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Effect of the Degree of Hydrolysis of Polyacrylamide on Its Interactions with Poly(ethylene oxide) and Poly(vinylpyrrolidone)

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ABSTRACT: Intermolecular interactions between polyacrylamides hydrolyzed to varying degrees and poly(vinylpyrrolidone) or poly(ethylene oxide) are investigated by using fluorescence spectroscopy. At low degrees of hydrolysis, interactions between hydrolyzed polyacrylamide and poly(vinylpyrrolidone) are weak, but at higher degrees of hydrolysis, the interactions are strong and similar to that in the presence of poly(acrylic acid). At higher degrees of hydrolysis and low pH values, interpolymer complexation between the carboxylic acid group of the hydrolyzed polyacrylamide and the poly(vinylpyrrolidone) is predominant over intramolecular complexation between the acid and the amide groups. There are no interactions between hydrolyzed polyacrylamide and poly(ethylene oxide) over the entire range of hydrolysis studied.

Introduction

The use of natural and synthetic polymers is gaining prominence as a viable tool in several mineral processing operations such as flocculation and selective flocculation. Polyacrylamides, PAM, are particularly popular because of their low cost and the ability of acrylamide to copolymerize with other monomers into flocculant-grade polymers. Anionic polyacrylamides with 20–30% ionized groups are the most common of the high molecular weight polymers used in mining and other industries.[1] In recent years, there have been several experimental as well as theoretical studies on the adsorption of PAM and hydrolyzed polyacrylamide (HPAM) on oxide minerals.[2-6] The interactions of PAM with other synthetic water-soluble polymers such as poly(acrylic acid) (PAA) and poly(vinylpyrrolidone) (PVP) have also been studied.[7,8] In this paper, we have investigated the effect of the hydrolysis of polyacrylamide on its interactions with poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) using fluorescence spectroscopy. Fluorescence methods based on the properties of fluorophore-labeled polymers have proven to be more informative and sensitive than the conventional techniques of viscometry and potentiometry.[9,10]

Experimental Section

Pyrene-labeled polyacrylamide was synthesized in the laboratory. Mixtures of acrylamide and the pyrene source, 2-[[4-(1-pyrenyl)butanoyl]amino]propenoic acid, were copolymerized by using precipitation polymerization in DMF at 65 °C using azobis(isobutyronitrile) as initiator. The pyrene source was synthesized as per the method of Turro and Arora.[11] The concentration of acrylamide was 0.6 M, and that of the pyrene-containing monomer was 0.008 M. The initiator concentration was 0.4% based on the total monomer concentration. Pyrene-labeled hydrolyzed polyacrylamide was obtained by controlled hydrolysis of labeled polyacrylamide.[12] The extent of hydrolysis was determined by potentiometric titration.[13] The pyrene content of the polymers was estimated from UV absorption spectra.[11] Synthesis of pyrene-labeled poly(acrylic acid) was carried out also according to the method of Turro and Arora.[11] Intrinsic viscosities were obtained from linear η_{sp}/C vs C plots and used to determine molecular weights by using Mark–Houwink constants available in the literature.[12]

Poly(ethylene oxide) and poly(vinylpyrrolidone) were used as received. Characteristics of all the polymers used are presented in Table I. Fisher Scientific A.C.S. reagent-grade hydrochloric acid and sodium hydroxide were used for pH adjustments.

All samples were prepared in triply distilled water and at a salt concentration of 0.005 M sodium chloride. The concentration of polymers in all fluorescence experiments was maintained at 10 ppm.

Fluorescence spectra were recorded on a Photon Technology Inc. (PTI) LS-100 spectrophotometer. The excitation wavelength was 335 nm. Monomer emission was monitored at 376 nm and the excimer emission at approximately 480 nm. The sample cells were of 10-mm path length, and suitable correction was applied to avoid interference from the lamp.

The fluorescence experiments were carried out a temperature of 23 ± 2 °C.

