Macroinorganics. 9.[†] Enthalpies of Protonation and Copper(II) Complex Formation of Some Poly(amido amines)

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ABSTRACT: The heats of protonation and complex formation with Cu(II) of two classes of poly(amido amines) have been measured calorimetrically at 25 °C in 0.1 M NaCl solution, and the corresponding entropy values have been calculated. The heats of complex formation have been determined by titration with acid, base, or free metal ion, and the results of the different techniques are in good agreement with each other. The effect of lengthening the aliphatic chain between the aminic groups has been studied for both classes of polymers. The different complexing abilities of the two classes of polymers are attributed to the participation of carbonyl groups, in addition to participation of the amino groups, to the complexation only in symmetrically substituted polymers. The heats of hydrolysis of the CuL^{2+} complexes have also been determined.

Introduction

In previous papers we have found that poly(amido amines) are quite unusual polyelectrolytes, since their repeating units behave independently toward protonation[1] and complex formation with heavy-metal ions.[2,3] This allows determination of sharp basicity and stability constants for poly(amido amines), because the basicity and complexing ability of the aminic nitrogens belonging to each repeating unit do not depend on the overall state of the macromolecule. Poly(amido amines) as a class have been found to be useful in several applications: for instance, in the biomedical field as heparin complexing agents,[4] as ion-exchange resins (when in a cross-linked form),[5] and, more recently, as oxidation catalysts when in the form of their Cu^{2+} complexes.[6] Our studies have been mainly concerned with the determination of basicity and stability constants. However, a very useful point of view is to consider the basicity or complexing ability of a compound as arising from two independent contributions, i.e., the enthalpy term and the entropy term. Such a point of view allows a better understanding of the structural origins of the reaction processes, and it is for this reason that simultaneous potentiometric and calorimetric measurements are usually undertaken for low molecular weight compounds.[7] However, few studies have been published to date on the protonation enthalpies of polyelectrolytes,[8] and, to the best of our knowledge, no complex formation enthalpies of polyelectrolytes have been reported due to the complexity and difficulty of understanding the complex formation process. On the other hand, the peculiar behavior of poly(amido amines) allows a fully thermodynamic study. Therefore the aim of this paper is to report a calorimetric study on the protonation and Cu^{2+} complex formation of six poly(amido amines) belonging to two different classes (Chart I).

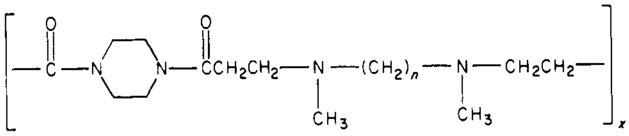
Experimental Section

Materials. All the polymers studied in this paper have been synthesized as previously described.[1c]

Other Reagents. CO_2-free NaOH solutions were prepared, stored, and standardized as described elsewhere.[9] Stock solutions of 0.1 M NaCl were prepared from sodium chloride (C. Erba, ACS grade) without further purification and were used as the ionic medium for the calorimetric measurements. The copper(II) nitrate solution was prepared with decarbonated water using a C. Erba RPE grade product. Before each measurement the copper(II) content was analyzed gravimetrically.[10] To prevent hydrolysis, the solution was slightly acidified with nitric acid, and the acidity was determined potentiometrically.

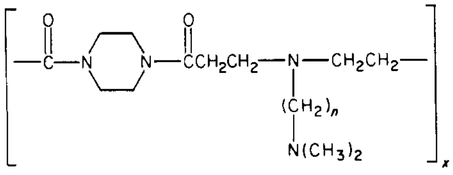
Chart I

A. First Class



$n = 2$, L_1
$n = 3$, L_2
$n = 4$, L_3

B. Second Class



$n = 2$, L_4
$n = 3$, L_5
$n = 4$, L_6

Calorimetric Measurements. Calorimetric titrations were carried out at 25 °C with either a Tronac 550 or a Tronac 450 calorimeter. Two or more duplicate runs were made for each system studied. In order to determine the enthalpies of protonation, isothermal and isoperibol calorimetric titrations were performed with 25- or 50-mL reaction vessels, respectively. These titrations were performed either by adding HCl to the solutions of the polymers in 0.1 M NaCl or by adding NaOH to a solution of polymer hydrochlorides. In each case, the titer of the polymer solutions was checked by pH-metric titration just before the calorimetric titrations. The titrant solutions were delivered through a Gilmond buret driven by a synchronous motor. Two blank runs were performed before each experiment in order to check the apparatus. Three different techniques have been used for the determination of complex formation enthalpies in connection with either isothermal or isoperibolic measurements. In the first method a solution of the free polymer was titrated by $Cu(NO_3)_2$, in the second one a solution of the polymer containing known amounts of Cu(II) and HCl was titrated by NaOH, and finally, in the third method the complex CuL was destroyed by titration with HCl.

