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Ionic and ionizable synthetic polymers: interactions in aqueous solutions

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CONTENTS

A. INTRODUCTION

The theory of polyelectrolytes deals with the molecular interpretation of the macroscopic properties of solutions of highly charged ions [1]. In fact, polyelectrolytes are defined as natural and/or synthetic macromolecules containing a large number of ionic and/or ionizable groups [2]. The attachment of a large number of ionized groups to the backbone of a molecular chain produces such striking modifications in the polymer characteristics that the contributions of chain properties to the properties of polymers have often been neglected. Whenever an uncharged polymer is converted by titration to a polyion containing a large number of ionized groups attached to the polymer "backbone", chain extension is obtained and revealed by viscometric data [3].

The variation of acidity/basicity constants with pH depends largely on the conformation assumed by the polymer in the different ionization states. In some cases, the variation can be expressed by a linear relationship with the degree of protonation, α, the so-called generalized Henderson–Hasselbalch equation [4]:

$$\log K = \log K^{\circ} + (n-1)\log[(1-\alpha)/\alpha] \qquad (1)$$

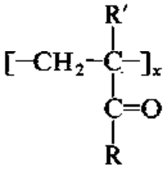
where the value of n takes into account the electrostatic interactions amongst charged groups [5], and the $(n-1)$ value quantitatively indicates the deviation from the behaviour of charged groups independent of each other, i.e. the typical ionization behaviour of small, physically separate molecules. An occurrence analogous to the ionization behaviour could be represented by the complex ion formation with the polymer as a ligand. If the coordinating groups are well separated from one another along the polymer chain, the monomeric units will behave independently of one another, like low molecular weight chelating agents. Unfortunately, much more complicated situations arise in complex formation studies with polymers [6], generally because:

(a) the coordinating groups are spread evenly along the polymer chain and the metal ion may coordinate with more than two such groups;

(b) the great number of functional groups present on the polymer chain increases the number and type of interactions with the metal ion;

(c) the presence of a microheterogeneous region occupied by the polymer chain alters the physico-chemical characteristics of the aqueous environment.

Nevertheless, the behavioural study of polymers undergoing ionization and complex formation is fascinating. We wanted to give a summary of our contribution to the interpretation of some physico-chemical data of polyelectrolytes with poly(vinyl) backbone purposely synthesized by us, in aqueous solution:



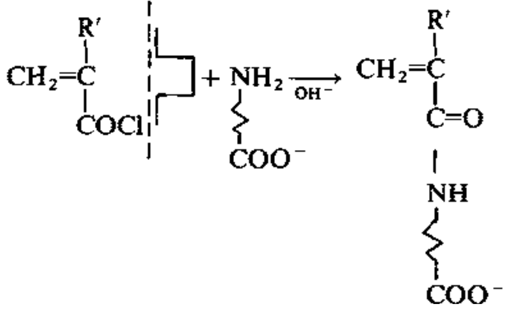
$$[-CH_2-\overset{\displaystyle R'}{\underset{\displaystyle \underset{\displaystyle R}{C=O}}{C}}-]_x$$

where R = $NH{-}(CH_2)_m{-}COOH$, $m = 1,2,5$; $NH{-}CH_2{-}CO{-}NH{-}CH_2{-}COOH$;
$NH{-}(CH_2)_m{-}NH_2$, $m = 2,3$; $\overline{\underline{N\quad N}}{-}H$; $\overline{\underline{N\quad N}}{-}CH_3$
$R' = H$; CH_3

relative to both protonation and Cu(II) complex formation [7–14].

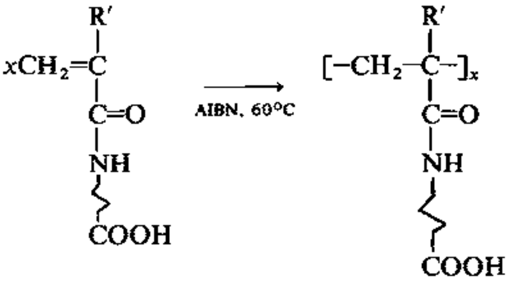
B. SYNTHESIS AND STRUCTURES

Functional groups (amido, carboxyl) can be readily introduced via amino-acid acylation by treatment with acryloyl or methacryloyl chloride in the presence of sodium hydroxide [15].



(R′ = H, CH$_3$)

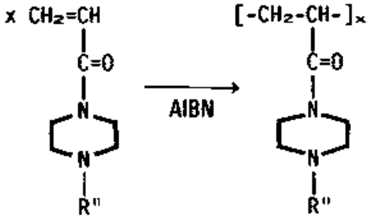
The usual route to obtain vinyl polymers is via radical polymerization using the corresponding monomers. Radicals to initiate polymerization are usually generated by the thermal or photochemical decomposition of an azo compound [16].



Radical polymerization involves several random processes and thus offers rather limited possibilities for the control of polymer molecular weight, molecular weight distribution and microstructure. In fact, polymers made by radical polymerization have polydispersities and are usually atactic. In contrast to the crystalline monomers, the corresponding polymers are amorphous under X-ray examination and do not have a definite melting point [7,17].

Acrylates, being more reactive than methacrylate, have greater attendant problems. They generally lead to polymers with broader molecular weight distributions [16]. However, the average molecular weight is lower for the methacrylate series. For steric reasons, crotonil monomers are quite inert toward polymerization. The limiting viscosity number (intrinsic viscosity) is the quantity usually correlated with molecular weights. Table 1 shows the structure of the monomers and of the repeating units of the corresponding poly(acrylic) and poly(methacrylic) acid derivatives with the intrinsic viscosities of the polymers.

Two synthetic routes have been followed in order to obtain vinyl polymers with amino groups in the side chain [10,11]. The synthesis of polymers I and H (Table 2) involves the usual radical polymerization mechanism:



R'' = CH_3 (polymer I)
= $C(C_6H_5)_3$

polymer H being obtained after removal of the triphenyl methyl group with HCl in aqueous 1,4-dioxan [10].

Moreover, polymers F and G have been obtained using poly(*N*-acryloylbenzotriazole) as a polymeric precursor [11].

