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Thermodynamics of the copper complexation of a polyelectrolyte derived from lysine

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Abstract

Calorimetric measurements have been made at 25 °C in 0.1 M $NaClO_4$ in order to determine the heats of dissociation and the copper coordination of a polyampholyte derived from L-lysine, a natural aminoacid. Combining these values with data from potentiometric titrations, the enthalpy of formation of each of the two ligand–metal complexes formed in this system could be determined. These values were compared with those of the model small molecule in order to account for the polyelectrolyte effect.

INTRODUCTION

The protonation of natural or synthetic polyelectrolytes has been widely studied in the past decades. Except when a conformational transition occurs [1–12], these polymers behave as normal polyelectrolytes, i.e. they undergo a progressive expansion of the macromolecular chain when dissociation of the ionizable groups occurs. Many papers have dealt with the thermodynamics associated with the protonation and metal coordination of such synthetic polycarboxylic acids [13–18] and polybases [19–22] or natural polymers [23–25]. In most cases, all the thermodynamic values are dependent on the ionization state of the polymer due to the mutual interactions of neighbouring ionizable side chains, and the thermodynamic data are more difficult to explain than for the corresponding small molecules.

By comparison, few data are available for polyampholytes and we report here the study of a synthetic polymer derived from lysine, poly (*N*-methacryloyl-L-lysine) (PNML) in which each side chain bears a carboxyl and an amino group which ionize in very different pH ranges (see Scheme 1).

The thermodynamic data for this polymer will be compared with those of the model molecule NIBL determined in a previous work [26].

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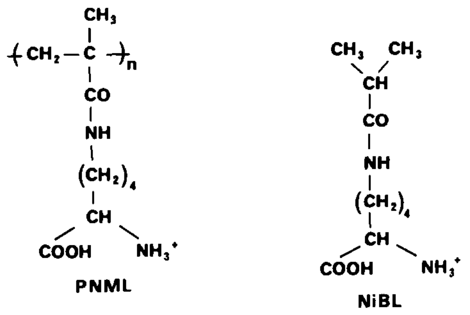


Scheme 1.

EXPERIMENTAL

Materials

The synthesis and purification of the PNML polymer have been described in a previous paper [27].

Aqueous solutions were prepared by weighing and dissolution of the samples in 0.1 M $NaClO_4$ and their exact titre was determined by acid–base titration to take account of the hydration water.

Copper perchlorate (99.9% purity, Fluka) was used as the metal ion source.

Methods

Potentiometric titrations

Potentiometric titrations were performed at 25 ± 0.1° C, using a fully automatic titration apparatus, made up of a Radiometer pHM 65 pHmeter, a Gilmont microsyringe and a Schott N 65 combined electrode. The titration was monitored by an HP 9825 computer.

In the case of copper–ligand coordination, the species distribution curve, giving the concentration of each complex as a function of pH, was calculated with the MUCOMP program [28].

Calorimetric measurements

Calorimetric measurements were made at 25 ± 0.01° C with a Calvet-type batch differential microcalorimeter (Setaram, France), and 100 ml inox cells containing a glass or pyrex inner tube of varying volume were used. This allows the mixing of solutions with various volume ratios, although in most cases the volume ratio was 1:1. The molar ratio, ligand/$HClO_4$, ligand/NaOH or ligand/$Cu(ClO_4)_2$, was adjusted by changing the concentrations of the solutions.

Before being introduced into the calorimeter, the cells were pre-heated to a temperature as close as possible to the inner temperature. When thermal equilibrium was attained, the calorimeter was rocked two or three times to ensure complete mixing of the solutions. The heat signal was amplified and recorded as a function of time. The heat effect (in Joules) was obtained after integration of the experimental curve.

When dealing with the reactions of the carboxyl group of PNML, heats of protonation rather than heats of dissociation were recorded to avoid the contribution from the heat of formation of water ($\Delta H = 55.815$ kJ mol^{-1}) [13] which is 10–15 times larger than the mean heat of dissociation of the COOH group.

For the reaction of the amino group of PNML in alkaline medium, heats of dissociation could be recorded because the enthalpy of the reaction $NH_3^+ \rightarrow NH_2$ is high.

Thus most experiments were made starting from the isoelectric point of the polymer (around pH 5.9) and adding either $HClO_4$ or NaOH.

