

Viscometric and Conductometric Studies of Poly(vinyl alcohol)-*g*-Polyacrylamide Composites

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SYNOPSIS

Poly(vinyl alcohol)-*g*-polyacrylamide composites have been prepared by γ -radiation-initiated polymerization of acrylamide (AAm) in the presence of poly(vinyl alcohol) (PVA) in aqueous medium by the mutual method in air. Percentage conversion of AAm has been studied as a function of total dose, monomer concentration, and amount of water. Optimum conditions leading to maximum percent conversion of the monomer to give the composite have been evaluated. The products of polymerization of AAm in the presence of PVA consisted of unreacted PVA, the graft copolymer, PVA-*g*-PAAm, and the homopolymer polyacrylamide, PAAm, and this mixture is referred to as PVA-*g*-PAAm composite. AAm was also polymerized in the absence of PVA under similar conditions, and optimum conditions leading to maximum conversion of AAm to PAAm have been evaluated. A comparative study of the polyelectrolytic behavior of PVA, PAAm, and the composite has been made by viscometric and conductometric methods. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In recent years increasing interest has arisen in the determination of the structure and composition of water-soluble random or graft copolymers which could be used more efficiently as displacement fluids during enhanced oil recovery (EOR) processes. In EOR practice, high solution viscosities in aqueous solution must be maintained at a low concentration of polymer and the polymer in solution should permeate through the porous medium to displace residual oil without degradation or absorption. Polyacrylamide (PAAm) and poly(vinyl alcohol) (PVA) cause more pronounced changes in the rheology of their aqueous solutions as their molecular weight increases. PVA aqueous solutions are surface active and therefore can stabilize various kinds of hydro-sols.¹ Its main use as a colloid stabilizer is in polymer dispersion.² The principal uses of PAAm continue to be in water treatment, mining, and paper manufacture. Recently, potential use of PAAm in EOR has been reported³ and it is used in partially hydro-

lyzed form containing 10–50% carboxylic groups. However, PAAm loses its viscosity in salty injection waters and it is more sensitive to degradation at higher rates of shear encountered during the actual injection into the oil reservoir at the bottom of the well. These drawbacks can be overcome by use of water-soluble graft copolymers. Starch-*g*-PAAm copolymers have been evaluated as agents to increase the viscosity of aqueous fluids^{4–6} and the graft copolymer may find uses in EOR processes. Saponified starch-*g*-polyacrylonitrile copolymers are useful as thickening agents and as water absorbents, but it has been found to remain in the form of highly swollen insoluble gel after saponification.⁷ Starch-*g*-PAAm composites have been prepared by the γ -irradiation method and the viscometric behavior of the composite showed polyelectrolytic behavior, which suggests that it could function as a good candidate polymer for use in the EOR process.⁸ PVA has been proposed as a pigment binder in clay coatings to replace other water-soluble binders such as starch, casein, or proteins. Fully hydrolyzed medium viscosity PVA is most suited for use as pigment binder. The high adhesive and cohesive strength of PVA coatings is probably due to the presence of many hydroxyl groups. Graft copolymers of PVA

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and acrylamide (AAm) appear to have combined properties of both the polymers and as such would offer a more promising polymer for effective oil recovery agent. Grafting of water-soluble monomers such as acrylic acid and acrylamide onto PVA backbone has not been extensively studied. In the present paper, graft copolymerization of acrylamide onto PVA by the γ -radiation method and polymerization of acrylamide under similar conditions have been studied, the solution properties of the graft copolymer composite with respect to the viscosity and conductance behavior have been investigated, and the results have been compared with those of PAAm.

EXPERIMENTAL

Materials and Method

Pure PVA (BDH) with a viscosity average molecular weight of 14,000 has been used. AAm (Sisco) was recrystallized from methanol before use. All the reactions were carried out in an aqueous medium using distilled water; ^{60}Co was used as the γ -ray source for irradiation in air.

