.21(5)	21.76(5)	21.83(5)
	3	30.18(3)		29.99(2)	30.00(7)	29.92(2)
	4	34.4(1)		34.34(8)	32.9(1)	32.6(2)
A5	1		12.6(1)	12.2(1)	12.2(1)	12.2(2)
	2		23.26(8)	23.2(1)	23.3(1)	23.46(9)
	3		33.38(5)	33.51(5)	33.47(4)	33.68(4)
	4		37.7(1)	38.0(1)	36.7(2)	36.5(2)
A6	1		12.3(1)	12.0(2)	12.6(2)	12.3(1)
	2		22.89(3)	23.09(9)	22.6(1)	22.86(9)
	3		32.63(1)	32.36(5)	32.38(5)	32.73(5)
	4		37.26(3)	36.91(9)	35.3(2)	36.3(1)
A7	1	12.71(7)		12.7(2)	12.4(1)	13.0(2)
	2	23.55(2)		23.38(8)	23.17(7)	23.49(9)
	3	33.23(5)		33.30(3)	33.30(1)	33.72(1)
	4	37.73(8)		37.67(5)	36.22(8)	37.41(3)
A8	1		11.9(1)	12.2(1)	12.2(2)	12.3(1)
	2		21.84(2)	22.40(8)	21.92(3)	22.18(3)
	3		29.12(1)	29.45(5)	23.23(3)	29.36(2)
	4		33.58(5)	34.18(9)	31.97(6)	32.6(1)
A9	1	10.1[c]		10.5(2)	10.5(1)	10.7(2)
	2	19.14		19.71(6)	19.74(9)	20.42(8)
	3	24.44		24.48(9)	23.15(8)	24.17(9)
	4	26.4		28.4(2)	26.2(1)	26.8(1)
A10	1		11.9(1)	12.0(2)	11.6(2)	11.8(1)
	2		21.32(8)	21.50(8)	21.61(8)	21.26(9)
	3		30.29(2)	30.02(5)	30.59(3)	30.44(3)
	4		34.83(6)	34.4(2)	33.1(2)	33.78(6)
A11	1	10.5[c]		11.2(1)	11.1(1)	11.2(1)
	2	19.49		19.94(7)	19.87(5)	20.10(7)
	3	25.61		25.62(5)	25.30(6)	25.56(3)
	4	29.69		29.92(8)	28.41(9)	29.18(8)
	5	31.7		33.2(1)	31.1(1)	30.7(2)

[a] ±3 SD in parentheses. [b] Index refers to the reaction $A^0 + L^{2-} + rH^+ = ALH_r^{(2-r)-}$. [c] Reference 19.

Significance of Polyamine−Dicarboxylate Species. To give a picture of the formation percentages of mixed species formed in mixed dicarboxylic ligand−polyamine solutions, Figures 1−3 show the distribution diagrams of the A2-toda, A5-aza, and A11-oda systems. Under the conditions in these diagrams, similar to experimental conditions, the species with higher yields, in our experimental conditions, are between 15 and 25% of the amine present in solution. They coincide with the complexes, normally with zero charge, deriving from probable reactions for which the value of ζ

$$\zeta = |z_{\mathrm{cation}} z_{\mathrm{anion}}|$$

is the highest possible. It is also interesting to evidence two important factors affecting the formation of dicarboxy-

Table 4. Partial Fomation Constants of ALH$_r$ Complexes, at T = 25 °C and I = 0 mol·dm^{-3}