Results and Discussion

The excimer-forming capability of pyrene, attached randomly along the hydrolyzed polyacrylamide chain, was used as an indicator of polymer rigidity and/or conformation. An excimer (or excited dimer) is formed when an excited pyrene group interacts with a ground-state pyrene group when they approach each other within 0.4–0.5 nm. The excimer is a distinct photochemical dimer that exists only in the excited state and has its own characteristic fluorescence. It is observed as a broad spectral band centered around 480 nm that is red-shifted with respect to the monomer emission (370–400 nm).[14] Ground-state aggregation of pyrene groups due to hydrophobic attraction is known to be insignificant in samples with very low pyrene contents.[10] In dilute solutions the intramolecular excimer formation between an excited-state pyrene and a ground-state pyrene is mainly through a diffusion-controlled cyclization process.[15] Since the pyrene molecule is covalently attached to the polymer chain, the distance

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Table I
Characteristics of Polymer Samples Used in the Study

polymer sample	mol wt, $\times 10^{-4}$	pyrene content wt %	pyrene content mol %	% hydrolysis (EH), mol %	supplier
hydrolyzed polyacrylamide, HPAM-1	5.75[a]	0.83	0.3	8.0	*c*
hydrolyzed polyacrylamide, HPAM-2	7.62[a]	0.81	0.29	22.6	*c*
hydrolyzed polyacrylamide, HPAM-3	6.58[a]	0.70	0.25	37.2	*c*
hydrolyzed polyacrylamide, HPAM-4	6.48[a]	0.70	0.25	42.8	*c*
pyrene-labeled polyacrylamide, PAM	7.32[a]	3.67	1.31		*c*
pyrene-labeled poly(acrylic acid), PAA	4.48[a]	1.35	0.48		*c*
poly(ethylene oxide), PEO	86.5[b]				*d*
poly(vinylpyrrolidone), PVP	36.0[b]				*e*

[a] M_v. [b] M_w. [c] Laboratory Synthesis. [d] Polymer Laboratories, Ltd. (U.K.). [e] Sigma Chemical Co. (St. Louis, MO).

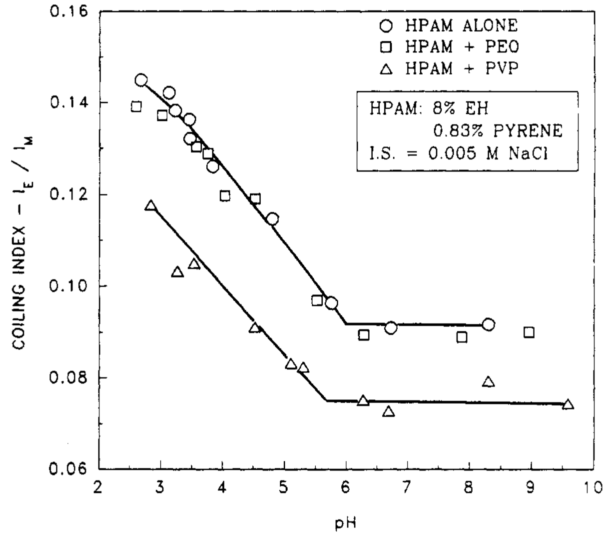

Figure 1. Interactions between 8% hydrolyzed polyacrylamide and poly(ethylene oxide) (PEO) or poly(vinylpyrrolidone) (PVP).

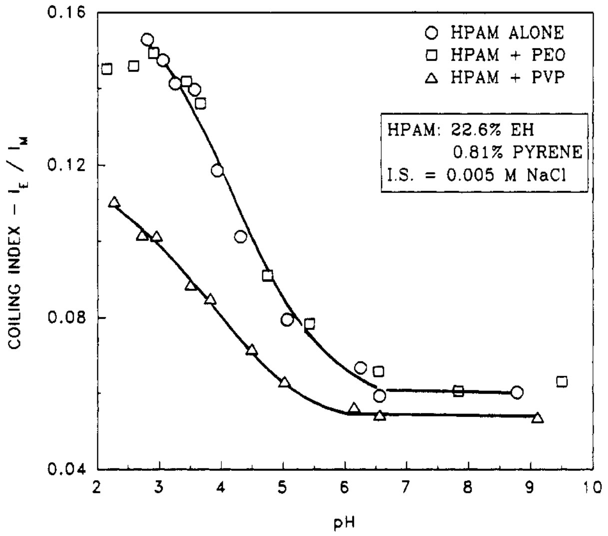

Figure 2. Interactions between 22.6% hydrolyzed polyacrylamide and PEO or PVP.