Table I Effect of Total Dose, Monomer Concentration, and Amount of Water on Weight Percentage of PVA-*g*-PAAm Composite^a

| Series No. | Total Dose (Mrad) | [AAm] $\times 10^{-2}$ mol | H ₂ O (mL) | Weight Percentage |
|------------|-------------------|----------------------------|-----------------------|-------------------|
| 1 | 0.116 | 0.28 | 20 | 364 |
| 2 | 0.132 | 0.28 | 20 | 382 |
| 3 | 0.348 | 0.28 | 20 | 420 |
| 4 | 0.464 | 0.28 | 20 | 302 |
| 5 | 0.348 | 0.21 | 20 | 303 |
| 6 | 0.348 | 0.24 | 20 | 438 |
| 7 | 0.348 | 0.31 | 20 | 382 |
| 8 | 0.348 | 0.24 | 15 | 362 |
| 9 | 0.348 | 0.24 | 25 | 377 |
| 10 | 0.348 | 0.24 | 30 | 348 |

^a PVA = 200 mg.

Synthesis of PVA-*g*-PAAm

A solution of PVA was prepared by dissolving 200 mg of PVA granules in 20 mL distilled water in a conical flask heated to 90°C. The temperature of the PVA solution was brought to room temperature and a known amount of AAm was added and dissolved to get a clear solution. The reaction mixture

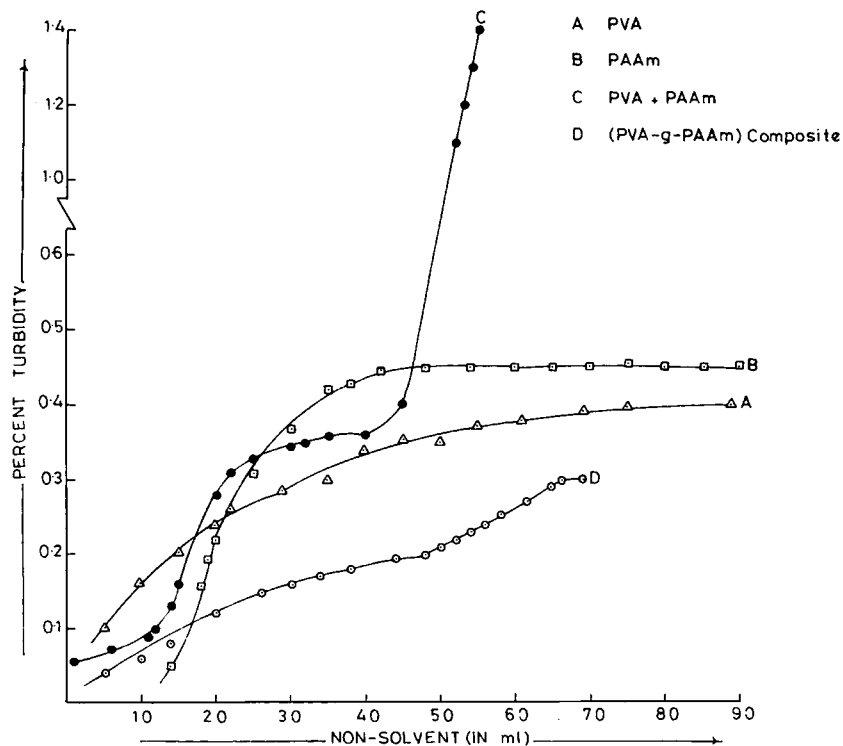


Figure 1 Variation in percent turbidity with added nonsolvent (methanol).

was irradiated by γ -rays for different time periods at a constant dose rate of 0.29 Mrad/h in air. After the completion of the reaction the flask was removed from the gamma chamber and an excess of purified methanol was added to the reaction mixture to precipitate the unreacted PVA, the homopolymer, i.e., PAAm, and the graft copolymer. All attempts to separate the graft copolymer from the homopolymer by the solvent extraction method were unsuccessful, since both the graft and the homopolymer are soluble in water. The product, therefore, is not a true graft copolymer but rather a composite comprising an ungrafted PVA, graft copolymer PVA-*g*-PAAm, and homopolymer, PAAm; the product is referred to as PVA-*g*-PAAm composite.