TABLE 1

Structure of monomers and corresponding vinyl poly(acids)

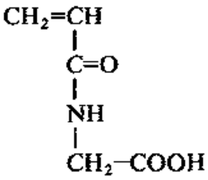
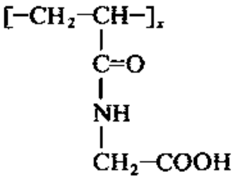
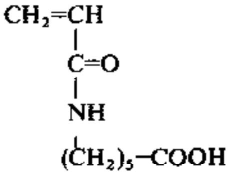
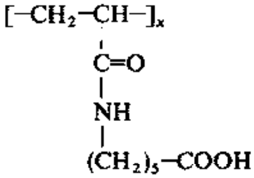
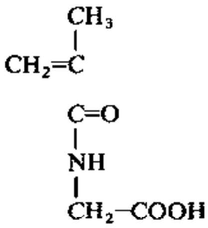
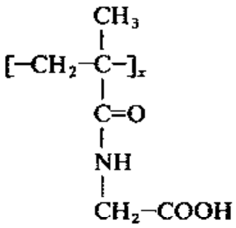
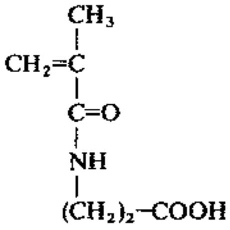
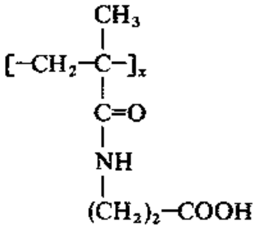
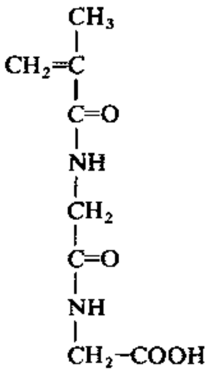
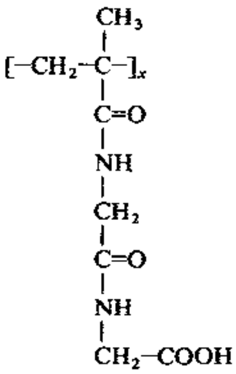
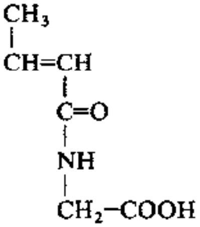
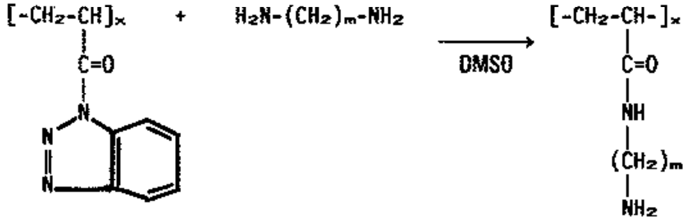
Monomer		Polymer		$[\eta]$[a] (dl g^{-1})	Ref.
 $CH_2{=}CH{-}C({=}O){-}NH{-}CH_2{-}COOH$	1	 $[-CH_2-CH(-C({=}O)-NH-CH_2-COOH)-]_x$	A	0.66	7
 $CH_2{=}CH{-}C({=}O){-}NH{-}(CH_2)_5{-}COOH$	2	 $[-CH_2-CH(-C({=}O)-NH-(CH_2)_5-COOH)-]_x$	B	0.58	7
 $CH_2{=}C(CH_3){-}C({=}O){-}NH{-}CH_2{-}COOH$	3	 $[-CH_2-C(CH_3)(-C({=}O)-NH-CH_2-COOH)-]_x$	C	0.27	9
 $CH_2{=}C(CH_3){-}C({=}O){-}NH{-}(CH_2)_2{-}COOH$	4	 $[-CH_2-C(CH_3)(-C({=}O)-NH-(CH_2)_2-COOH)-]_x$	D	0.20	9
 $CH_2{=}C(CH_3){-}C({=}O){-}NH{-}CH_2{-}C({=}O){-}NH{-}CH_2{-}COOH$	5	 $[-CH_2-C(CH_3)(-C({=}O)-NH-CH_2-C({=}O)-NH-CH_2-COOH)-]_x$	E	0.25	[b]

TABLE 1 (*continued*)

Monomer	Polymer	$[\eta]$[a] (dl g^{-1})	Ref.
 $CH_3-CH=CH-C(=O)-NH-CH_2-COOH$	6		[b]

[a] Intrinsic viscosity in DMF at 30°C.
[b] Unpublished data.



m = 2 (polymer F)
m = 3 (polymer G)

An excess of simple diamine is necessary to avoid crosslinking.

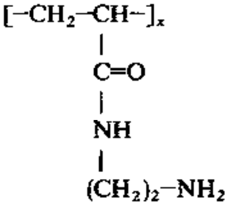
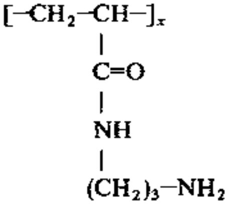
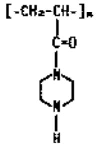
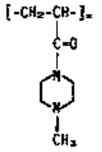
C. PROTONATION

The protonation behaviour of vinyl polymers in aqueous solution was investigated by potentiometry, calorimetry, viscometry and IR spectroscopy, and compared with that of the corresponding monomers [8–11,13]. This approach is necessary to rationalize the protonation equilibria of polymeric species and to distinguish the polymeric behaviour from the structural requisite of the repeating unit.

Without taking into account the specific macromolecular conformation, when dealing with polyanions, the approach of the proton will be enhanced by the electrostatic attraction of the neighbouring carboxylate groups, whilst with polybases, the hydrogen ions will be repelled by the polycation. In the former case, the basic strength of the polyelectrolyte will increase with its charge density; the opposite occurs in the latter case.

TABLE 2

Structure of vinyl polymer with basic functional groups

Polymer		$[\eta]^a$ (dl g^{-1})	Ref.
 $\begin{array}{l}[-CH_2-CH-]_x\\ \qquad\mid\\ \qquad C{=}O\\ \qquad\mid\\ \qquad NH\\ \qquad\mid\\ \qquad (CH_2)_2-NH_2\end{array}$	F	2.4	11
 $\begin{array}{l}[-CH_2-CH-]_x\\ \qquad\mid\\ \qquad C{=}O\\ \qquad\mid\\ \qquad NH\\ \qquad\mid\\ \qquad (CH_2)_3-NH_2\end{array}$	G	2.6	11
	H	0.26^b	11
	I	0.28^b	10

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[a] Intrinsic viscosity at 30°C in $CH_3OH:H_2O$ (10:1).

[b] Intrinsic viscosity at 30°C in $CHCl_3$.

(i) Vinyl polymers with carboxyl groups

The strength of a poly(carboxyl acid) is known to result from both the intrinsic equilibrium constant log K° and the electrostatic interaction from the ionized groups [4,5,18]. The value of log K° is mainly influenced by the inductive effect of the other carboxyl groups and the conformation of the polyelectrolyte. We have to consider these two effects when we compare our polymer with the other polyelectrolytes and with the corresponding low-molecular-weight analogues [8,9,19]. The intrinsic equilibrium constant is a quantity which applies to a hypothetical uncharged polymer with the log K value extrapolated to a degree of protonation $\alpha = 1$, but its determination, which is never experimental, involves many difficulties [20]. The high-molecular-weight poly(acid) in solution at $\alpha = 1$ assumes a compact coil conformation that cannot be expected to be similar to that of the low-molecular-weight analogue. With decreasing α, however, the polymer uncoils and the availability of the carboxylate groups for protonation becomes closer to that of the non-macromolecular monomer.