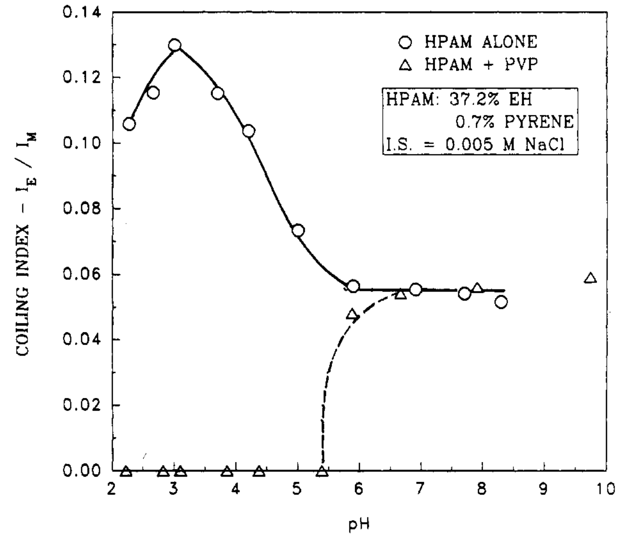

Figure 3. Interactions between 37.2% hydrolyzed polyacrylamide and PVP.

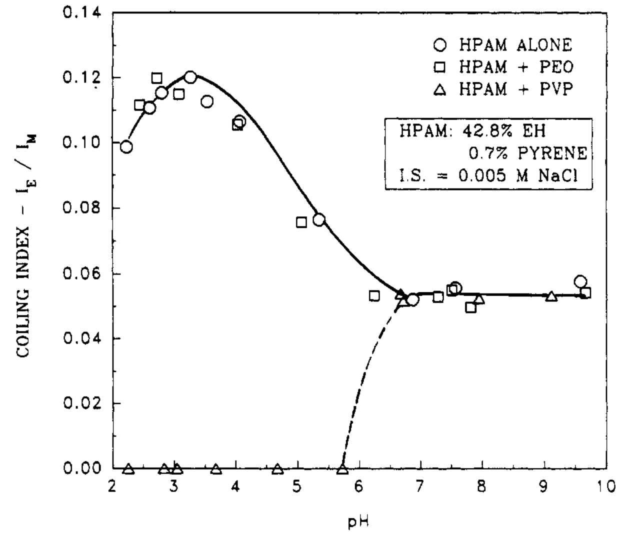

Figure 4. Interactions between 42.8% hydrolyzed polyacrylamide and PEO or PVP.

between the pyrene molecules will be determined by the conformation and mobility of the polymer chains. The extent of intramolecular excimer formation (given by the ratio of excimer to monomer intensities, I_e/I_m) therefore reflects the statistical conformation of the labeled polymer chain and will be termed here as the *coiling index*. A large value of I_e/I_m suggests polymer chain contraction, whereas a small value of I_e/I_m suggests polymer expansion and/or rigidity.

Figures 1–5 depict interactions of hydrolyzed polyacrylamide with poly(ethylene oxide) and poly(vinylpyrrolidone) as a function of its degree of hydrolysis and pH. It is observed that the conformation of HPAM is sensitive to changes in pH. At low pH values, the ionizable groups present on the polymer chain are undissociated and the polymer adopts a coiled conformation (high I_e/I_m). As the pH is raised, the carboxylate groups on the polymer are ionized and repulsion between the charged groups results in an expanded polymer chain (lower I_e/I_m). At higher degrees of hydrolysis, the conformational behavior of the HPAM is different from that of the samples with lower degree of hydrolysis, particularly at low pH values (Figures 3 and 4). Below pH 3, the polymers show a decrease in I_e/I_m even in the absence of PEO and PVP.

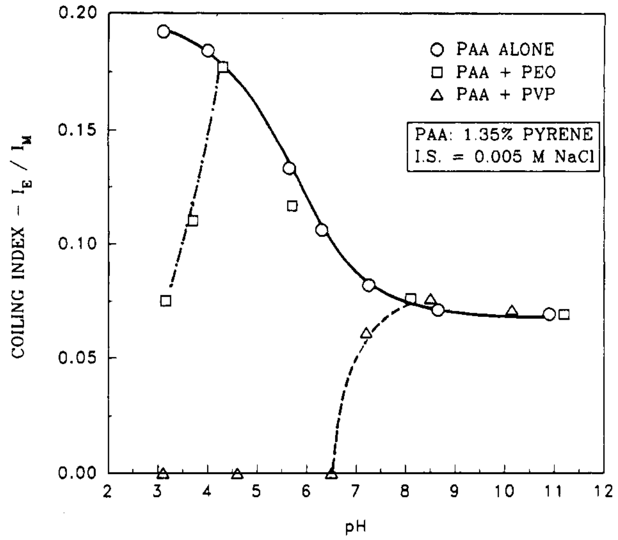

Figure 5. Interactions between poly(acrylic acid) (PAA) and PEO or PVP.