The dissociation coefficient α was taken as 0 for the fully protonated state, 1 for the isoelectric point and 2 for the fully deprotonated state, corresponding to the steps $LH_2^+ \rightarrow LH \rightarrow L^-$.

In the determination of the heats of protonation or dissociation, 1 volume of the sample solution at a concentration of 2–3 wt.% at a degree of dissociation α, and 1 volume of an $HClO_4$ or NaOH solution were placed in the two compartments of the mixing cell. The concentration of $HClO_4$ or NaOH was adjusted so that the change in the degree of dissociation α_1 to α_2 ($\Delta\alpha$) was not larger than 0.06 in each experiment. This procedure is essential because the heat of protonation (or dissociation) of a polyacid depends on its degree of dissociation. In addition, overall heats of dissociation (from $\alpha = 0$ to $\alpha = 1$ or from $\alpha = 1$ to $\alpha = 2$) were measured. pH changes during the experiments were also recorded.

Separate dilution experiments were also carried out on all the sample solutions, replacing one of the two solutions by water (1:1 dilutions). The results were used to correct the protonation data for sample dilution effects.

In the following, the results are presented as $\Delta H_{\mathrm{diss}} = f(\alpha)$ where $\alpha = (\alpha_1 + \alpha_2)/2$ and ΔH_{diss} is the enthalpy of dissociation at a given α value, calculated as

$$\Delta H_{\mathrm{diss}} = (Q - Q_{\mathrm{d1}} - Q_{\mathrm{d2}})/m$$

where Q is the recorded heat effect obtained by adding m mol of acid or base to a solution of the partially neutralized sample, Q_{d1} is the heat of dilution of the polymer and Q_{d2} is the heat of dilution of the reactant.

For the measurements of heats of ligand–metal interaction, a known volume of PNML and metal solution at a given alkaline pH was placed in one compartment of the cell and a known volume of acid solution was placed in the other. After the experiment, the final pH was carefully measured. The concentration change of the different complex species was

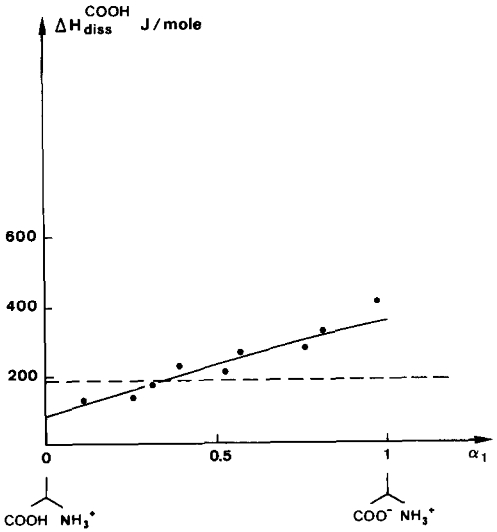


Fig. 1. Variation of the enthalpy of neutralization of the carboxyl group of PNML versus the degree of dissociation α. The dotted line is the reference value for the model small molecule.

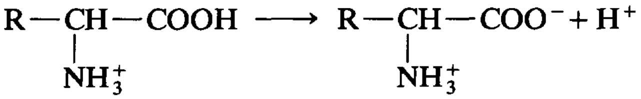
deduced from the pH change and the species distribution curve. Separate dilution experiments were also carried out for correction purposes.

The calorimeter was electrically calibrated by Joule effect and tested by measuring the heat of dilution of NaCl solutions [29].

RESULTS AND DISCUSSION

Heats of dissociation

As expected for a small molecule containing only two ionizable groups with ionization in very different pH ranges, the heat of dissociation of NIBA does not depend on the average degree of dissociation, as shown in Fig. 1. Partial and overall protonation experiments give similar results: $\Delta H_{diss} = +210$ J mol^{-1} for the process shown in Exhibit 1, and $\Delta H_{diss} = +44.8$ kJ mol^{-1} for the process shown in Exhibit 2 in agreement with



$$\underset{\displaystyle NH_3^+}{R{-}\overset{}{C}H{-}COOH} \longrightarrow \underset{\displaystyle NH_3^+}{R{-}CH{-}COO^-} + H^+$$

$$(LH_2^+ \longrightarrow LH + H^+)$$

Exhibit 1.