This is why the thermodynamic functions of protonation of the polymer obtained at $\alpha = 1$ and the non-macromolecular model cannot be correctly compared. We prefer to consider log K, ΔG°, ΔH°, and ΔS° obtained at at least two different α values: $\alpha = 0.5$ and $\alpha = 1$. For comparison between polymers, only the values at $\alpha = 0.5$ will be considered.

The classic way of measuring polyion expansion of charged polymer chains is by viscometry [2]. This property can be related to several factors such as aggregation, hydration, ion pairing and so forth, all strongly dependent on the ionic strength and polymer concentration. The data reported in this study concern very dilute solutions of polyelectrolytes (less than 0.01 M) at a constant ionic strength (0.1 NaCl), which maintains the same screening effect of the charges. Reduced viscosity η/C (η = specific viscosity; C = polymer concentration in g dl^{-1}) expresses the average dimension of a macromolecule and is related to the electrostatic interaction between ionized groups on the polymer chain. This property depends on the charge density and charge distribution of the polymer chain.

The macromolecules listed in Table 1 contain many carboxylate groups and exhibit the highest viscosity in the fully ionized state, reflecting maximum extension of the macromolecule [8,9]. Decreasing pH leads to a regular decrease in η/C. The successive and gradual neutralization of COO− groups determines lower electrostatic repulsion between negatively charged groups on the macromolecular chain, allowing the polymer to assume a compact coil conformation rather than extended conformation. This regular decrease is a trend usually observed in the polyelectrolyte domain. A strict comparison between the two classes of polymer (A and B, C and D, Table 1), differing in the methyl group on the backbone chain, cannot be made due to the remarkable difference in reduced viscosity. Nevertheless, the C and D polymers seem to compel the macromolecule into a more compact coil upon protonation, as shown by the negligible viscosity value at $\alpha = 1$ (Fig. 1). Long range attractive interaction of hydrophobic groups may provide powerful assistance to chain contraction.

In fact, the slope of η/C vs. α for polymer B, containing a long methylene chain, is steeper than for polymer A with a shorter chain (Fig. 1). When the polymer B reaches a relatively low charge density at $\alpha = 0.6$, it precipitates because the hydrophobic moiety overcomes the hydrophilic quality of the amido and carboxylic groups.

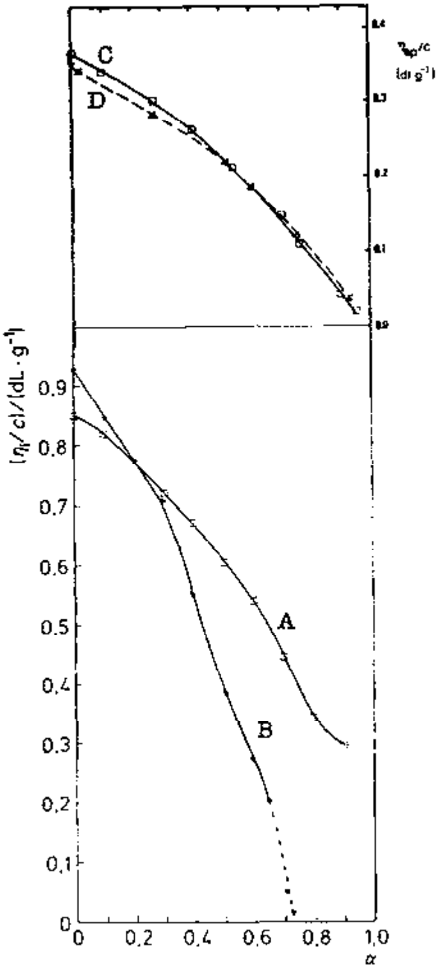


Fig. 1. Reduced viscosity for poly(acrylic acid) derivatives (A and B) and for poly(methacrylic acid) derivatives (C and D) versus α at 25°C in 0.1 M NaCl.

A similar pattern of η/C vs. α is shown by the two polymers C and D, containing CH_3 groups in the main chain, and differing only by a CH_2 moiety in the side chain.

The relevance of hydrophobic interactions to the protonation behaviour of such polymers is also revealed by infrared studies in aqueous solution [8,9]. The frequency and relative intensity of the components of the amide I vibration (combination of the vibrational modes of the C=O, N—H and C—N groups of the amide moiety) are generally used in the structurally induced interactions study of polymeric compounds carrying amide groups.

Hydration of the amide group is reflected by absorption at about 1650 cm^{-1}, whereas non-hydration leads to absorption at higher frequencies [8,21]. Moreover, hydrogen bonding interactions between neighbouring amide moieties are revealed by the presence of absorptions below 1650 cm^{-1} [8,21]. Table 3 summarizes the main amide I components observed for protonated and unprotonated A, B, C and D polymers together with their assignments. Figure 2 shows the difference spectra of these polymers in (a) the protonated and (b) the unprotonated forms. The increase of the methylene groups in the side chain from A to B causes an increase of the 1696 cm^{-1} band intensity and a decrease of the 1650 cm^{-1} band intensity in the ionized polymer; this means that a lower hydration of the amide group of polymer B occurs at high pH.

Lowering the pH, a new band appears at 1628 cm^{-1} in the spectrum of polymer B. This shows that the amide group is involved in strong hydrogen bonds. Due to the hydrophobic character of this polymer, the side chains become closer upon partial charge neutralization so that we may attribute this band to the H-bonding interaction between amide moieties of neighbouring pendant chains [8]. The insolubility of polymer B at $pH < 5.0$ may be thus explained in terms of the strong interactions between neighbouring side chains. Their cohesions appear so strong that they stabilize a compact form even at relatively high charge densities.

The increase in the methylene side chain from C to D, in poly(acid)s containing a methyl group on the macromolecule backbone, is reflected in an unexpected increase in hydrophilic character [9].

The infrared spectra at high pH reveal that the solvation of the amide group is much more pronounced for polymer D than polymer C. The longer aliphatic chain of polymer D renders its side substituent more flexible, allowing the carboxylate

TABLE 3

Amide I components for polymers A, B, C, D in the protonated and unprotonated forms

Compound	Wavenumber (cm^{-1})[a] at pH				Assignment
	2.5	5.5[b]	10.5	11.0	
A			1696 vw		"Free" amide C=O stretch
	1650 m		1650 s		"Hydrated" amide C=O stretch
B		1696 sh		1694 m	"Free" amide C=O stretch
		1647 sh		1650 sh	"Hydrated" amide C=O stretch
		1628 vs			"Strongly H-bonded" amide C=O stretch
C				1696 m	"Free" amide C=O stretch
	1620 m				"Strongly H-bonded" amide C=O stretch
D				1696 sh	"Free" amide C=O stretch
	1648 sh			1658 m	"Hydrated" amide C=O stretch
	1620 s			1620 sh	"Strongly H-bonded" amide C=O stretch

[a] vs = very strong, s = strong, m = medium, vw = very weak, sh = shoulder.

[b] pH before precipitation.

