Physicochemical Study of the Complexation of Poly(acrylic acid) with Cu^{2+} Ions in Water

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ABSTRACT: The complexation of poly(acrylic acid) (PAA) with Cu^{2+} ions in a dilute aqueous solution has been investigated as a function of the mixing molar ratio of the two species and the neutralization degree (i) of PAA by means of turbidimetry, viscometry, potentiometry, and ultraviolet–visible (UV–vis) spectrophotometry. Turbidimetry reveals that, for $i > 0.1$, phase separation takes place when the mixing ratio approaches the critical value of two carboxylate ions per Cu^{2+} ion, which is indicative of the formation of a 2 : 1 polymer/metal complex. This complex is very compact, as evidenced by the very low reduced viscosity values obtained just before phase separation. The variation of the fraction of complexed carboxylate anions and complexed Cu^{2+} ions can be followed as a function of the mixing ratio and i from the analysis of the potentiometric results for $i < 0.5$. Finally, the combination of the potentiometric and UV–vis spectrophotometric results supports the idea that both mononuclear and binuclear PAA/Cu^{2+} complexes are formed in an aqueous solution, depending on the mixing ratio and i. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 769–776, 2008

Key words: metal-polymer complexes; polyelectrolytes; solution properties; UV-vis spectroscopy; water-soluble polymers

INTRODUCTION

Polymer–metal complexes often offer significant advantages over nonpolymeric metal complexes or metal salts in a variety of applications. For instance, polymer–metal complexation is used for the removal of toxic metal ions in wastewater treatment[1–8] and for the preparation of improved catalysts in catalytic reactions.[9–11] Moreover, the exploitation of polymer–metal complexation in hydrogels or polymer-modified surfaces is very promising for several potential smart applications, such as redox actuators,[6] metal-ion-selective electrodes,[12–14] and electroswitchable devices.[15]

The complexation of Cu^{2+} ions with carboxyl-containing polymers or gels, such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA), has been widely studied with a variety of techniques, both in water and in the solid state.[1,3,9,16–21] The exact mechanism of complexation, as well as the stoichiometry of the reaction and the complex that is formed, is still an open question. However, for the description of the complexation reactions in this work, just for simplicity we will adopt the usually accepted stoichiometry:

complexation involves two carboxylate groups per Cu^{2+} ion.[22–26] Thus, keeping always in mind that this may not be the case as far as it concerns the stoichiometry, when PAA is mixed with Cu^{2+} ions in water, we can describe the polymer–Cu^{2+} complexation by the following overall interaction:

$$2COOH + Cu^{2+} \underset{\longleftarrow}{\longrightarrow} [COO]_2Cu + 2H^+ \qquad (1)$$

In fact, this equation is the sum of two simpler reactions, the complexation of carboxylate anions with Cu^{2+}

$$2COO^- + Cu^{2+} \underset{\longleftarrow}{\longrightarrow} [COO]_2Cu \qquad (2)$$

and the dissociation of carboxylic groups of PAA

$$COOH \underset{\longleftarrow}{\longrightarrow} COO^- + H^+ \qquad (3)$$
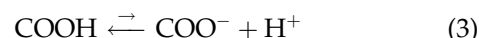
As a result, when the polyacid is not neutralized or moderately neutralized, the complexation with Cu^{2+} through eq. (2) favors the dissociation of carboxylic units and the liberation of H^+ ions in the solution [eq. (3)].[27,28] This observation has made potentiometry maybe the most popular technique for the characterization of the PAA/Cu^{2+} system in aqueous solutions.[29–32] The usual potentiometric approach is the titration of a given PAA/Cu^{2+} solution (with the polyacid at a large excess to ensure the solubility of the complex), and the results are analyzed with the modified Henderson–Hasselbach expression for polyelectrolytes.[33]

Ultraviolet–visible (UV–vis) spectrophotometry in solution is another popular technique, as the complexation of PAA with Cu^{2+} is evidenced by the appearance of new absorption bands at ~ 260, ~ 370, and ~ 700 nm and the disappearance of the band at ~ 800 nm (corresponding to free Cu^{2+}).[34,35] Nevertheless, to our knowledge, correlating the UV–vis results with the potentiometric ones has never been attempted. On the contrary, the combination of the UV–vis results with more elaborate techniques, such as electron paramagnetic resonance (EPR), gives sufficient evidence that in an aqueous PAA/Cu^{2+} solution, apart from the free Cu^{2+} ions, there coexist two kinds of polymer-bound copper species, namely, mononuclear and binuclear PAA/Cu^{2+} complexes. In fact, Francois et al.[25] managed to determine from these combined results the extinction coefficients at 710 nm of these two polymer-bound species and to calculate the variation of the fractions of all copper species in a PAA/Cu^{2+} solution at a given mixing ratio with the neutralization degree (i) of the polyacid.