A series of polymerization reactions of acrylamide in aqueous medium were also carried out in the absence of PVA, under identical conditions to synthesize polyacrylamide for comparative studies. The procedure followed for polymerization and precipitation of the polymer was the same as for the graft copolymerization reaction. Optimum conditions for the synthesis of the PVA-*g*-PAAm composite and PAAm were evaluated as a function of total dose, monomer concentration, and amount of water. Weight percentage of PVA-*g*-PAAm composite was determined from weight increase in PVA after polymerization of AAm in the presence of PVA while the percentage of polymer (PAAm) formed was determined from the initial weight of the monomer used.

$$\text{Weight percentage (W \%)} = \frac{W_2}{W_1} \times 100$$

where

W_2 = weight of grafted PVA + weight of ungrafted PVA + weight of PAAm formed

W_1 = initial weight of PVA used

$$\% \text{ total polymer formed} = \frac{W_3}{W_4} \times 100$$

where

W_3 = total weight of PAAm formed

W_4 = initial weight of AAm used

RESULTS AND DISCUSSION

Turbidimetric Titration

Turbidimetric titrations of PVA, PAAm, PVA-*g*-PAAm composite, and a physical mixture of PVA

Table II Effect of Total Dose, Monomer Concentration, and Amount of Water on Percent Conversion of AAm

| Series No. | Total Dose (Mrad) | [AAm] $\times 10^{-2}$ mol | H ₂ O (mL) | Percent PAAm Formed |
|------------|-------------------|----------------------------|-----------------------|---------------------|
| 1 | 0.116 | 0.28 | 20 | 229 |
| 2 | 0.132 | 0.28 | 20 | 215 |
| 3 | 0.348 | 0.28 | 20 | 272 |
| 4 | 0.464 | 0.28 | 20 | 169 |
| 5 | 0.348 | 0.21 | 20 | 160 |
| 6 | 0.348 | 0.24 | 20 | 200 |
| 7 | 0.348 | 0.31 | 20 | 236 |
| 8 | 0.348 | 0.28 | 15 | 176 |
| 9 | 0.348 | 0.28 | 25 | 191 |
| 10 | 0.348 | 0.28 | 30 | 101 |

and PAAm in aqueous solution were carried out using methanol as the precipitating solvent. A total of 20 mL of standard solutions (0.1%) each of PVA, PAAm, and PVA-*g*-PAAm composite were prepared. The physical mixture of PVA and PAAm were prepared by mixing equal amounts (0.05 g) of each polymer. To these standard solutions, 1 mL portions of methanol were added and the optical density of the solution after each addition was measured at 540 nm until complete precipitation occurred. Percent turbidity of solution was defined as the percent ratio of optical density of solution to the optical density at complete precipitation.⁹ Percent turbidity was plotted against volume of the precipitant and the results are presented in Figure 1. Curves A, B, C, and D in Figure 1 represent, respectively, the turbidimetric titrations of aqueous solutions of PVA, PAAm, physical mixture of PVA and PAAm, and PVA-*g*-PAAm composite under identical conditions. It is seen that in curve C, the turbidity increases rapidly with addition of 10–20 mL and again on addition of 40–55 mL of methanol. These jumps may be attributed to the precipitation of PVA and PAAm fractions, respectively, in the physical mixture. However, in the case of the composite (curve D), increase in turbidity is more or less continuous and no well defined inflexion was observed. But with the addition of about 50 mL of methanol, there is a little increase in the turbidity, which may be due to the presence of the homopolymer, i.e., PAAm in the composite. Upon comparison of the shapes of curves, it is observed that curve D is different from the rest. This indicates that grafting has occurred. Curve A due to PVA shows continuous precipitation on addition of the precipitant while turbidimetric titration

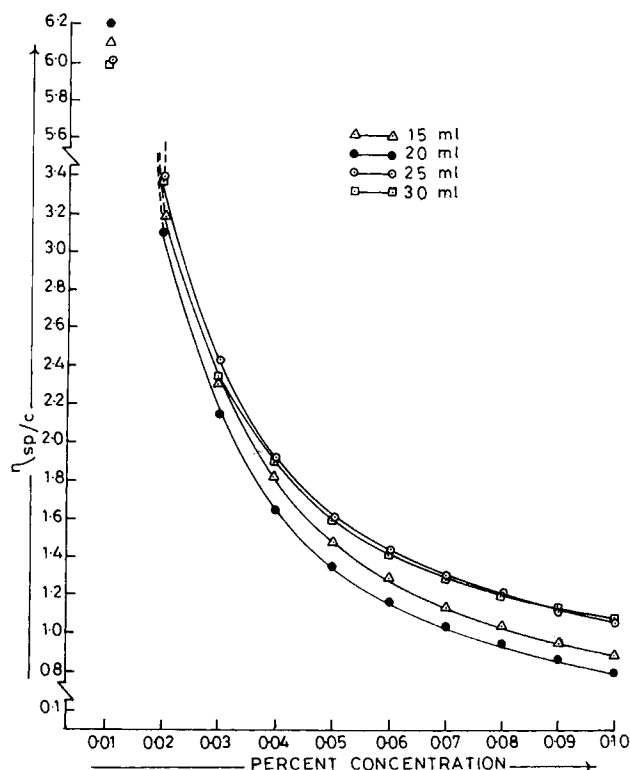


Figure 2 Effect of amount of water on $\eta_{sp/c}$ of [PVA-g-PAAm] composite.

