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ADSORPTION STUDIES OF COPPER SULFATE ON HYDROGELS OF POLY(AMIDO-AMINES)

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ABSTRACT

The interaction between the active groups of polymeric gels of poly(amido-amines) such as poly(acrylamide-diallyldiethyl ammonium chloride) "cationic gel p(AM-DADEAmCl)" and poly-(acrylamide-sodium acrylate-diallyldiethyl ammonium chloride) "amphoteric gel p(AM-AANa-DADEAmCl)" with copper sulfate have been carried out by using polymeric gels of different swelling degree and different amine percent.

The capacity toward cations decreases with increasing the amine percent and the swelling degree but the capacity toward anions such as $(\text{SO}_4)^{2-}$ decreases with increasing swelling degree and increases with increasing the amine percent. These polymeric gels interact with copper sulfate at pH value >5 to form a crosslinked structures. Spectroscopic studies showed that the mechanism of crosslinking formation is a bond formation between the active group of polymeric chains and copper sulfate. The bond formation depends on the nature of the polymer chain. It was also found that the amide groups form complexes with hydrated cations, while both carboxylate and ammonium groups interact by ion-exchange mechanisms.

INTRODUCTION

In the previous works [1-7], water-soluble polymers such as polyacrylamide (PAM), polysodium acrylate (PAANa), poly(acrylamide-sodium acrylate)

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p(AM-AANa), poly(acrylamide-diallylamine hydrochloride) p(AM-DAA HCl), poly(acrylamide-diallylethylamine hydrochloride) p(AM-DAEA HCl), poly(acrylamide-diallyldiethyl ammonium chloride) p(AM-DADEAmCl) and poly(acrylamide-sodium acrylate-diallyldiethyl ammonium chloride) p(AM-AANa-DADEAmCl) and the resin of poly(acrylamide-acrylic acid) p(AM-AA) and poly(amido-amines) were used in wastewater treatment for recovery of cations and radioactive isotopes from aqueous solutions.

It was found that there is no effect of heat and radiation on the formed floc or solid phase which is formed between ions of the solution and polymeric chains. This may be attributed to the formation of a crosslinked structure as a result of bond formation between the active groups of polymeric chains and these ions which might be present in the waste solution. The bond formation depends on the nature of the polymer.

In this work, polymeric gels such as cationic gels, poly(acrylamide-diallyldiethyl ammonium chloride) "p(AM-DADEAmCl)" and amphoteric gel of poly(acrylamide-sodium acrylate-diallyldiethyl ammonium chloride) "p(AM-AANa-DADEAmCl)" were used in treatment of wastewater of aqueous solution of copper sulfate. The mechanism of interaction of gels with copper sulfate was studied.

Materials and Experimental Technique

Polymeric gels such as poly(acrylamide-diallyldiethyl ammonium chloride) "p(AM-DADEAmCl)" and poly(acrylamide-sodium acrylate-diallyldiethyl ammonium chloride) "p(AM-AANa-DADEAmCl)" were prepared at different swelling degrees and amine percent by gamma radiation-induced polymerization of the corresponding monomers as described previously [8].

40 mg of the prepared polymeric gels were added to 20 ml of copper sulfate (0.04M), the pH of the mixture was adjusted to pH~8 by NaOH. Then the mixture was agitated, the floc was formed instantaneously. After settlement of the floc, the absorbance of the supernatant solution for Cu^{2+} was determined spectrophotometrically using a Beckman Model D-6360 spectrophotometer. The capacity of the polymeric gels was determined as described previously [6]. The formed floc was dried in vacuum oven at 50°C and was investigated by infrared spectra.

