

## Thermodynamics of copper binding with some polycarboxylic acids derived from natural amino acids

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### Abstract

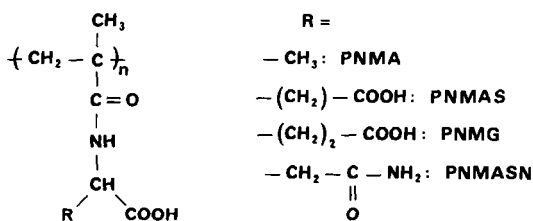
Copper(II) binding data for four polycarboxylic acids in 0.1 M NaClO<sub>4</sub> at 25 °C obtained by calorimetric measurements are reported. The polymers studied were poly(*N*-methacryloyl-L-alanine), poly(*N*-methacryloyl-L-aspartic acid), poly(*N*-methacryloyl-L-glutamic acid) and poly(*N*-methacryloyl-L-asparagine) obtained from the corresponding natural amino acids. Two different pH domains were studied to account for the formation of different kinds of complexes. In the low pH range where only (RCOO)<sub>2</sub>Cu complexes are formed for the four polymers, the enthalpy of copper binding is positive, rather low and nearly the same for all the polymers. At higher pH, in the domain where the polymer side chain undergoes deprotonation of the amide group induced by copper, the metal binding is an even more endothermic process. Thus, the binding of copper to these polymers is entirely entropy-driven. In fact, the entropy change, obtained from combination of calorimetric data and potentiometric data, is largely positive in every case and indicates an extensive desolvation of copper ion and carboxylate groups during the binding process.

### INTRODUCTION

The measurements of enthalpy changes accompanying the interaction of polycarboxylates with metal ions, gives insight into the energetics of chelate formation between the metal ion and the carboxylate groups. Provided that data of potentiometric titrations are also available, the combination of enthalpy and free enthalpy change (from stability constants) allows a complete description of the thermodynamics of the process, including entropy changes.

This method has been applied mainly to the interaction of synthetic polycarboxylic acids with various metal ions, especially copper [1–6] and, in few cases, to natural polymers such as polysaccharides [7,8]. In all cases considered, the enthalpy and entropy changes on copper binding are both positive, thus making this process entirely entropy-driven.

In a previous paper, we reported the results of calorimetric and potentiometric measurements on the protonation of a series of polycarboxylic



acids derived from various natural amino acids [9]: poly(*N*-methacryloyl-L-alanine) (PNMA) from alanine, poly(*N*-methacryloyl-L-aspartic acid) (PNMAS) from aspartic acid, poly(*N*-methacryloyl-L-glutamic acid) (PNMG) from glutamic acid and poly(*N*-methacryloyl-L-asparagine) (PNMASN) from asparagine.

When considering the copper binding to these polymers, the situation is much more complicated than for simple polycarboxylic acids because, at high pH, copper is able to deprotonate the NH of the amide group [10,11] and an additional contribution to the enthalpy of reaction is expected.

The purpose of this paper is to report the results of a thermodynamic study of these systems.

## EXPERIMENTAL

### Materials

The polymer samples used in this study were prepared as previously described [10,11].

Stock solutions of these polymers were prepared in 0.1 M NaClO<sub>4</sub>. Because the samples contain as much as 5% of water even after freeze drying, the exact concentrations of the solutions were obtained from acid-base titrations in 1 M NaClO<sub>4</sub>. The pH of the solutions was adjusted with HClO<sub>4</sub> or NaOH.

Copper perchlorate was used as the metal ion source. The concentration of the stock solution of copper was determined by acid-base titration after exchange of copper on a cationic ion-exchanger.

### Methods

The calorimetric experiments were carried out at 25°C using a Calvet batch-type microcalorimeter, closely following a procedure already described [9].

Two series of experiments were carried out for the binding of copper to the polymers: in the first series, measurements were made near pH 4.5, i.e. in a range where only (R-COO)<sub>2</sub>Cu complexes are formed [10,11], in order

to determine the heat of formation of this simple chelate; in a second series, the pH was adjusted to about 7.5, i.e. where the major species in solution is a complex in which copper is bound to one carboxyl and one peptide nitrogen (see below).

