

Viscometric, Conductometric, and Ultrasonic Studies of Gelatin-g-polyacrylamide Composite

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SYNOPSIS

Polymerization of acrylamide in aqueous medium in the presence of gelatin has been carried out by the mutual method in air. All attempts to separate graft copolymer from the homopolymer and unreacted gelatin were unsuccessful as all the components were soluble in water. Hence the mixture comprising unreacted gelatin, homopolymer, polyacrylamide (PAAm), and the graft copolymer of gelatin and PAAm is referred to as the gelatin-g-PAAm composite. Solution properties of the composite with respect to viscosity, conductivity, and ultrasonic velocities were studied and the results were compared with those of PAAm prepared under identical conditions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Although gelatin enjoys a wide range of usage in diverse industrial applications certain properties of the gelatin limit their use and eliminate them for consideration in specific processes. Modification of gelatin by graft copolymerization can bring about improvements in properties broadening the overall usefulness of this important protein. Various types of chemical derivatives of gelatin have been prepared through interaction with specific reagents. Keinchington¹ studied the esterification of carboxyl groups and acylation of amino acid and the histidine group. Organic acid anhydride and acid chloride have been reacted with gelatin to form derivative for several uses in photographic² and pharmaceutical³ applications. Klasek et al.⁴ and Kwajima et al.⁵ grafted methyl methacrylate onto gelatin using redox initiator and radical initiator, respectively. Misra et al.^{6,7} have successfully grafted acrylate monomers onto gelatin using redox initiators. In the present communication we report on grafting of acrylamide onto gelatin using gamma rays as initiator by the mutual method. Physical properties such as viscosity, conductance, and ultrasonic velocities of the

composite and PAAm in aqueous solution have been investigated.

EXPERIMENTAL

Material and Methods

Gelatin (Oxoid, England) was in the form of granules and was used as received. Acrylamide (SISCO) recrystallized from methanol was used. Distilled water was used as solvent in all the grafting experiments.

Graft Copolymerization

Gelatin (100 mg) was dissolved in a definite amount of boiled distilled water in 50-mL conical flask. The temperature of the reaction mixture was brought to room temperature. A definite amount of acrylamide was dissolved in it and the reaction mixture was irradiated from a ⁶⁰Co source for different time periods at a constant dose rate of 0.2 Mrad/h. After the completion of the reaction excess methanol was added to the reaction mixture in order to precipitate the grafted gelatin, the homopolymer, PAAm, and any unreacted gelatin and filtered.

All attempts to separate the grafted gelatin from the homopolymer by solvent extraction were unsuccessful since both the graft and the homopolymer

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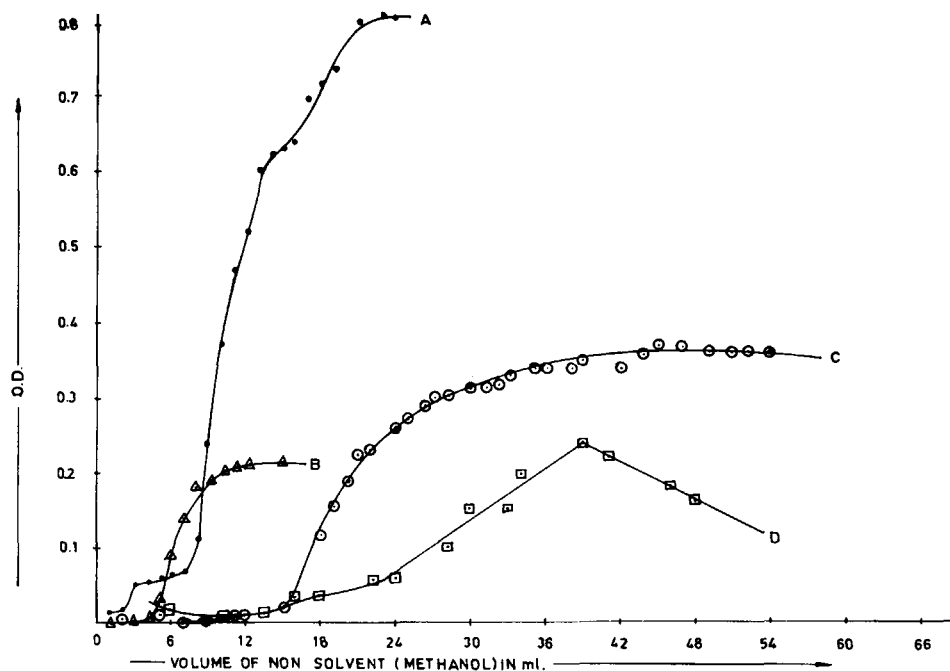


Figure 1 Turbidimetric titration of PAAm (○), gelatin-*g*-PAAm composite (●), physical mixture of gelatin + PAAm (△), and gelatin (□).

are soluble in water. The product, therefore, is not a true graft copolymer but rather a mixture of ungrafted gelatin, PAAm, and gelatin-*g*-PAAm graft copolymer. This mixture is referred to as gelatin-*g*-PAAm composite.