RESULTS AND DISCUSSION

The Influence of Swelling Degree and Amine Percent

The influence of swelling degree and amine percent on the capacity of cationic gel p(AM-DADEAmCl) and amphoteric gel p(AM-AANa-DADEAmCl)

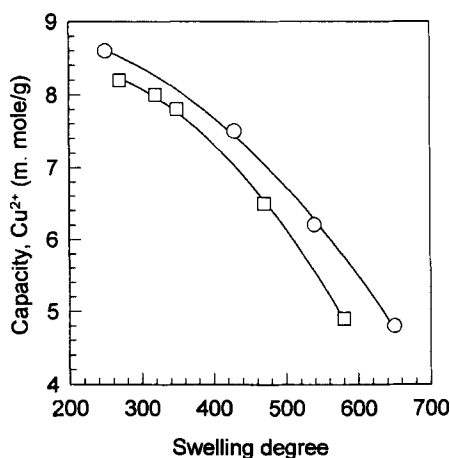


Figure 1. Influence of the swelling degree on the capacity of the resin toward Cu^{2+} p(AM-DADEAmCl) (○) p(AM-AANa-DADEAmCl) (□)

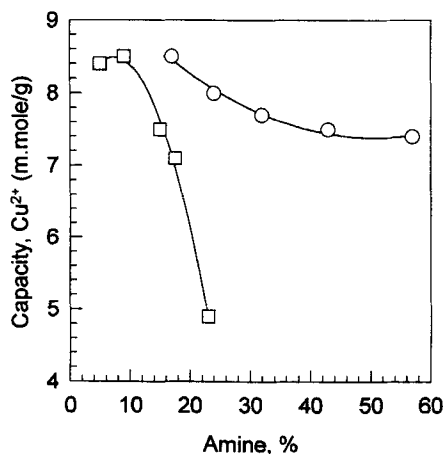


Figure 2. Influence of the amine percent on the capacity of the resin toward Cu^{2+} p(AM-DADEAmCl) (○) p(AM-AANa-DADEAmCl) (□)

toward Cu^{2+} are shown in Figures 1 and 2. Generally, it can be seen that the capacity of the gels decreases with increasing both swelling degree and amine percent. As a consequence of increasing crosslinking density, the swelling degree of the gel decreases, this will increase the probability of interaction of Cu^{2+} with the active groups, hence, the capacity of the gel increases as the swelling decreases. On the other hand, the capacity of the gels decreases with increasing the amine percent.

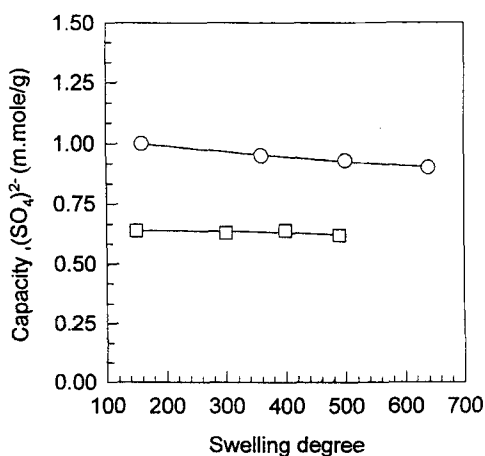


Figure 3. Influence of the swelling degree on the capacity of the resin toward $(\text{SO}_4)^{2-}$
 ○ p(AM-DADEAmCl) □ p(AM-AANa-DADEAmCl)

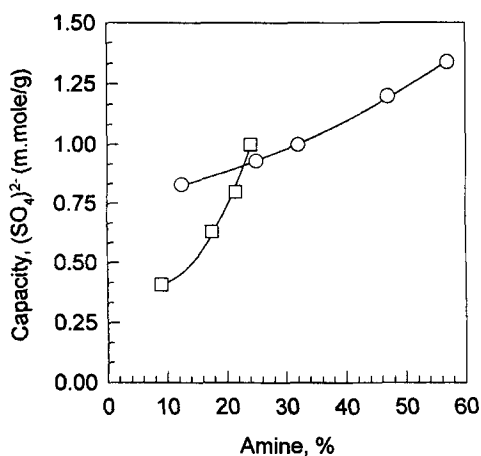


Figure 4. Influence of the amine percent on the capacity of the resin toward $(\text{SO}_4)^{2-}$
 ○ p(AM-DADEAmCl) □ p(AM-AANa-DADEAmCl)