[†] Part 8 is ref 3.

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Table I
Heats of Protonation: Experimental Details of Calorimetric Measurements at 25 °C in 0.1 M NaCl

compd	reaction	run	pH range	titrant concn[a] C_{H^+/OH^-}, mol dm^{-3}	T_L, mmol	no. of points	buret rate, mL min^{-1}	method	$-\Delta H^\ominus$,[b,c] kcal mol^{-1}
L_2	$L + H^+ \rightleftharpoons LH^+$ $LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	1	5.83-8.10	0.1043	0.1388	25	0.0833	isothermal	8.52 (5) 8.34 (5)
		2	6.43-9.48	0.3593	0.2535	35	0.3334	isoperibolic	8.56 (18) 8.14 (23)
L_3	$L + H^+ \rightleftharpoons LH^+$	1	6.65-8.18	0.2131	0.1669	25	0.0833	isothermal	9.07 (12) 8.49 (10)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	2	7.73-9.22	-0.1400	0.1684	20	0.0833	isothermal	8.84 (2) 8.83 (3)
L_5	$L + H^+ \rightleftharpoons LH^+$	1	6.11-8.85	0.1043	0.1625	26	0.0833	isothermal	8.66 (5) 8.20 (7)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	2	7.24-9.93	-0.1388	0.1626	31	0.0833	isothermal	8.49 (3) 8.54 (8)
L_6	$L + H^+ \rightleftharpoons LH^+$	1	6.99-9.21	0.1040	0.1614	25	0.0833	isothermal	9.68 (4) 9.65 (8)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	2	6.76-9.15	0.1040	0.1503	25	0.0833	isothermal	9.70 (8) 9.56 (10)

[a] Negative values indicate titrations with NaOH. [b] All values are corrected for heats of dilution. [c] Values in parentheses are standard deviations.

Table II
Heats of Cu(II) Complex Formation: Experimental Details of Calorimetric Measurements at 25 °C in 0.1 M NaCl

			titrant concn[a]								
compd	reaction	run	C_{H^+/OH^-}, mol dm^{-3}	$C_{Cu^{2+}}$, mol kg^{-1}	T_L, mmol	T_M, mmol	T_{H^+}, mmol	no. of points	buret rate, mL min^{-1}	method	$-\Delta H^\ominus$,[b,c] kcal mol^{-1}
L_1	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	1	0.2131		0.3000	0.1535	0.2557	28	0.0833	isothermal	8.11 (35) *d*
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	2	-0.1863		0.2210	0.2196	0.2226	28	0.3334	isoperibolic	7.96 (39) 2.8 (7)
L_2	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$ $CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$ $CuL^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2L$	1	-0.1871		0.2535	0.0601	0.4491	32	0.3336	isoperibolic	7.1 (4) *d* *d*
L_4	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	1		0.1009	0.1744		0.0000	24	0.0833	isothermal	7.51 (4) 5.3 (1)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	2	0.2131		0.2089	0.1018	0.1705	30	0.0833	isothermal	7.63 (8) *d*

[a] Negative values indicate titrations with NaOH. [b] All values are corrected for heats of dilution. [c] Values in parentheses are standard deviations. [d] Complex present in solution in negligible percentages.

The procedure for the different titrations was the same as in the case of protonation. The corrections for the heats of dilution were made by adding HCl, NaOH, or $Cu(NO_3)_2$ solutions to a 0.1 M NaCl solution. All the operations were governed by a North-Star CCP 930 computer connected to the instrument, using either the program ISOTHERM, delivered by Tronac Inc., or our modified version of the program ISOPER, also supplied by Tronac.