In this study, we attempt a systematic reexamination of the PAA/Cu^{2+} complexation, mainly aiming at the combination of the potentiometric and spectrophotometric results. For our investigation, we follow a different procedure from that usually applied in the potentiometric studies so far: instead of fixing the mixing ratio of PAA and Cu^{2+} and titrating with a base, we fix i of PAA and we titrate with Cu^{2+} ions. In this way, we are able to follow the PAA/Cu^{2+} complexation as a function of the mixing ratio, covering the whole neutralization range, $0 \leq i \leq 1$.

It is well known that the PAA/Cu^{2+} complexation is accompanied by a significant viscosity decrease,[36,37] revealing the shrinkage of the polymer chain,[20] and finally leads to the formation of water-insoluble products. Therefore, the first step of our study was the systematic turbidimetric and viscometric investigation of the PAA/Cu^{2+} complexation as a function of i.

EXPERIMENTAL

Materials

PAA was purchased as an aqueous 25% (w/v) solution from Polysciences (Warrington, PA). This solution was diluted with an aqueous 0.01M HCl solution and purified with a dialysis membrane (cut-off: 12,000; Sigma-Aldrich Inc., St Lewis, MO) (Sigma; 12,000). Water was changed daily until its conductivity reached values close to that of ultrapure water (<10 μS/cm). Finally, the polymer was recovered by freeze drying. The number-average molecular weight of PAA was determined viscometrically to be 90,000 g/mol.[38] CuSO$_4$ was purchased from Aldrich (Milwaukee, WI) and used as received. A copper(II) standard solution (10.00 g/L) was purchased from Fluka (Buchs, Swit-

zerland). Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga water purification unit (Vivendi Water Systems, Bucks, UK).

Preparation of stock solutions

A mother PAA solution was prepared by the dissolution of PAA in pure water under gentle stirring overnight. From this solution, stock solutions of PAA at different values of i ($0 \leq i \leq 1$) were prepared through mixing with a standard aqueous NaOH solution and subsequent dilution to obtain a final concentration of PAA equal to 20 mM, which is expressed in acrylic acid units under the acid form. These solutions were titrated with a relatively concentrated aqueous CuSO$_4$ solution (0.100M). In this way, the concentration of PAA throughout titration changed just slightly ($\sim 20\%$). In all physicochemical studies, some selected samples were measured twice. The reproducibility of the experiments was found to be better than 90%.

The CuSO$_4$ solution was standardized spectrophotometrically at 820 nm. Standard aqueous CuSO$_4$ solutions were used for the calibration curve.

Turbidimetry

The optical density of dilute aqueous PAA/Cu^{2+} solutions was monitored at 490 nm with a Hitachi model U 2001 spectrophotometer (Hitachi Instruments, Tokyo, Japan).

UV–vis spectrophotometry

The UV–vis spectra of aqueous PAA/Cu^{2+} solutions in the region of 190–1100 nm were obtained with a Hitachi model U 1800 spectrophotometer. All spectroscopic measurements were performed in quartz glass cuvettes (1 cm).

Viscometry

The reduced viscosity (η_{red}) studies at 25°C were carried out with an automated viscosity measuring system (AVS 300, Schott-Gerate, Mainz, Germany) equipped with an Ubbelohde type I viscometer (the flow time of water at 25°C was ~ 85 s).
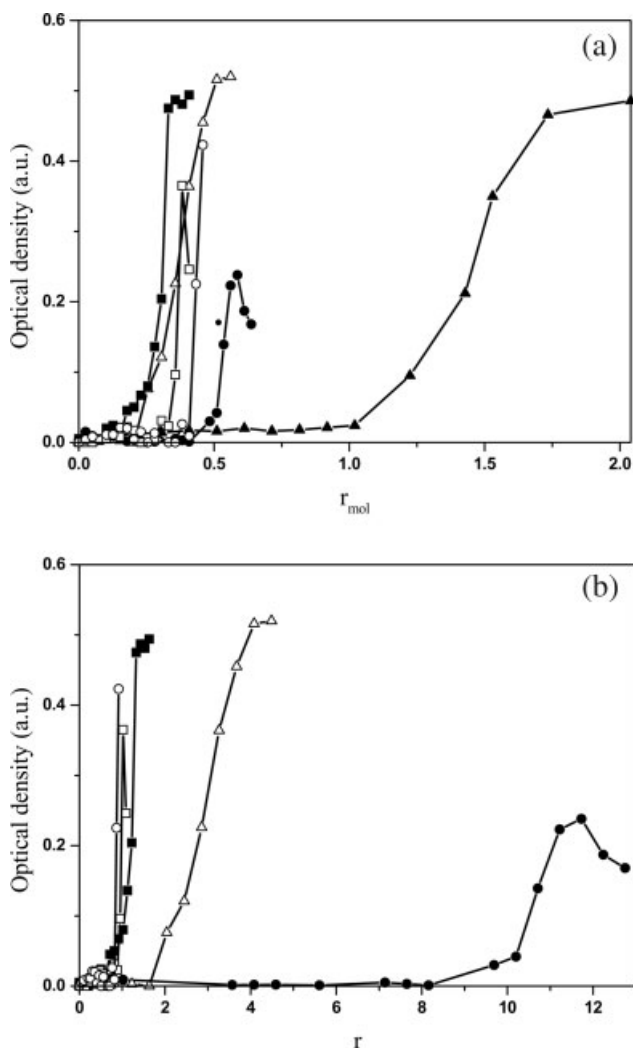
Potentiometry

The pH measurements were obtained with a Mettler–Toledo Seveneasy pH meter (Mettler-Toledo, Inc., Columbus, OH).