	log K						log K				
reacns	mal	succ	aza	oda	toda	reacns	mal	succ	aza	oda	toda
$A1H^+ + L^{2-}$	0.9	1.1		0.7	1.0	$A2H^+ + L^{2-}$	1.2	1.1		1.5	1.7
$A1H_2^{2+} + L^{2-}$	2.0	2.0		2.1	2.1	$A2H_2^{2+} + L^{2-}$	1.9	1.8		2.2	2.6
$A1H_2^{2+} + HL^-$	1.0	1.2		1.2	1.3	$A2H_2^{2+} + HL^-$	1.3	1.4		1.2	2.0
$A3H^+ + L^{2-}$	0.9			0.9	1.4	$A4H^+ + L^{2-}$	0.7		1.7	1.2	1.1
$A3H_2^{2+} + L^{2-}$	2.3			2.1	2.2	$A4H_2^{2+} + L^{2-}$	1.8		2.3	1.9	2.0
$A3H_2^{2+} + HL^-$	1.4			1.3	1.8	$A4H_3^{3+} + L^{2-}$	3.2		3.0	3.0	2.9
						$A4H_3^{3+} + HL^-$	1.7		1.8	1.5	1.4
$A5H^+ + L^{2-}$		1.4	1.0	1.1	1.0	$A6H^+ + L^{2-}$		1.4	1.1	1.7	1.4
$A5H_2^{2+} + L^{2-}$		1.8	1.8	1.9	2.0	$A6H_2^{2+} + L^{2-}$		2.0	2.2	1.7	2.0
$A5H_3^{3+} + L^{2-}$		2.6	2.8	2.7	3.0	$A6H_3^{3+} + L^{2-}$		2.9	2.7	2.7	3.0
$A5H_3^{3+} + HL^-$		1.3	1.7	1.6	1.5	$A6H_3^{3+} + HL^-$		1.9	1.7	1.3	2.4
$A7H^+ + L^{2-}$	1.5		1.5	1.2	1.8	$A8H^+ + L^{2-}$		1.5	1.9	1.8	1.9
$A7H_2^{2+} + L^{2-}$	2.1		1.9	1.7	2.0	$A8H_2^{2+} + L^{2-}$		2.2	2.8	2.3	2.5
$A7H_3^{3+} + L^{2-}$	2.6		2.6	2.6	3.1	$A8H_3^{3+} + L^{2-}$		3.1	3.3	3.2	3.3
$A7H_3^{3+} + HL^-$	1.4		1.5	1.2	2.5	$A8H_3^{3+} + HL^-$		1.9	2.6	1.5	2.3
$A9H^+ + L^{2-}$	0.9		1.3	1.3	1.5	$A10H^+ + L^{2-}$		1.8	1.9	1.5	1.6
$A9H_2^{2+} + L^{2-}$	1.7		2.3	2.3	3.0	$A10H_2^{2+} + L^{2-}$		2.0	2.2	2.3	1.9
$A9H_2^{2+} + HL^-$	1.3		1.6	1.4	2.6	$A10H_3^{3+} + L^{2-}$		3.1	2.8	3.4	3.2
$A9H_3^{3+} + HL^-$	1.8		4.0	3.0	3.7	$A10H_3^{3+} + HL^-$		2.0	1.7	1.5	2.3
$A11H^+ + L^{2-}$	1.3		2.0	1.9	2.0						
$A11H_2^{2+} + L^{2-}$	2.2		2.6	2.5	2.7						
$A11\ H_3^{3+} + L^{2-}$	3.5		3.5	3.2	3.5						
$A11H_3^{3+} + HL^-$	1.9		2.3	2.0	2.8						
$A11H_4^{4+} + HL^-$	3.3		5.0	4.1	3.8						

Table 5. Literature Data for Formation Constants of ALH$_r$ Complexes, at T = 25 °C and I = 0 mol·dm^{-3}

	log K			
reacns[a]	mal	mala[b]	tar[c]	refs
$enH^+ + L^{2-}$	0.9	0.7	0.9	17, 20
$enH_2^{2+} + L^{2-}$	2.5	2.1	2.2	
$enH_2^{2+} + HL^-$	1.7	0.9	0.9	
$1,2dapH^+ + L^{2-}$	1.0	0.7[d]	1.2[e]	20
$1,2dapH_2^{2+} + L^{2-}$	2.6	2.5[d]	2.6[e]	
$1,2dapH_2^{2+} + HL^-$	1.8	1.5[d]	1.4[e]	
$ptrH^+ + L^{2-}$		1.7	2.0	6
$ptrH_2^{2+} + L^{2-}$		2.5	2.9	
$ptrH_2^{2+} + HL^-$		1.6	2.4	
$cdvH^+ + L^{2-}$	1.5	1.1	1.3	6
$cdvH_2^{2+} + L^{2-}$	2.3	2.1	2.2	
$cdvH_2^{2+} + HL^-$	0.9	0.9	1.0	
$dienH^+ + L^{2-}$	1.1	1.0		21
$dienH_2^{2+} + L^{2-}$	2.1	1.9		
$dienH_2^{2+} + HL^-$	1.9	1.9		
$dienH_3^{3+} + HL^-$	1.9	1.9		
$trienH^+ + L^{2-}$	1.4	1.8	1.7	3
$trienH_2^{2+} + L^{2-}$	2.3	2.6	2.5	
$trienH_3^{3+} + L^{2-}$	3.4	3.4	3.4	
$trienH_3^{3+} + HL^-$	2.4	2.3	2.9	
$trienH_4^{4+} + HL^-$	2.9	3.2	3.1	
$spdH^+ + L^{2-}$	0.8			4
$spdH_2^{2+} + L^{2-}$	1.7			
$spdH_3^{3+} + L^{2-}$	2.9			
$spdH_3^{3+} + HL^-$	1.5			
$sperH^+ + L^{2-}$	1.2	1.4	1.7	4
$sperH_2^{2+} + L^{2-}$	2.3	2.1	2.4	
$sperH_3^{3+} + L^{2-}$	3.1	3.0	3.2	
$sperH_4^{4+} + L^{2-}$	3.7	3.6	3.8	
$sperH_4^{4+} + HL^-$	1.7	1.9	2.4	

