Synthesis and behaviour of two copolymers of poly[acrylamide-*co*-(*N*-(hydroxymethyl)acrylamide)] in ultrafiltration experiments

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SUMMARY

The synthesis of two copolymers of poly[acrylamide-*co*-(*N*-(hydroxymethyl)acrylamide)] is described. Polymer analogous reactions have been used as well as direct radical polymerization. The two copolymers have been fractionated and ultrafiltered in the presence of Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and an excess of Na^+. It has been found that Na^+ ions do not interact with the copolymers. The effect of the different composition of the copolymers is noted in the study of Cu^{2+} and Pb^{2+}, but there is no difference in the retention profiles obtained for the rest of the metal ions.

INTRODUCTION

The synthesis of polymers by polymer analogous reactions has been extensively used (1-7). As a consequence of the properties associated with the polymer, the polymer analogous syntheses result sometimes in unexpected final products or in particular reaction mechanisms. Examples of this are the dehydrohalogenation of poly(vinyl chloride) or the assisted hydrolysis of poly(vinyl acetate) (1). This technique could be advantageous to obtain polymers with a variety of functional groups. In this context, polymers with chelating or ion exchange groups have been employed for the removal of metal ions from diluted solutions (5-7). Investigations that imply the use of polymers in solution in metal separation science are of great importance nowadays. A number of techniques have been described to recover metals from water using water-soluble polymers (8-10). The ultrafiltration technique has been efficiently used to selectively concentrate metal ions that form soluble complexes with water-soluble polymers of high molecular weight, and to selectively separate traces of metal ions from diluted solutions (10-13). Many water-soluble polymers have been synthesized by both direct polymerization and polymer analogous reactions. For ultrafiltration experiments, the polymers are previously fractionated by the same method and the highest molecular weight fractions are used. Metal ions with high interaction rates with the polymer stay retained by the polymer, which is not able to pass through the ultrafiltration membrane, while other ions are eluted through the membrane. When solutions of mixtures of metal ions are put in contact with the polymer solution, a profile for the retention of the different metal ions by the polymer during filtration with pure water can be obtained. Some previous theoretical work has been made by the authors in order to get information from these retention profiles (14). Under some

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assumptions, it is possible to quantify the concentration of ions both bound to the polymer and free in the solution in every instant.

In this work, two different copolymers of poly[acrylamide-*co*-(*N*-(hydroxymethyl)acrylamide)] (AAm-HMAAm) have been synthesized, and their behaviour in ultrafiltration experiments in the presence of Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and an excess of Na^{+} is discussed.

EXPERIMENTAL PART

Synthesis of AAm-HMAAm-a
Commercially available *N*-(hydroxymethyl)acrylamide (HMAAm) (Sigma) (47.7 mmol) was diluted with bidistilled water to 80 ml. Ammonium persulfate (11 mg, 0.05 mmol) was added and the solution deoxygenated under a N_2 stream. The solution is heated by 8 hours at 90°C. The white gel obtained is filtered and the filtrate is ultrafiltered over an ultrafiltration membrane of a cut off of 10.000 g mol^{-1} (Filtron). A water-soluble polymer is isolated by lyophilization of the ultrafiltration cell solution (1.9 mmol, 4 % yield of soluble fraction). It contains a 76 % of acrylamide units and a 24 % of *N*-(hydroxymethyl)acrylamide units as shown by ^{1}H-NMR.

Synthesis of AAm-HMAAm-b
Poly(acrylamide) (1005 mg, 14.14 mmol of amide groups), whose synthesis has been referred elsewhere (15), was dissolved in 140 ml bidistilled water and the pH was adjusted to 12 with the aid of Na_2CO_3. Formaldehyde (1.6 ml of 36 % wt. water solution, 20.93 mmol) was added and the solution was heated for 3 h at 50°C. The solution is neutralized and ultrafiltered over a membrane of an exclusion rating of 10.000 g mol^{-1} (Filtron). After lyophilization of the ultrafiltered solution, a water soluble polymer is obtained (7.3 mmol, 51 % yield) that contains 62 % of acrylamide units and 38 % of *N*-(hydroxymethyl)acrylamide units as shown by ^{1}H-NMR.