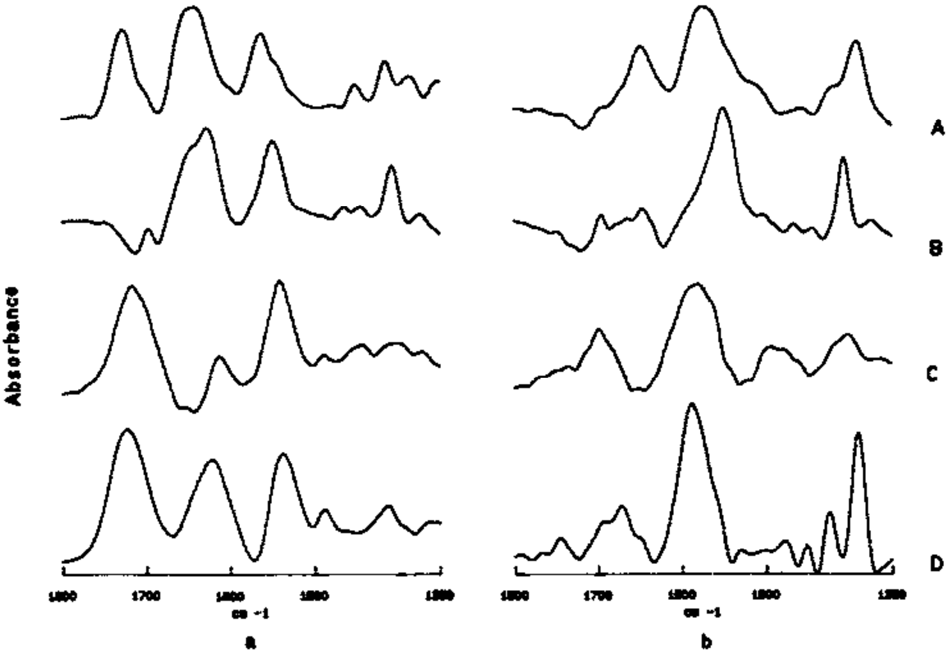


Fig. 2. Difference infrared spectra of polymers A, B, C, D in aqueous solution in both (a) protonated and (b) unprotonated form.

group to lie much closer to the amide moiety, so they can interact through hydrogen bonds. It also allows the two CH_2 groups to lie nearer to the CH_3 group of the main chain (hydrophobic interaction).

The protonation constants of all the poly(carboxylic acids) decrease linearly with increasing degree of protonation, α. This means that the electrostatic free energy required for the uptake of an equivalent amount of protons depends linearly on the degree of ionization, i.e. the negative charge density. Table 4 shows the parameters of the modified Henderson–Hasselbalch equation for all the vinyl poly(carboxylic acid)s together with the log K of the corresponding non-macromolecular analogues. The equilibrium constant, log K°, is higher for the half-ionized polymer than the log K for the corresponding monomer as a consequence of the close negative charge of the polyelectrolyte chain. This also occurs at $\alpha = 1$ when the polymer assumes a neutral form. The values are always higher than those of the corresponding monomers. The electronic withdrawal of the vinyl double bond of the latter compounds further reduces the values of the protonation constants, albeit slightly. The increase in methylene groups from A to B and from C to D is reflected in a higher log K° value for the polymer with the longer chain. The same occurs for the corresponding non-macromolecular analogues. Polymers carrying the same lateral glycinate moiety, but differing in the methyl group on the backbone of the macromolecule, show almost the same value of log K° (polymers A and C). The same behaviour is observed

TABLE 4

Basicity constant values for poly(acids) and corresponding monomers at 25°C in 0.1 M NaCl α = degree of protonation.

Compound	$\log K$ ($\alpha = 1$)	$\log K^{\circ}$[a] ($\alpha = 0.5$)	n[a]
A	3.75	4.32	1.50
B	5.10	5.42	1.31
C	3.85	4.26	1.40
D	4.25	4.92	1.61
E	3.90	4.90	1.96
1	3.53		
2	4.67		
3	3.60		
4	4.33		
5	3.50		
6	3.58		

[a] All listed polymers follow the modified Henderson–Hasselbalch equation: $\log K = \log K^{\circ} + (n-1)\log[(1-\alpha)/\alpha]$. The $\log K$ values at $\alpha = 1$ are extrapolated values.

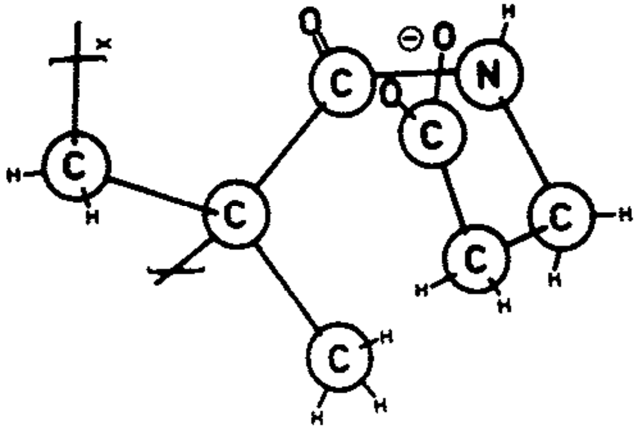
with $\log K$ values for the monomers 1, 3, and 6, which show striking structural similarity. The presence of two amido groups in 5 does not alter the protonation behaviour of the carboxylate group, which behaves like the other carboxylate groups.

Comparing the n values of eqn. (1) in the series of poly(acid)s considered, a close relationship is observed between this parameter and the hydrophilic character of the polymers [9]. High hydrophilicity corresponds to high polyelectrolyte behaviour [5], and the value of n exceeds 1 and approaches a value of 2. Vinyl polymers with a lateral amido group always show $n > 1$ [9]. When the hydrophilic character of the monomer unit is increased, e.g. by introducing an amido group, then n value sharply increases. The introduction of further hydrophobic groups on the backbone chain, or on the side chain, always leads to a decrease in n values. This is a trend usually observed when no other phenomenon occurs during the protonation of polymers.

We found that polymer D behaved in a peculiar manner. This polymer, showing increased hydrophobic character with respect to polymer C due to the insertion of a further $-CH_2-$ group on the side chain, has a higher n value [9].

The previously hypothesized structure of polymer D well explains the unexpected hydrophilic character (Scheme 1).

The dependence of protonation behaviour on α presents a much more complex pattern if we compare the heat effects accompanying the protonation of our polymers [8,9]. Previous data show that $-\Delta H^{\circ}$, characterizing the protonation of a carboxylate anion in a polymer, tends to become less negative with increasing α.



Scheme 1.