of PAAm (curve B) shows an initial rise in turbidity with addition of 10–35 mL of methanol, beyond which it becomes constant. Generally, the chemical nature of the polymer has a much greater influence on its solubility than its molecular weight. The meager data available in the literature indicate that a graft copolymer will normally display solubility characteristics intermediate between those of the constituent homopolymers. However, in the present case, it is observed that the composite shows turbidimetric behavior different from that of either PVA or PAAm, and this tends to indicate that the product is not a true graft copolymer and consists of the mixture of PVA, PAAm, and grafted PVA, which exhibits properties entirely different from those of individual polymers, i.e., PVA and PAAm.

Synthesis of PVA-g-PAAm composite and the homopolymer, PAAm, has been studied as a function of total dose, monomer concentration, and the amount of water, and the results are presented in Tables I and II, respectively.

It is observed from the tables that the weight percentage of composite and percent PAAm formed increases with increasing total dose, reaches maximum, and then decreases. Maximum weight percentage of composite (420%) (Table I) and maximum percent homopolymer formation (272%)

(Table II) occur at an optimum total dose of 0.348 Mrad. Weight percentage of composite and percent PAAm formation have been studied as a function of monomer concentration and it is observed from Tables I and II that maximum weight percentage of composite (438%) and PAAm formation (272%) occurred at $[AAM] = 0.24 \times 10^{-2}$ and 0.28×10^{-2} mol, respectively, beyond which these decrease. Under optimum conditions, maximum weight percentages of composite (438%) and polyacrylamide formation (272%) were obtained in 20 mL of water, beyond which these decrease.

Viscometric Behavior of PVA-g-PAAm and PAAm

The viscosity measurements of aqueous solutions of PVA-g-PAAm composite and PAAm were made at $30 \pm 0.02^\circ\text{C}$ using an Ubbelohde viscometer. Reduced viscosity was determined as a function of the concentration of the composite and PAAm and the results are presented in Figures 2 and 3. Examinations of the plots of reduced viscosity $\eta_{sp/c}$ versus concentration of polymeric solutions (Figs. 2 and 3) of PVA-g-PAAm composite and PAAm prepared using varying amount of water reveals that there is a continuous rise of $\eta_{sp/c}$ values of PAAm upon dilution. The same trend is observed for the aqueous