RESULTS AND DISCUSSION

Turbidimetry

We first investigated the influence of the mixing ratio of the two species on the phase behavior of

Figure 1 Variation of the optical density of aqueous PAA/Cu^{2+} solutions with (a) r_{mol} or (b) r at different values of i of PAA: (▲) $i = 0$, (●) $i = 0.1$, (△) $i = 0.25$, (■) $i = 0.5$, (□) $i = 0.75$, and (○) $i = 1$.

mixtures of PAA and Cu^{2+} in water at various values of i of the polyacid covering the whole neutralization range ($0 \leq i \leq 1$). The variation of the optical density of aqueous PAA/Cu^{2+} solutions is presented in Figure 1(a) as a function of the molar mixing ratio (r_{mol}):

$$r_{mol} = C_{Cu^{2+}}/C_{PAA} \tag{4}$$

where $C_{Cu^{2+}}$ and C_{PAA} are the molar concentration of Cu^{2+} ions and the unit molar concentration of PAA, respectively. As expected,[39] all solutions are transparent and homogeneous at low r_{mol}, and they turn turbid, indicating the formation of water-insoluble PAA/Cu^{2+} complexes, upon the addition of Cu^{2+} ions. The turbidity onset is observed at high r_{mol} for $i = 0$, and it is displaced to lower r_{mol} values as i increases up to $i = 0.5$. However, this trend is

inversed as the polyacid is further neutralized, and a gradual increase of the critical molar mixing ratio for phase separation is observed as i increases toward unity.

As discussed previously [eq. (2)], the PAA/Cu^{2+} complexation takes place in reality between the Cu^{2+} cations and the carboxylate anions (COO$^-$) and not the carboxylic acid groups (COOH). Therefore, it would be more meaningful to present the aforementioned results with the charge ratio (r) instead of r_{mol}. r is defined as

$$r = 2C_{Cu^{2+}}/C_{COO^-} \tag{5}$$

where C_{COO^-} is the unit molar concentration of the carboxylate anions in the solution. The carboxylate anions originate from both the dissociation and neutralization of the carboxylic acid groups of PAA. With the exception of the experiment for $i = 0$, in all other cases, i is rather high, so the dissociation of PAA may be neglected in the calculation of C_{COO^-}:

$$C_{COO^-} = iC_{PAA} \quad \text{for } i \geq 0.1 \tag{6}$$

The optical density results of Figure 1(a) are presented in Figure 1(b) as a function of r. Obviously, using this representation, we cannot plot the results for $i = 0$. However, the rest results are now more concise. In fact, we see that the optical density onset is observed at the same value of r for $i \geq 0.5$, and it is displaced to significantly higher values as the neutralization of the polyacid decreases.

The critical charge ratio (r_{cr}) for phase separation (defined as the value of r at the optical density onset) is plotted in Figure 2 as a function of i of PAA. For high values of i (≥ 0.5), phase separation takes places at a constant charge ratio close to unity
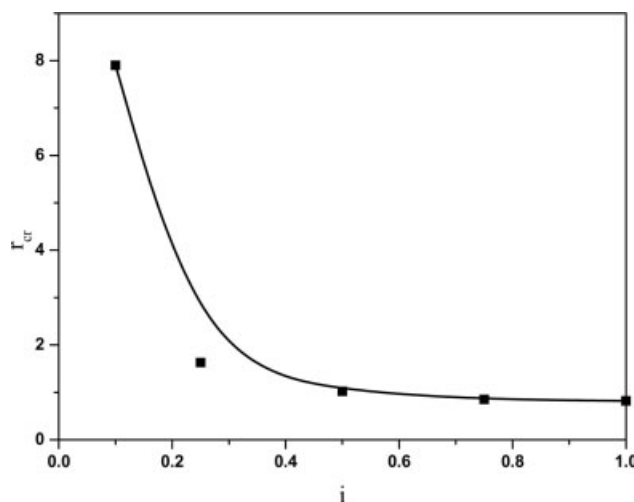
Figure 2 r_{cr} for the phase separation of the PAA/Cu^{2+} complex as a function of i of PAA.
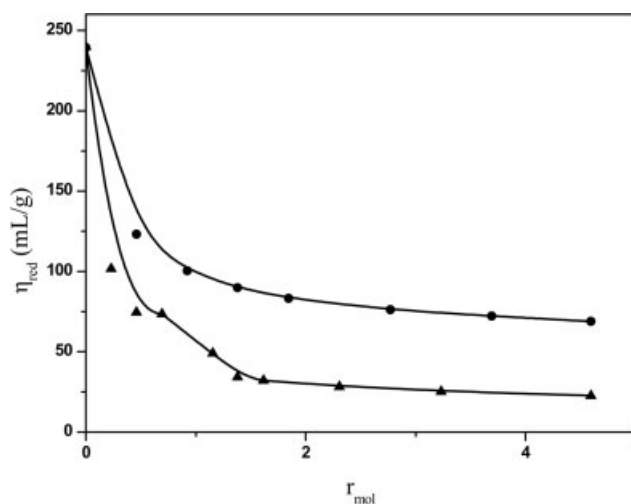
Figure 3 Variation of η_{red} of PAA at $i = 0$ with r_{mol} upon the addition of (▲) $CuSO_4$ or (●) Na_2SO_4.