A series of polymerization reactions of acrylamide in aqueous medium were also carried out in the absence of gelatin under identical conditions for com-

parative studies. The procedure for polymerization and precipitation was the same as for the graft copolymerization.

Weight percentage of gelatin-*g*-PAAm composite was determined from the weight increase in gelatin after grafting while the percentage of total homopolymer of acrylamide formed was calculated from the initial weight of acrylamide used.

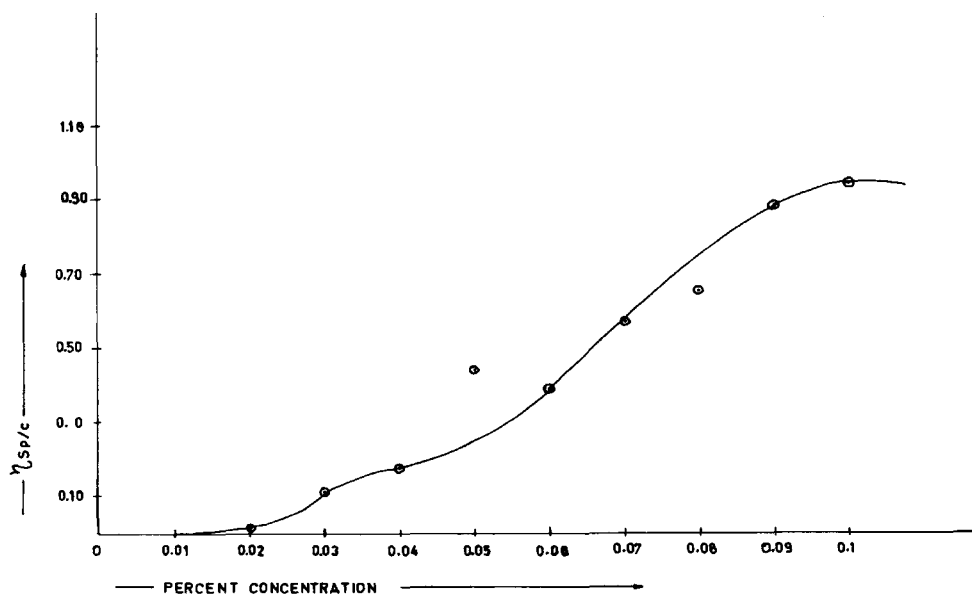


Figure 2 η_{sp}/c vs. percent concentration of pure gelatin.

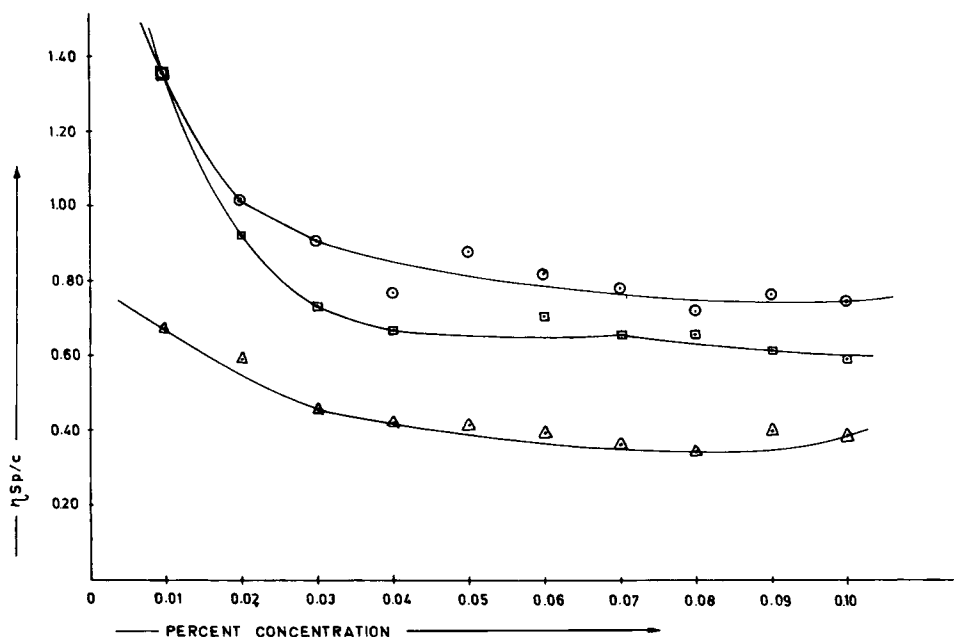


Figure 3 $\eta_{sp/c}$ vs. percent composition of PAAm prepared as a function of total dose. (○) 0.168 Mrad; (□) 0.28 Mrad; (△) 0.224 Mrad.