Experimental details for protonation and Cu^{2+} complex formation are given in Tables I and II. Figure 1 shows typical plots of temperature vs. pH for the protonation of the polymer L_2 obtained in either isothermal and isoperibolic modes. As for the isothermal mode, it can be observed that at pH values lower than 8, the constancy of temperature is assured to a very good extent. The same remark applies to all the other polymers studied, and only the points in the region of constant temperature have been used for the successive computation of protonation enthalpies. Figure 2 shows the corresponding plot $-Q$ vs. pH together with the distribution curves. Finally, a typical plot $-Q$ vs. pH for the titration of a solution of polymer L_1 (containing Cu(II) and a small amount of acid) with NaOH in the isoperibolic mode is shown in Figure 3, together with the distribution curves of the species CuL and Cu(OH)L.

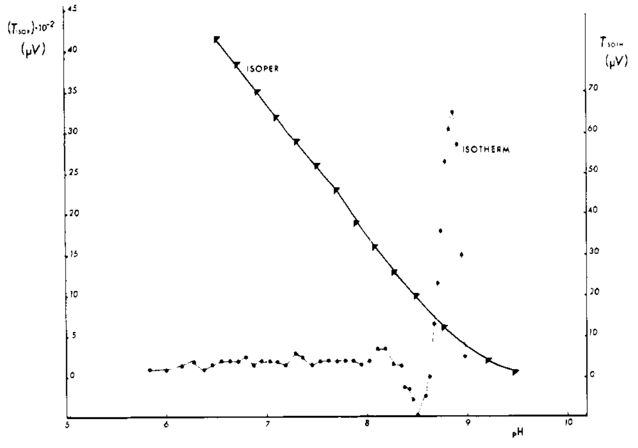

Figure 1. Plots of temperature (μV) vs. pH for the protonation of polymer L_2.

Method of Calculation

The enthalpies have been obtained by the program FIT, which is a generalization of the program FITH[11] previously employed for the determination of protonation enthalpies. The data are obtained by a titration of T_L millimoles of the free ligand L (eventually containing T_{H^+} millimoles of acid and T_M millimoles of metal) with a strong acid of concentration C_{H^+} or with a metal of concentration C_M. Alternatively, it is possible to titrate T_L millimoles of the fully protonated species LH_n^{n+} (eventually containing T_{H^+} millimoles of acid and or T_M millimoles of metal) with a strong base of concentration C_{OH} or with a metal of concentration C_M. The different species present in the solution have general formula $L_iH_jM_k$ (hereafter we omit

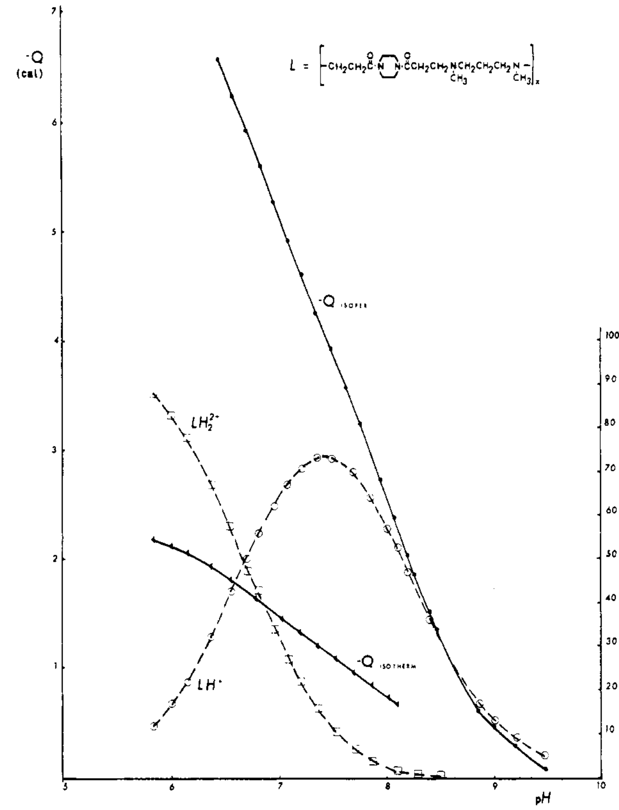

Figure 2. Plots of $-Q$ (calories) vs. pH (solid lines) and distribution curves of the different species present in solution (dotted lines) for the protonation of polymer L_2.

