Viscometric Studies of Starch-g-Polyacrylamide Composites

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SYNOPSIS

Composites of starch-g-polyacrylamide, starch, and polyacrylamide have been prepared by gamma radiation-initiated polymerization of acrylamide in the presence of starch in aqueous medium. The polymerization was studied as a function of the (i) amount of water (ii) monomer concentration, and (iii) total dose. The optimum conditions for maximum conversion of the monomer to homopolymer and graft copolymer have been evaluated. Percentage of grafting of polyacrylamide could not be determined precisely as both the homopolymer and the graft are soluble in common solvents and all attempts to separate the graft from the homopolymer were unsuccessful. However, the formation of the starch-g-polyacrylamide copolymer was confirmed by the turbidimetric studies using acetone as a nonsolvent. The products of polymerization of acrylamide in the presence of starch consisted of unreacted starch, starch-g-polyacrylamide, and polyacrylamide and is referred to as the composite. Acrylamide was also polymerized in the absence of starch using γ-rays as means of initiation and the optimum conditions for maximum conversion of acrylamide to polyacrylamide have been evaluated. Viscosity behavior of the composite and polyacrylamide was studied in aqueous medium at $30 \pm 0.04°C$. The reduced specific viscosity of the aqueous solution of acrylamide and the composite as well was found to increase with increasing dilution, the effect being more pronounced in the composite. This tends to indicate that both the homopolymer and the composite behave as polyelectrolytes. An attempt has been made to explain the polyelectrolytic behavior of the homopolymer and the composite. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Use of polyacrylamide in various aspects has grown enormously. The principal outlets continue to be water treatment, mining, and paper manufacturing. Besides these uses, polyacrylamide is extensively used in enhanced oil recovery (EOR) processes to reduce the mobility of water in porous media.[1,2] Different types of water-soluble polymers used in EOR applications include xanthum gum polysaccharide and partially hydrolyzed polyacrylamide. The purpose of these polymers is to reduce the mobility of injected fluids during flow through the reservoir.[3] Xanthum gum and polyacrylamide reduce the mobility principally by increasing the viscosity of the injected fluid. Polyacrylamide used in EOR generally contains 10–50% carboxyl groups and possesses molecular weights averaging a few hundred or thousands to many millions. It is known that these water-soluble polymers offer greater resistance to flow than that expected from their viscosity behavior. During injections and flow through the reservoir rock, polymer solutions are required to be stable under high shear rate. The usual EOR agent such as polyacrylamide degrades at a high shear rate as well as in the presence of salty waters that contain a significant concentration of divalent ions.[4] This drawback can be overcome by the use of water-soluble organic graft copolymers. In recent years, increasing interest has arisen in determining the structure and composition of a water-soluble random or graft copolymer that would be more efficient for use as displacement fluids during EOR processes. The many requirements necessary for a candidate polymer to perform adequately in this application is that high-solution viscosities (large hydrodynamic dimensions) in aqueous solution must be maintained at low concentrations of polymer.[5] Additionally, the polymer
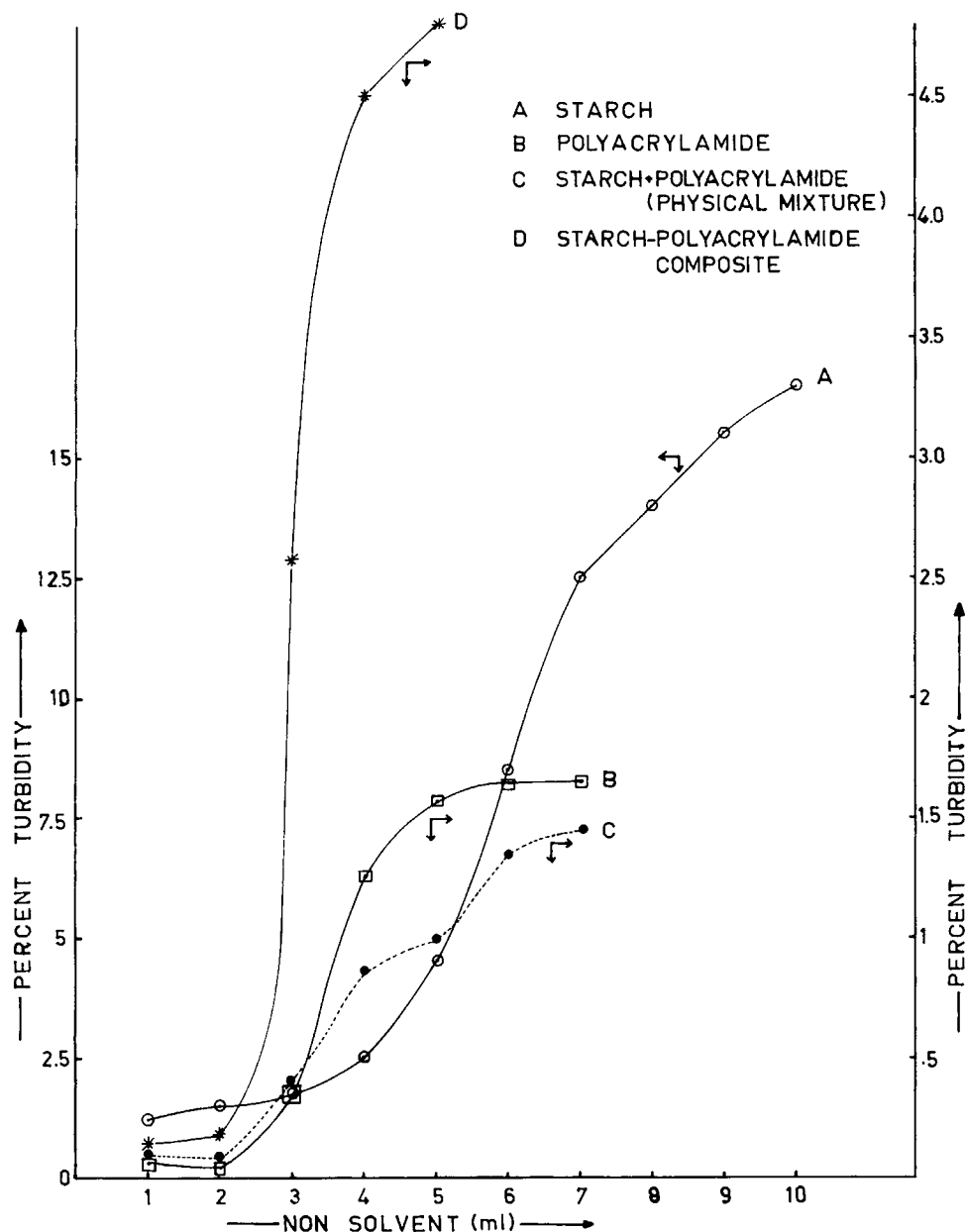