The enthalpies of neutralization of polymers A and B are both endothermic and pH-independent, while for polymers C and D, protonation is exothermic, as for the corresponding monomers 3 and 4, and pH-dependent (Fig. 3, Table 5). Moreover, the variation of $-\Delta H^\circ$ vs. α follows an opposite trend in the last two polymers: the slope of $-\Delta H^\circ/\alpha$ is positive for C, but negative or almost constant for D [9]. All this means that the slopes observed in the plot log K vs. α for the polymers A, B and D are reflected in the slope of $\Delta S/\alpha$, indicating that the cooperative effect is really a cooperation between the hydration shells of different COO^- groups. The slope difference D > A > B can be attributed to the greater penetration of hydration shells belonging to neighbouring side chains. It is particularly interesting to note that polymer D shows the greatest slope. The neutralization process of D provokes a larger desolvation effect than A and B due to the peculiar structure of this polymer (Scheme 1), which renders the amide moiety more open and free to hydration. The difference in slope observed between polymers A and B can be attributed to the closer proximity of the COO^- groups in polymer A. The first COO^- groups to be neutralized liberate more water molecules than the rest. This does not prevent the entropy change of B from always being the largest in the series. The solvent exclusion effect of long aliphatic chains is well known [8,19]. For C, the exothermic effect increases with increasing α because, during neutralization, the release of water molecules, already low, becomes progressively smaller and the exothermic effect, due to the $-COO^- + H^+ \rightleftharpoons COOH$ bond formation, becomes greater.

(ii) Vinyl polymers with amino groups

Structurally related vinyl polymers, but with amino groups, have so far been studied from a thermodynamic standpoint [10,11]. The structure of the polymers is listed in Table 2, whilst the thermodynamic functions of protonation are shown in

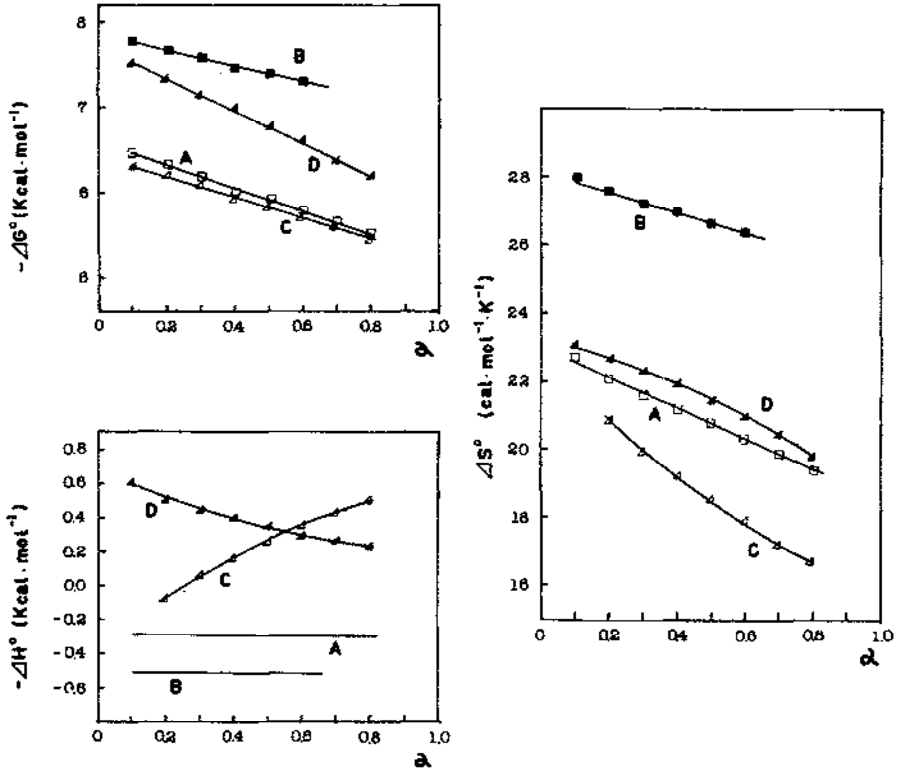


Fig. 3. Dependence of the thermodynamic values of protonation on the degree of protonation α for polymers A, B, C, and D.

TABLE 5

Thermodynamic changes of protonation for poly(acids) and monomers at 25°C in 0.1 M NaCl

Compound	$-\Delta G^{\circ a}$ (kcal mol^{-1})	$-\Delta H^{\circ a}$ (kcal mol^{-1})	$\Delta S^{\circ a}$ (cal mol^{-1} K^{-1})
A	5.90	−0.29[b]	20.8
B	7.38	−0.55[b]	26.5
C	5.81	0.26	18.6
D	6.71	0.37	21.3
E	6.68	–	–
3	4.90	0.95	13.3
4	5.90	0.96	16.6

[a] Calculated at $\alpha = 0.5$ for polymers.

[b] Values independent of α.

Table 6. The log K° values are observed in the range of aliphatic primary, secondary and tertiary amines [22], thus they obey the order G > F > H > I. The insertion of a methylene group in the aliphatic chain or a methyl group in the acylpiperazine unit of the side chain not only affects the values of the basicity constant but determines a decrease in *n*. Such an insertion imparts enhanced hydrophobic character to the polymer. In polymers F and G, $-\Delta H^\circ$ is independent of the degree of protonation, and the variation of the basicity constants with α depends on the variation of ΔS°. The value of ΔS° is small and positive up to $\alpha = 0.5$ and assumes negative values for $1 > \alpha > 0.5$ (Fig. 4). The desolvation effect accompanying the protonation process is relatively modest and decreases with increasing number of protonated nitrogen groups. This behaviour is completely different from that observed in poly(carboxylic acids) and reflects the different magnitudes of hydration shells of the two reaction products, the ammonium group and the carboxylic acid [23,24].

$$-NH_2(H_2O)_x + H^+(H_2O)_y \rightleftharpoons -NH_3^+(H_2O)_{x+y-z} + zH_2O$$

The release of water molecules in the above reaction is hindered by the greater solvation of the ammonium group, which also picks up some H_2O molecules belonging to the H^+ ion. With increasing number of protonated nitrogens in the polymeric chain, desolvation becomes more difficult in the presence of water molecules tightly bound to the $-NH_3^+$ up to $\alpha = 0.5$, where ΔS° for both polymers is zero.

Beyond this α value the ordering effect, caused by the repulsion between neighbouring positive poles, progressively reduces the conformational freedom, and hence the entropy value. A different effect on the $-\Delta H^\circ$ pattern is clearly shown for polymers H and I. The $-\Delta H^\circ$ values are dependent on α with an increasing trend for both polymers up to $\alpha = 0.5$. As protonation proceeds, the compact coil of the uncharged macromolecule breaks down and gradually uncoils into a more extended state. This leads to easier accessibility or easier protonation of the residual basic amino groups reflected by the increase in $-\Delta H^\circ$.

The gradual extension due to charge repulsion leads to a greater hydration

TABLE 6

Thermodynamic values for the protonation of vinyl polymers with amino groups at 25°C in 0.1 M NaCl

Compound	log K°	*n*	$-\Delta G^{\circ a}$ (kcal mol^{-1})	$-\Delta H^{\circ a}$ (kcal mol^{-1})	$\Delta S^{\circ a}$ (cal mol^{-1} K^{-1})
F	8.23	1.48	11.22	11.2[b]	0
G	9.31	1.37	12.70	12.7[b]	0
H	7.13	1.40	9.72	9.29	1.44
I	6.09	1.27	8.30	6.78	5.10

[a] Calculated at $\alpha = 0.5$.