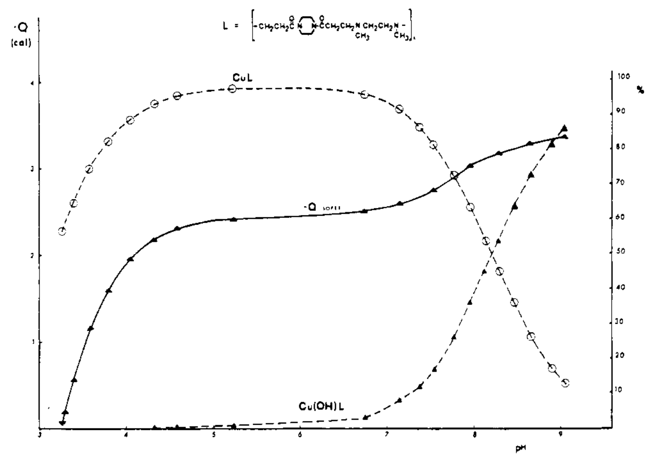

Figure 3. Plots of $-Q$ (calories) vs. pH (solid line) and distribution curves of the species CuL and Cu(OH)L (dotted lines) for the Cu(II) complex formation of polymer L_1.

charges for clarity) and their concentrations at the equilibrium are given by

$$[L_iH_jM_k] = \beta_{ijk}[L]^i[H]^j[M]^k \tag{1}$$

where the β_{ijk} are overall formation constants and i, j, and k are integers (k can also assume negative values). With this labeling the first basicity constant of the ligand will be β_{110} and the OH^- ion can be indicated as $[H^+]^{-1}$ with a formation constant $\beta_{0,-1,0} = K_w$. For each point in the titration the stoichiometric equations are

$$C_L = [L] + \sum_i \beta_{ijk}[L]^i[H]^j[M]^k \tag{2a}$$

$$C_H = [H] + \sum_j \beta_{ijk}[L]^i[H]^j[M]^k \tag{2b}$$

$$C_M = [M] + \sum_k \beta_{ijk}[L]^i[H]^j[M]^k \tag{2c}$$

where C_L, C_H, and C_M are computed by the program from the analytic data and the buret rate and nonlinear eq 2a–c in the unknowns [L], [H], and [M] are solved at each point by the Newton–Raphson method[12] using the results at the previous point as initial guesses. Then eq 1 gives the concentration of all the species at equilibrium. The program can be stopped at this point (in order to obtain distribution curves) or proceed to determine by a least-squares method any set of observables F_{ijk} that are linear functions of the concentrations at equilibrium. In the particular case of the protonation enthalpies, the difference $\Delta(p,q)$ between the measured heats at points p,q (previously stored on a floppy disk by the ISOTHERM program or by a modified version of the ISOPER program) is given by

$$\Delta(p,q) = \Delta(\text{dil}) + \Delta W + \sum_{n=1}^{N_T}([L_iH_jM_k]_q - [L_iH_jM_k]_p)\Delta H^\ominus_{ijk} \tag{3}$$

where Δ(dil) is the difference between the dilution heats of the titrant at the points p,q (also stored on a floppy disk by ISOTHERM in a calibration titration), ΔW is the differential heat due to the formation of water, and N_T is the number of different species (except M, L, H, and OH).

The whole set of linear equations (3) in N_R unknowns (N_R may be lower than N_T if some of the formation enthalpies, e.g., the protonation enthalpies, do not need to be refined) for the N measured points ($N > N_R$) is solved to give the $\Delta H^\ominus_{ijk}$ and their standard deviations σ_{ijk}

$$\sigma_{ijk} = V\{a_{PP}/(N - N_R)\}^{1/2}$$

as the square roots of the diagonal terms of the variance–covariance matrix.[13] At this stage the points with the largest errors can be automatically removed (one by one) and the evaluation of the enthalpies repeated. In its present form the program can handle 50 points and 12 enthalpies (10 of which are refined).

Results and Discussion

Protonation. The thermodynamic functions relative to the protonation of all the poly(amido amines) studied in this work are reported in Table III and Figure 4. For purposes of comparison, in Figure 5 we report the thermodynamic functions for the protonation of low molecular weight diamines with different aliphatic chains.

It can be observed that the basicities ($\Delta G^\ominus$) of both classes of polymers show similar trends with lengthening of the aliphatic chain between the amino groups present in the monomeric units.