Figure 1   Variation in percent turbidity with added nonsolvent.

in solution must permeate the porous medium to displace residual oil without degradation or adsorption. To obtain more detailed information on structure–property relations, a series of model acrylamide copolymers have been synthesized under controlled conditions and investigated with respect to solution viscosity behavior. Some of the acrylamide copolymers are synthesized by graft copolymerization.[6] Some typical hydrophilic backbone polymers are starch, dextran, cellulose, PVA, poly(N-vinyl pyrolidinone). Some of these polymers find uses as flocculants, oil recovery agents, and adhesives.

Starch is probably the most abundant and low-cost polymer commercially available. Research on starch and modified starches as extenders or replacements for petroleum-derived polymers has resulted in several new technologies. Some of these new technologies provide new polymeric systems for use in pharmaceuticals and agriculture. 2-Hydroxy-3-methacryloyloxypropyltrimethylammonium chloride was grafted onto whole wheat starch using Ce^{4+} and Fenton's reagent by Fanta et al.[7] The graft copolymers were tested as flocculating agents for diatomaceous silica and nonmagnetic iron ore. Grafting

Table I Effect of Total Dose, [AAm], and Amount of Water on Percent Weight Increase and Total Monomer Conversion during Polymerization of Acrylamide in the Presence and Absence of Starch

Sample No.	Water (mL)	Total Dose (MR)	[AAm] (Mol $\times 10^{-3}$)	Percentage of Increase in Presence of Starch[a] (%)	Total Monomer Conversion in Absence of Starch
1	15	0.34	3.5	250	150
2	15	0.52	3.5	254	117.5
3	15	0.86	3.5	261	96.4
4	15	1.20	3.5	247	98.6
5	15	1.38	3.5	244	71.7
6	15	0.86	2.1	145	171.3
7	15	0.86	2.8	245	164
8	15	0.86	4.2	330	139.6
9	15	0.86	4.9	499	138.8
10	5	0.86	3.5	259	234
11	10	0.86	3.5	253	181
12	20	0.86	3.5	244	132.6
13	25	0.86	3.5	235	85.1

[a] Starch = 100 mg.