^{1}H-NMR (D_2O) δ (ppm) 1.70 and 2.18 (vinyl protons), 4.72 (CH_2 lateral chain).
^{13}C-NMR (D_2O) δ (ppm) 35.61 (CH_2 main chain), 43.11 (CH main chain), 63.57 (CH_2 lateral chain), 178.12 and 180.20 (C=O amides).
FT-IR (KBr) wave numbers (cm^{-1}) 3430 (OH and NH), 1670 (C=O amide), 1030 (C-O).

Equipment
The unit used for retention studies consisted of a filtration cell with a magnetic stirrer, a membrane with an exclusion rating of 3,000, 10,000, or 100,000 g / mol (Filtron), a reservoir, a selector, and a pressure source. Metal ion concentrations were measured by atomic absorption on a Perkin Elmer 3100 spectrometer. The pH was controlled on a pH meter H. Jürgens & Co. The NMR spectra were obtained in a Bruker AC 250 P spectrometer. FT-IR spectra were obtained in a Nicolet Magna IR-550 spectrometer.

Procedure for ultrafiltration experiments
One experiment has been done for each copolymer. The ultrafiltered copolymers (1.0 mmol of total amide groups) and $NaNO_3$ (480 mg, 5.6 mmol) were dissolved in bidistilled water, and

$Cu(NO_3)_2$, $Cd(NO_3)_2$, $Co(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$ were added. The exact quantities are shown in Table 1. The solution was brought to 20 ml of total volume respectively, and the pH was adjusted. The pH of the cell solutions and the reservoir containing only water were adjusted to pH 5 with a pH meter H. Jürgens & Co. The ultrafiltration runs were carried out over a membrane with an exclusion rating of 3,000 g mol^{-1} under a total pressure of 3 Bar, keeping constant the total volume in the cell by creating a continuous flux of liquid through the cell solution from the reservoir. Filtration fractions were collected and the metal concentrations were analyzed by atomic absorption on a Perkin Elmer 3100 spectrometer.

Table 1: Initial metal ion amounts

copolymer	Initial metal ion amounts (μmol)					
	Cu^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
AAm-HMAAm-a	44.9	53.8	65.2	56.3	47.5	43.6
AAm-HMAAm-b	45.2	48.9	57.2	53.7	44.2	45.3

RESULTS AND DISCUSSION

Determination of the copolymer compositions

The two copolymers synthesized are described by the general formula **1**. The ^{1}H-NMR and ^{13}C-NMR spectra of the copolymers are described in the experimental part. The signal at 4.72 ppm corresponds to the metylene group of the hydroxymethyl substituent. The determination of the copolymer composition has been made comparing the integration area corresponding to this peak with the integration area of the vinyl protons at 1.70 and 2.18 ppm. Thus, AAm-HMAAm-a contains 76 % of acrylamide units and a 24 % of *N*-(hydroxymethyl)acrylamide units, while AAm-HMAAm-b contains 62 % of acrylamide units and 38 % of *N*-(hydroxymethyl)acrylamide units.
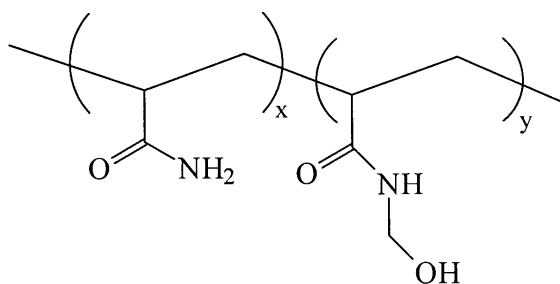
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Ultrafiltration results

