



Spectral characterization of PA-Cu under two polymeric forms and their complex PA-Cu

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Abstract

Metal complexes the type sodium polyacrylate and copper (PA-Cu) were prepared and studied. The characterization of the two complexes formed was performed by IR spectroscopy. IR spectroscopic investigation by comparing the spectra of the complexes with those ligands only serves to better understand the mechanism by which sodium polyacrylate fixed Cu²⁺ ions. Structural changes in the two complexes are observed. Indeed, the regressions of some bands have been observed, indicating the coordination of the COO⁻ group to the metal ion by cation exchange, according to the following reaction: $2\text{COO}^- + \text{Cu}^{2+} \rightarrow [\text{COO}]_2\text{Cu}$.

Keywords: sodium polyacrylate, PA-Cu complexes, copper, complexation of Cu²⁺ ions.

1. Introduction

Sodium polyacrylate superabsorbent polymer is a part of the compounds of polyelectrolytes ionizable groups capable of dissociating in a polar solvent (usually water) [1]. The presence of charged groups increases solubility chains and has an important role in industrial applications [2] and in biological processes [3-6]. These systems are important applications especially in agriculture [7;8], hygiene products [9], medicine [10,11], pharmaceuticals [12-15], the cosmetics industry and the paper industry or also the oil industry [16].

The wastewater treatment uses the properties of the polyelectrolyte flocculation phenomenon [17-20]. The use of superabsorbent polymers in the complexation implements a very wide range of application [21-27].

The metal cations by complexation polyelectrolytes gels have been subject of several studies [28-34]. Indeed, recovery of elements harmful to the environment, as copper complexing polymethacrylic acid gels [35], the extraction of uranium from aqueous solutions by ion exchange gels, extraction of silver by polyacrylic acid, sodium polyacrylate [36], the extraction of cobalt nitrate medium and recovering cesium, strontium and europium by polyacrylic acid gels [37], is an important application fields. As the recovery of organic matter [38].

Our work aims to determine the nature of the complexes formed by the fixing of Cu²⁺ ions on based on supports sodium polyacrylate, using spectroscopic technique such as infrared Fourier transform (FTIR).

2. Materials and methods

2.1. Used materials

The samples used in this work are superabsorbent polymers which are presents in two different forms:

- Spherical beads transparent, of non-porous surface aspect of wich diameters are varied between 2 and 3.5 mm. They introduce themselves in many colors from which the name: SEVEN COLOR CRYSTAL BOLL, reference SJQ-007, are supplied by the company Xinchang Chengtan Magic Bean & Grass Doll Artware Factory of Origin: Zhejiang, China (Mainland).

- The powder form of white fine grains is commercialized under the name: Sodium Polyacrylate Powder, under reference: Model Number SNN560-011, supplied by the company Henan CXH Purity Industrial And Trading Co., Ltd. On Origin: Henan, China (Mainland).

2.2. Analytical method

Infrared spectra were recorded by means of a Fourier transform spectrometer (FTIR) Model Vertex 70 in the spectral region between 400 and 4000 cm^{-1} .

The samples were prepared following the method of KBr discs, using the technique recommended by Cabridge (1956), potassium bromide is used for special KBr infrared spectrometry, preserved in a dry atmosphere. At first the samples were ground and sieved, and then mixed with about three hundred milligrams of bromide. The mixture is homogenized with a hydraulic press under a pressure of 10 t/cm². Potassium bromide exhibits no peak in the area operated, all the bands of vibrations recorded are specific to polymers.

2.3. Preparation of complexes

Each mass of 30 g of the two polymeric forms is placed in a beaker containing a concentration of 1000 ppm of copper nitrate solution; it is agitated until the polymers saturation into copper. The complexes formed were taken, and then dried in an oven at 50°C.

3. Results and discussion

3.1. IR spectra of the two forms of the free polymer

Figures (1) and (2) represent the infrared absorption spectra of the two forms of free polymer studied. In Tables (1), and to ease interpretation, we give the frequencies of the characteristic absorption bands corresponding to the vibrations of different molecules in the composition of both forms of PANa.