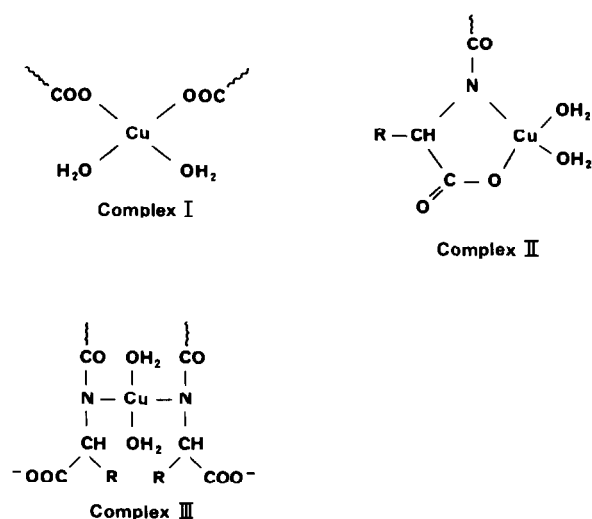
The concentrations of the polymer and copper solutions in the two compartments of the calorimetric cell were adjusted so that in the final mixture, the ratio  $R$  defined by  $[\text{Cu}^{2+}]/[\text{COO}^-]$  ranged between 0 and 0.5.

The  $\Delta H$  values for the enthalpy of binding were normalized to one mole of carboxyl group and the enthalpy of binding per mole of bound copper was deduced from the slope of the curves of  $\Delta H$  versus  $R$ .

By measurements of free copper concentration using copper-selective electrodes [11] it was confirmed that at least 98% of the added copper was bound to the polymer under our experimental conditions.

## RESULTS AND DISCUSSION

In previous papers [10,11] dealing with the coordination of copper to the above polymers, it was shown, by various spectroscopic and potentiometric methods, that three types of complex are formed for each polymer-Cu system, depending on the pH of the solution. At low pH, around 4.5, only a 2:1 ligand: metal complex is formed involving two carboxyl groups and one metal ion (complex I, Scheme 2). With PNMA and PNMASN, which contain one carboxyl group per side chain, formation of the complex requires the participation of two side chains, whereas in the case of PNMAS and PNMG, two carboxyl groups of the same side chain or of different side chains can form the complex. This difference is reflected in



Scheme 2.

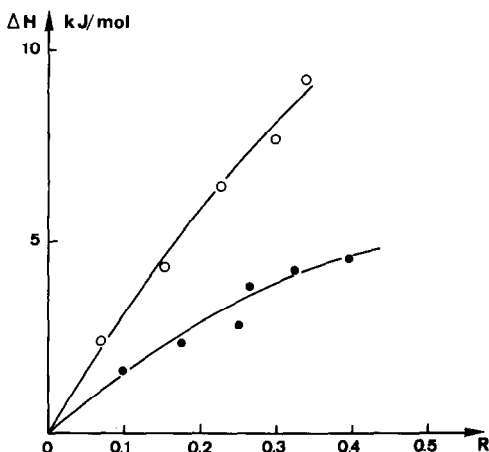


Fig. 1. Variation of  $\Delta H$  versus  $R$  for PNMA: ●, pH 4.5; ○, pH 7.5.

the values of the stability constant  $K_2$  of the complexes which are slightly higher for PNMA and PNMG [11]. Complex II has maximum concentration around pH 8 but is never the only species in solution, which also contains non-negligible amounts of complex I and also complex III. The latter complex becomes the major species around pH 10 and undergoes hydrolysis, i.e. conversion of bound water into OH ligands, at still higher pH.

Therefore, as a result of these considerations, the heat of formation of complex I can be measured with good precision. In contrast, data obtained at higher pH will contain contributions from the simultaneous formation of different species. Therefore, the results will only indicate qualitatively the additional contribution of the deprotonation of the amide group to the overall heat of reaction.

Figures 1–4 give the results obtained for the four polymer–Cu systems at pH 4.5 and 7.5.  $\Delta H$  is given in kJ per mole of carboxyl group and is plotted versus the concentration ratio  $R = [\text{Cu}^{2+}]/[\text{COO}^-]$ . The enthalpy of binding  $\Delta H_b$  is obtained from the slope of the curves and is expressed in kJ per mole of added copper, that is per mole of copper bound, because separate measurements have shown that, in these conditions, over 98% of the added copper is actually bound to the polymer.

At pH 4.5 where the  $(\text{RCOO})_2\text{Cu}$  complex is formed, the values of  $\Delta H_b$  are 15, 17.5, 18.75 and 21  $\text{kJ mol}^{-1}$  for PNMA, PNMA SN, PNMG and PNMA S respectively. Thus the binding process is an entirely entropy-driven process.

Our values are in qualitative agreement with those reported previously for copolymers of maleic acid with various comonomers, 15–18.4  $\text{kJ mol}^{-1}$  [3,12], and are also close to those for the copper–succinate system, 19  $\text{kJ mol}^{-1}$  [12]. For natural polyelectrolytes, the values seem to be somewhat lower, 9–10  $\text{kJ mol}^{-1}$  [7,8].