Turbidimetric Titrations

Turbidimetric titrations of 20 mL of 0.1% aqueous solutions each of gelatin, PAAm, gelatin-*g*-PAAm composite, and the physical mixture of gelatin and PAAm in aqueous medium were carried out using methanol as a nonsolvent. 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, that is the ratio of optical density of the solution to the optical density at complete precipitation, was plotted against volume of the precipitant added and the results are presented in Figure 1 Curves A, B, C, and D, respectively, represent the precipitation of gelatin-*g*-PAAm composite, physical mixture of gelatin and PAAm, PAAm, and gelatin. It is observed from curves C and D that upon addition of the nonsolvent to PAAm solution (curve C), an increase in optical density occurs, while in case of gelatin (curve D) increase in the optical density with increasing amount of methanol is sharp up to 39 mL and then it decreases. The physical mixture (curve B), however, shows an early precipitation with the addition of 15 mL methanol only. However, there is a sharp rise in optical density of the composite up to the addition of 8 mL MeOH beyond which it increases continuously (curve A), indicating that the composite behaves quite differently from the other sample solutions. Increase in the optical density of com-

posite with addition of MeOH up to 7 mL experiences a steep rise in the optical density followed by another sharp rise with further addition of MeOH up to 14 mL, beyond which the increase in optical density is regular. Complete precipitation occurs with 24 mL of methanol. The pattern of the precipitation curve of the composite indicates that the composite is not only a mixture of PAAm and gelatin but also contains some gelatin-*g*-PAAm.

RESULTS AND DISCUSSION

Irradiation of an aqueous mixture of gelatin and acrylamide by gamma rays was carried out in air. Upon irradiation active sites are generated onto gelatin where PAAm is grafted. Grafting of polyacrylamide onto gelatin and polymerization of acrylamide have been studied as a function of different reaction parameters such as total dose, monomer concentration, and amount of water. Maximum percentage of composite formation (293%) occurs at 0.28 Mrad while maximum homopolymer formation (243%) occurs at 0.224 Mrad. Studies of the effect of concentration of acrylamide on graft copolymerization reveal that the weight percentage of composite formation increases continuously with increasing monomer concentration. Formation of polyacrylamide also increases with increasing monomer concentration giving maximum percentage of 243% at

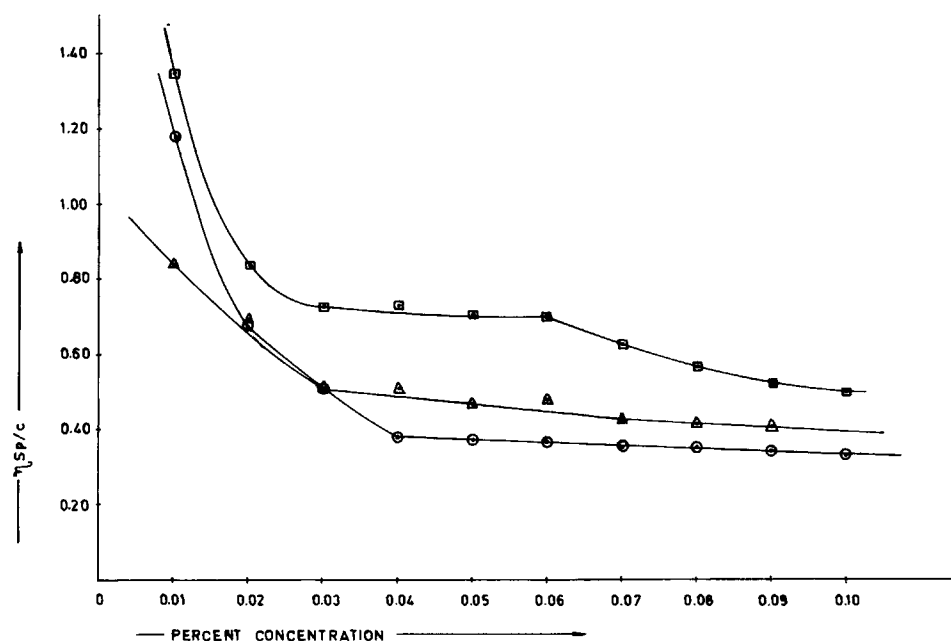


Figure 4 $\eta_{sp/c}$ vs. percent composition of gelatin-*g*-PAAm composite prepared as a function of total dose. (○) 0.224 Mrad; (□) 0.28 Mrad; (△) 0.392 Mrad.

[AAm] = 0.211×10^{-2} mol. It is further observed that maximum weight percentage of composite formation (293%) and homopolymer formation (243%) occurred when 10 mL of water was used, beyond which percent conversion to composite and homopolymer decreased.

Viscometric Behavior of Gelatin, Gelatin-*g*-PAAm Composite, and PAAm

The viscosity measurements of aqueous solutions of gelatin, gelatin-*g*-PAAm composite, and PAAm were made at $30 \pm 0.2^\circ\text{C}$ using an Ubbelohde viscometer. Reduced viscosity, $\eta_{sp/c}$ was determined as a function of concentration of aqueous solutions of gelatin, gelatin-*g*-PAAm composite, and PAAm and the results are presented in Figures 2–9.