Figure 1 shows the ultrafiltration results corresponding to all the metal ions and both copolymers. In this figure, retention (R_Z) is plotted versus the filtration factor (*F*). The retention is defined for any species of metal ions of valence *Z* as the fraction per unit of metal ion remaining in the cell. The filtration factor is defined as the volume ratio of the filtrate, V^f, versus the volume in the cell, V^c. It is noted that no Na^+ is retained by the copolymers at *F*

values over 6. The retention profiles found for the rest of the metal ions are very similar from one polymer to the other because they have similar structures. In the case of Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, they are coincident. An explanation of this fact could be the participation on the interaction mechanism of the amide groups, whose concentration is constant in both copolymers. However it has been shown that poly(acrylamide) (15) itself does not interact with these metal ions. By contrary, the retention profiles of Cu^{2+} and Pb^{2+} change from one copolymer to the other. The retention profiles corresponding to the copolymer with higher content of hydroxy groups show higher values of the retention for a definite F value.

The theoretical work made previously by the authors (14) allow the calculation of the concentration of ions both bound to the polymer and free in the solution in every instant. To do this, the retention functions, defined as the functions whose plot fits the best with the experimental retention profiles, are searched. The retention functions corresponding to the retention profiles shown in Figure 1 are listed in Table 2.

Table 2: Expressions of the Retention Functions

Divalent Metal Ion	Copolymer	Retention Function	u_Z	v_Z	k_Z
Cu^{2+}	AAm-HMAAm-a	$R = 0.97 + 0.03 \exp(-0.5\,F)$	0.71	0.29	0.5
Cu^{2+}	AAm-HMAAm-b	$R = 0.71 + 0.38 \exp(-0.5\,F)$	0.97	0.03	0.5
Cd^{2+}	AAm-HMAAm-a	$R = 0.56 + 0.44 \exp(-0.7\,F)$	0.56	0.44	0.7
Cd^{2+}	AAm-HMAAm-b	$R = 0.56 + 0.44 \exp(-0.7\,F)$	0.56	0.44	0.7
Co^{2+}	AAm-HMAAm-a	$R = 0.70 + 0.30 \exp(-0.8\,F)$	0.70	0.30	0.8
Co^{2+}	AAm-HMAAm-b	$R = 0.70 + 0.30 \exp(-0.8\,F)$	0.70	0.30	0.8
Pb^{2+}	AAm-HMAAm-a	$R = 0.23 + 0.77 \exp(-0.7\,F)$	0.23	0.77	0.7
Pb^{2+}	AAm-HMAAm-b	$R = 0.74 + 0.26 \exp(-0.5\,F)$	0.74	0.26	0.5
Ni^{2+}	AAm-HMAAm-a	$R = 0.72 + 0.28 \exp(-0.8\,F)$	0.72	0.28	0.8
Ni^{2+}	AAm-HMAAm-b	$R = 0.72 + 0.28 \exp(-0.8\,F)$	0.72	0.28	0.8
Na^{+}	AAm-HMAAm-a	$R = \exp(-F)$	0	1	1
Na^{+}	AAm-HMAAm-b	$R = \exp(-F)$	0	1	1
Zn^{2+}	AAm-HMAAm-a	$R = 0.69 + 0.31 \exp(-0.8\,F)$	0.69	0.31	0.8
Zn^{2+}	AAm-HMAAm-b	$R = 0.69 + 0.31 \exp(-0.8\,F)$	0.69	0.31	0.8

They are functions of the type:

$$R_Z = u_Z + v_Z \exp(-k_Z F) \qquad\qquad (1)$$

where the u_Z, v_Z, and k_Z are experimental parameters called the *retention parameters*. The values of the molarity of metal ion not bound to the polymer chain (C_Z), the concentration of metal ions bound to the polymer (c_Z^b) and the dissociation constant related to the equilibrium between these two variables (K_Z^{diss}) defined as C_Z / c_Z^b, can be calculated with the following equations:

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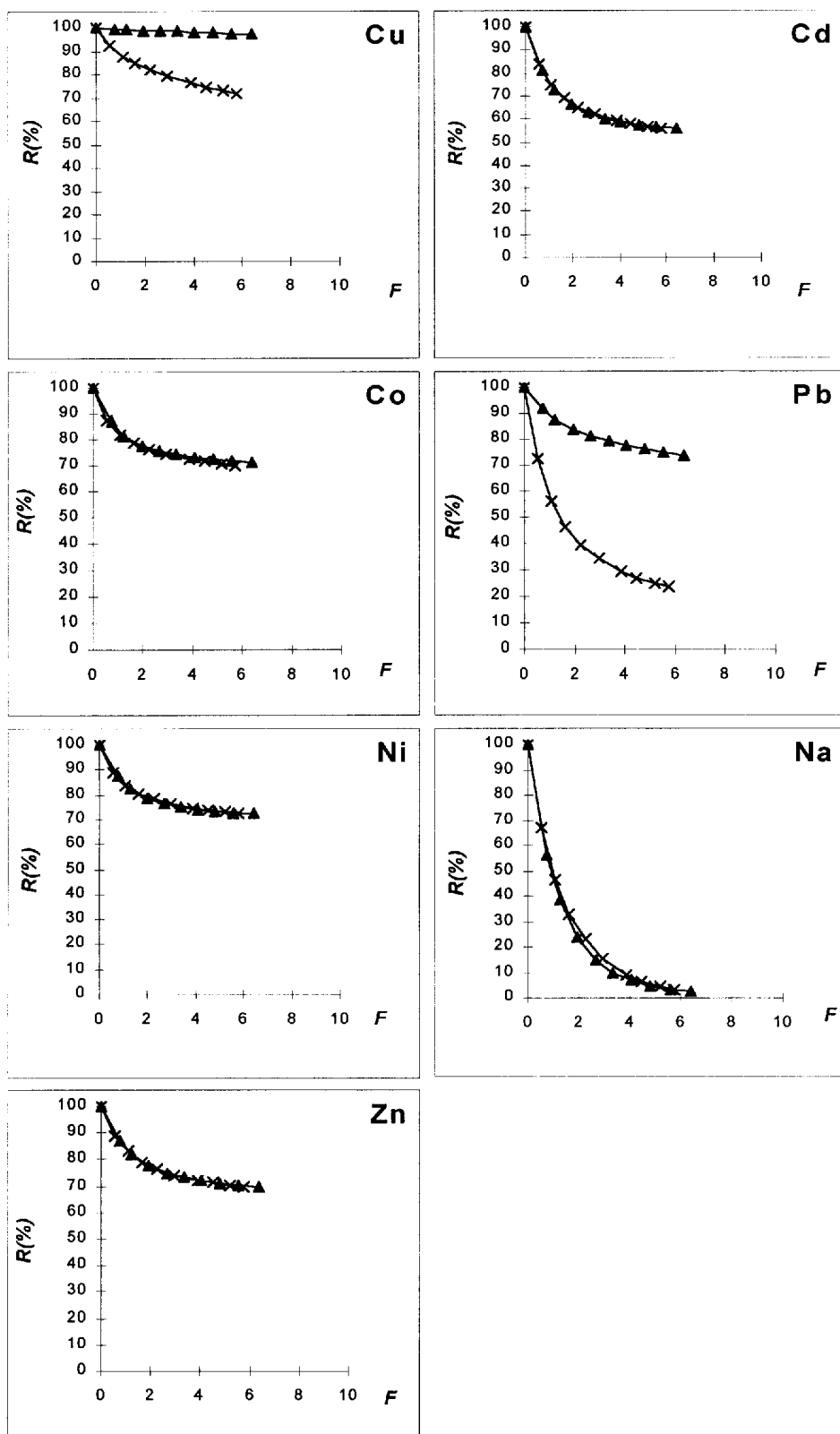
Figure 1. Retention profiles for the metal ions Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and an excess of Na^+. ($\times$) AAm-HMAAm-a; ($\blacktriangle$) AAm-HMAAm-b

$$c_Z^b(F) = \frac{R_Z c_Z^{init}}{\left[1 + K_Z^{diss}\right]} = \frac{c_Z^{init}}{k_Z^m}\left[k_Z^m u_Z + \left(k_Z^m - k_Z\right)v_Z \exp(-k_Z F)\right] \qquad (2)$$