On the other hand, previous viscosimetric and ^{13}C NMR studies revealed significant differences in the behavior of the two classes of polymers toward protonation.[1c] Such a difference is well evidenced by the enthalpy and entropy terms, so that the similar trend of basicity constants results from a balance between opposite trends of $\Delta H^\ominus$ and $\Delta S^\ominus$. As a general trend, it may be observed that both the basicity constants and the protonation enthalpies increase with the number of methylenic groups (n) between the two tertiary nitrogen atoms. This is in agreement with all the previous data on diamines[14] and is mainly due to the increased distance of the other amino group (either free or protonated) from the basic center that undergoes protonation.[15,16]

By considering the corresponding terms of the two classes of polymers, we may observe that the $|\Delta H_1^\ominus|$ of L_4 is lower than that of L_1, but there is no difference in this respect between L_5 and L_2, while the $|\Delta H_1^\ominus|$ of L_6 is definitely higher than that of L_3. Moreover, for the polymers of the first class, the largest difference in both log K_1 and

Table III
Thermodynamic Functions of Protonation at 25 °C in 0.1 M NaCl

compd	reaction	log K^a	$-\Delta G^{\ominus a,b}$	$-\Delta H^{\ominus a,b}$	$\Delta S^{\ominus a,c}$
L_1	$L + H^+ \rightleftharpoons LH^+$	8.09 (2)	11.03 (3)	7.35 (12)	12.3 (3)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	4.54 (5)	6.19 (7)	6.09 (11)	0.3 (6)
L_2	$L + H^+ \rightleftharpoons LH^+$	8.172 (6)	11.14 (1)	8.54 (23)	8.7 (7)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	6.691 (9)	9.12 (1)	8.24 (28)	3.0 (9)
L_3	$L + H^+ \rightleftharpoons LH^+$	8.715 (8)	11.88 (1)	8.95 (14)	9.8 (4)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	7.689 (9)	10.49 (1)	8.65 (18)	6.2 (6)
L_4	$L + H^+ \rightleftharpoons LH^+$	8.87 (1)	12.10 (1)	7.05 (12)	16.9 (4)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	4.10 (2)	5.59 (3)	7.09 (21)	-5.0 (6)
L_5	$L + H^+ \rightleftharpoons LH^+$	8.755 (8)	11.94 (1)	8.57 (8)	11.3 (3)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	6.30 (2)	8.59 (3)	8.38 (15)	0.7 (6)
L_6	$L + H^+ \rightleftharpoons LH^+$	9.196 (6)	12.54 (1)	9.69 (12)	9.6 (4)
	$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	7.189 (17)	9.80 (2)	9.60 (24)	0.7 (7)

[a] Values in parentheses are standard deviations computed as the sum of the standard deviations for the different runs. [b] kcal mol^{-1}. [c] cal K^{-1} mol^{-1}.

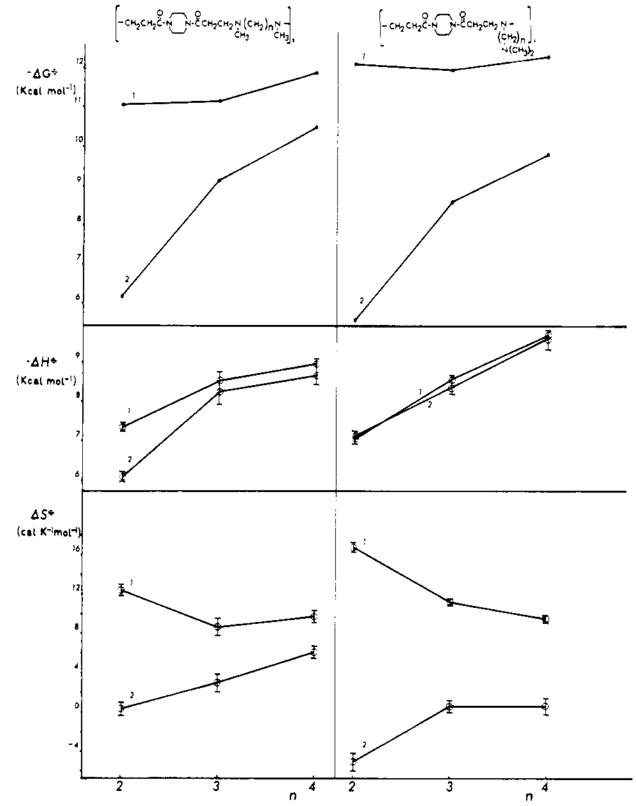

Figure 4. Plots of the thermodynamic functions $-\Delta G^\ominus$, $-\Delta H^\ominus$, and $\Delta S^\ominus$ relative to the protonation of the poly(amido amines) vs. n (the number of methylene groups between the tertiary nitrogen atoms).