Examination of the plots of reduced viscosity, $\eta_{sp/c}$ versus concentration of aqueous solutions of PAAm (Fig. 3) and gelatin-*g*-PAAm composite (Fig. 4) prepared at different total doses reveals that the reduced viscosity of both the polymeric solutions remains constant up to a concentration of 0.04%. Upon further dilution reduced viscosity of both the polymeric materials increases. Maximum $\eta_{sp/c}$ for both the samples prepared at a total dose of 0.28 Mrad was observed. The reduced viscosity values of the composite are higher than those of PAAm at higher dilution suggesting strong polyelectrolytic behavior of the composite.

Reduced viscosity of the homopolymer and the composite samples prepared as a function of monomer concentrations are presented in Figures 5 and 6 respectively. It is observed from Figure 8 that the reduced viscosity of PAAm remains constant up to 0.04% concentration, below which there is a rise in the reduced viscosity with further dilution. The behavior of the aqueous solutions of composite upon dilution is different with different samples (Fig. 6). It is observed from Figure 6 that the reduced viscosity curve of samples with 142 and 163 wt % of the composite (curves A and D) resembles the reduced viscosity curve of ungrafted gelatin (Fig. 2), suggesting that the presence of a small amount of PAAm as grafted chains in gelatin does not significantly change the viscosity behavior of the composites and the solution behaves as a nonpolyelectrolyte. However, when the percent weight of the composite increases to 293% (curve C) and 326% (curve B), reduced viscosity upon dilution below 0.03% concentration experiences an increase, indicating the polyelectrolytic behavior.

Plots of reduced viscosity versus concentration of aqueous solutions of PAAm and the composite samples prepared using varying amount of water are presented in Figures 7 and 8, respectively. It is observed from Figure 7 that the aqueous solutions of PAAm show rise in reduced viscosity upon dilution below 0.05% concentration. However, the samples prepared using 25 mL of water show a continuous

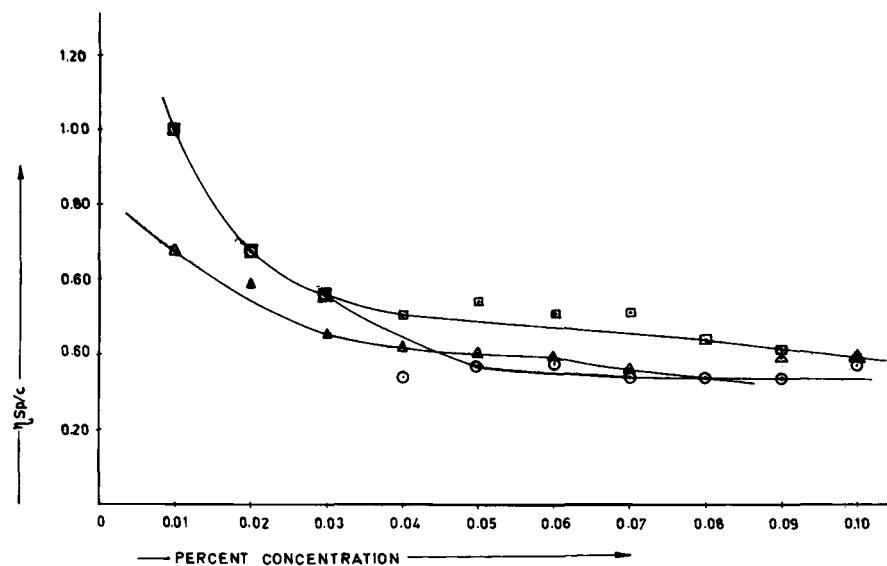


Figure 5 η_{sp}/c vs. percent composition of PAAm prepared as a function of [AAm]. (△) 0.211×10^{-2} mol; (○) 0.28×10^{-2} mol; (□) 0.35×10^{-2} mol.

rise in reduced viscosity, which drops sharply after 0.03% concentration indicating a nonpolyelectrolytic behavior. The reason for such behavior of this particular sample may be due to the fact that the specific viscosity of the samples prepared using different amounts of water shows that the sample prepared with 25 mL water has minimum specific viscosity and this indicates that no gel formation occurs and as such the sample behaves as a linear neutral

polymer. The plots of reduced viscosity versus concentration of the aqueous solution of the composite (Fig. 8) indicate that the reduced viscosity starts increasing below 0.08% concentration, indicating a strong polyelectrolytic behavior of the composite upon dilution.

From the foregoing discussion it is clear that gelatin, which itself does not show polyelectrolytic behavior, upon grafting with PAAm behaves as a poly-

