Polymer–Polymer Complexation in Dilute Aqueous Solutions: Poly(acrylic acid)–Poly(ethylene oxide) and Poly(acrylic acid)–Poly(vinylpyrrolidone)

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Fluorescence spectroscopy of pyrene-labeled poly(acrylic acid) (PAA) was used to study its interactions with poly(ethylene oxide) (PEO) and poly(vinylpyrrolidone) (PVP) in aqueous solutions. The effects of molar ratio, molecular weight, and solvent were also investigated. Hydrogen bonding is the primary mechanism of interaction among these polymers. Excimer fluorescence studies show that the PVP–PAA complex is stronger than and exists in a more constricted form than the PEO–PAA complex. Interactions between PVP and PAA are prevalent over a wider pH range than those of PAA and PEO. The higher electronegativity of the oxygen in the pyrrolidone group is attributed as the reason for the stronger interaction of PVP with poly(acrylic acid).

Introduction

Cooperative interaction between synthetic water-soluble polymers has been a topic of investigation worldwide because of their importance from both scientific and practical viewpoints. Interpolymer complexes resulting from these interactions possess unique properties which are different from those of the individual components and find various applications, for example, in dialysis, ultrafiltration, reverse osmosis, and production of blood-compatible materials and batteries.[1,2] Synthetic water-soluble polymers such as polyacrylamide, poly(acrylic acid), poly(ethylene oxide), and poly(vinylpyrrolidone) are also increasingly being used in mineral-processing operations such as flocculation and dewatering, effluent treatment, selective flocculation,[3] and flotation.[4] A natural development in this area has been the use of polymer mixtures in mineral processing. In a recent study, poly(vinylpyrrolidone) (PVP) was found to be a better dispersant than poly(ethylene oxide) (PEO) and sodium silicate for selective flocculation of iron oxide from clay using poly(acrylic acid) (PAA) as flocculant.[5] Complexation between PVP, PEO, and PAA has been investigated earlier but the studies have concentrated on the biological aspect of these complexes. The interactive forces responsible for complexation between two chemically different macromolecules are usually secondary forces due to electrostatic, hydrogen-bonding, or hydrophobic interactions. Hydrogen bonding in the poly(acrylic acid)–poly-(ethylene oxide) system is perhaps the most well established[6,7] and is used as a quantitative method for estimating ppm levels of PEO or PAA. Earlier studies suggested the association to be between the ether oxygen of the poly-(ethylene oxide) and the carboxyl group of the poly(acrylic acid), which approaches 1:1 stoichiometry.[8] Cooperative interaction among active sites in PEO–PAA complex formation was later verified by several techniques.[9] It has also been suggested that the driving force for the formation of a hydrogen bond between an ether and a carboxylic acid in aqueous solution is very small and a stable PAA–PEO complex can be formed only by the cooperative interactions between many such groups.[10] The formation of hydrogen bonds is also considered to be the dominant force in the interactions between PVP and PAA.[11,12] A stronger association of PAA–PVP than that of PEO–PAA was observed and attributed to the contribution of hydrophobic and Coulombic interactions in the PAA–PVP association.

The present study was conducted to investigate the interactions between PAA and PEO and between PAA and PVP using fluorescence spectroscopy. Effects of changes in complexation conditions such as pH, polymer molecular weight, and solvent are also discussed. It has been demonstrated that fluorescence spectroscopy is a more sensitive and informative technique than other conventional methods such as viscometry, potentiometry, and turbidimetry, which provide information only on average properties representing the whole system.[13–18]

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Table I. Characteristics of the Polymers Used in the Study

polymer	MW × 10⁻⁴	notation	pyrene content, wt %	supplier
pyrene-labeled poly(acrylic acid)			1.35	laboratory synthesis
poly(ethylene oxide)				Polymer Lab. Ltd., U.K.
poly(ethylene oxide)				Scientific Polymer Products, Inc., New York
poly(vinylpyrrolidone)				Sigma Chemicals Co., St. Louis, MO
poly(vinyl pyrrolidone)				Aldrich Chemical Co., Milwaukee, WI

Experimental Section

Synthesis of 2-[4-(1-pyrenyl)butanoyl]aminopropenoic acid, which was used as the pyrene source, is described elsewhere.[13] Acrylic acid monomer purchased from Aldrich was vacuum distilled at 50–51 °C to free it from inhibitor. It was then copolymerized with pyrene-containing monomer (2-[4-(1-pyrenyl)butanoyl]aminopropenoic acid) in DMF at 65 °C with azobis(isobutyronitrile) as the initiator for 9 h. The concentrations of the acrylic acid and the pyrene-containing monomer were 72.8 and 1.07 mM, respectively. The concentration of AIBN was 0.3 mol %, and the amount of DMF was 35.5 mL. The pyrene content of the polymers was estimated from UV absorption spectra.[13] Intrinsic viscosities were obtained from linear η_{sp}/C vs C plots and used to determine molecular weights by use of Mark–Houwink constants available in the literature.[19]

Poly(ethylene oxide) and poly(vinylpyrrolidone) were obtained from various suppliers and used as received. Characteristics of the polymers used are presented in Table I.