Table II $[\eta]_{sp}$ of Starch-*g*-PAAm Composite and Polyacrylamide at Various Concentrations

Sample No.	Reaction Variable (Total Dose) (MR)	Polymer Sample	$[\eta]_{sp}$ at									
			0.01%	0.02%	0.03%	0.04%	0.05%	0.06%	0.07%	0.08%	0.09%	0.1%
1	0.34	Starch-*g*-PAAm	0.55	0.72	0.65	0.70	0.78	0.81	0.93	1.08	1.28	1.75
2	0.52		0.69	0.92	0.98	1.63	1.91	2.02	2.16	2.44	2.57	3.33
3	0.86		1.75	3.3	3.5	3.04	3.7	4.26	4.97	5.8	6.9	8.2
4	1.20		0.37	0.59	0.68	0.80	0.86	1.06	1.11	1.34	1.55	1.69
5	1.38		0.59	0.86	0.92	0.85	1.0	1.0	1.14	1.32	1.21	1.58
6	0.34	PAAm[b]	0.03	0.05	0.09	0.10	0.13	0.15	0.20	0.2	0.24	0.25
7	0.52		0.03	0.06	0.09	0.11	0.13	0.15	0.18	0.21	0.23	0.26
8	0.86		0.34	0.41	0.46	0.5	0.55	0.58	0.67	0.68	0.72	0.79
9	1.20		0.58	0.66	0.74	0.78	0.82	0.92	0.98	1.04	1.06	1.11
10	1.38		0.13	0.23	0.27	0.34	0.4	0.48	0.52	0.55	0.57	0.77

Reaction conditions—a: starch = 100 mg, AAm = 3.5 $\times$ 10^{-3} mol, H_2O = 15 ml; b: AAm = 3.5 $\times$ 10^{-3} mol; H_2O = 15 mL.

Table III $[\eta]_{sp}$ of Starch-*g*-PAAm Composite and Polyacrylamide at Various Concentrations

Sample No.	Reaction Variable (Monomer Conc Mol)	Polymer Sample	$[\eta]_{sp}$ at									
			0.01%	0.02%	0.03%	0.04%	0.05%	0.06%	0.07%	0.08%	0.09%	0.10%
1	2.1 $\times$ 10^{-3}	Starch-*g*-PAAm composite	0.20	0.31	0.37	0.37	0.45	0.48	0.51	0.59	0.7	0.86
2	2.8 $\times$ 10^{-3}		0.70	1.24	1.29	1.35	1.41	1.46	1.51	1.56	1.58	1.6
3	3.5 $\times$ 10^{-3}		1.75	3.3	3.5	3.04	3.7	4.26	4.97	5.8	6.9	8.2
4	4.2 $\times$ 10^{-3}		7.02	7.10	7.20	7.28	7.34	7.42	7.43	7.54	7.58	7.65
5	4.9 $\times$ 10^{-3}		8.8	8.94	9.00	9.05	9.11	9.20	9.28	9.31	9.37	9.43
6	2.1 $\times$ 10^{-3}	PAAm[b]	0.03	0.07	0.09	0.12	0.14	0.16	0.17	0.19	0.21	0.24
7	2.8 $\times$ 10^{-3}		0.08	0.14	0.18	0.21	0.24	0.27	0.31	0.35	0.38	0.44
8	3.5 $\times$ 10^{-3}		0.34	0.41	0.46	0.5	0.55	0.58	0.67	0.68	0.72	0.79
9	4.2 $\times$ 10^{-3}		1.20	1.27	1.33	1.37	1.46	1.48	1.52	1.58	1.62	1.60
10	4.9 $\times$ 10^{-3}		1.51	1.58	1.63	1.71	1.77	1.83	1.86	1.9	1.94	1.97

Reaction conditions—a: starch = 100 mg, H_2O = 15 mL, total dose = 0.86 MR; b: H_2O = 15 mL, total dose = 0.86 MR.