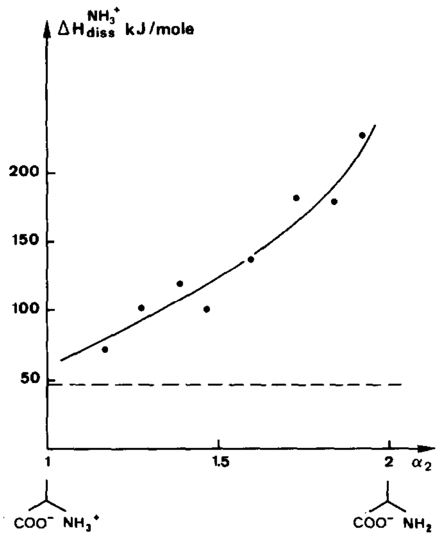
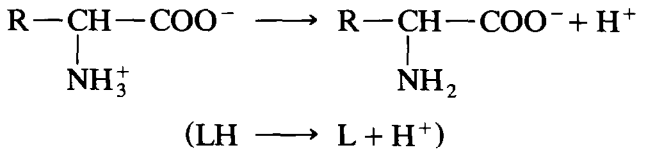


Fig. 2. Variation of the enthalpy of neutralization of the amino group of PNML versus the degree of dissociation α. The dotted line is the reference value for the model small molecule.

literature data on ionization of carboxyl and amino groups in amino acids [30].



$$\underset{\displaystyle NH_3^+}{R-\underset{|}{C}H-COO^-} \longrightarrow \underset{\displaystyle NH_2}{R-\underset{|}{C}H-COO^-} + H^+$$

$$(LH \longrightarrow L + H^+)$$

Exhibit 2.

In contrast, the heat of dissociation of the polymer does depend on the degree of dissociation (Figs. 1 and 2). Between $\alpha = 0$ and 1 where ionization of the COOH groups occurs, ΔH_{diss} increases regularly when α increases and is about twice as high as the value for the model molecule at $\alpha = 1$. At low α value, the removal of a proton from the side chain is more easy than in the small molecule because the accumulation of positive charges exerts a highly repulsive action on the proton. Therefore the enthalpy of ionization is less positive.

At values of α near 1, however, most of the carboxyl groups are ionized, the repulsive effect of the NH_3^+ groups is attenuated and ΔH increases.

The overall heat of ionization between $\alpha = 0$ and 1 measured in separate experiments is $\Delta H = +230$ J mol^{-1}. The overall process of ionization of the carboxyl group is thus only slightly more difficult in the polymer than in the model molecule ($\Delta H = +210$ J mol^{-1}).

The second part of the ionization process between $\alpha = 1$ and 2 (Fig. 2) concerns the amino groups. The partial heat of dissociation of NH_3^+ into NH_2 and H^+ is always higher than for the model molecule and increases sharply when approaching $\alpha = 2$.

Two effects must be taken into account: firstly, the strong electrostatic field of the COO^- groups that are fully ionized and exert a strong attraction on the proton; and secondly, the disappearance of the positive NH_3^+ charges which help ionization at lower α values.

The overall heat of ionization between $\alpha = 1$ and 2 measured in separate experiments is $\Delta H = +132.5$ kJ mol^{-1}. Thus, in the case of PNML, the overall ionization of the amino group is much higher than in the model molecule ($\Delta H = +44.8$ kJ mol^{-1}). This enhancement of the enthalpy of ionization of the polymer compared to small molecules is usually observed [13–22].

These results may be compared with literature data concerning polybases such as poly(vinylamine) or poly(iminoethylene) [31]. In both cases, the ΔH value for the ionization of the NH_3^+ or NH_2^+ group is also positive (around 40 kJ mol^{-1}) but tends to decrease when α increases. This difference can be attributed to the presence of the COO^- group in our polymer.

Entropy change of the ionization

The entropy change during the ionization of the COOH and NH_3^+ groups may be estimated using the equations [18]

$$pK_{app} = pH - \log(\alpha/(1-\alpha))$$

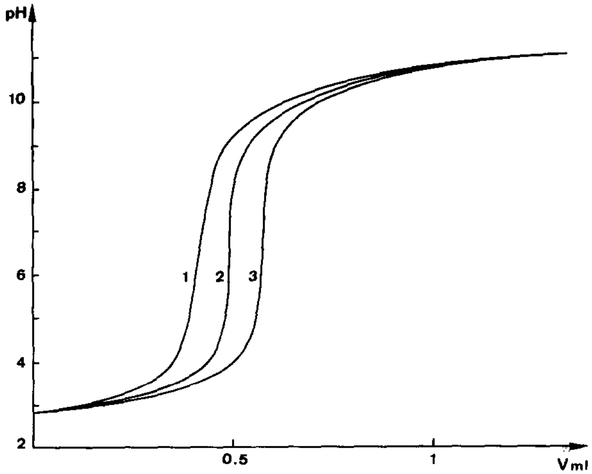


Fig. 3. Titration curves of PNML in 0.1 M $NaClO_4$: curve 1, no copper; curve 2, [PNML]/[copper] = 10; curve 3, [PNML]/[copper] = 5.