This can be attributed to decrease the number of active amide groups and increasing the number of inactive quaternary ammonium groups (completely substituted ammonium groups). Consequently, the probability of complex formation between amide groups and Cu^{2+} decreases. This agrees with the previous finding in

treatment of $[P(\text{AM-AA-DAA})^+.\text{Cl}^-]$ and $[p(\text{AM-AA-DAEA})^+.\text{Cl}^-]$ resins with copper sulfate [7-9]. The Figures (1 and 2) also show that the capacity of cationic gel toward Cu^{2+} was relatively higher than amphoteric one. This can be explained in terms of pH. At higher pH-values, the carboxylate and ammonium groups of amphoteric gel are in the ionized form [10-12]. Accordingly, the interaction between these groups leading to decrease the affinity of these groups to interact with Cu^{2+} ions. This may elucidate the decrease in the capacity of amphoteric gel toward Cu^{2+} compared to that of cationic gel.

The influence of swelling degree and amine percent of the cationic gel $p(\text{AM-DADEAmCl})$ and amphoteric gel $p(\text{AM-AANa-DADEAmCl})$ toward $(\text{SO}_4)^{2-}$ are shown in Figures 3 and 4. It can be seen that the capacity of the cationic gel slightly decreases with increasing the swelling degree but the capacity of the amphoteric gel is almost the same at different swelling degree. This can be attributed to the anion-exchange occur at Cl^- which is coordinated with the quaternary ammonium group. Consequently, there is no effect of the nature of the polymeric chain on the capacity of the gels toward $(\text{SO}_4)^{2-}$. On the other hand, the capacity of the gels toward $(\text{SO}_4)^{2-}$ increases with increasing the amine percent. This can be attributed to increasing the percent of chloride ion which increases the probability of anion-exchange between Cl^- and $(\text{SO}_4)^{2-}$. This agrees with the previous finding in the treatment of $[p(\text{AM-AA-DAA})^+ \text{Cl}^-]$ and $[p(\text{AM-AA-DAEA})^+ \text{Cl}^-]$ with copper sulfate [7, 9].

Mechanism of the Interaction Between the Polymeric Gels and the Ions in Aqueous Solution

The infrared spectral data of $p(\text{AM-DADEAmCl})$, and $p(\text{AM-AANa-DADEAmCl})$ of the formed floc produced from the interaction of polymeric gels with copper sulfate are summarized in Table 1. The data in Table 1 shows that the shift in the adsorption bands of $>\text{NH}$ stret. of the amide group to a lower wavenumber may be due to hydrogen bond formation between the amide groups in the polymer chains (plurimolecular aggregates in acrylamide and acrylic acid polymers) [13-16]. The same shift in the absorption bands characteristic for $-\text{OH}$ group to a lower wavenumber, is due to the presence of water molecules which is coordinated with the polymeric chains or ions of copper sulfate. The spectra show also that the absorption bands characteristic for $-\text{CH}_2$ group of the repeated methylene group along the polymeric chains and the presence of $-\text{CH}_3$ bend. in the spectrum of $p(\text{AM-DADEAmCl})$ and $p(\text{AM-AANa-DADEAmCl})$ is due to the presence of the ethyl group in the quaternary ammonium group.

TABLE 1. IR Spectral Data of Polymeric Gels with Copper Sulfate

Absorption bands of original groups, cm^{-1}	Experimental Absorption bands, cm^{-1}	
	p(AM-DADEAmCl)	p(AM-AANa-DADEAmCl)
<u>Amide:</u> <u>amide II:</u> Free >NH stret., 3500, 3400 bonded >NH stret., 3350, 3180 >NH bend., 1620-1590 <u>amide I:</u> >C=O stret., 1650 <u>Aliphatic:</u> CH ₂ Stret. 2960-2870 CH ₃ bend, 1380, 1460-1420 CH ₂ bend., 1300-1100, 1470-1400, 790-720	 3415 1616, 1576 1646 1472, 1457 1339,1489,1472,1418	 3439 1558, 1540 1653 1472,1457 1472,1418
<u>Hydroxyl:</u> Free -OH Stret., 3700-3650 Bonded -OH Stret., 3400-3200	3710, 3688, 3669, 3648 & 3415	----- 3439
<u>Carboxylic:</u> -COOH Stret., 1725-1700 -COOH bend.,1420, 1300-1200 & 920 Free -OH Stret., 3550 Bonded -OH Stret., 3300-2500		

In the spectrum of p(AM-AANa-DADEAmCl), the appearance of the absorption bands characteristic for -COO-, >C=O stret. of the ester group and -COOH group is due to the interaction of -COONa group with ions.