An increase in the number of acid groups on the acrylamide chain will enhance intramolecular bonding between the amide and acid groups of the same molecule. The decrease in intramolecular excimer formation in the low-pH region can be attributed to the decreased mobility of the HPAM chains due to such intramolecular hydrogen bonding. As the pH is raised, the ionization of the carboxylate groups breaks up the hydrogen bonding between the amide and the acid groups, and the behavior is similar to that of HPAM of lower extents of hydrolysis. Similar observations have been reported for intermolecular interactions between polyacrylamide and poly(acrylic acid).[7] At low degrees of hydrolysis the number of carboxyl groups is very low and randomly distributed: any hydrogen bonds formed will be unable to sustain a stable intramolecular complex.

PEO does not interact with HPAM over the range of hydrolysis studied (see Figures 1-4). Interactions are observed with PAA (Figure 5), which in effect is a 100% hydrolyzed polyacrylamide. It has been reported that PEO does not interact with PAM.[16] The same was observed in our studies. This could be due to the fact that PAM is a weak proton donor. Hydrogen bonding between PEO and PAA has been well established.[17,18] It has also been suggested that the driving force for the formation of a hydrogen bond between an ether oxygen and a carboxylic acid in aqueous solution is very small and a stable PAA-PEO complex can be formed only by the cooperative interaction of many such groups.[19] In addition, the strength of the complex will depend upon the distance between two hydrogen-bonded groups. In hydrolyzed polyacrylamides, it has been shown that, depending upon the hydrolysis conditions employed, the distribution of acrylic acid and acrylamide monomer units is very randon.[20] When the HPAM and PEO interact, the hydrogen bonds between the ether oxygen and the carboxylic acid will be few and far apart. The segmental mobility of the polymer will be sufficient to break up these bonds, and hence the complex will be very unstable. A stable complex can only be formed when the hydrogen bonds are many and close together, preventing any segmental mobility. Such is the case in the poly(acrylic acid)-poly(ethylene oxide) system under conditions where the acrylic acid is undissociated (Figure 5). It can also be seen that in the PEO-PAA system the presence of dissociated carboxyl groups (above pH 4) prevents any interactions between PAA and PEO.

The behavior of HPAM in the presence of poly(vinylpyrrolidone) is different from that in the presence of poly(ethylene oxide). The interactions between HPAM and PVP are significant under all conditions, but at low degrees of hydrolysis (8 and 22.6%) the expansion of the HPAM coils is less than that at higher degrees (37.2 and 42.8%). At degrees of hydrolysis of 37.2 and 47.8%, the I_e/I_m value of HPAM reaches a value of zero (Figures 3 and 4) and the behavior is similar to that in the case of the PAA-PVP system (Figure 5). Using a pK_a of 4.5 for the acid groups, the degree of dissociation of the -COOH groups even for the 8% HPAM is negligible (0.3%) at a value of pH 2. Therefore, at the low degrees of hydrolysis and low pH values, it is not the dissociation of -COOH groups that prevents interactions with PVP. It can be suggested that there is a critical number of -COOH groups required for complexation with PVP. The interactions between the -COOH groups of the hydrolyzed polyacrylamide and the bulky functional groups of the PVP could cause steric hindrances, resulting in decreased mobility of the complex and a more rigid chain (lower I_e/I_m). The hydrogen bond between -COOH of the hydrolyzed polyacrylamide and PVP will be strong on account of the high electronegativity of the oxygen of PVP due to the presence of nitrogen. These strong interactions are evident from the observation that the HPAM-PVP complex is stable between pH 2.5 and 5.5 where ionized carboxyl groups are present (Figures 3 and 4). Interactions are absent only when all the -COOH of the HPAM are ionized (>pH 7). In Figures 3 and 4, it can be seen that at low pH values (below pH 3) interpolymer interactions between PVP and -COOH groups are favored over the intrapolymer interactions between the amide and the acid groups. This reinforces earlier observations that interactions between PVP and the polyacid are stronger than those between PAM and the polyacid.[8]