$$\Delta G_{\text{diss}} = 2.303RT(\text{pK}_{\text{app}})$$

$$\Delta S_{\text{diss}} = (\Delta H_{\text{diss}} - \Delta G_{\text{diss}})/T$$

This calculation has been made for $\alpha = 0.5$ and 1.5 (half-dissociation of the carboxyl and amino groups) using 3.1 and 9.83 as $\text{p}K_{\text{app}}$ values obtained from the titration curve in Fig. 3. The values $\Delta S_{\text{diss}} = -59$ and $+227$ J K^{-1} mol^{-1} were obtained respectively.

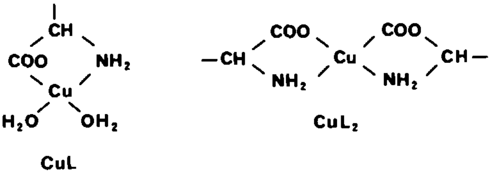
The value for the dissociation of the carboxyl group is two to three times lower than for pure polycarboxylic polymers. The presence of the positively charged amino group in this pH range decreases the net charge of the side chain and likewise decreases the immobilization of water molecules around the polymer.

The positive value obtained in the second case reflects the neutralization of the amino group as observed for other polybases [31].

Heats of complexation

The addition of the copper ion to a solution of PNML at a given pH induces a strong decrease in the pH of the solution as shown in Fig. 3.

In a previous study [27] it was shown that two complexes are formed in the PNML–Cu system with 1:1 and 2:1 ligand–metal stoichiometries, referred to hereafter as CuL and CuL_2 (see Scheme 2).



Scheme 2.

The decrease in the pH is due to the displacement of the following reactions with liberation of H^+

$$\text{LH}_2^+ + \text{Cu}^{2+} \rightarrow \text{CuL}^+ + 2\text{H}^+$$

$$2\text{LH}_2^+ + \text{Cu}^{2+} \rightarrow \text{CuL}_2 + 4\text{H}^+$$

$$\text{LH} + \text{Cu}^{2+} \rightarrow \text{CuL}^+ + \text{H}^+$$

$$2\text{LH} + \text{Cu}^{2+} \rightarrow \text{CuL}_2 + 2\text{H}^+$$

Therefore, in the calorimetric experiments the recorded heat effect contains not only the heats of formation of each of these complexes but also a change in the concentrations of the LH_2^+, LH and L^- species.

The heat quantity Q_c, corrected for dilutions effects, is then expressed by

$$Q_c = Q_{\text{LH}_2} + Q_{\text{LH}} + Q_{\text{CuL}} + Q_{\text{CuL}_2}$$

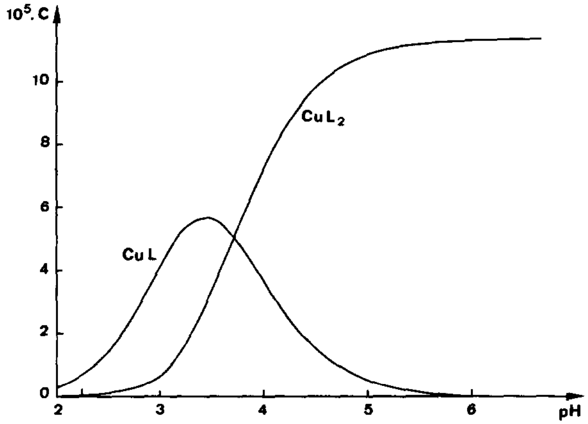


Fig. 4. Species distribution curve for the PNML/Cu^{2+} system.