[a] en = ethylenediamine; 1,2dap = 1,2-diaminopropane; ptr = putrescine; cdv = cadaverine; dien = diethylenetriamine; spd = spermidine; trien = triethylenetetramine; sper = spermine. [b] mala = malate. [c] tar = tartrate. [d] succ. [e] oxalate.

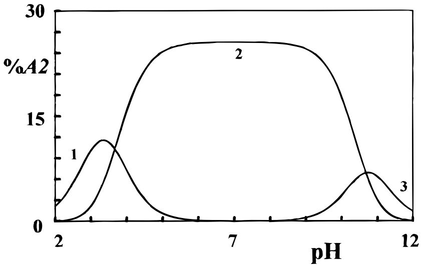

Figure 1. Distribution of the species vs pH in the system H$^+$−toda−A2. Species: (1) A2(toda)H$_3^+$; (2) A2(toda)H$_2^0$; (3) A2(toda)H$^-$. Analytical conditions: C_{A2} = 5 mmol·dm^{-3}; C_{toda} = 10 mmol·dm^{-3}; C_{NaCl} = 0.1 mol·dm^{-3}.

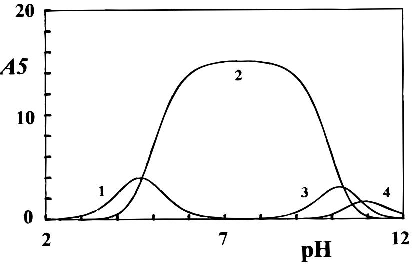

Figure 2. Distribution of the species vs pH in the system H$^+$−aza−A5. Species: (1) A5(aza)H$_4^{2+}$; (2) A5(aza)H$_3^+$; (3) A5(aza)H$_2^0$; (4) A5(aza)H$^-$. Analytical conditions: C_{A5} = 5 mmol·dm^{-3}; C_{aza} = 10 mmol·dm^{-3}; C_{NaCl} = 0.1 mol·dm^{-3}.

lic ligand−polyamine species, namely the concentration of components and the interference of other anions and cations. The first factor can be accounted for by plotting formation percentages (at constant pH) vs concentration. Figure 4 shows the sum of the percentages (Σ%) of A10LH$_r$ species vs −log C_{oda} for the system H$^+$−A10−oda, at pH = 7 and C_{A10} = 1 μmol·dm^{-3}. The curve represents a continuous decreasing function: Σ% decreases slowly for pC_{oda} = 1−2 (Σ% = 95−75), and for pC_{oda} > 2 the curve becomes steeper and tends for pC_{oda} > 3 asymptotically to zero. Note that even at C_{oda} = 10^{-4} mol·dm^{-3}, about 10% of the amine is present as complex species; this means that these species may have an important role in the speciation of natural and biological fluids.

The interference of other anions and cations must be considered in the experiments when a background salt is added to the solutions under study (constant medium method) or when considering biological and natural fluids where several salts are dissolved. As an example, Figure 5 shows the sum of percentages vs concentration of NaCl

Table 6. Mean Values of log *K* for Different ζ Values

ζ	log $\bar{K}$	$s/\sqrt{N}$[a]	*N*	ref
2	1.40	0.05	58	this work
3	1.99	0.12	32	this work
4	2.30	0.09	43	this work
6	3.02	0.05	28	this work
2	1.33	0.07	33	see Table 5
3	2.14	0.16	7	see Table 5
4	2.38	0.08	25	see Table 5
6	3.20	0.07	7	see Table 5
8	3.70	0.05	3	see Table 5

[a] *s* = standard deviation; *N* = number of formation constants considered.

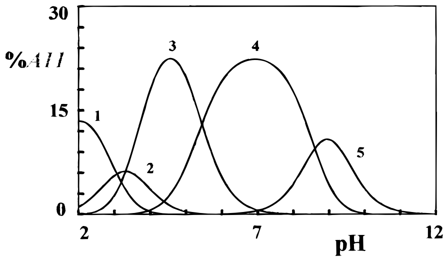

Figure 3. Distribution of the species vs pH in the system H^+–oda–A11. Species: (1) $A11(oda)H_5{}^{3+}$; (2) $A11(oda)H_4{}^{2+}$; (3) $A11(oda)H_3{}^{+}$; (4) $A11(oda)H_2{}^{0}$; (5) $A11(oda)H^{-}$. Analytical conditions: C_{A11} = 5 mmol·dm^{-3}; C_{oda} = 10 mmol·dm^{-3}; C_{NaCl} = 0.1 mol·dm^{-3}.