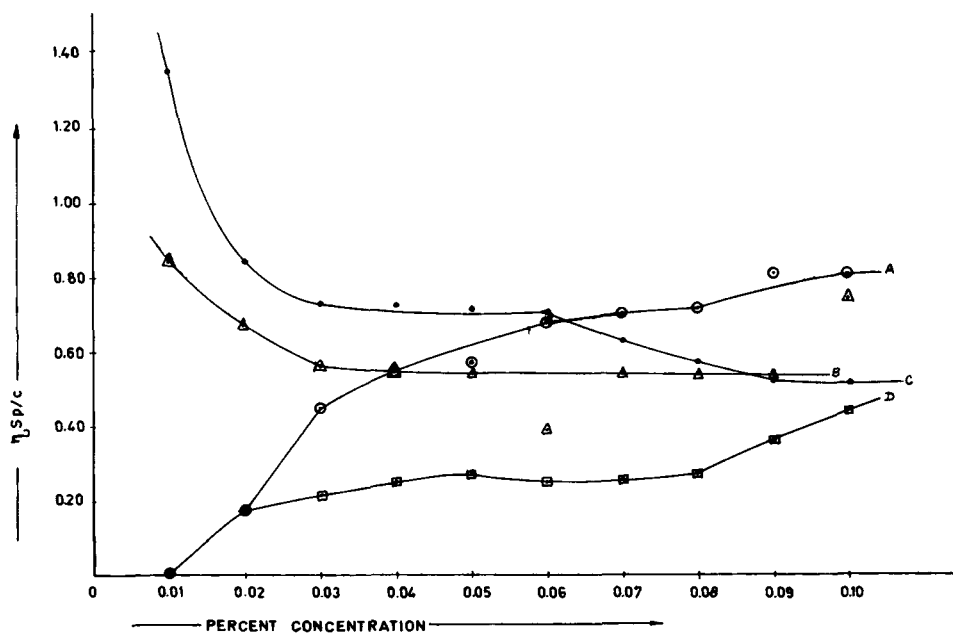


Figure 6 η_{sp}/c vs. percent composition of gelatin-*g*-PAAm composite prepared as a function of [AAm]. (○) 0.07×10^{-2} mol; (△) 0.28×10^{-2} mol; (●) 0.211×10^{-2} mol; (□) 0.14×10^{-2} mol.

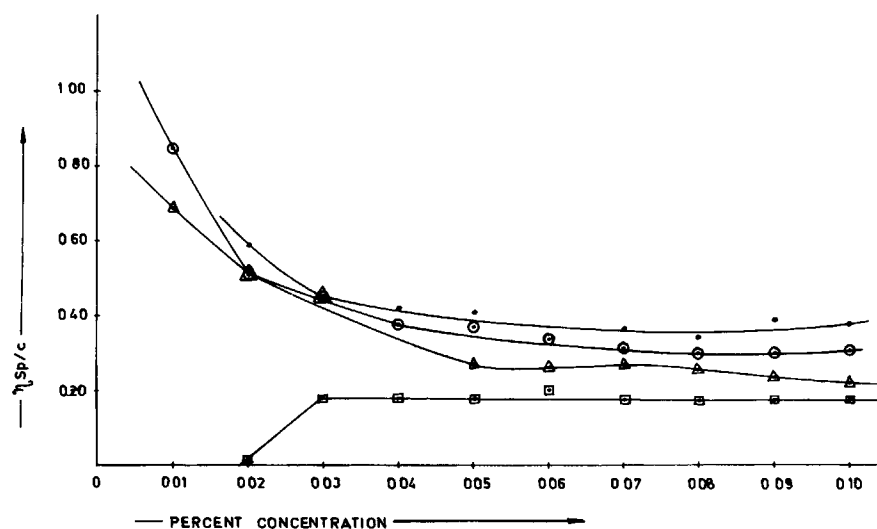


Figure 7 $\eta_{sp/c}$ vs. percent composition of PAAm prepared as a function of amount of water. (○) 15 mL; (●) 20 mL; (□) 25 mL; (△) 30 mL.

electrolyte. These facts were further confirmed when the viscosities of the various solutions of PAAm and the composite were measured in the presence of strong electrolyte, potassium bromide, and the results are presented in Figure 9. The solutions of the composite and the homopolymer were diluted by the addition of 40% aqueous solution of KBr. It is observed from the figure that the added salt solution depresses the viscosity of polyelectrolyte solutions of both the PAAm (curve a) and the composite (curve b). The general effect of the simple salt is to depress the viscosity of the polyelectrolyte solution over the entire range of concentrations. This indicates that the addition of the electrolyte neutralizes the ionic groups on the grafted gelatin and PAAm, thereby making them behave like a neutral polymer solution.

Conductance Studies of Gelatin, Gelatin-*g*-PAAm Composite, and PAAm Aqueous Solutions

The conductance of aqueous solutions of gelatin, polyacrylamide, and gelatin-*g*-PAAm composites has been measured at 1 kHz with a digital conductivity cell with a cell constant 0.568 cm^{-1} .

The specific conductance of aqueous solutions of gelatin-*g*-PAAm composite, prepared as a function of total dose and monomer concentration, has been measured and the results are presented in Figure 10. It is observed from the figure that the specific conductance (k) of gelatin-*g*-PAAm composite prepared as a function of total dose decreases sharply upon dilution. Maximum value has been obtained with the sample prepared at a total dose of 0.224 Mrad.

On the other hand, the aqueous solutions of PAAm samples prepared as a function of varying total doses (Fig. 10) show constant k values up to 0.08%; upon further dilution it decreases sharply. Maximum k value is obtained with PAAm sample prepared at 0.208 Mrad.