The following method was used. As explained in the experimental section above, a given amount of acid or base was added to a mixture of PNML and Cu^{2+}. The variation of pH allows the variation of the dissociation coefficient α to be calculated from Fig. 3. The heat effect associated with the concentration changes of the LH_2^+ and LH species is then calculated from Figs. 1 and 2 ($Q_{LH_2} + Q_{LH}$).

The heat effect Q_c' related to the formation of the complexes may be calculated and expressed as a function of the variation of the number of moles of each complex and the corresponding enthalpy changes

$$Q_c' = Q_c - Q_{LH_2} - Q_{LH} = \Delta n(CuL_2)\Delta H_{CuL_2} + \Delta n(CuL)\Delta H_{CuL}$$

$$Q_r = Q_c'/\Delta n(CuL) = \Delta H_{CuL} + \Delta H_{CuL_2}[\Delta n(CuL_2)/\Delta n(CuL)]$$

Values of ΔH_{CuL_2} and ΔH_{CuL} are then obtained from the slope and intercept of the curve

$$Q_r = f(R_c)$$

with $R_c = \Delta n(CuL_2)/\Delta n(CuL)$.

Different values of R_c are obtained by varying the initial and final pH of the experiment, the concentration changes of the two complexes being obtained from the species distribution curve (Fig. 4).

The plot of Q_r versus R_c is given in Fig. 5 and values of -12.5 and -7.8 kJ mol^{-1} are obtained from the intercept and slope.

ΔH_{CuL} corresponds to the reaction

$$CuL^+ + 2H^+ \rightarrow Cu^{2+} + LH_2$$

which is the sum of

$$CuL^+ \rightarrow Cu^{2+} + L^- \qquad (-\Delta H_f)$$

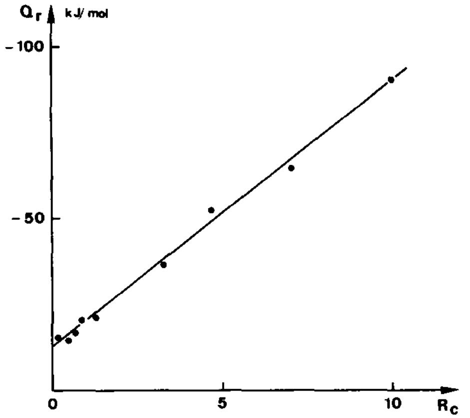


Fig. 5. Plot of Q_r versus R_c.

and

$L^- + 2H^+ \rightarrow LH_2^+ \qquad (\Delta H_{LH_2})$

Therefore, ΔH_f for formation of the CuL complex is given by

$\Delta H_f = \Delta H_{LH_2} - \Delta H_{CuL} = -44.4 - (-12.5) = -31.9 \text{ kJ mol}^{-1}$

In the same way, ΔH_f for the CuL_2 complex is given by

$\Delta H_f = 2\Delta H_{LH_2} - \Delta H_{CuL_2} = -2 \times 44.4 - (-7.8) = -81 \text{ kJ mol}^{-1}$

From these results, it appears that the coordination of a second ligand to the metal ion (formation of CuL_2 from CuL + L in the second step) is

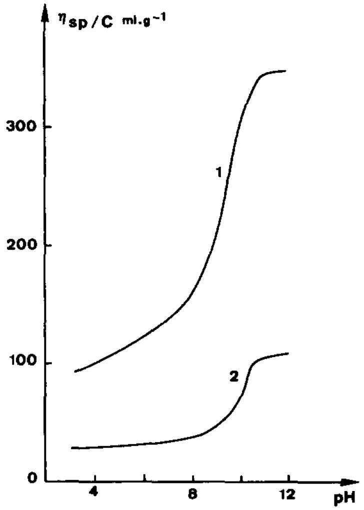


Fig. 6. Reduced viscosity of PNML versus pH in 0.1 M $NaClO_4$: curve 1, no copper; curve 2, [PNML]/[copper] = 15.

much more exothermic (-40.1 kJ mol^{-1}) than the coordination of the first. With small molecules the reverse situation is generally observed, i.e. the second coordination step is more difficult than the first [26]. This difference must be ascribed to the polymeric nature of PNML. The high local concentration of ligand along the polymer chain strongly favours the formation of the CuL_2 complex. The fall in viscosity of the polymer solutions when adding the metal ion, especially at high pH where CuL_2 complex forms, suggests that the formation of this complex occurs between the metal and two non-neighbouring side chains, resulting in the collapse of the polymer chain (Fig. 6).

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