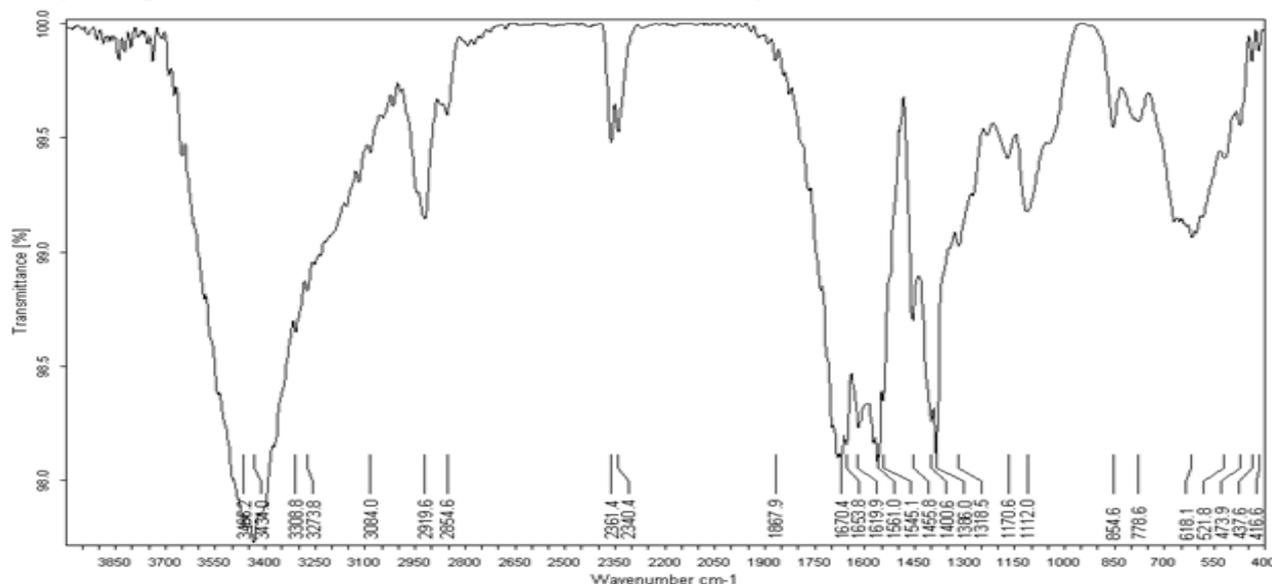


Figure 1: IR spectrum of the polymer in the form of bead.

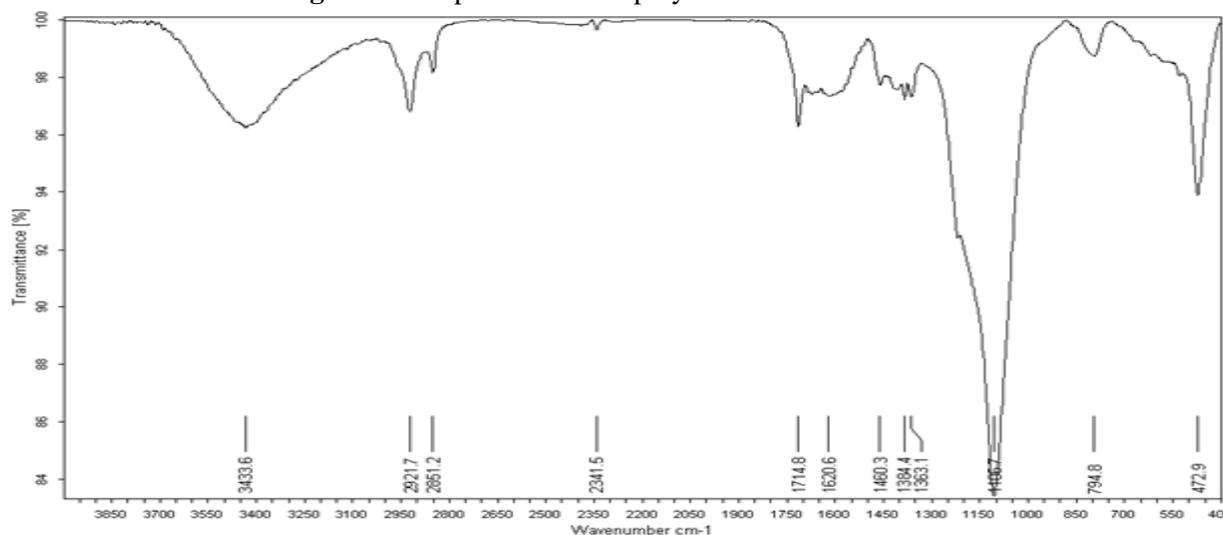


Figure 2: IR spectrum of the polymer powder.