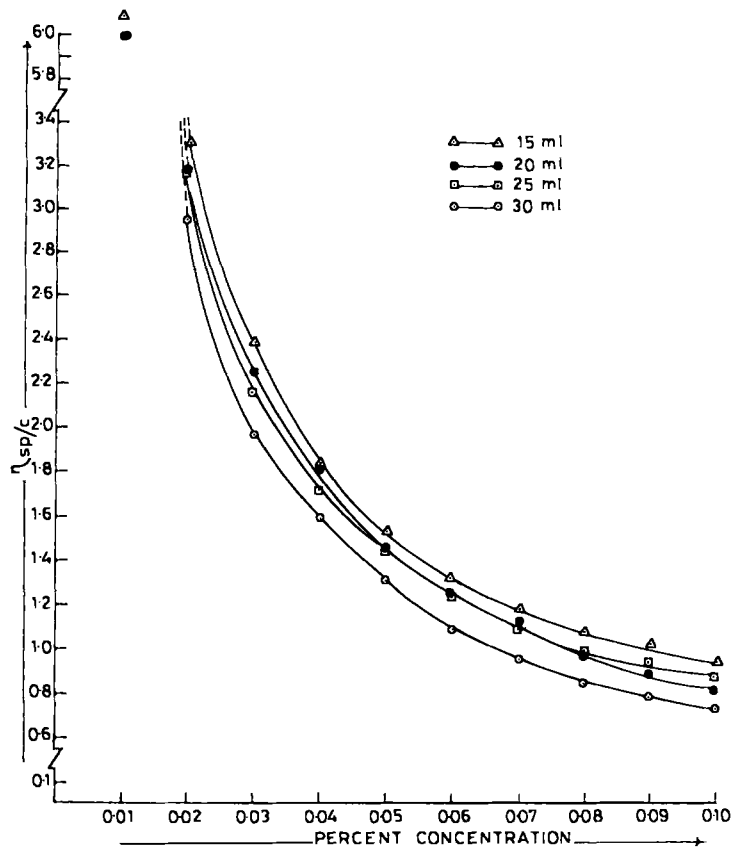


Figure 3 Effect of amount of water on η_{sp}/c of PAAm.

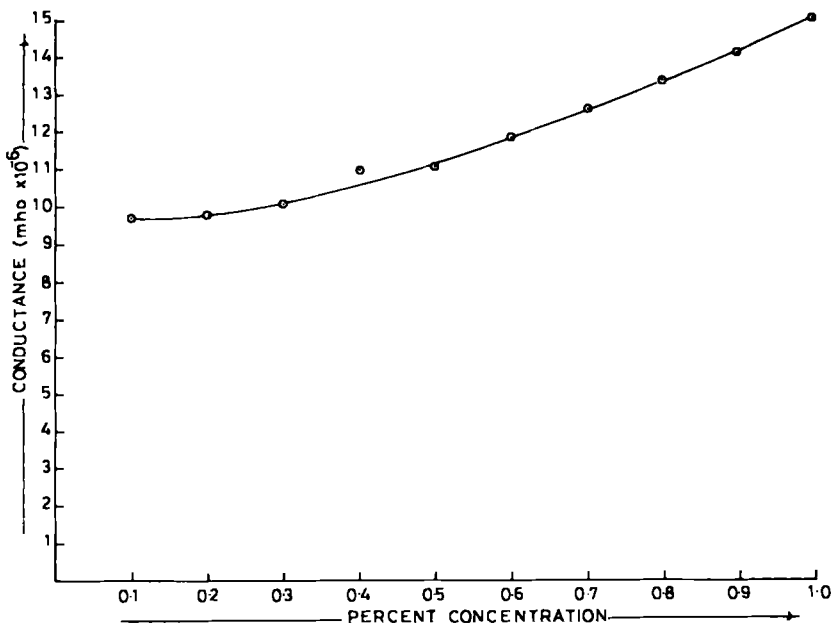


Figure 4 Conductance as a function of [PVA].

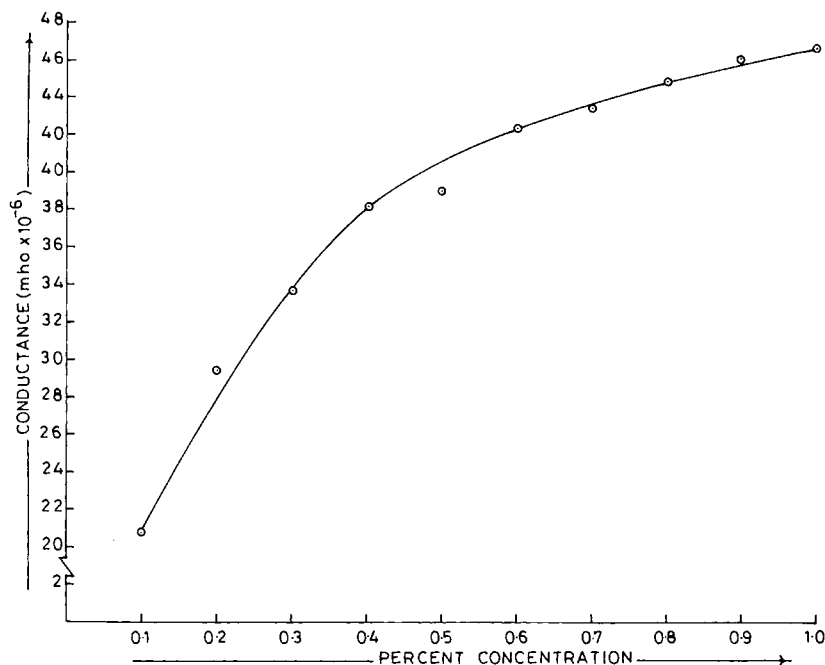


Figure 5 Conductance as a function of [PAAm].

solution of the composite, but the extent of increase of η_{sp}/c for composite is much higher than that observed for PAAm, suggesting that the composite shows stronger polyelectrolytic behavior than PAAm.