The concentration of polymers in all the fluorescence experiments was maintained at 10 ppm. Only in cases where the effect of molar ratio was studied, was the concentration varied.

All samples were prepared in triply distilled water and at a salt concentration of 0.005 M sodium chloride.

Fisher Scientific ACS reagent grade hydrochloric acid and sodium hydroxide were used for pH adjustments. Urea crystals were purchased from Amend Drug and Chemical Co., and dimethyl sulfoxide (DMSO) was from Fisher Scientific. Both were ACS reagent grade.

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

Results and Discussion

Poly(acrylic acid) (PAA) behaves as a random coil in dilute solutions in the presence of simple electrolytes. The randomly distributed pendant pyrene groups on the polymer chain, at low concentrations, do not significantly affect the dissolution characteristics. Pyrene groups are constantly in motion due to the high mobility of the polymer segments to which they are covalently attached. The distance between the pyrene groups on the polymer chain is determined by its conformation and the mobility of the segments. An excited pyrene group interacts with a ground-state pyrene group to form an excimer when they approach each other within about 4–5 Å. The formation of an excimer will depend upon the conformation of the polymer, and hence, the extent of intramolecular excimer formation (given by the ratio of excimer to monomer intensities or I_e/I_m) provides a measure of the statistical conformation of the labeled polymer chain and its intramolecular overlap. It can therefore be referred to as the *coiling index*. A large value of the I_e/I_m ratio
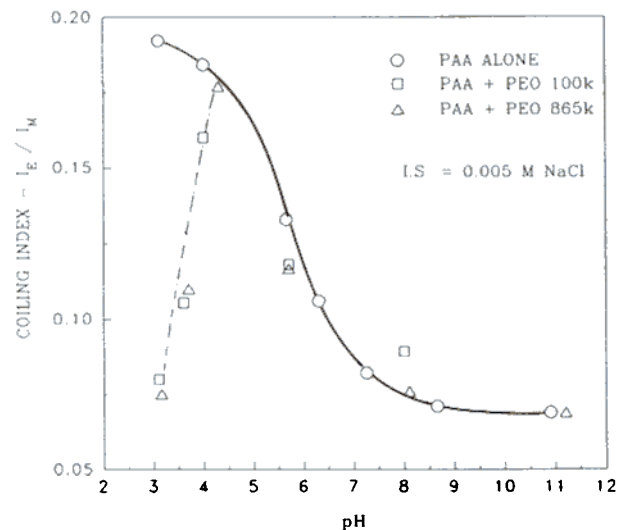

Figure 1. Interactions between poly(acrylic acid) and poly(ethylene oxide) of two molecular weights, 100 000 and 865 000.

suggests polymer chain contraction, whereas a small value of I_e/I_m suggests polymer expansion and/or segmental rigidity. Under the dilute polymer concentrations employed, all excimer formation was intramolecular and hence the I_e/I_m value can be taken as a true indication of polymer segmental mobility.

The change in the conformation of poly(acrylic acid) as a function of pH is shown in Figure 1. At low pH values, the acid groups of the PAA are undissociated and therefore the polymer exists as a compact coil (high I_e/I_m). When the pH of the solution reaches the pK_a of PAA (4–4.5), some of the COOH groups of the PAA are ionized. This generates some repulsion between adjacent groups and as a result the polymer coil expands. The presence of a neutral electrolyte shields some of the charge and decreases the repulsion. This is reported as a gradual decrease in the I_e/I_m value with increase in pH. Above a pH value of 8.5 all the acid groups on the PAA are ionized and the polymer is in its most expanded state. As a result, there is no further decrease in I_e/I_m and it remains at a constant value.