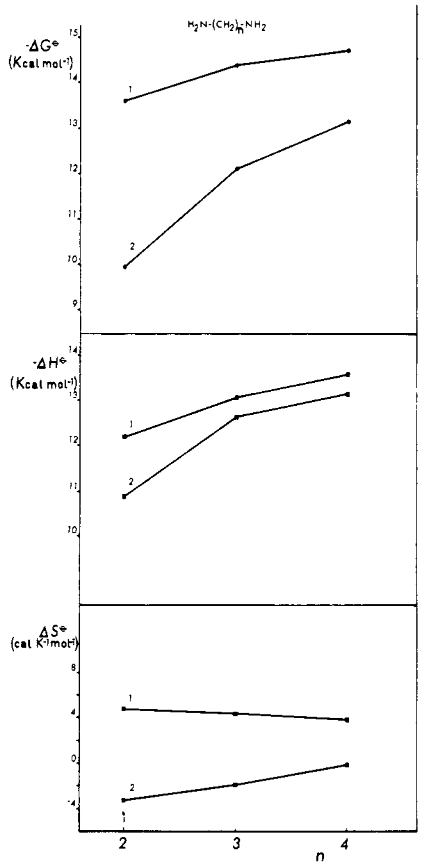

Figure 5. Plots of the thermodynamic functions $-\Delta G^\ominus$, $-\Delta H^\ominus$, and $\Delta S^\ominus$ relative to the protonation of low molecular weight diamines vs. n (the number of methylene groups between the nitrogen atoms).

$|\Delta H_1^\ominus|$ occurs between $n = 2$ and $n = 3$, exactly as in the case low molecular weight diamines (Figures 4 and 5). On the contrary, for the polymers of the second class, both log K_1 and $|\Delta H_1^\ominus|$ increase monotonically with n up to, at least, $n = 4$.

As for the second step, the trend of the protonation enthalpies is very similar to that observed in the first step, but $|\Delta H_2^\ominus| < |\Delta H_1^\ominus|$ for the polymers of the first class, while $|\Delta H_2^\ominus| \simeq |\Delta H_1^\ominus|$ for the polymers of the second class. Furthermore, the changes of $\Delta S_2^\ominus$ with n closely resemble the corresponding changes of low molecular weight diamines for the polymers of the first class, while this is not the case for the polymers of the second class.

In order to gain further insight into this behavior, let us consider the detailed protonation mechanism of the two classes of polymers.

In the first class the two aminic nitrogens are equivalent and very near the carbonyl groups, with which the onium ions obtained upon protonation can form very effective hydrogen bonds.[1c] Their behavior is thus related to that of diamines, because the thermodynamic contribution of hydrogen bridges is constant along the whole series and the increase of the protonation enthalpy with n is related in both cases to the corresponding increasing in the net charge of the nitrogen atoms,[15,16] which affects both the N^+–H bond strength and the solvation enthalpy.[15b] The decrease of $\Delta S_1^\ominus$ with n is larger in the case of the polymers because the first protonation (upon formation of intramolecular hydrogen bridges) reduces very much the conformational freedom of the whole macromolecule, and this reduction increases between $n = 2$ and $n = 3$ and then remains nearly constant.[16] In the second protonation step, the situation remains unchanged for the enthalpies, but as in low molecular weight diamines, the increase of n allows a larger conformational freedom due to the in-

Table IV
Thermodynamic Functions of Copper(II) Complexes at 25 °C in 0.1 M NaCl

compd	reaction	log K^a	$-\Delta G^{\ominus\ a,b}$	$-\Delta H^{\ominus\ a,b}$	$\Delta S^{\ominus\ a,c}$
L_1	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	8.96 (10)	12.22 (14)	8.04 (39)	14.8 (8)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	5.52 (25)	7.53 (34)	2.8 (7)	15.9 (1.2)
L_2	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	5.36 (2)	7.31 (3)	7.1 (4)	0.7 (1.2)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	5.14 (8)	7.01 (11)	*d*	*d*
	$CuL^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2L$	10.25 (5)	13.98 (7)	*d*	*d*
L_4	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	8.47 (5)	11.55 (7)	7.57 (8)	13.4 (3)
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	6.1 (1)	8.3 (1)	5.3 (1)	10.1 (8)