The marked difference in interactions between PVP and HPAM at low and high degrees of hydrolysis should be noted. At 8 and 22.6% hydrolysis, interactions between HPAM and PVP are weak but exist over the entire range of pH values studied. For the 37.2, 47.8, and 100% hydrolyzed polyacrylamides, the interactions between PVP and HPAM are strong at low pH values but are absent above pH 6. In Figure 1 it can be seen that the I_e/I_m value of 8% HPAM is lowered by a near-constant amount over the entire pH range in the presence of PVP. However, for 22% HPAM, the decrease in I_e/I_m in the presence of PVP is greater at lower pH values (<pH 6) than at higher pH values (>pH 6). When the degree of hydrolysis is 37.2% and higher, there is no interaction between PAM and PVP above pH 6. A possible explanation of this lies in the number of amide and acid groups present on the polymers. At low degrees of hydrolysis the number of amide groups is much higher than that of the acid groups. Interactions between the few widely scattered -COOH groups and the pyrrolidone groups will be weak. Poly(vinylpyrrolidone) will interact with the amide groups, and this weak interaction results in only a slight decrease in the segmental mobility of HPAM. This interaction will be independent of pH because both PVP and PAM are nonionic. As the number of -COOH groups increases (higher percent hydrolysis and lower amide groups), interaction between -COOH and PVP will increase and HPAM will behave more like poly(acrylic acid). Under these conditions, the number of amide groups is apparently too low for any significant interaction with PVP and interactions between PVP and the -COOH group dominate. The interactions between polyacrylamide hydrolyzed to high degrees and

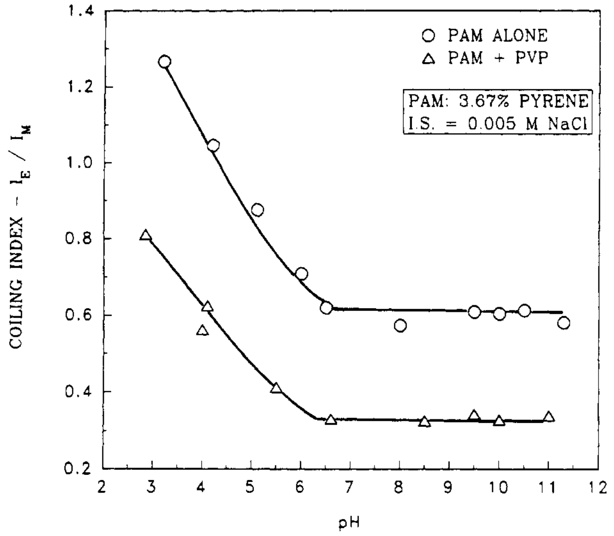

Figure 6. Interactions between polyacrylamide (PAM) and PVP.

poly(vinylpyrrolidone) serve to delineate the selectivity of macromolecular complexation. Interactions between PVP groups and the -COOH groups are stronger and favored over PVP-PAM or PAM-PAA complexation. It is observed that the decrease in the excimer formation (or decrease in segmental mobility) of pyrene-labeled hydrolyzed polyacrylamide on its interaction with poly(vinylpyrrolidone) is proportional to the extent of hydrolysis, particularly in the low-pH region. The higher the degree of hydrolysis, the larger the number of hydrogen bonds and therefore the lesser the segmental mobility of the complex.

Complexation between polyacrylamide and poly(vinylpyrrolidone) was studied in order to determine the nature of interactions between the amide group and the PVP. The results are plotted in Figure 6. The pyrene content of the PAM was 3.67 wt %, which is much higher than that in all the hydrolyzed polyacrylamides. The carboxyl group in the pyrene-containing monomer is the cause of the change in the conformation of PAM with pH. It can be seen that, in the presence of PVP, the behavior of PAM is similar to that of 8% HPAM. The decrease in the I_e/I_m of PAM in the presence of PVP is constant over the entire pH range studied, which could be due to the weak interactions between the amide groups and the functional group in PVP.

Conclusions

Excimer fluorescence measurement is a sensitive and informative technique for the study of interpolymer complexation. Using pyrene-labeled polyacrylamides hydrolyzed to different degrees, the effect of hydrolysis on the interactions between polyacrylamide, poly(vinylpyrrolidone), and poly(ethylene oxide) was determined. There are no detectable interactions between HPAM and PEO over the entire range of hydrolysis and pH studied. For lower degrees of hydrolysis, interactions between HPAM and PVP are measurable even though weak, but for high degrees of hydrolysis, the interactions are strong below pH 6 and similar to those in the case of the PAA-PVP system. Interaction between PVP and -COOH groups is stronger than those between $-CONH_2$ and -COOH.

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Registry No. PEO, 25322-68-3; PVP, 9003-39-8.