[b] Values independent of pH.

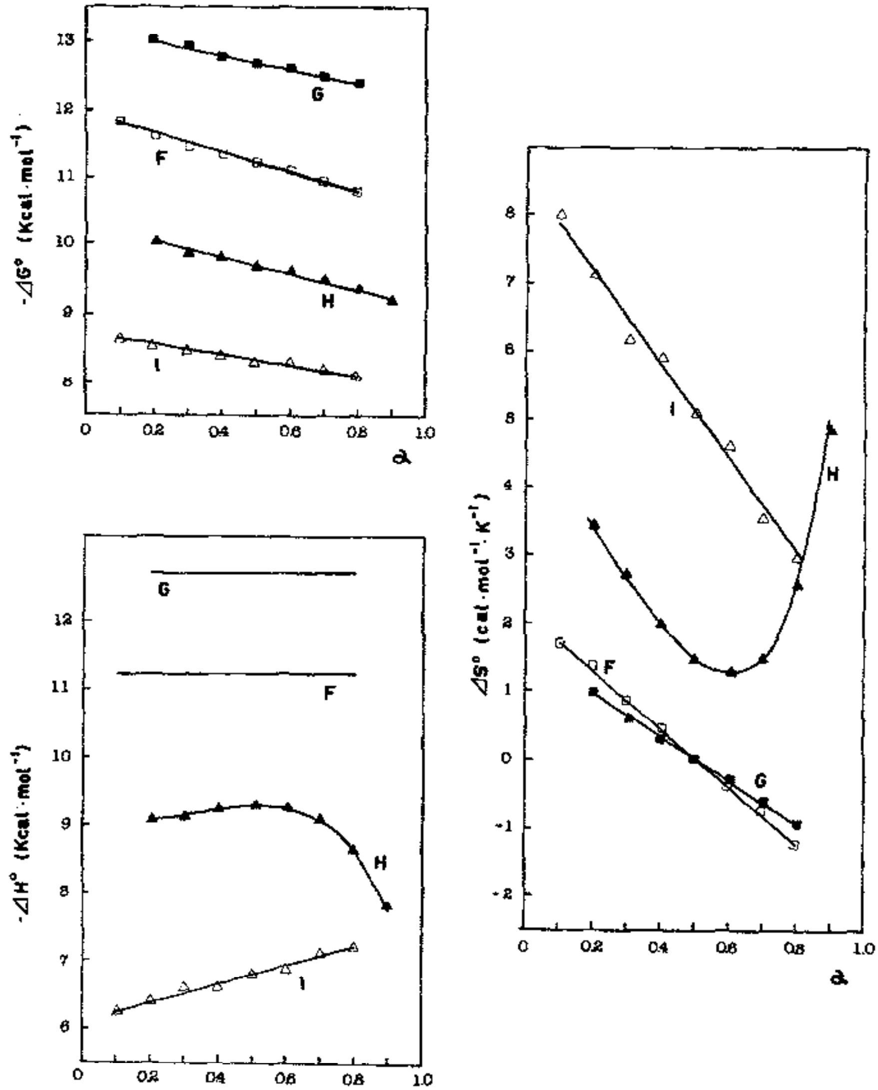
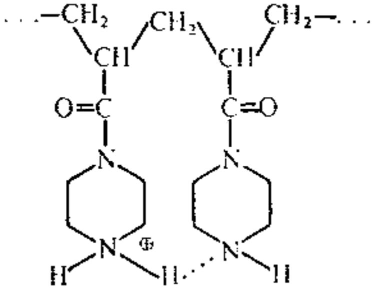


Fig. 4. Dependence of the thermodynamic values of protonation on the degree of protonation α for polymers F, G, H, and I.

and to a decrease in conformational freedom of the macromolecule, causing a sharp drop in ΔS° with α. At $\alpha > 0.5$, the $-\Delta H^\circ$ value of polymer H sharply decreases. This peculiar behaviour may be explained by the formation of hydrogen bonds between a protonated nitrogen and an unprotonated nitrogen of a neighbouring unit as shown in Scheme 2. This proceeds up to $\alpha = 0.5$ when all units are engaged. The

H-bonded structure is then destroyed by further addition of H^+ ions which protonate the engaged amino groups, and $-\Delta H^\circ$ decreases.



Scheme 2.

As a matter of fact, ΔS gradually diminishes with α to $\alpha = 0.5$, then sharply increases. This is related to an increase in chain rigidity due to the formation of hydrogen bonds and then a decrease in rigidity due to the destruction of the same bond [10,23,24].

D. COPPER(II) COMPLEX FORMATION

Stability constants of polyelectrolytes complexing heavy metal ions are usually evaluated by the modified Bjerrum method [25]. The modification was necessary because the polyelectrolytes show "apparent" basicity constants, i.e. pH-dependent. Even so, the formation constant log β values reported in the literature for polyelectrolytes with metal ions do not completely describe the complexing behaviour [14]. The equilibrium constants relative to Cu^{2+} complex formation of some polymers with amino-acid residues have recently been calculated on the basis of the pH dependence of the protonation constants [26,27]. In these specific examples, the two protonation constants, calculated for each repeating unit, refer to the protonation of the tertiary nitrogen and carboxylate groups, following a linear trend with respect to pH via the modified Henderson–Hasselbalch equation. Choosing a pH region in which only one complex species is present, i.e. the spectrophotometric region in which λ_{max} of the complex species remains unchanged, it was possible to evaluate the stability constant at each titration point. Using the previously calculated basicity constants and an estimated stability constant value (see Sect. E) together with the analytical data as input, a system of mass balance equations can be solved for each titration point, giving the equilibrium concentrations of all the species present in solution [28] and, in particular, a calculated value of pH (pH_{calcd}). The program refines a stability constant value of a specified species present at each point of the titration curve with respect to the previous point by choosing the pH as titre parameter and successively solving the equation:

$$pH_{obsd} = pH_{calcd} + (\delta pH/\delta\beta)\Delta\beta$$

In the case of vinyl polymers, only some are capable of forming complex species with the Cu^{2+} ion in aqueous solution [13]. On the contrary, none of the low molecular weight analogues show this property. The characteristic feature of the polymer to form complex species is due to the specific nature of the polymer chain. The reaction between a macromolecule and metal ion proceeds in a microheterogeneous region, the so-called domain. The domain shows physico-chemical properties completely different from that of the bulk solution [29], for instance a different dielectric constant. Both the domain and the nature of the complex species change continuously as the reaction proceeds. This fact is usually ascertained in the literature for a strictly related vinyl polymer, namely poly(*N*-methacryloyl-L-alanine).