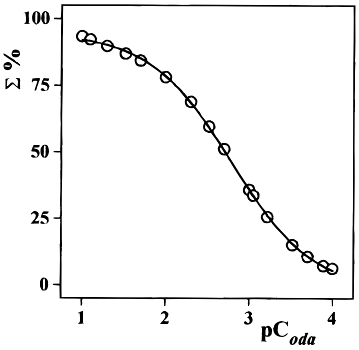

Figure 4. Sum of the percentages of $A10LH_r$ species vs −log C_{oda}. Analytical conditions: C_{A10} = 1 μmol· dm^{-3}; C_{Na} = C_{Cl} = 10 mmol·dm^{-3}; pH = 7.

at pH 7 and 8. It is evident that the ions Na^+ and Cl^- interfere with the formation of the complex species A10-(oda)H_r. On the basis of the model proposed by us, when C_{NaCl} = 1 mol·dm^{-3}, interactions between protonated amines and dicarboxylic acids are pratically negligible, since the two components are almost completely involved in complexation with chloride and with sodium, respectively. As C_{NaCl} decreases, the reactions between protonated amine and dianion become significant, and the formation percentages reach about 70% at pH = 7.

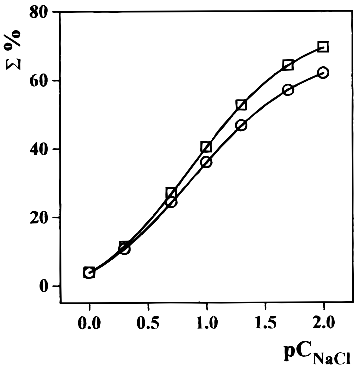

Figure 5. Sum of the percentages of $A10LH_r$ species vs −log C_{NaCl}: (○) for values determined at pH = 7; (□) for values determined at pH = 8. Analytical conditions: C_{A10} = C_L = 10 mmol·dm^{-3}.

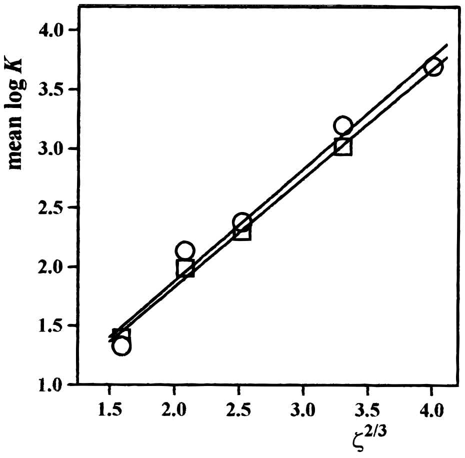

Figure 6. Mean log *K* values as function of z_{anion} and z_{cation}.

Stability–Charge Relationships. In previous works we studied other dicarboxylic ligand–polyammonium cation systems, and the formation constants of the complexes formed are shown in Table 5. Stability data from both Tables 4 and 5 indicate that when reactant charges are the same, the resulting complexes show quite close formation constants. Table 6 shows mean values of log *K* as a function of the empirical parameter ζ.

Standard errors on the mean ($s/\sqrt{N}$; *s* = standard deviation, *N* = number of formation constants considered) are quite low, confirming the strict dependence of log *K* on charges involved in the formation reaction. Moreover, values obtained from data in this work are very close to

Table 7. Empirical Parameter a for Stability-charges Relationships Relative to the Equation log *K* = a $\zeta^{2/3}$

mal	mala	tar	MD	SD	amines considered[a]
0.90 ± 0.03	0.91 ± 0.04	1.00 ± 0.04	0.32	0.40	en, 1,2dap, ptr, cdv, dien, spd, trien, sper
0.95 ± 0.05	0.95 ± 0.06	1.02 ± 0.07	0.35	0.44	en, 1,2dap,dien, trien
0.84 ± 0.04	0.87 ± 0.04	0.99 ± 0.04	0.27	0.34	cdv, ptr, spd, sper

mal	succ	aza	oda	toda	MD	SD	amines considered[a]
0.84 ± 0.04	0.84 ± 0.05	0.97 ± 0.04	0.88 ± 0.03	0.99 ± 0.03	0.35	0.50	A1-A11
0.91 ± 0.09		1.24 ± 0.10	1.03 ± 0.09	1.20 ± 0.09	0.48	0.66	A3, A9, A11
0.80 ± 0.07	0.92 ± 0.05	0.92 ± 0.04	0.86 ± 0.04	0.98 ± 0.04	0.26	0.33	A7, A8
0.78 ± 0.04	0.79 ± 0.03	0.84 ± 0.03	0.79 ± 0.03	0.87 ± 0.03	0.20	0.26	A1, A2, A4, A5, A6, A10