Table IV $[\eta]_{sp}$ of Starch-g-PAAm Composite and PAAm at Various Concentrations

Sample No.	Reaction Variable (Amount of H₂O [ml])	Polymer Sample	$[\eta]_{sp}$ at									
			0.01%	0.02%	0.03%	0.04%	0.05%	0.06%	0.07%	0.08%	0.09%	0.10%
1	5	Starch-g-PAAm composite[a]	1.7	2.56	2.62	2.66	2.75	2.80	2.90	2.9	3.10	3.39
2	10		1.65	2.72	2.79	2.85	2.89	2.93	2.6	3.07	3.10	3.13
3	15		1.75	3.3	3.5	3.04	3.7	4.26	4.97	5.8	6.9	8.2
4	20		1.06	1.13	1.18	1.24	1.27	1.34	1.43	1.46	1.46	1.51
5	25		1.0	1.06	1.15	1.20	1.22	1.24	1.27	1.30	1.32	1.41
6	5	PAAm[b]	0.13	0.22	0.28	0.32	0.36	0.39	0.45	0.48	0.60	0.60
7	10		0.18	0.24	0.28	0.32	0.38	0.42	0.5	0.51	0.55	0.62
8	15		0.34	0.41	0.46	0.5	0.55	0.58	0.67	0.68	0.72	0.79
9	20		0.19	0.31	0.36	0.42	0.51	0.51	0.56	0.60	0.69	0.74
10	25		0.17	0.22	0.27	0.34	0.39	0.45	0.48	0.52	0.55	0.58

Reaction conditions—a: starch = 100 mg, AAm = 3.5×10^{-3} mol, total dose = 0.86 MR; b: AAm = 3.5×10^{-3} mol, total dose = 0.86 MR.

of acrylamide and N,N,N-trimethylaminoethyl-methacrylate methyl sulfate onto starch was also studied by Fanta et al.[8] by simultaneous irradiation from Co^{60}. In the present article, an attempt has been made to synthesize water-soluble composites consisting of starch, polyacrylamide (PAAm), and starch-g-PAAm that may find uses in EOR processes and as speciality polymers.

EXPERIMENTAL

Pure starch (BDH) and distilled water was used in all experiments. Acrylamide was recrystallized from water. CO^{60} 2100 Ci has been used as the source of gamma radiation.

Pure and dry starch powder (100 mg) was dissolved in a known amount of water at 90°C. The temperature of the reaction flask was brought to room temperature and a known amount of acrylamide was added. The reaction mixture was irradiated for different time periods at a constant dose rate of 0.17 MR/h. After the completion of the reaction, methanol was added to the reaction mixture until complete precipitation occurred and the contents filtered. The precipitated residue is a mixture of ungrafted starch, starch-g-PAAm, and the homopolymer, PAAm. All attempts to separate the graft copolymer from the homopolymer were unsuccessful since both the graft and the homopolymer are soluble in common organic solvents. Therefore,

the product that is not a true graft copolymer but a mixture of graft copolymer with homopolymer and unreacted starch is referred to as starch-g-PAAm composite. The formation of graft during irradiation is confirmed by turbidimetric titrations. PAAm has also been synthesized separately by using gamma radiations as means of initiation under identical conditions. A comparative study of the viscosity behavior of starch-g-PAAm composite and PAAm has been made.

Turbidimetric Titrations

Turbidimetric titrations of starch, PAAm, starch-g-PAAm composites and a physical mixture of starch and PAAm in aqueous medium were carried out using acetone as the precipitating solvent. Standard solutions of each substrate is prepared by dissolving 0.1 g of each sample in 100 mL of distilled water. The physical mixture of starch and PAAm was prepared by dissolving 0.05 g of starch and 0.05 g of PAAm in 100 mL of water. To these standard solutions, a 1 mL portion of acetone was added in succession, and optical density of the solution was measured at 380 nm after each addition until complete precipitation took place. Percent turbidity is the ratio of optical density of the solution to optical density at complete precipitation.[9]