[a] Values in parentheses are standard deviations computed as the sum of the standard deviations for the different runs. [b] kcal mol^{-1}. [c] cal K^{-1} mol^{-1}. [d] Not possible to determine the formation enthalpies and entropies because complex concentration was too low.

creased distance between the two positively charged onium groups which, at low *n*, are frozen in a fully extended conformation due to the strong electrostatic repulsion. As a consequence, $\Delta S_2^{\ominus}$ increases with *n* in nearly the same way for polymers and diamines.

For polymers of the second class, it must be remembered that the first protonation occurs on the side nitrogen atom,[17] which is not able to form hydrogen bonds with distant carbonyl groups.[1c] As a consequence the exothermic effect due to lengthening of the aliphatic chain is more effective, and $\Delta S_1^{\ominus}$ is larger than for polymers of the first class; the second protonation cannot lead to effective hydrogen bridges because each onium group is near two carbonyl groups[1c] but gives rise to a local situation of charges of alternating sign (two negative carbonyl oxygens and a central positive onium ion) closely resembling that met in the second protonation step of triamines (two positively charged terminal onium ions and a negatively charged central amino group).

We have previously suggested that the presence of three alternating charges can generate a new orientation of water molecules around the base, which provides a further exothermic contribution due to specific solute–solvent interactions.[15b]

This effect balances the energy required to add a positive charge on an already charged compound and leads to $|\Delta H_1^{\ominus}| \simeq |\Delta H_2^{\ominus}|$. The strong organization of the solvent in the second protonation step of the second class of polymers is in agreement with the fact that the $\Delta S_2^{\ominus}$ are always lower than those of the corresponding polymers of the first class.

Cu(II) Complex Formation. The thermodynamic functions for Cu^{2+} complex formation of the studied poly(amido amines) are reported in Table III.

Previous potentiometric studies established that only some polymers are able to form stable complexes in aqueous solution.[3] The corresponding complex formation enthalpies have been determined by the three different techniques described in the Experimental Section.

The results were always in close agreement, and the enthalpies have been computed separately from the three techniques and the results averaged only at the end.

For polymer L_1 the formation of the hydroxo complex Cu(OH)L at high pH values is well evidenced by the calorimetric titration curve (Figure 3). Similar results have been obtained also for polymer L_4; however, it has not been possible to determine the enthalpies of the Cu(OH)L and $Cu(OH)_2L$ hydroxo complexes for polymer L_2.

This is due to the precipitation of hydroxide complexes before a significant amount of the Cu(OH)L complex formed. The independence of the monomeric units toward complexation and the previous discussion on the protonation allows us to analyze the behavior of the poly(amido amines) with special reference to low molecular weight polyamines.[7] As a first point, the values of Table IV show that CuL complexes are more stable for polymers of class I than for polymers of class II, the difference being due mainly to the enthalpy terms. This effect is probably due to the involvement of the carbonyl groups in the complexes of the class, while this is not the case for the unsymmetrically substituted compounds of class II, due to high steric hindrance.[3] The entropy term is not strongly influenced because the mobility of amidic groups in the CuL complexes is very low for steric reasons, even if not directly involved in the complex. The decrease of the complexing ability with the lengthening of the aliphatic chain was already observed for several low molecular weight compounds[7,18,19] and was related to the increased steric strain when going from five-membered to six-membered chelate rings. In this case the decrease of stability is mainly due to the decrease of enthalpy where, in the case of polymers the entropy term dominates, probably because the reduction of conformational freedom is much larger for polymers than for low molecular weight compounds. For the Cu(OH)L complexes, the thermodynamic functions of polymer L_4 are similar to those of *N*,*N*-diethylethylenediamine.[20] On the contrary, the corresponding values for the polymer L_1 are in the range of the values observed for low molecular weight tetramines,[7,21] thus confirming the involvement of more than two coordinating groups.

Registry No. L_1 (copolymer), 29930-20-9; L_1 (repeating unit), 70559-28-3; L_2 (copolymer), 78567-54-1; L_2 (repeating unit), 78567-68-7; L_3 (copolymer), 78567-51-8; L_3 (repeating unit), 78567-67-6; L (copolymer), 52383-88-7; L_4 (repeating unit), 72982-31-1; L_5 (copolymer), 78567-52-9; L_5 (repeating unit), 78567-69-8; L_6 (copolymer), 78567-53-0; L_6 (repeating unit), 78567-70-1; Cu, 7440-50-8.