($r_{cr} \cong 0.9$). This is a good indication that the stoichiometry of the complex that is formed is two carboxylate anions per Cu^{2+} ion. On the contrary, for $i < 0.5$, r_{cr} gradually increases and takes values significantly higher than unity as i decreases toward zero. Although this could be an indication that the stoichiometry of the water-insoluble complex that is formed gradually changes with i at low values of i, it is most likely that at low i the complexation process becomes more gradual and the remaining large fraction of the uncomplexable hydrophilic carboxylic units suffices to maintain the complex in solution even when the mixing ratio is larger than stoichiometry.

Viscometry

The variation of η_{red} of PAA upon complexation with Cu^{2+} ions has been studied in the region in which the solubility in water is maintained, that is, for $r < r_{cr}$. The results for $i = 0$ are presented in Figure 3 as a function of r_{mol}. For comparison, we also performed identical experiments using a noncomplexing sulfate salt of a monovalent cation, that is, Na_2SO_4, instead of $CuSO_4$ to discriminate the effect of complexation from the well-known ionic strength effect on the polyelectrolyte behavior of PAA.[40] The result of this ionic strength effect is the significant decrease of η_{red} of PAA observed in Figure 3, especially in the initial stages of addition of Na_2SO_4. However, the addition of $CuSO_4$ leads to a much more pronounced continuous decrease of η_{red} of PAA. As a result, η_{red} of the PAA/Cu^{2+} system just before phase separation is only ~ 20 mL/g, whereas η_{red} of the PAA/Na_2SO_4 system is maintained at much higher values (~ 60 mL/g). This very low viscosity, first mentioned by Flory and Osterheld,[36] is

the result of the compact nature of the PAA/Cu^{2+} complex. In fact, the evolution of PAA/Cu^{2+} complexation leads to continuous shrinkage of the PAA chain and finally to the precipitation of the water-insoluble complex at somewhat higher r_{mol} values, as already seen in Figure 1(a).

Identical viscometry experiments have been performed for the whole neutralization range of PAA ($0 \leq i \leq 1$) upon the addition of $CuSO_4$, and they have been compared with the respective behavior upon the addition of Na_2SO_4. In all cases, the addition of $CuSO_4$ provoked a much more significant viscosity decrease than Na_2SO_4. For simplicity, in Figure 4 we do not show the results for Na_2SO_4 but show just the results concerning the PAA/Cu^{2+} complexation. Because of the polyelectrolyte character of PAA, its η_{red} value increases significantly with i. For this reason, we have chosen to present in Figure 4 relative results, using the reduced viscosity ratio term ($r_{\eta red}$):