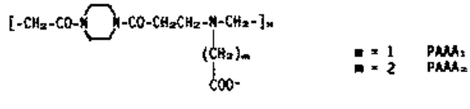
Unlike the corresponding non-macromolecular model, *N*-isobutyroyl-L-alanine, which shows only a simple complex species in a narrow low pH range of CuL stoichiometry, the polymer forms complex species involving one or two adjacent monomeric units [30]. However, the cooperation of several repeating units does not occur for our Cu(II) polymer complex as shown by the stoichiometry.

Of the several vinyl compounds studied, only polymers A, C, and F showed an ability to form complex species with copper(II) ions, irrespective of the structure of the main skeleton. The two poly(acids) form a CuL^+ complex species (L^- is the monomer unit of the polymer) with the same λ_{max} and very similar stability constants (Table 7). None of these parameters change with pH in the range reported, even though the

TABLE 7

Results of Cu(II) complex formation with polymeric ligands (0.1 M NaCl at 25°C) L = monomer unit of the polymer.

Compound	Reaction	pH range	log β	λ_{max} (kK)
A	$Cu^{2+} + L^- \rightleftharpoons CuL^+$	2.8–4.0	3.30	13.5
	$CuL^+ + OH^- \rightleftharpoons Cu(OH)L$	4.2–6.0	9.8–7.6	13.7
	$CuL^+ + 2OH^- \rightleftharpoons Cu(OH)_2L^-$	6.5–10.0	14.5–11.3	14.9
1	No complex-species formed			
C	$Cu^{2+} + L^- \rightleftharpoons CuL^+$	2.7–4.0	3.47	13.5
	$CuL^+ + OH^- \rightleftharpoons Cu(OH)L$	4.5–6.8	9.0–7.0	13.9
3	No complex-species formed			
$PAAA_1$[a]	$Cu^{2+} + L^- \rightleftharpoons CuL^+$	2.5–4.0	9.0–8.3	13.6
$PAAA_2$[a]	$Cu^{2+} + L^- \rightleftharpoons CuL^+$	4.0–6.4	6.5–5.8	13.4

[a]


curves were obtained at different polymer/Cu^{2+} molar ratios. This means that the structure of the complex involves only the coordinating groups present in each repeating unit, excluding any cooperation of neighbouring units. The d–d adsorption spectrum of the CuL^+ complex species is shifted to higher energies than those of the hydrated Cu^{2+} ion and close to those of the previously studied CuL^+ complexes with poly(amidoglycine) ($PAAA_1$) and poly(amido-β-alanine) ($PAAA_2$). In the previously studied complexes, coordination clearly occurs through the tertiary amino nitrogen and the carboxylate group [26] of the same monomer unit (Table 7). The hypothesis formulated is that polymers A and C coordinate to the Cu^{2+} ion via the negatively charged oxygen of the COO— group and the amido group. The remaining coordination positions are occupied by water molecules. Due to the low percentage of formation of the CuL^+ species in the narrow low pH range, we cannot be sure that the stability constant is really "sharp". At higher pH, further hydroxylate species of Cu(OH)L stoichiometry seem to form for A and C (Fig. 5). One dihydroxyl species,

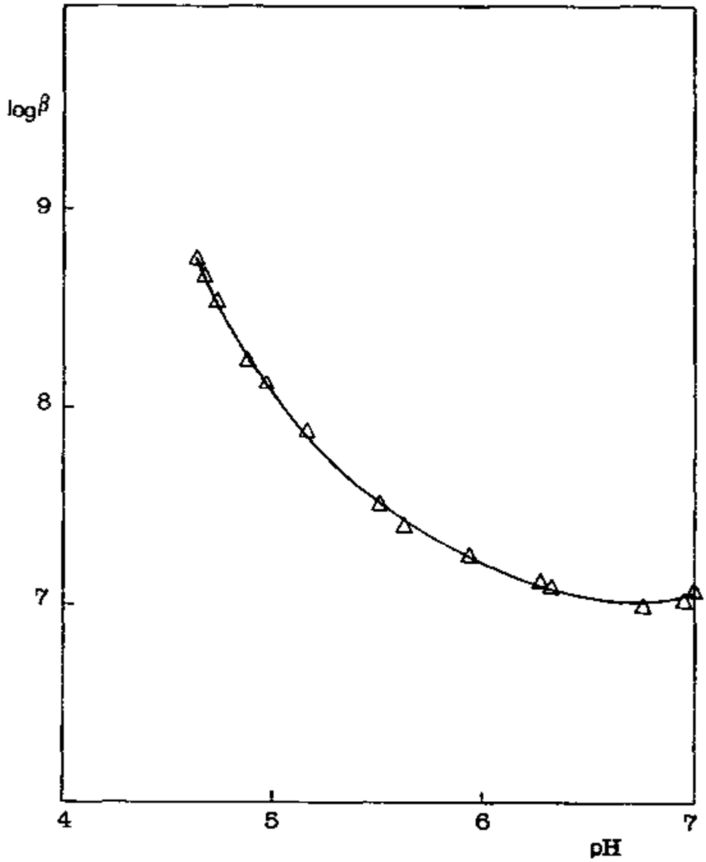


Fig. 5. Variation of the Cu(OH)L stability constant (log β) vs. pH (L is the monomer unit of polymer C). Curve obtained at L/Cu^{2+} = 3 molar ratio.

$Cu(OH)_2L^-$, of A is revealed at higher pH values (Fig. 6). All three stability constants decrease with pH. For C, at pH > 7 the stability constants of the equilibrium

$$CuL^+ + OH^- \rightleftharpoons Cu(OH)L$$

tend to rise (Fig. 5). This means that, beyond this point, new complex species are formed but are hard to discriminate. The stability constant variations observed for the above reaction can be attributed to electrostatic effects [26]. At the beginning, the high positive charge density on the CuL^+ polymer allows the negatively charged OH^- ions to approach more easily, giving a higher stability constant. As the reaction proceeds, charge neutralization of the Cu-polyion occurs and the approach of the other OH^- ions becomes more difficult. For both polymers A and C, the Cu(OH)L complex species show many similarities, so that the same stoichiometry can be reasonably hypothesized with an OH^- group replacing a water molecule in the coordination sphere.