It can also be seen from Figure 1 that the conformation of poly(acrylic acid) is affected by the presence of poly(ethylene oxide) (PEO), but only below pH 4.5. Undissociated COOH groups play a significant role in PAA–PEO interactions, and the presence of a few dissociated acid groups on the PAA is sufficient to break up hydrogen bonding between PAA and PEO. The strength of a single hydrogen bond between an ether oxygen of the poly(ethylene oxide) and a carboxylic acid of the poly(acrylic acid) is very low. The total strength of a PAA–PEO complex will therefore depend upon the number of hydrogen bonds formed as well as the distance between two hydrogen-bonded groups. The interaction between PAA and PEO is a cooperative phenomenon, and the stability of the complex will depend on the predominance of hydrogen bonding over thermal or Brownian motion. At low pH values (<3) the number of dissociated COOH groups on the PAA is very low and there are a large number

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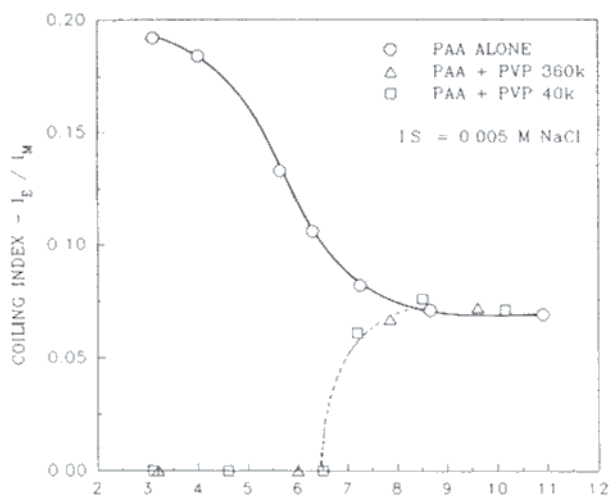(14) Arora, K. S.; Turro, N. J. *J. Polym. Sci., Part B* **1987**, *25*, 243–262.
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Figure 2. Interactions between poly(acrylic acid) and poly(vinylpyrrolidone) of two molecular weights, 360 000 and 40 000.

of hydrogen bonds. The large number of hydrogen bonds and the small separation between hydrogen-bonded groups will result in a strong complex and also prevent any segmental mobility. The associated chains, therefore, are very stiff and this results in a very low value of the coiling index. With an increase in the pH, some of the acid groups of the PAA will dissociate and break up the hydrogen bonds with the ether oxygen of the PEO at these points. As a result, the distance between some hydrogen-bonded groups will increase and the segmental mobility of the associated chains will also increase slightly. The measured coiling index will be slightly higher, as is seen in Figure 1. Finally, at a pH value of 4.5, the number of dissociated acid groups on the PAA is very high, the segmental mobility becomes large enough to overcome the strength of the hydrogen bonds, and the complex between PAA and PEO is broken. This can be seen from Figure 1, where the coiling index of PAA above pH 4.5 is similar in the presence as well as the absence of PEO. It can also be seen from Figure 1 that there is no effect of molecular weight of poly(ethylene oxide) on its interactions with poly(acrylic acid), at least in the ranges of molecular weight, concentration, and time investigated in this study. This implies that the distance of separation between hydrogen-bonded groups rather than the overall number of bonds is the critical factor governing the stability of the PAA–PEO complex.

In the presence of poly(vinylpyrrolidone) (PVP), the coiling index (I_e/I_m) of PAA reaches a value of zero (Figure 2). This suggests that the PAA chain associated with PVP is stiffer than the one associated with PEO. The pH range over which the PAA–PVP complex is stable is wider than the corresponding range for the PAA–PEO complex. These results suggest that the interactions between PAA and PVP are stronger than those between PAA and PEO. The hydrogen bonding between PAA and PVP could be stronger than that between PAA and PEO due to the higher electronegativity of the oxygen of the PVP caused by the presence of nitrogen in the functional group. Therefore the PAA–PVP complex will remain stable with fewer hydrogen bonds and over a wider pH range than the PAA–PEO complex. During interactions between PAA and PVP, the bulky functional group of the PVP could cause steric hindrances leading to a more rigid chain (resulting in a lower I_e/I_m). The PVP ring is known to be hydrophobic (presence of three methylene groups), but this does not appear to play a significant role in its interactions with PAA, as can be postulated from the lack of effect of

PVP molecular weight (Figure 2). In the complexation between PAA and PVP and between PAA and PEO, it is evident that the stability of the complex is determined by the strength of the individual H bonds as well as the distance between hydrogen-bonded groups. The stronger H bond in the PAA–PVP system results in that complex being stable over a wider pH range. Only above a pH value of 8, where all the acid groups of the PAA are ionized, are the interactions between PAA and PVP absent. Possible interactions between PAA, PEO, and PVP are schematically illustrated in Figure 3.