$$r_{\eta red} = \eta_{red}/(\eta_{red})_0 \qquad (7)$$

where η_{red} is the actual reduced viscosity of the PAA/Cu^{2+} mixture and $(\eta_{red})_0$ is the reduced viscosity of the initial PAA solution in the absence of Cu^{2+} ions. At a first approximation, with this definition, values of $r_{\eta red}$ lower than unity indicate the shrinkage of the PAA chain upon the addition of Cu^{2+} ions. As can be seen in Figure 4, in all cases, the ratio $r_{\eta red}$ decreases rather sharply and takes values very close to zero as r approaches r_{cr}, that is, close to phase separation. As discussed previously, this very low value of $r_{\eta red}$ is partly due to the ionic strength effect on the PAA chain but is mostly indicative of the very compact structure of the PAA/
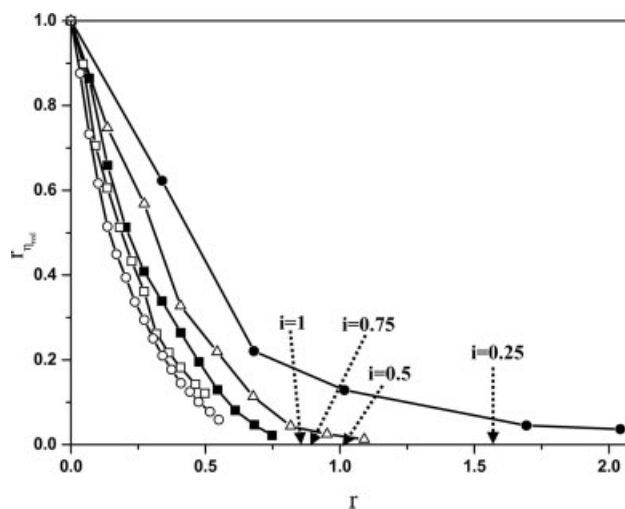
Figure 4 Variation of $r_{\eta red}$ as a function of r at different values of i of PAA: (●) $i = 0.1$, (△) $i = 0.25$, (■) $i = 0.5$, (□) $i = 0.75$, and (○) $i = 1$. The arrows indicate r_{cr} for each value of i.
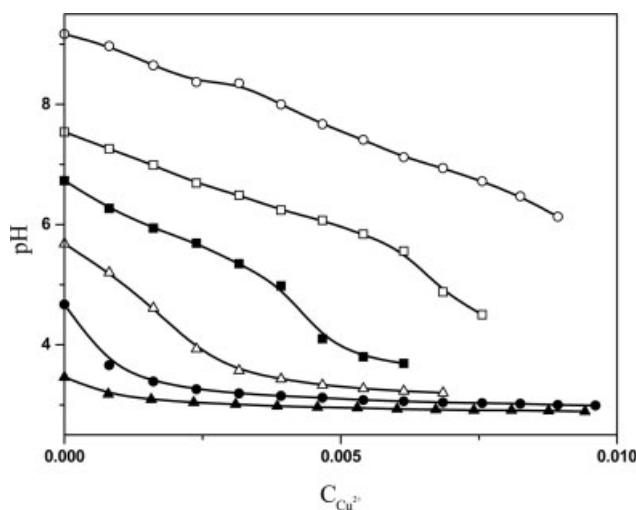
Figure 5 Variation of the pH during the titration of aqueous PAA solutions with a CuSO$_4$ solution at different values of i of PAA: (▲) $i = 0$, (●) $i = 0.1$, (△) $i = 0.25$, (■) $i = 0.5$, (□) $i = 0.75$, and (○) $i = 1$.

Cu^{2+} complex formed in all cases. In addition, we observe that the rate of decrease of $r_{\eta red}$ is less sharp for $i = 0.1$ and gradually increases up to $i = 0.5$. However, for higher values of i ($0.5 \leq i \leq 1$), all curves practically coincide, and this is similar to the turbidimetric behavior reported in Figure 1(b).

Potentiometry

In Figure 5, we present the variation of pH during the titration of aqueous PAA solutions with a CuSO$_4$ solution, covering the whole neutralization range of the polyacid, $0 \leq i \leq 1$. The value of pH of the pure polyacid solution increases from ~ 3.5 up to ~ 9 as it is gradually neutralized from $i = 0$ up to $i = 1$, respectively. On the other hand, we have checked the pH of pure aqueous CuSO$_4$ solutions in the concentration range studied, and pH was found to take a value of about 5.5. As shown in Figure 5, an important pH decrease is observed upon the addition of CuSO$_4$, regardless of the i value of the polyacid. In addition, we see that when PAA is moderately neutralized, the pH change is sharper during the first stages of titration with Cu^{2+} ions and results in clearly more acidic solutions, indicating the liberation of hydrogen ions (H$^+$) in the solution, as a result of the complexation of PAA with Cu^{2+}, according to eqs. (1)–(3). Although the pH change at $i = 0$ is not as significant, it still expresses an important liberation of H$^+$ ions, as the initial pH value is now much lower. On the contrary, when PAA is highly or fully neutralized, the majority of carboxylate anions have already been formed, and PAA/Cu^{2+} complexation can readily occur through eq. (2), not necessarily involving an important shifting of

eq. (3) to the right-hand side. Indeed, in these cases (see, for instance, the results in Fig. 5 for $i = 0.75$ and $i = 1$), just a gradual decrease of the pH is observed from slightly basic values to neutral or slightly acidic values, revealing just a marginal liberation of H$^+$ ions in the solution in comparison with the concentration of PAA or Cu^{2+} ions. It is, therefore, evident that the further exploitation of the pH data is not possible for $i \geq 0.5$, as the error introduced into the relevant calculations will be very important. For this reason, in the following, the discussion will be mainly based on the pH results for the PAA/Cu^{2+} systems with $i < 0.5$.

For further calculations, the dissociation constant (K_d) of PAA, described by eq. (3), is also needed. As it is known that K_d is apparent and depends on i of the polyacid as well as the ionic strength of the solution and the polymer concentration, its value in every PAA/Cu^{2+} mixture was estimated with the Kern approximation[33] for $i = 0$ or the modified Hendersson–Hasselbach equation[33] for $i = 0.10$ and $i = 0.25$. Thus, applying the conservation laws and electroneutrality for the system described by eqs. (2) and (3), we can calculate the concentration of the carboxylate anions that disappeared from the solution ([COO$^-$]$_{com}$) because of the complexation with Cu^{2+} ions. From these results, the fraction of complexed acrylic acid groups (f_{PAA}) can be calculated as follows:

$$f_{PAA} = [COO^-]_{com}/C_{PAA} \qquad (8)$$

We should note that no considerations about the stoichiometry of complexation are made for the calculation of f_{PAA}. On the other hand, assuming that the stoichiometry of the complex is two carboxylate groups per Cu^{2+} ion, the fraction of complexed Cu^{2+} ions (f_{Cu}) can be calculated as follows:

$$f_{Cu} = 0.5\,[COO^-]_{com}/C_{Cu^{2+}} \qquad (9)$$

The results concerning f_{PAA} and f_{Cu} are presented in Figure 6 as a function of r_{mol} for $i = 0$, $i = 0.1$, and $i = 0.25$. As expected, f_{PAA} starts from zero at the limit of $r_{mol} = 0$, that is, in the absence of Cu^{2+} ions, and increases upon the addition of Cu^{2+} ions in the solution. In contrast, f_{Cu} starts asymptotically from unity when r_{mol} tends to zero, that is, when PAA is in large excess, and decreases sharply as r_{mol} increases. Moreover, Figure 6 nicely demonstrates that the neutralization of the polyacid favors significantly complexation: at any given value of r_{mol}, both f_{PAA} and f_{Cu} increase considerably as i increases. It is interesting to note that when Cu^{2+} is in large excess, that is, at high r_{mol}, the values of f_{PAA} are somewhat higher than 0.1 and 0.25 for $i = 0.1$ and $i = 0.25$, respectively. This indicates that when the carboxy-
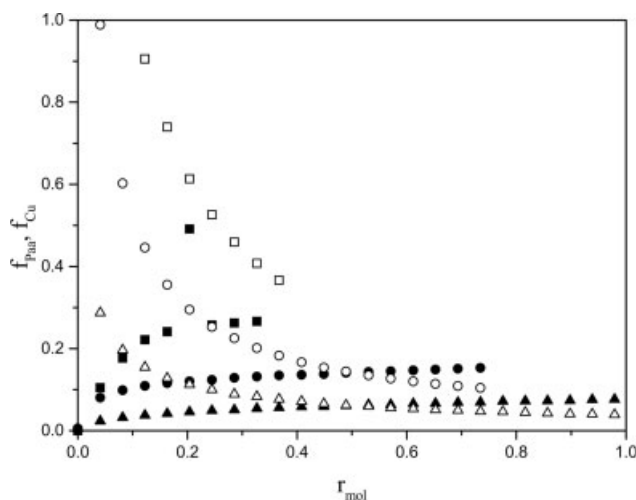
Figure 6 Variation of f_{PAA} (solid symbols) and f_{Cu} (open symbols) with r_{mol} of PAA with Cu^{2+} for ($\blacktriangle,\triangle$) $i = 0$, ($\bullet,\circ$) $i = 0.1$, and ($\blacksquare,\square$) $i = 0.25$.

late anions are preformed through neutralization, they all are practically complexed with the Cu^{2+} ions; that is, eq. (2) is to a large extent quantitative under these conditions. In fact, only when PAA is slightly neutralized or is not neutralized at all does the polymer/Cu^{2+} complexation induce considerably the dissociation of PAA, as described by eq. (3). For this reason, the deviation of f_{PAA} from the respective i value becomes smaller as i increases. Because of the limitations of the method applied, our results are limited to the region of $0 \leq i \leq 0.25$. Nevertheless, our conclusions should also hold for higher i values of the polyacid.

UV–vis spectrophotometry

As reported, the PAA/Cu^{2+} complexation has significant effects on the corresponding UV–vis spectrum. This is evident in Figure 7, in which typical UV–vis spectra of an aqueous PAA/Cu^{2+} solution are plotted in the region of 190–1100 nm upon neutralization from $i = 0$ up to $i = 1$. For comparison, we have also plotted in the same figure the spectrum of a pure aqueous $CuSO_4$ solution with the same concentration, 1 mM. As known,[41] the aqueous $CuSO_4$ solutions have a blue color, and the corresponding absorbance maximum is situated around 800 nm. However, at this very low $CuSO_4$ concentration applied in this experiment, the pure salt solution is almost transparent, and the absorbance peak in the visible region with the maximum at 810 nm is just detected. On the contrary, the peak in the UV region, situated at $\sim$ 230 nm, can be well observed. The aqueous pure PAA solution, on the other hand, is colorless, and it has just a sharp peak in the UV region situated at $\sim$ 210 nm, as shown in Figure 7 for $i = 0$

and $i = 1$. When $CuSO_4$ is mixed with PAA in water, a new strong peak, centered at 260 nm, appears. However, under the concentration conditions of our experiments, this strong peak is already saturated for $i = 0$. As a result, the visible region of the spectrum is the most interesting under these concentration conditions. As seen, because of the complexation of PAA with Cu^{2+}, the hardly visible peak at $\sim$ 810 nm can now be clearly observed but is shifted at $\sim$ 720 nm. The gradual neutralization of the polyacid, up to $i = 0.5$, leads to an important absorption enhancement, in agreement with the conclusion from potentiometry that the neutralization of the polyacid favors significantly the PAA/Cu^{2+} complexation. Nevertheless, it is observed that the further neutralization of the polyacid leads to a gradual decrease of the intensity of the peak at $\sim$ 720 nm. Such a behavior has already been mentioned for the complexation of Cu^{2+} with PAA or PMAA in water, and it has been attributed to the existence of mononuclear and binuclear PAA/Cu^{2+} complexes and to the variation of their relative proportions with i.[25]