Table 1: Characteristic absorption bands of the two polymeric forms

<i>Binding</i>	C=O	C-O	CH	CH ₂	H ₂ O
<i>Wavenumber (cm⁻¹)(bead form)</i>	1670	1112	2854.6	2919.6	3434 - 3466.2
<i>Wavenumber (cm⁻¹)(powder form)</i>	1714.8	1106.7	2851.2	2921.7	3433.6

The spectra of the free PANA ligands have five important bands features. We notice a strong band to medium located at 1670 - 1714.8 cm⁻¹ assigned to the stretching vibration of C=O group in bead form, in the powder form, respectively. The symmetric stretching vibration of C-O bond, gives a strong band to medium located in 1112 cm⁻¹ for bead form and 1106.7 cm⁻¹ for the powder form. A weak band at the 2854.6 cm⁻¹ (bead form) and 2851.2 cm⁻¹ (powder form) is characteristic stretching vibration of the CH molecule. Besides, the band attributed to the vibration of the CH₂ group is medium towards 2919.6 cm⁻¹ for the bead form and towards 2921.7 cm⁻¹ for the powder form.

The presence of water of hydration in the two polymeric forms is demonstrated by the appearance of bands in the region 3433-3466 cm⁻¹. This sample support has the drawback of being hygroscopic.

The infrared spectra of the polymers also contain other bands in the region 1386 cm⁻¹ strong in bead form and 1384.4 cm⁻¹ weak in the powder form, attributed to the stretching vibration of the group-COO⁻ [39-43].

It should be noted that the same molecule does not behave in the same way according to its environment, where the distinction found between the vibrations of the same molecules in the two forms of polymer, because the bead form is organized in comparison with the powder form.

3.2. IR spectra of the two forms of the polymer saturated copper

The object of this study is to understand the fixing mechanism of Cu²⁺ ions by sodium polyacrylate PA-Na. The study is based on the comparison of the spectra of the free polymers to those of the complexes.

PA-Cu complexes are obtained as a fine blue powder color proof to the complexation polymeric supports of made of copper. The Analysis of the obtained infrared spectra allows the characterization of two complex, figures (3) and (4).