The effect of molar ratio of the interacting polymers (PAA–PEO and PAA–PVP) was also studied, and the results are given in Figure 4. It has been stated that the interpolymer complexes formed are stoichiometric. This is true for the PAA–PEO system, where it can be seen that the plateau I_e/I_m value of 0.08 is reached at a molar ratio of 1.0. In the PAA–PVP system, however, complete stretching of the complex occurs at a molar ratio as low as 0.01. This result is very surprising, and at the present moment we do not have any explanation for this behavior. These results lend support to the earlier hypotheses that the interactions between PAA–PVP are stronger than those in the PAA–PEO system and that a stable PAA–PEO complex requires a 1:1 stoichiometry.

It was also observed that the interpolymer complexes formed were totally reversible. Instead of a new sample being prepared at every pH, the same sample was taken through a cycle of pH 2–10 and back. The ability to form, break, and re-form became clear from this behavior.

The solvent can play an important role in determining the nature of polymer complexes formed by hydrogen bonding because it also can interact with the polymer via hydrogen bonds.[2] Complexation in the presence of such solvents, therefore, can be regarded as a three-component reaction involving a proton-donating polymer, a proton-accepting polymer, and a solvent. The effect of such a solvent, dimethyl sulfoxide (DMSO), on polymer–polymer complexation is depicted in Figure 5. The poly(acrylic acid) is mostly undissociated at a pH value of 3.0, and DMSO being a better solvent than water causes the coil to expand. The value of the coiling index for PAA alone in water is higher than that in DMSO. In the case of the PAA–PEO system, a combined effect of both the solvent molecules and PEO on the stretching of the PAA (lower I_e/I_m than that for the PAA–PEO complex in water) is possible at low DMSO content. As the DMSO content is raised, interactions between DMSO and PAA become stronger since the amount of DMSO is much larger than that of the proton-accepting groups of the poly(ethylene oxide). Also, the mobility of the DMSO molecules is higher than the segmental mobility of the poly(ethylene oxide) chain. Eventually, at 40% DMSO all PAA–PEO bonds are replaced by PAA–DMSO bonds. In the case of PAA–PVP, the bonding is stronger than that between PAA–PEO and hence a higher amount of DMSO is required to replace the interaction between poly(acrylic acid) and poly(vinylpyrrolidone) than is required to replace PAA–PEO interactions. Interpolymer complexation was also studied in the presence of urea, but the effect was not as pronounced as that in the case of dimethyl sulfoxide.

Conclusions

Interactions between poly(acrylic acid), poly(ethylene oxide), and poly(vinylpyrrolidone) in aqueous solution were studied by fluorescence spectroscopy. Hydrogen bonding is the primary mechanism of interaction between these polymers, and the interactions between PAA and
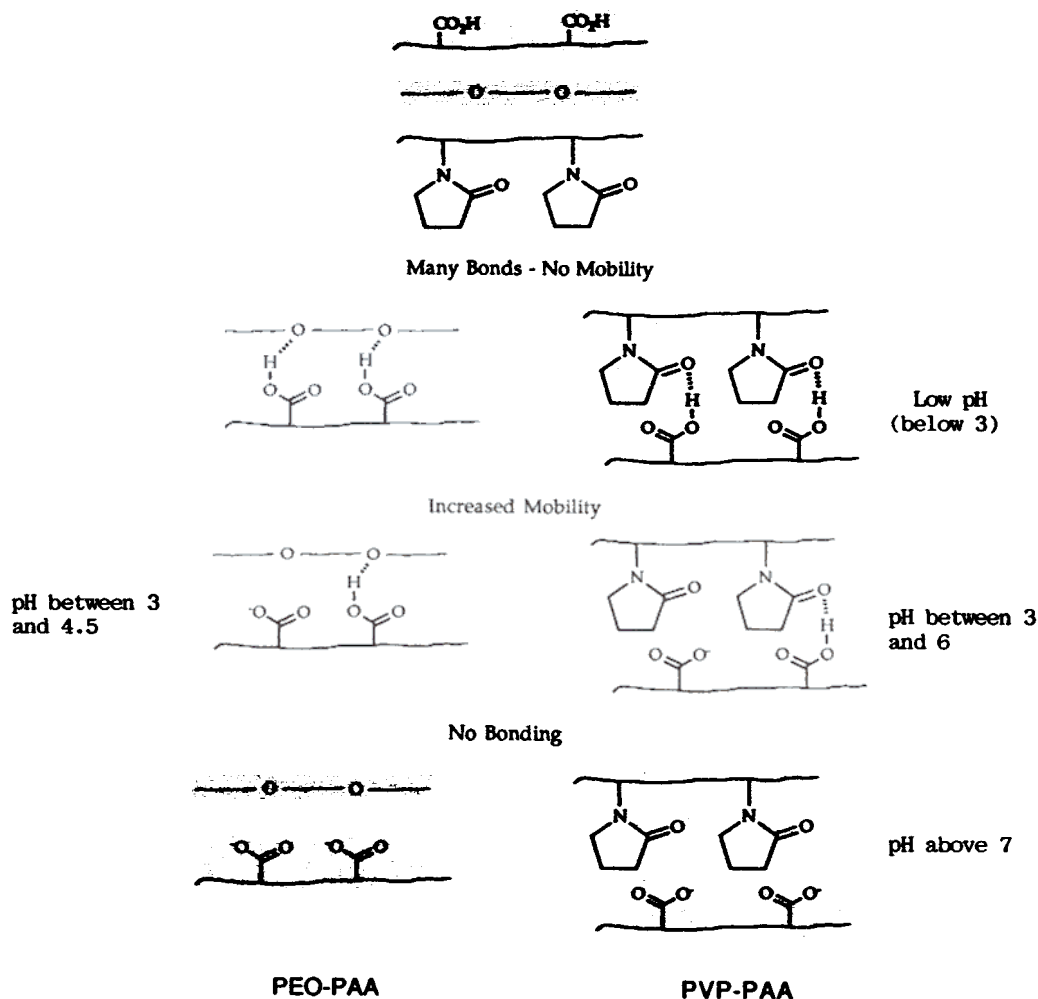
Many Bonds - No Mobility