The complexation of PAA with Cu^{2+} was investigated in detail as a function of r_{mol} and i of the polyacid under conditions identical to those of the potentiometric experiments. An attempt to correlate the spectrophotometric results with the potentiometric results is shown in Figure 8, in which the absorbance at 710 nm is presented as a function of the term $f_{cu}C_{Cu^{2+}}$ expressing the concentration of complexed Cu^{2+} species, under the considerations of validity of eq. (9), that is, assuming that the stoichiometry of the complex is two carboxylate groups per Cu^{2+} ion. Because of the limitations of the potentiometric method discussed previously, the results in Figure 8 are restricted in the neutralization region of $0 \leq i \leq$
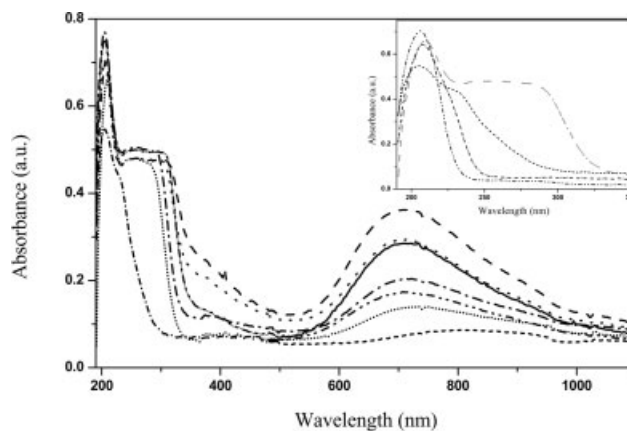
Figure 7 Typical UV–vis spectra of aqueous PAA/Cu^{2+} solutions at different values of i of PAA: ($\cdots$) $i = 0$, (– ·) $i = 0.1$, ($\cdot\cdot\cdot$) $i = 0.25$, (– – –) $i = 0.5$, (—) $i = 0.75$, and (– · ·) $i = 1$. The spectra of (- - -) a pure aqueous $CuSO_4$ solution and a pure PAA solution at ($\cdots$) $i = 0$ and ($\cdots$) $i = 1$ are also shown. C_{PAA} is 20 mM, and $C_{Cu^{2+}}$ is 1 mM.
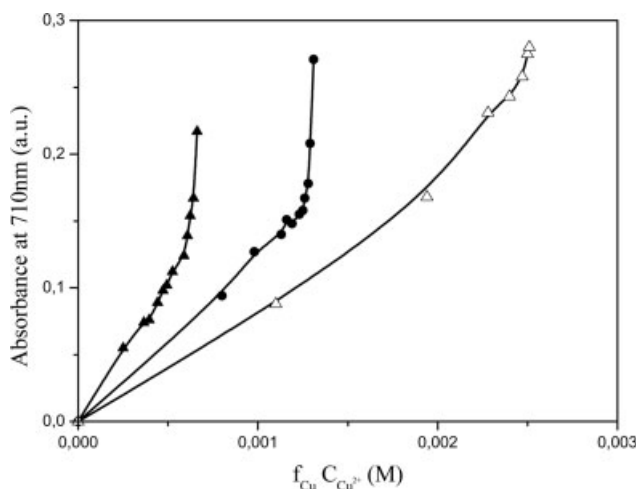
Figure 8 Absorbance at 710 nm of aqueous PAA/Cu^{2+} solutions as a function of the concentration of complexed Cu^{2+} species ($f_{cu}C_{Cu^{2+}}$) at different values of i of PAA: (▲) $i = 0$, (●) $i = 0.1$, and (△) $i = 0.25$.

0.25. We should note that within the $CuSO_4$ concentration range studied, the absorbance of a pure $CuSO_4$ solution at 710 nm is negligible, so we can consider that the absorbance detected originates strictly from the PAA/Cu^{2+} complex. As a result, if just one complexed Cu^{2+} species were present in the solution, all results should follow the same straight line, the slope of which is the extinction coefficient of the PAA/Cu^{2+} complex at 710 nm. On the contrary, it is observed that the results follow a different curve for each value of i, whereas the obtained curves are not straight. From the initial slopes of the curves, we can see that the corresponding extinction coefficients increase from ~ 40 up to ~ 80 M^{-1} cm^{-1}. These values are quite comparable to the extinction coefficients of the mononuclear complexed Cu^{2+} species ($\varepsilon_1 = 46$ M^{-1} cm^{-1}) and binuclear complexed Cu^{2+} species ($\varepsilon_2 = 255$ M^{-1} cm^{-1}), as determined by Francois et al.,[25] who combined spectrophotometric and EPR results.