The data in Table 1 shows that the appearance of the adsorption bands characteristic for ionic sulfate for all polymers and the appearance of the char-

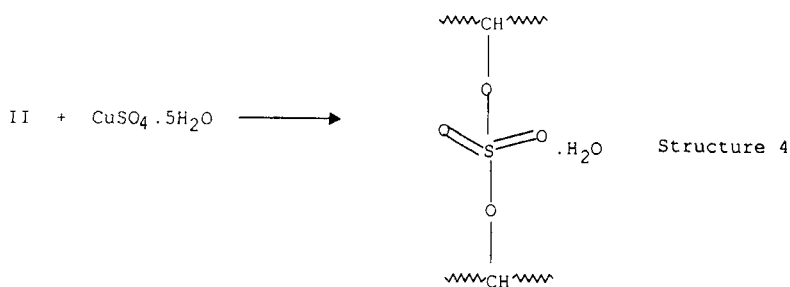
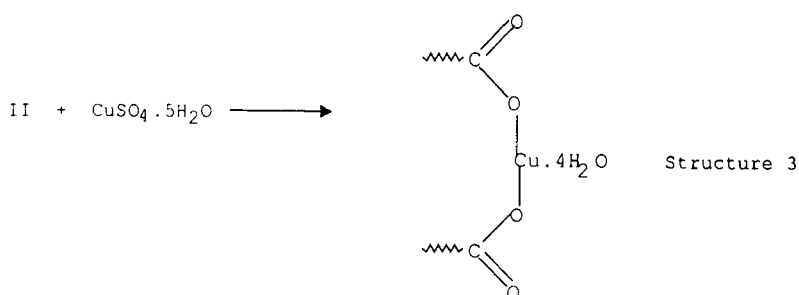
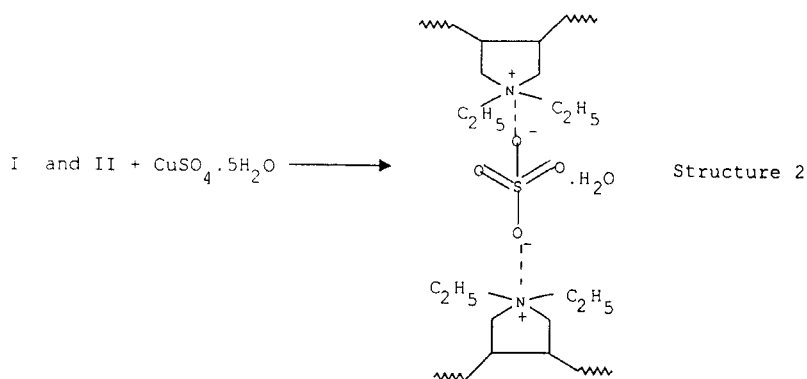
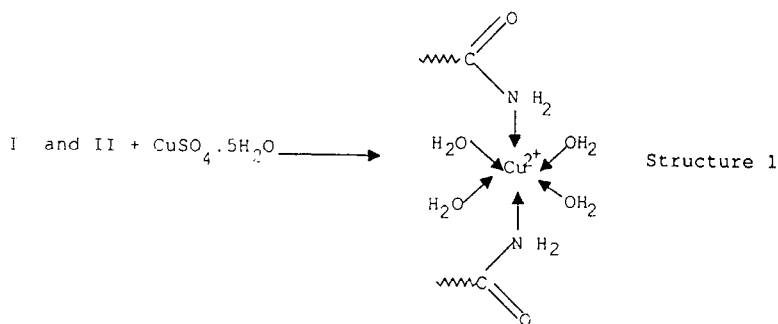
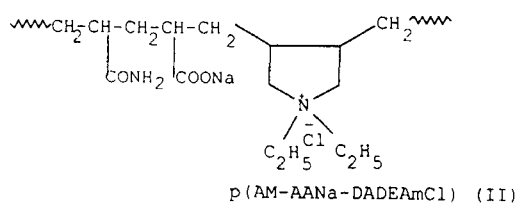
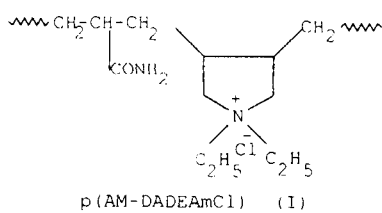
TABLE 1. Continued