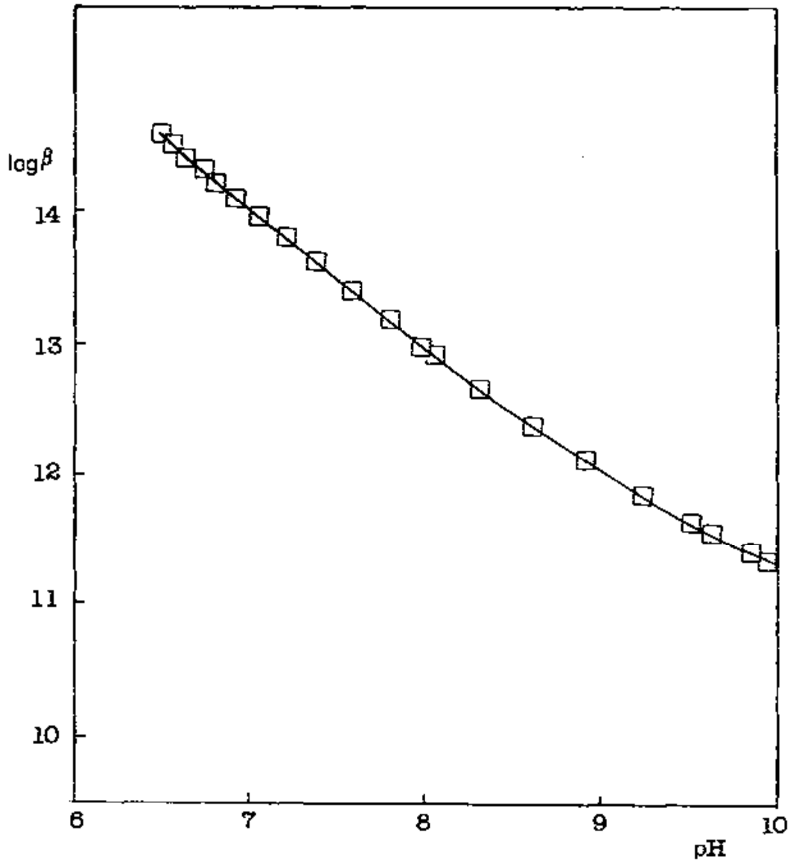


Fig. 6. Variation of the $Cu(OH)_2L^-$ stability constant (log β) vs. pH (L is the monomer unit of polymer A). Curve obtained at $L/Cu^{2+} = 1.5$ molar ratio.

A vinyl polymer carrying an amido and a primary amino group (polymer F) only shows a log β value at low pH [12]. The increase in pH leads to further deprotonation of the amido group of the same monomer unit. In fact, in the alkaline region $\lambda_{max} = 16$ kK has been recorded with no formation of hydroxylate species. The CuL^+ complex species has been fully characterized in the pH range 4–6. All the thermodynamic values are "real" and the low free-energy and enthalpy terms are consistent with coordination involving the primary amino and the amido C=O groups (Table 8). The value of log β we found is very low indeed if we consider the stability constants of other Cu(II) complexes with similar ligands. For example, for glycinamide, in which a Cu^{2+} anchors to the primary amino nitrogen and chelates the peptide oxygen to form a five-membered ring, log β is 5.40 [31]. From calorimetric measurements, only an approximate enthalpy change value can be obtained because of the small amounts of the complex species formed before precipitation occurs. The value of ΔH° is lower than that observed for the Cu(II)-glycylglycine complex in which coordination occurs via a primary amino group and the amido C=O to form a five-membered chelate ring [32]. In the Cu(II)-polymer system, the lower enthalpy value is in agreement with a hypothetical seven-membered chelate ring which is not very stable, as is also shown by the relatively small value of log β. The calculated value for ΔS° reported in Table 8 may be attributed to a release of water molecules around the solvated metal ion during the complexation reaction. The Cu^{2+} ions, in fact, are unable to hydrate to the same extent when bound to the ligand. This is due to the hydrophobic nature of the polymer, which determines a higher ΔS° value than with the formation of the glycylglycine complex. On the other hand, polymer G does not form complex species at all. This shows that even a flexible polymer chain is not a sufficient condition for the formation of various complexes with different stoichiometry, such as, for example, poly(4-vinyl-pyridine) [33]. In our case, the lack of cooperative interaction between the side chains of the same polymer chain is clear both from the formation of a single complex with polymer F and from the failure of polymer G to form a complex with Cu^{2+}.

E. METHOD OF CALCULATION

At each point of the titration curve, an equilibrium is established between different species whose general formula is $H_pM_qL_r$ (charges are omitted for clarity

TABLE 8

Thermodynamic results of Cu(II)–vinyl polymers with amino groups (0.1 M NaCl at 25°C) L = monomer unit of the polymer.

Compound	Reaction	pH range	log β	λ_{max} (kK)	$-\Delta H^\circ$ (kcal mol^{-1})	ΔS° (cal mol^{-1} K^{-1})
F	$Cu^{2+} + L^- \rightleftharpoons CuL^+$	4.0–6.0	4.83	13.5	2.3	14

and the OH ion is indicated by H^-). The concentration of $H_pM_qL_r$ is given by:

$$[H_pM_qL_r) = \beta_{pqr}[H]^p[M]^q[L]^r \tag{1}$$

where β_{pqr} is the formation constant of the species under consideration and [H], [M], and [L] are the equilibrium concentrations of the hydrogen ion, the free metal ion, and the free ligand, respectively. For each point, the mass balance equations (2)–(4) must hold:

$$C_M = [M] + \Sigma q\beta_{pqr}[H]^p[M]^q[L]^r \tag{2}$$

$$C_L = [L] + \Sigma r\beta_{pqr}[H]^p[M]^q[L]^r \tag{3}$$

$$C_H = [H] + \Sigma p\beta_{pqr}[H]^p[M]^q[L]^r \tag{4}$$

where C_M, C_L, and C_H are the analytical concentrations of metal, ligand and acid, respectively, the sum being extended over all the species $H_pM_qL_r$ assumed to be present in solution. For a given value of the formation constants, the set of simultaneous equations (2)–(4) is solved for the unknowns [H], [L] and [M] at each titration point by the Newton–Raphson method [34].

In the case of "sharp" stability constants, i.e. pH-independent, their refinement is then usually accomplished by the minimization of $U = \Sigma[y_i(\text{obsd}) - y_i(\text{calcd})]^2$, where y is a titre parameter [35]. In the case of polyelectrolytes, the "apparent" stability constants depend on pH [2] so that each titration point must be treated independently unless the functional dependence of the stability constants is known in advance. This is actually the case for protonation constants if we use the generalized Henderson–Hasselbalch equation, eqn. (1), which contains embodied stepwise constants. The latter equation is merely a convenient manner of representing the variation of log K with charge. This makes it possible to perform the refinement of protonation constants by standard methods with only minor modifications. A similar generalized expression is not known in the case of metal complexes, so we wrote a Basic program, which refines the stability constants of the species at each titration point with respect to the previous point by taking pH as titre parameter [36] and successively solving the equation:

$$\text{pH}_{\text{obsd}} = \text{pH}_{\text{calcd}} + (\delta\text{pH}/\delta\beta)\Delta\beta \tag{5}$$

in the form:

$$\Delta\beta = (\text{pH}_{\text{obsd}} - \text{pH}_{\text{calcd}})/(\delta\text{pH}/\delta\beta)$$

where the derivative is evaluated numerically. The convergence of the procedure is usually very rapid and, for "sharp" constants, the results compare very well with those obtained by the program SUPERQUAD [37]. Furthermore, the plot of log β values computed at the different titration points oscillates around a mean value for sharp constants, and has a monotonic trend for "apparent" constants. This allows unbiased discrimination of the two situations.

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