The specific conductance of aqueous solutions of gelatin-*g*-PAAm composite prepared as a function of monomer concentration (Fig. 11) also shows a decrease in k values upon dilution. It is observed that there is an optimum value (228%) of wt % of the composite at which k values are maximum. At the higher weight percentage (326%) a decrease in specific conductance is observed. PAAm samples prepared as a function of monomer concentration does not show marked difference in the specific conductance values. These observations indicate that the composite has more ionic ends in its structure as compared to PAAm and therefore shows stronger polyelectrolytic behavior in comparison to PAAm. This may be due to the fact that aggregation of the polyanion structure of PAAm breaks upon dilution, thereby decreasing specific conductance while such aggregation of PAAm in the composite is absent since, in the composite, grafted PAAm groups are separated by other functional groups of the gelatin backbone. Therefore, higher specific conductance values are obtained for the composite. These results support the viscosity results and confirm that the polyelectrolytic behavior of the composite is more pronounced than that of PAAm.

Conductance studies of aqueous solutions of gelatin shows that conductance increases with increasing dilution (Fig. 12) indicating that gelatin does

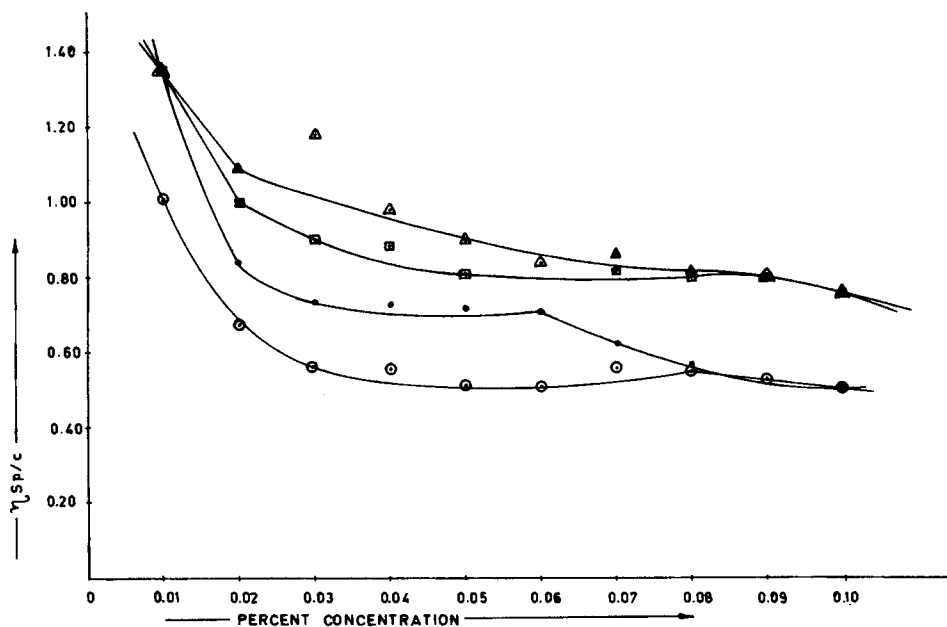


Figure 8 η_{sp}/c vs. percent composition of gelatin-*g*-PAAm composite prepared as a function of amount of H₂O. (○) 10 mL; (◻) 15 mL; (●) 20 mL; (△) 25 mL.

not show polyelectrolytic behavior. When specific conductance of the aqueous solutions of composite and PAAm is measured in the presence of strong electrolyte, potassium bromide (Fig. 13), it is observed that the specific conductance decreases sharply in both the cases. The values of k for composite and PAAm are much higher than the k values

of both the polymeric solutions in the absence of KBr. It is further observed (Fig. 13) that in the presence of KBr the specific conductance of PAAm is higher than the specific conductance of composite, but the reverse is true in the absence of KBr. This indicates that the composite shows more pronounced polyelectrolytic behavior than PAAm.