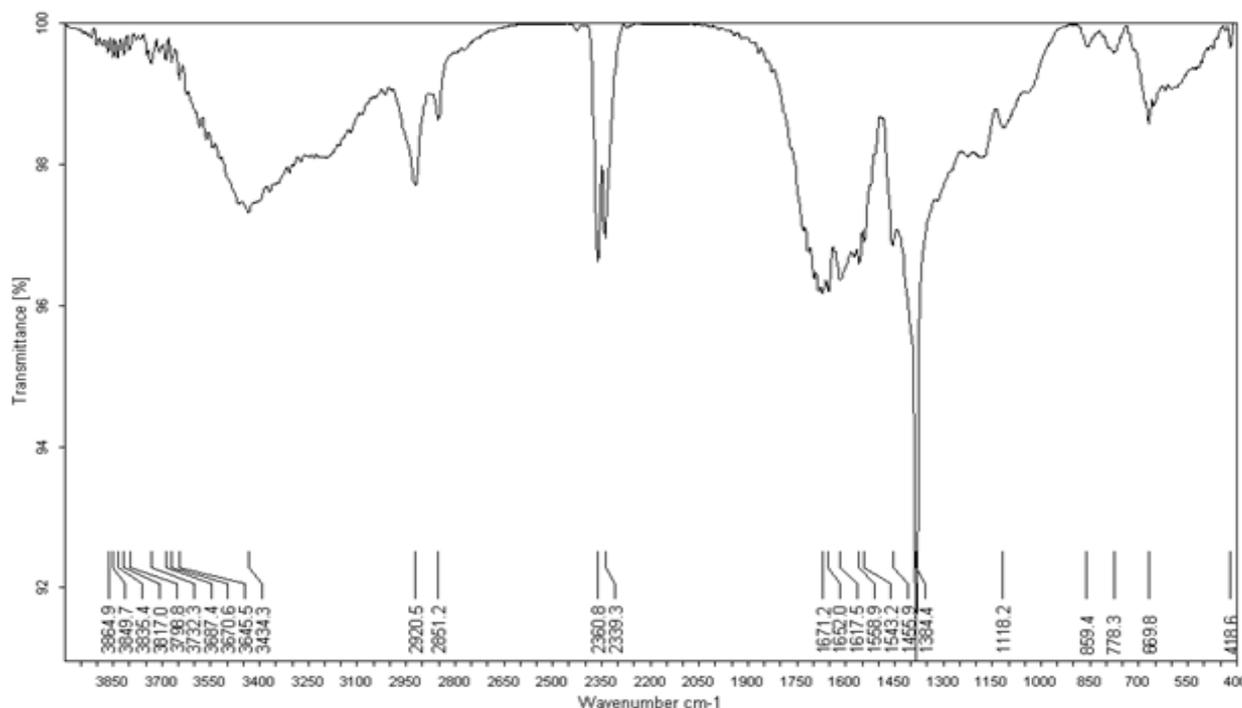


Figure 3: IR spectrum of the polymer in the form of bead saturated with Cu²⁺.

Structural changes in both complexes are observed by comparing the infrared spectra of the complexes (Figures 3 and 4) with those of the two forms of the free polymer (Figures 1 and 2). It is clear that a change in intensity involves a conformational change as suggested by the spectra. Indeed, even if the bands movements are not surprising, there by regression against certain bands.

The first change observed here concerns the vibration ν (C = O), the band is intense in the free polymers and less intense in the presence of copper, this can be attributed to the reorganization of the molecule after complexation. Lowering the frequency ν (CO) in the infrared spectra of the complexes is in agreement with the coordination of Cu^{2+} to the oxygen atom.