Increased Mobility

Low pH
(below 3)

pH between 3
and 4.5

pH between 3
and 6

No Bonding

pH above 7

PEO-PAA

PVP-PAA

Figure 3. Schematic representation of interpolymer complexation.
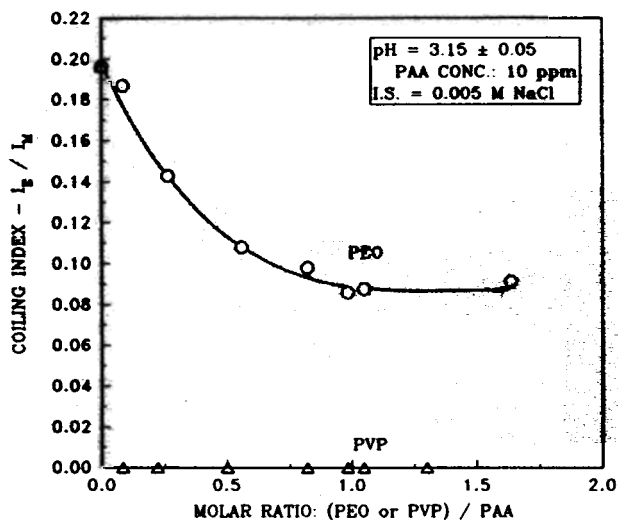
Figure 4. Effect of molar ratio on interpolymer complexation.

PVP were stronger than those between PAA and PEO. This was attributed to the stronger hydrogen-bonding capability of the pyrrolidone group in the PAA–PVP system. In the presence of DMSO, the interpolymer complexes were replaced by a solvent–PAA complex at high solvent concentrations, the amount of DMSO required being higher in the case of PVP than that in the case of PEO. Formation of a stable PAA–PEO complex required 1:1 stoichiometry but a stable PAA–PVP complex was formed even at very low PVP to PAA ratios. The complexation process was found to be reversible upon chang-
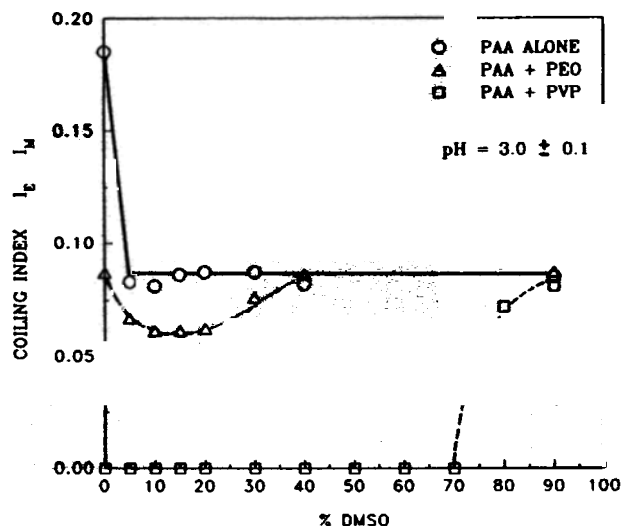
Figure 5. Effect of solvent (DMSO) on interpolymer complexation.

ing pH of the solutions. Under the conditions studied, there was no detectable effect of molecular weight of either the PEO or the PVP on its interaction with PAA.