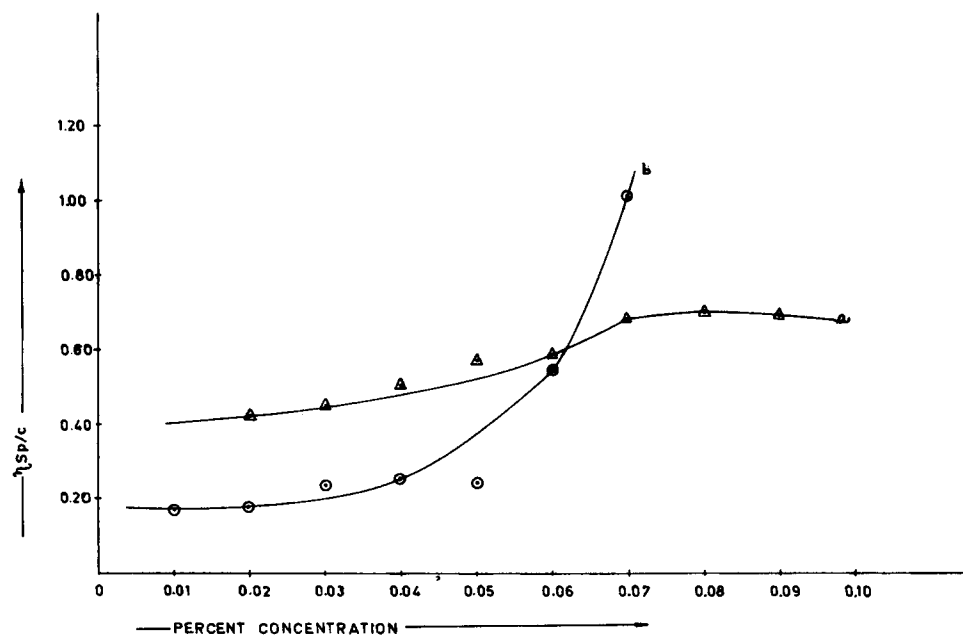


Figure 9 Effect of KBr on η_{sp}/c vs. percent composition curves of PAAm (△) and gelatin-*g*-PAAm composite (○).

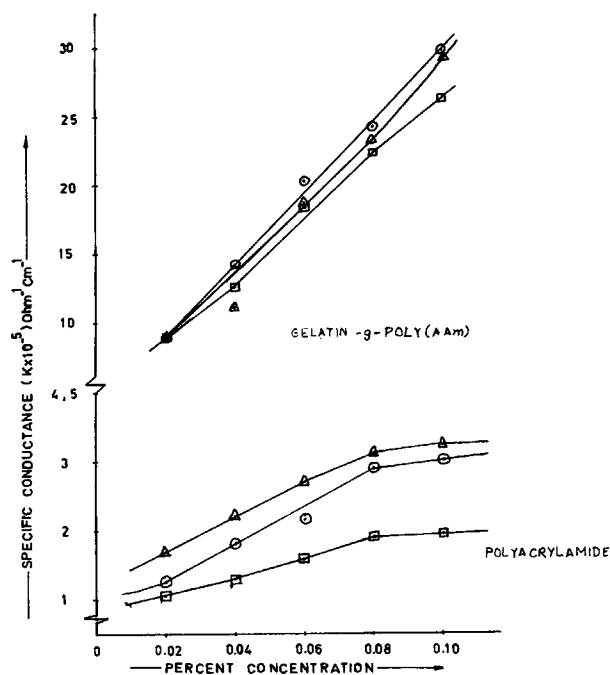


Figure 10 Specific conductance versus percent composition of PAAm (\odot 0.168 Mrad; \triangle 0.208 Mrad; \square 0.224 Mrad) and gelatin-*g*-PAAm composite (\odot , 0.224 Mrad; \triangle 0.392 Mrad; \square 0.280 Mrad) prepared as a function of total dose.

Ultrasonic Studies of Gelatin, Gelatin-*g*-PAAm Composite, and PAAm

Ultrasonic velocities, v (ms^{-1}), in 0.1% aqueous solutions each of 0.1% gelatin, gelatin-*g*-PAAm

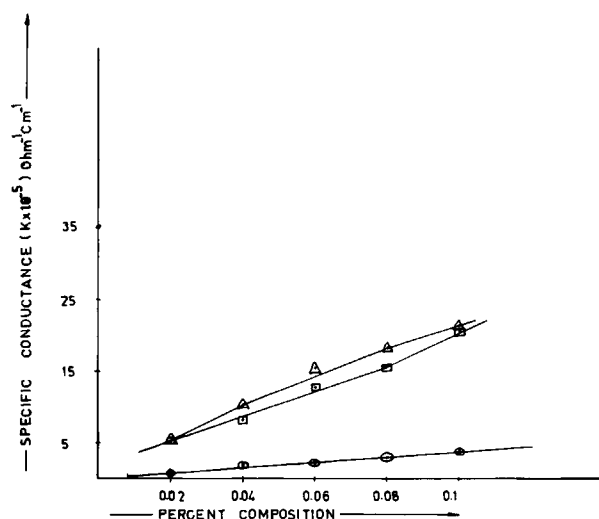


Figure 11 Specific conductance vs. percent composition of PAAm (\odot , 0.35×10^{-2} mol) and gelatin-*g*-PAAm composite (\square , 0.14×10^{-2} mol; \triangle , 0.28×10^{-2} mol) prepared as a function of [AAm].

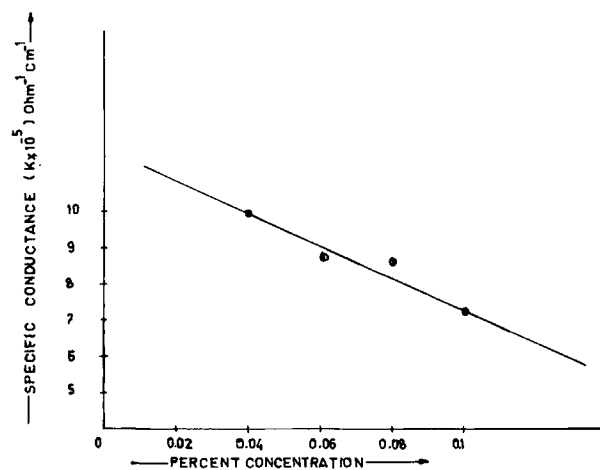


Figure 12 Specific conductance vs. percent composition of pure gelatin.