<u>Carboxylate:</u> -COO ⁻ Stret., 1610-1550 -COO ⁻ bend, 1400-1300		1558 1418
<u>Ester:</u> >C=O Stret 1750-1735 >C-O Stret., 1300-1100		1771, 1731
<u>Amine:</u> C-N Stret., 1410 >NH Stret., 3000-2700 & 2700-2500	1418	1418
<u>Sulfate:</u> Ionic, 1140-1170, 480-400 Covalent, 1450-1350, 1230-1150 and 650-550	1118, 482, 458	1118, 480 1450, 1418, 668, 60 0
<u>Chelate Compounds:</u> 3200-2400	2360	2361

acteristic for the covalent sulfate for p(AM-AANa-DAEAmCl) only may be due to anion-exchange between-COONa and (SO₄)²⁻. On the other hand, the appearance of the band characteristic for the chelate compound due to the formation of Cu²⁺ with -CONH₂ group. Consequently, these absorption bands can arrive to the conclusion that:

p(AM-DADEAmCl) Interacts with Copper Sulfate According to the Following Mechanisms:

(a) Amide group forms complexes with Cu²⁺ by formation of the coordinated bonds between the nitrogen atom of the amide group and Cu²⁺ as shown in Structure (1). This is in agreement with the previous finding [1-7] in interaction of water-soluble polyacrylamide, acrylamide copolymers and acrylamide-acrylic acid resin with Cu²⁺ and the finding of other authors [17-21] in interaction of poly(4-vinylpyridine) (PVP), polyethyleneimine (PEI), polyvinylimiazole (PVI), poly(ethylenepyridine-2-aldimine), polyvinylamine poly(amido-amine), poly(N,N,N',-



N'-tetramethylethan-1,2-diamine), (4-(3,4-dihydroxyphenyl)-L-alanine) and poly-dioximes with cations such as Cu, Ni, Cd, Fe, Cr and Hg and polyacrylamide with metal.

(b) Ammonium groups interact with copper sulfate through anion-exchange between Cl^- and $(\text{SO}_4)^{2-}$ as shown in Structure 2. This is in agreement with the previous finding in interaction of poly(amido-amines) with copper sulfate [1-7] and finding of other authors [14,15].

p(AM-AANa-DADEAmCl) Interacts with Copper Sulfate According to the Following Mechanisms:

(a) Amide and ammonium groups interact with copper sulfate as mentioned above for p(AM-DADEAmCl) as shown in Structures 1 and 2, respectively.

(b) Carboxylate group interacts with copper sulfate by cation-exchange between Na^+ and Cu^{2+} and anion-exchange between $-\text{COO}-$ and $(\text{SO}_4)^{2-}$ as shown in Structures 3 and 4. This is in agreement with the previous finding in interaction of anionic and amphoteric polymers with copper sulfate [1, 3-7] and finding of other authors [11, 22, 23]. Consequently, p(AM-DADEAmCl) and p(AM-AANa-DADEAmCl) gels interact with copper sulfate in aqueous solution as the corresponding water-soluble polymers as mentioned in the previous work [5]. Accordingly, acrylamide copolymer gels behave as water-soluble polymers and polymeric resins.

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