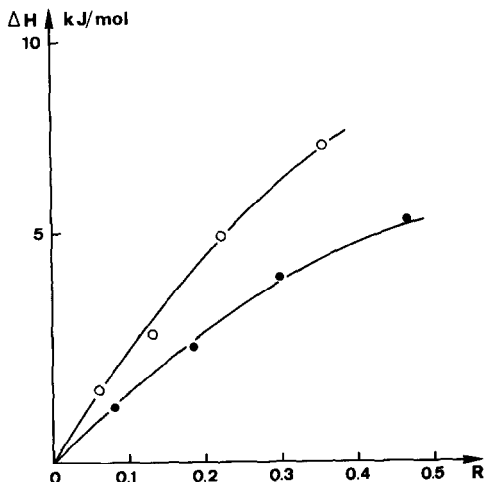


Fig. 2. Variation of  $\Delta H$  versus  $R$  for PNMASN: ●, pH 4.5; ○, pH 7.5.

The entropy change may be calculated from the following equations

$$\Delta G_b = -2.3RT \log K_2$$

$$\Delta S_b = (\Delta H_b - \Delta G_b)/T$$

and values are reported in Table 1. They are much higher than those reported for simple dicarboxylic acid-metal complexes [13] and are in good agreement with data for other polyelectrolytes [3,5]. This difference indicates that even at low  $R$  values, where not all the carboxylate groups are coordinated to copper, a long-range perturbation of the solvation layer of the polymer occurs, with a sharp increase in the mobility of water molecules.

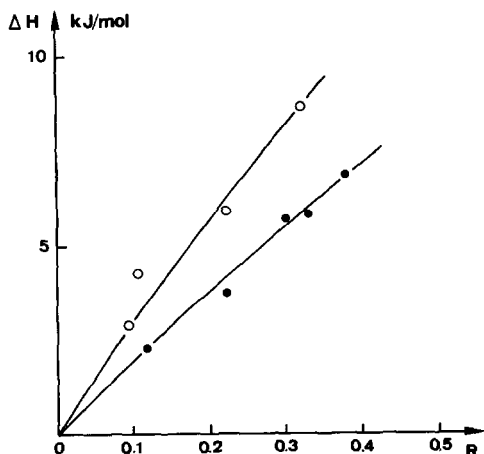


Fig. 3. Variation of  $\Delta H$  versus  $R$  for PNMG: ●, pH 4.5; ○, pH 7.5.

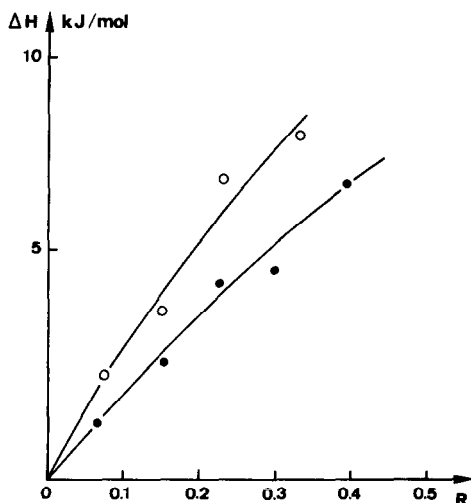


Fig. 4. Variation of  $\Delta H$  versus  $R$  for PNMA: ●, pH 4.5; ○, pH 7.5.

TABLE 1

Thermodynamic data of copper binding with four polycarboxylic acids

	PNMA	PNMASN	PNMG	PNMAS
$K_2$ [10,11]	$1.8 \times 10^7$	$5 \times 10^8$	$2.1 \times 10^8$	$3.3 \times 10^8$
$\Delta G$ (kJ mol <sup>-1</sup> )	-41.6	-49.8	-47.7	-48.8
$\Delta H$ (kJ mol <sup>-1</sup> )	+15	+17.5	+18.75	+21
$\Delta S$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )	+190	+225	+220	+235

In a higher pH range, where deprotonation of the peptide nitrogen occurs, the values of  $\Delta H_b$  are high: 31, 29, 30 and 34 kJ mol<sup>-1</sup> for PNMA, PNMASN, PNMG and PNMAAS respectively (Figs. 1-4). Despite the fact that these values are only indicative, for the reasons given above, it is clear that the deprotonation of the amide nitrogen is a very endothermic process. Although these values concern the binding of copper to polymeric ligands, they can also be interestingly compared with data for the deprotonation of the amide nitrogen in peptides, which range around +30 kJ mol<sup>-1</sup> [14-16].

## CONCLUSIONS

The results from this study emphasize the following points.

The binding of copper to carboxylate ions and to the deprotonated amide nitrogen are both endothermic processes;

The distinctive feature which makes the binding of copper to polycarboxylate ions much easier than to small dicarboxylates (reflected in the equilibrium binding constants) is the particularly favorable entropy change.

The strong increase in entropy on binding can be ascribed to a long-range perturbation of the ion dipole interaction resulting in the liberation of water molecules.

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