composite, and PAAm have been measured using an ultrasonic time intervalometer (UTI-101 model), based on a pulse-echo overlap (PEO) technique operating at a frequency of 2 MHz with an accuracy of 2 parts in 104 at 25, 35, and 45°C. The results are presented in Table I. Examination of the table shows that variation in weight percentage of PAAm and gelatin-*g*-PAAm composite prepared as a function of total dose and monomer

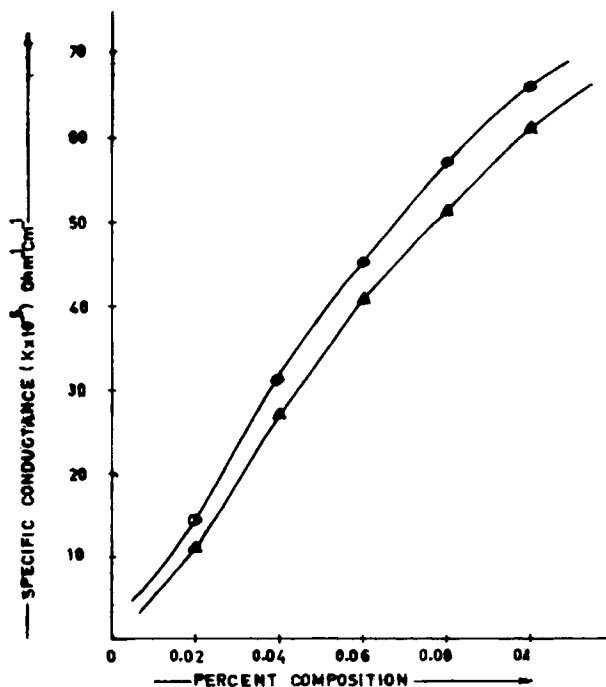


Figure 13 Effect of KBr on specific conductance vs. percent composition curves of PAAm (\odot) and gelatin-*g*-PAAm composite (\triangle) prepared as a function of total dose.

Table I Ultrasonic Velocities of (0.1%) Aqueous Solutions of Gelatin, PAAm, and Gelatin-*g*-PAAm Composite Prepared as a Function of Total Dose and Monomer Concentration^a

| Sample No. | Polymer Sample | Total Dose (Mrad) | (AAm) × 10 ² moles | Percentage Composition (%) | Ultrasonic Velocities (V/ms ⁻¹) | | |
|------------|-----------------------------------|-------------------|-------------------------------|----------------------------|---|--------|--------|
| | | | | | 25°C | 35°C | 45°C |
| | Pure gelatin | — | — | — | 1505 | 1527 | 1547 |
| 1 | PAAm | 0.168 | 0.211 | 167 | 1505.4 | 1527.8 | 1544.2 |
| 2 | PAAm | 0.208 | 0.211 | 187 | 1507.7 | 1530.8 | 1545.7 |
| 3 | PAAm | 0.224 | 0.211 | 243 | 1508.3 | 1530.5 | 1544.6 |
| 4 | Gelatin- <i>g</i> -PAAm composite | 0.224 | 0.211 | 228 | 1504.7 | 1528.6 | 1543.8 |
| 5 | Gelatin- <i>g</i> -PAAm composite | 0.392 | 0.211 | 242 | 1508.13 | 1527.8 | 1544.0 |
| 6 | Gelatin- <i>g</i> -PAAm composite | 0.392 | 0.211 | 293 | 1506.5 | 1527.7 | 1543.6 |
| 7 | PAAm | 0.224 | 0.35 | 221 | 1508.3 | 1530.5 | 1544.7 |
| 8 | PAAm | 0.28 | 232 | 1505.8 | 1529.5 | 1527.7 | 1543.7 |
| 9 | Gelatin-PAAm composite | 0.28 | 0.14 | 163 | 1505.5 | 1527.7 | 1543.7 |
| 10 | Gelatin-polyacrylamide composite | 0.28 | 0.28 | 326 | 1508.8 | 1527.4 | 1542.2 |

^a Gelatin = 100 mg, H₂O = 20 mL.

concentration does not significantly change the ultrasonic velocities.

It has been observed that the ultrasonic velocities in all three polymer samples increase with increasing temperature. This observation is contrary to expectations since ultrasonic velocities of polymer solution normally decrease with rise in temperature. Since as the temperature rises, intermolecular attraction forces decrease, a decrease in velocity is expected. In the present case, however, the composite and PAAm have the polyion structure in which ionic interaction as well as extensive intra- and intermolecular hydrogen bonding are present. With rise in temperature intramolecular and intermolecular hydrogen bonding breaks but the extended polyan ions of the composite and PAAm still have the intermolecular ionic interactions between the expanded polymeric chain carrying ionic groups, thereby the close association of polymeric chains remains intact and hence an increase in ultrasonic velocities with a rise in temperature is observed.

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