[a] A3, A9, A11 = substituted amines; A7, A8 = partially substituted amines; A1, A2, A4–A6, A10 = unsubstituted amines.

those obtained from previous data and are fitted by the simple equation

$$\log K = a\zeta^{2/3} \tag{2}$$

with $a = 0.925(\pm0.010)$ and $\sigma = 0.09$ (standard deviation on the fit), as shown in Figure 6.

Effect of Structure on Stability. From the results of the previous section it is evident that the structures of both the dicarboxylic anion and polyammonium cation have little effect on stability. Nevertheless, since a degree of error in general equations, which take into account only the charge contribution, may be attributed to structure effects, we performed some calculations on different groups of amines and for each dianion. Table 7 shows the results of these calculations. Some quantitative considerations can be made:

(a) Influence of Dianion Structure. The stability of all the dianion complexes (including results of previous works), in terms of $\log K/\zeta^{2/3}$, varies between 0.8 and 1.2. Two factors seem to have a little influence: (i) the distance between carboxylic groups, aza, toda > mal, succ; (ii) the presence of $-$OH or ethereal groups in the molecule, tar, toda, oda > mal, succ. These effects must be explained better by other experimental techniques.

(b) Influence of N-Alkyl Substitution. Recently we investigated the binding of polycarboxylic ligands by some substituted protonated polyamines and found the trend for stability substituted > unsubstituted. Factors which may influence the stability of these complexes are (i) solvatation effects and (ii) steric factors. *N*-Alkyl substitution implies a lower solvation, and this might increase the stability of complexes. On the other hand the steric hindrance of methyl groups should lower the stability. The resulting effect may be different for different types of amines and polyanions. The systems investigated in this work indicate an opposite though not statistically significant trend.

Moreover, we may also take into account the length of alkyl chains in the amine and their basicity. The ratio $R_{N/C}$, i.e. the ratio between N atoms and C atoms in the molecule, can account for the length of alkyl chains. By simply adding a linear term to the eq 2, we have

$$\log K_{ij} = a\zeta^{2/3} + bR_{N/C} \tag{3}$$

Calculations performed on all the formation constants of Tables 4 and 5 give $a = 0.88 \pm 0.02$ and $b = 0.19 \pm 0.09$, indicating that the length of the amine moleculas has a small effect. This can also be seen from Table 7 by comparing mean stability of en, 1,2dap, dien, and trien with that of cdv, ptr, spd, and sper: the stability of the first group of complexes is higher than that of the second group and $R_{N/C}$ for amines in the first group is higher than that of the second one. Nevertheless, on the basis of statistical considerations (decreasing variance), the introduction of the second term in eq 3 is not significant.

Basicity can also be taken into account by adding a linear term to eq 2 containing $\log \beta^H$:

$$\log K_{0n} = a\zeta^{2/3} + b \log {\beta_n}^H \tag{4}$$

By considering all the dicarboxylic$-$amine systems, and the species with $i = n$, we have $a = 2.59(\pm0.10)$ and $-0.197(\pm0.02)$. In this case the introduction of the second term in eq 4 is highly significant, with a variance ratio σ^2 (eq 2)/σ^2 (eq 4) = 3.5.

Final Remarks. Extensive data on the formation of polyammonium cation complexes with dicarboxylic anions have been reported. The body of results indicate that charges involved in the formation reaction are the main factor in determining stability, and the general equation $\log K = 0.925\zeta^{2/3}$ (eq 2) has been found. Less important factors are *N*-alkyl substitution and the distance between $-COO^-$ groups in dicarboxylic anions and between amino groups in polyammonium cations. A small effect is also due to the presence in the dicarboxylic anion of $-$OH or $-$O$-$ groups (this is particularly evident for toda). A fairly effective influence on the stability is shown by the basicity of the amine, and most of the differences between the stabilities of complexes of different amines disappear by using eq 4, which contains a linear term with protonation constants. By consideration of the simplest eq 2, an average $\Delta G°$ contribution per salt bridge (n) can be calculated: $\Delta G°/n = 5.3 \pm 0.1$ kJ·mol^{-1}, by assuming $n = \zeta^{2/3}$.

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