In fact, we can use these values for the extinction coefficients, and we can determine fractions f_1 and f_2 of the complexed mononuclear and binuclear Cu^{2+} species, respectively, as follows:

$$f_1 + f_2 = f_{Cu} \tag{10}$$

$$A = (\varepsilon_1 f_1 + \varepsilon_2 f_2)lC_{Cu^{2+}} \tag{11}$$

where A is the absorbance detected for each sample at 710 nm and $l = 1$ cm is the path length of the quartz cuvette. The variation of fractions f_1 and f_2 with r_{mol} is presented in Figure 9 for $i = 0$, $i = 0.1$, and $i = 0.25$. The fractions of both species decrease with r_{mol}, similarly to f_{CU}. Most of the complexed

Cu^{2+} ions are present as binuclear complexes at $i = 0$, whereas the fraction of mononuclear species is much lower. In addition, the fraction of both mononuclear and binuclear complexes increases upon neutralization of the polyacid. However, the increase of fraction f_1 of the mononuclear complexes with i is much more pronounced, so f_1 becomes clearly higher than f_2 at $i = 0.25$. Although we cannot follow the variation of f_1 and f_2 for $i > 0.25$, it is very likely that the observed trend will also hold upon further neutralization. Such a behavior, corroborated with the much lower extinction coefficient of the mononuclear complexes compared to that of binuclear complexes, can explain the gradual decrease in absorbance for $i > 0.5$, as reported in Figure 7.

CONCLUSIONS

The debate on the stoichiometry and, more generally, on the reaction scheme concerning the complexation of PAA with Cu^{2+} ions is strong and dates from the very early discovery that such metal ions can form complexes with poly(carboxylic acids). Among others, the formation of intermediate 1 : 1 complexes was suggested in some early studies, being in equilibrium with the 2:1 complexes formed between Cu^{2+} and PAA. Moreover, more recent studies based on EPR data have suggested the existence of mononuclear and binuclear PAA/Cu^{2+} complexes in aqueous solutions.

In this work, we have attempted a reexamination of the complexation between Cu^{2+} and PAA in water. Thus, we have studied the PAA/Cu^{2+} complexation as a function of r_{mol} and i of the polyacid by turbidimetry, viscometry, potentiometry, and UV–vis spectro-
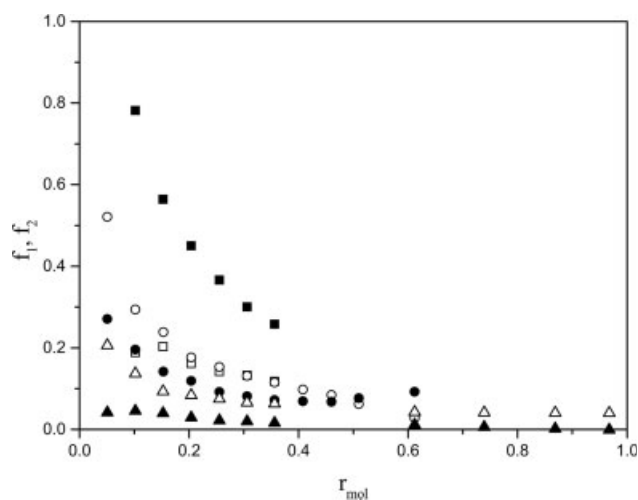
Figure 9 Variation of fractions f_1 (solid symbols) and f_2 (open symbols) of mononuclear and binuclear complexed Cu^{2+} species as a function of r_{mol} for (▲,△) $i = 0$, (●,○) $i = 0.1$, and (■,□) $i = 0.25$.

photometry. The turbidimetric study indicates that a 2:1 PAA/Cu^{2+} complex is formed, at least at high degrees of ionization. In addition, the complex that is formed is characterized by a very compact structure, as revealed by the very low η_{red} value of the PAA/Cu^{2+} mixture in water just before phase separation. From the potentiometric study, on the basis of the liberation of H^+ ions due to the PAA/Cu^{2+} complexation, it has been evidenced that reliable results may be obtained only for weakly neutralized PAA samples ($i < 0.5$). Thus, under these conditions, we were able to follow with r_{mol} and i the variation of f_{PAA} as well as the variation of f_{Cu}, considering a 2 : 1 stoichiometry. It has been shown that the neutralization of PAA enhances significantly its complexation with Cu^{2+}. Finally, the combination of the potentiometric and spectrophotometric results supports convincingly the suggestion that the complexed Cu^{2+} ions are present as mononuclear and binuclear PAA/Cu^{2+} complexes and that the ratio of the fraction of mononuclear complexes to the fraction of binuclear complexes is greatly influenced by i of PAA.

The aim of the study presented here was to better understand and increase our fundamental knowledge of the complexation between poly(carboxylic acids) and multivalent metal ions. We think that this knowledge is important to carefully design such water-soluble polymer/metal-ion complexes. These hybrid organic/inorganic nanomaterials would be promising candidates for potential uses in several fields, such as wastewater treatment, catalysis, and biological applications.

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