$$C_Z(F) = \frac{R_Z c_Z^{init} K_Z^{diss}}{\left[1 + K_Z^{diss}\right]} = \frac{c_Z^{init}}{k_Z^m} k_Z v_Z \exp(-k_Z F) \qquad (3)$$

$$K_Z^{diss}(F) = \frac{1}{\dfrac{k_Z^m}{k_Z} + \dfrac{u_Z k_Z^m}{v_Z k_Z \exp(-k_Z F)} - 1} \qquad (4)$$

where k_Z^m is related to the influence of the ultrafiltration membrane on the retention and is assumed to equal 1 for all the metal ions studied, and c_Z^{init} is the initial concentration of each metal ion.

From the analysis of the retention functions it can be inferred that Na^+ does not interact with the polymers since the value of K_1^{diss} is infinite as $u_1 = 0$ and $v_1 = k_1 = 1$. The physical meaning of k_Z is the absolute value of the variation of the logarithm of K_Z^{diss} with F when F is sufficiently large. The value of K_Z^{diss} is dependent on the variables of the equilibrium such as the ionic strength. It is possible to think that the value of k_Z is inherent to the polymer, although the influence of the different variables on this value is under investigation. In this sense, the two polymers under study have different values of k_Z for Pb^{2+}.

CONCLUSIONS

The synthesis of two copolymers of poly[acrylamide-*co*-(*N*-(hydroxymethyl)acrylamide)] has been described. Polymer analogous reactions have been used as well as direct radical polymerization. The two copolymers have been fractionated and ultrafiltered in the presence of Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, and an excess of Na^+. After a theoretical analysis of the retention profiles obtained it has been found that Na^+ ions do not interact with the copolymers. The effect of the different composition of the copolymers is noted in the cases of Cu^{2+} and Pb^{2+}. There is no difference, however, in the retention profiles obtained for the rest of the metal ions.

ACKNOWLEDGMENTS

References

1. E. M. Fettes, *Chemical Reactions of Polymers*, Interscience, 1964, New York.
2. J.H. Barnes, G.F. Esslemont, *Makromol. Chem*. **177**, 307 (1976)
3. L. McCormick, C.E. Hoyle, M.D. Clark, *Polymer* **33**, 243 (1992)
4. M. Valiente, X. Ribas, M. Hojjatie, H. Freiser, *Iranian J. Polym. Sci. Tech*. **3**, 105 (1994)
5. E. Bayer, K. Geckeler, K. Weingärtner, *Makromol. Chem.* **181**, 585 (1980)
6. K. Geckeler; E. Bayer; P.A. Grathwohl, *Angew. Makromol. Chem.* **113**, 141 (1983)
7. K. Geckeler, R. Zhou, *Macromol. Rapid Commun.* **15**, 55 (1994)
8. T. Tomida, T. Ikawa, S. Masuda, *J Chem: Eng. Jpn.* **26**, 575 (1993)
9. T. Tomida, T. Inoue, K. Tsuchiya, S. Masuda, *Ind. Eng. Chem. Res.* **33**, 904 (1994)
10. K. Geckeler, G. Lange, H. Eberhardt, E. Bayer, *Pure Appl. Chem.* **52**, 1883 (1980)
11. B.L. Rivas, K.E. Geckeler, *Adv. Polym. Sci.* **102**, 171 (1992)
12. Y. Uludag, H.O. Özbelge, L. Yilmaz, *J. Membrane Sci.* **129**, 93 (1997)
13. B.L. Rivas, I. Moreno-Villoslada, *J. Appl. Polym. Sci.* **69**, 817 (1998)
14. B.L. Rivas, I. Moreno-Villoslada, *J. Phys. Chem. B* **102**, 6994 (1998)
15. B.L. Rivas, I. Moreno-Villoslada, *Macromol. Chem. Phys.* **199**, 1153 (1998)