References and Notes

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Enthalpies of Transfer of the Alkali-Metal Poly(styrenesulfonates) from Water to Mixtures of Water and Dioxane

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ABSTRACT: Enthalpies of transfer of poly(styrenesulfonic acid) and its alkali-metal salts from water to dioxane–water mixtures containing up to 90% dioxane are reported. They were obtained from calorimetric experiments in which a dioxane–water mixture was mixed both with an aqueous polyelectrolyte solution and with water. The enthalpy of transfer does not depend on the nature of counterions; it is exothermic and its value sharply increases with the increasing content of dioxane in the binary solvent. It is shown that the electrostatic contribution to the transfer enthalpy is small compared to the chemical contribution.

Introduction

Synthetic polyelectrolytes have usually been studied in aqueous solutions,[1] and articles dealing with nonaqueous solvents or solvent mixtures, are rather scarce. In the field of solutions of simple electrolytes the most frequently used organic solvent was dioxane. It is miscible in all proportions with water, and since its dielectric constant is very low, the dioxane–water mixtures are very suitable as solvents for the study of the behavior of a solute in media of continuously and drasticly changing dielectric constant. From the point of view of any electrostatic theory the dielectric constant is the most important physical property of the solvent. It has a direct influence on the electrostatic interactions between charged particles and thus on the behavior of a charged macromolecule in solution. Therefore, studies of polyelectrolytes in solvent mixtures not only are attractive per se but should also provide an excellent test of those polyelectrolyte theories that taken into account only long-rang Coulombic forces.

One of the essential phenomena that determines the behavior of solute in a binary solvent is solvent sorting in the solvation shells of the solute, a consequence of the specific solute–solvent interactions. Changes of this preferential solvation are expected to be directly reflected in the enthalpy change accompanying the transfer of solute from an aqueous solution to a binary solvent. In this paper we describe the calorimetric procedure for obtaining the enthalpy of transfer of some alkali-metal poly(styrenesulfonates) from water to dioxane–water mixtures. From the experimental enthalpies the nonelectrostatic contribution to the transfer enthalpy due to the specific solute–solvent interactions was estimated, assuming for the electrostatic contribution the prediction derived from the cell model.[2,3]

Experimental Section

Materials. Poly(styrenesulfonic acid), HPSS, and its alkali-metal salts were all derived from one single sample of sodium poly(styrenesulfonate), NaPSS, obtained from Polysciences Inc. (Rydal, PA). According to the manufacturer's specification the NaPSS had a molecular weight of 100 000 and a degree of sulfonation of 1.00. For purification and preparation of polyelectrolyte solutions, dialysis and ion-exchange techniques were used as described in detail elsewhere.[4] The dioxane–water mixtures were prepared from distilled water and chromatographicly pure 1,4-dioxane (Riedel-De-Haen).

Apparatus. Calorimetric measurements were performed at 25 °C in an LKB 10700-2 batch microcalorimeter. Into compartments of the reaction cell 0.2 cm^3 of about 0.7 monomolar aqueous poly(styrenesulfonate) solution and 4 cm^3 of an appropriate dioxane–water mixture were pipetted. One compartment of the reference cell was filled with the amount of water equal to the water quantity in the 0.2 cm^3 of added poly(styrenesulfonate) solution and the other with 4 cm^3 of the same dioxane–water mixture. Since the two calorimetric cells are not thermally balanced (their thermal response differs by about 3.5%), a separate blank experiment had to be made for each transfer. In this experiment both cells were filled with the same amounts of water and mixed solvent as the reference cell in the main experiment. The observed thermal effect was accounted for in calculating the enthalpy of transfer, ΔH_t. In spite of this correction, the experimental error in ΔH_t is judged to be from 10% to 20%, due to the fact that the enthalpy of transfer is much smaller than the enthalpy of mixing of water and dioxane–water solvent.

The calibration of the instrument was performed by the electrical heating of the heater built in the reaction cell.

Thermodynamic Analysis

We use mathematical formalism and thermodynamic analysis similar to those of Pointud et al.[5] in their interpretation of the enthalpy of transfer of simple electrolytes