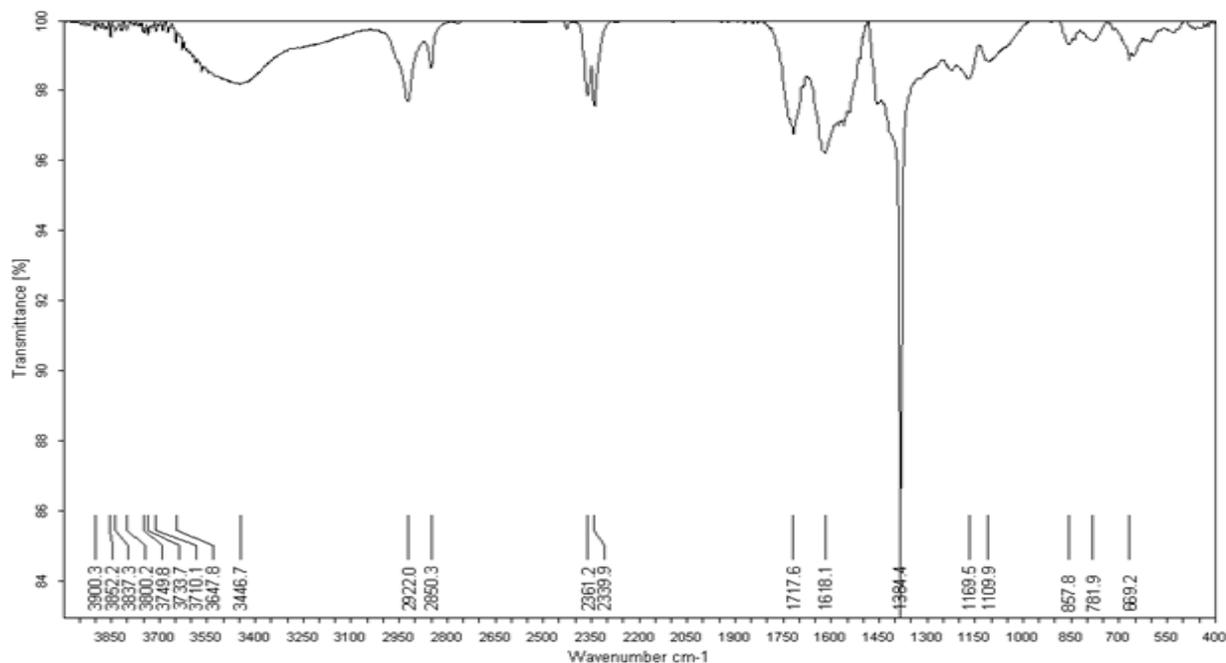


Figure 4: IR spectrum of the polymer in the form of powder saturated with Cu^{2+} .

Bands attributed to vibrations ν (CH), ν (CH_2) do not undergo the regressions in the infrared spectra of the complexes, indicating that they are not involved in coordination.

A regression is then observed in the regions 3434.3 cm^{-1} and 3446.7 cm^{-1} characteristic of the molecules of water, due to restructuring organized complex.

An increase of the band located at 1384.4 cm^{-1} in both complexes PA-Cu powder and bead, indicates the participation of the COO^- group in the formation of a new group by fixing Cu^{2+} .

The observations presented above show that the PA-Na acts as bidentate ligand [38], by coordinating with the metal center by two bonds (Figure 5), which leads to a chemical crosslinking of the polymer is therefore the repulsion of the hydration water molecules present in the polymer network, from which the regression of the band allocated to the water molecule in both complexes Cu-PA bead and PA-Cu powder.

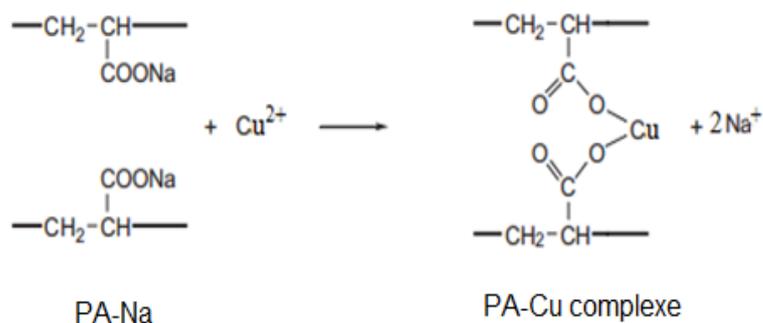


Figure 5: Reaction of chemical cross-linking between the polymer chains.

The spectral determinations have therefore allowed us to attribute to complex the following structural formula:

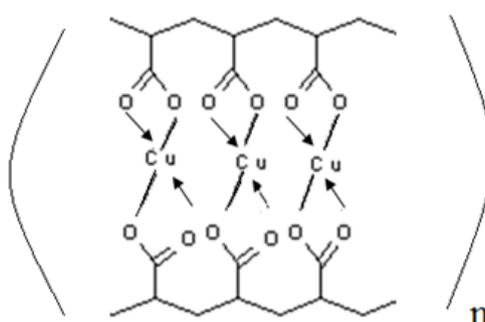


Figure 6: A complex formed between the carboxylate ions and Cu^{2+} ions.

Conclusion

The results obtained in this study provide a better understanding of the attachment mechanism of Cu^{2+} ions by the two polymeric forms of sodium polyacrylate.

The Analysis of infrared spectra was used to define the mechanism by which the fixed PANA Cu^{2+} ions, comparing infrared spectra of the complexes with those of the two forms of the free polymer. Indeed, the vibration bands of the C-H molecule and the CH_2 group undergo no change in the spectra of the complex, indicating that they are not involved in coordination. However, the regressions of the intensity of the bands attributed to molecules C=O and C-O were observed in the IR spectra of two complexes obtained, as well as the progression of the band allocated to the COO^- group. This change indicates the participation of the COO^- group in the formation of a new group by fixing the Cu^{2+} ions.

Based on the results of spectral analysis, it was concluded that the formation of complex coordination of this fact by Cu^{2+} ions to two COO^- molecule polymer promoting crosslinking of the latter, which undergoes collapse of its polymeric network which appears more pronounced at the end of the complexation. The complexation mechanism is modeled by the following reaction:



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