From the foregoing discussions it is observed that the aqueous solutions of both PAAm and PVA-*g*-PAAm composite do not behave as true nonionic polymeric solutions for which the plots of η_{sp}/c versus

concentration should have shown a linear relationship. The sharp increase in η_{sp}/c upon dilution is an indication of the fact that these polymer solutions are behaving as polyelectrolytes. The difference in viscometric behavior of polymeric solution reflecting the dependence of viscosity on polymer concentration reveals that dilution produces a continuous change in the nature of the electrostatic environment of individual polymers leading to major

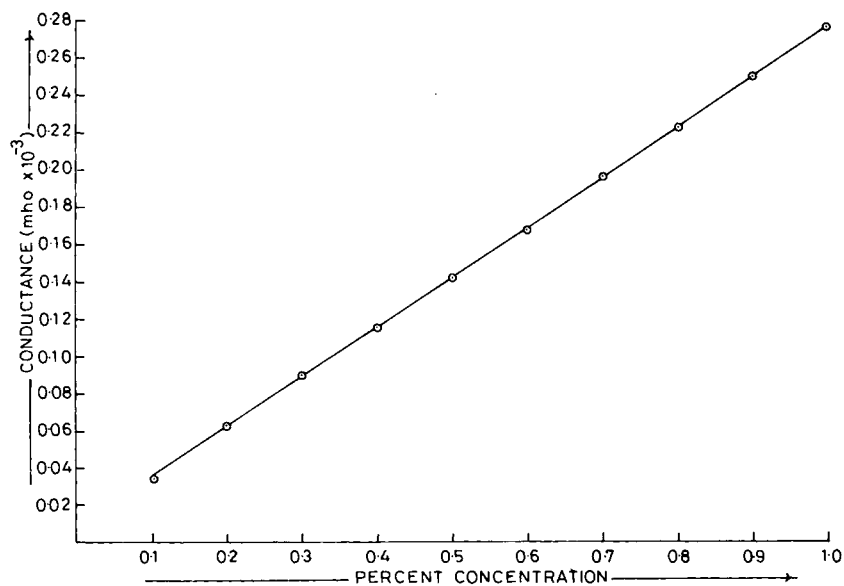


Figure 6 Conductance as a function of [PVA-*g*-PAAm] composite.

changes in both intra- and interpolyion interactions and hence gives rise to reduced viscosity curves which are fundamentally different from those of nonionic polymers. It is argued that dilution would promote increased counterion dissociation, thus augmenting the intrapolyions repulsive forces which act to dilute the polyion dimensions. The dimensions of polyion solution are strongly dependent on the concentration of the polyion. At a very low concentration macroions appear to be highly extended and probably adopt a rod like configuration in the limits of infinite dilutions.

Conductance Measurements

In order to further establish the polyelectrolytic behavior of PVA, PAAm, and PVA-g-PAAm composite, conductance measurements were made at $30 \pm 0.2^\circ\text{C}$ and the results are presented in Figures 4–6. It is observed from Figure 4 that the specific conductance of PVA decreases continuously between $15 \times 10^{-6} \Omega^{-1}$ to $9 \times 10^{-1} \Omega^{-1}$ upon dilution whereas PAAm shows a sharp decrease in specific conductance beyond 0.04% concentration of its aqueous solution (Fig. 5). Viscosity measurements also showed a sharp increase in reduced viscosity beyond 0.04% concentration of aqueous solution of PAAm, indicating that at this concentration of PAAm a significant change occurs. It is further observed that the specific conductance of PAAm is higher than that of PVA for all concentration ranges studied. Examination of the plot of conductance versus concentration of PVA-g-PAAm composite (Fig. 6) shows that the trend in change of specific conduc-

tance with dilution is different from that of PVA and PAAm. Conductance of PVA-g-PAAm decreases continuously with dilution and it bears a linear relationship with percent concentration of the aqueous solution of the composite. Specific conductance values of the composite are higher than those of PAAm.

Conductance measurement studies indicate that both the composite and the homopolymer, PAAm, behave as polyelectrolytes. The polyelectrolytic behavior of the composite, however, is more pronounced. PVA, on the other hand, behaves as a non-polyelectrolyte.

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