Percent turbidity was plotted against the volume of the precipitant added and the results are presented in Figure 1. Curves A and B represent the
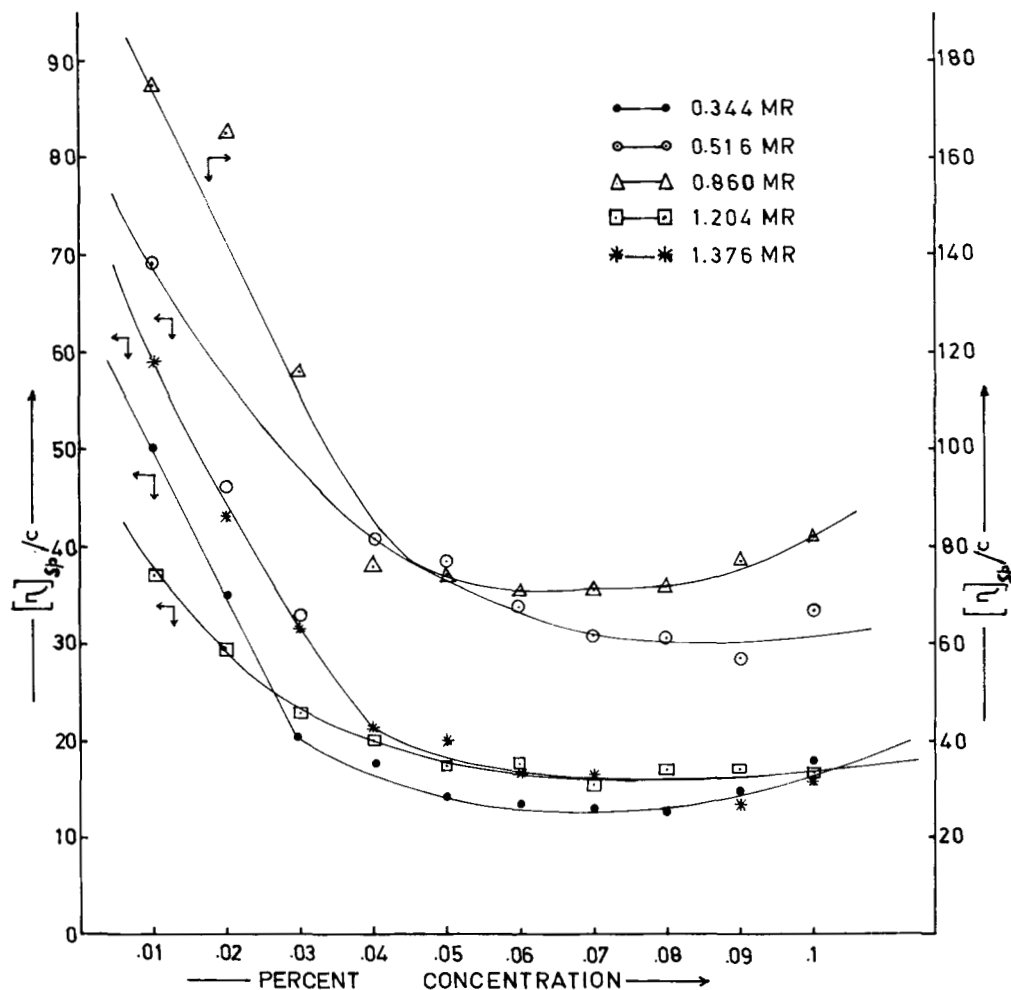
Figure 2   Effect of total dose on $[\eta]_{sp}/c$ of starch-*g*-PAAm composite.

titration of a solution of starch and PAAm, respectively; curve C, that of a physical mixture of starch and PAAm; and curve D, that of starch-*g*-PAAm composite under identical conditions. It can be seen that in curve C of the physical mixture the turbidity increases rapidly on addition of 2–4 mL of acetone and again on addition of 5–6 mL of acetone. These steps may be attributed to the precipitation of PAAm and starch, respectively. However, in case of the composite, curve D is more or less continuous and no well-marked inflection is observed. Generally, the chemical nature of the polymer has a much greater influence on its solubility. The meager data available in the literature indicate that a graft copolymer will generally display the solubility pattern intermediate between those of the homopolymers. But it is observed from the figure that the composite (curve D) does not have the intermediate solubility of the two polymers, suggesting, thereby, that the

product of grafting is not a true graft copolymer but rather a mixture of unreacted starch, starch-*g*-PAAm, and PAAm. Nayudamma and co-workers[9] also studied the solubility behavior of collagen and MMA-grafted collagen by turbidimetric titrations and found that the solubility of grafted collagen is intermediate between collagen and poly(methyl methacrylate).

RESULTS AND DISCUSSION

Synthesis of graft copolymers of starch essentially involves generation of active sites on the starch backbone upon which a suitable monomer is polymerized. In the present work, initiation of the starch backbone is carried out by using gamma radiation by the mutual method in the presence of a vinyl monomer, acrylamide, leading to the formation of graft copolymer.
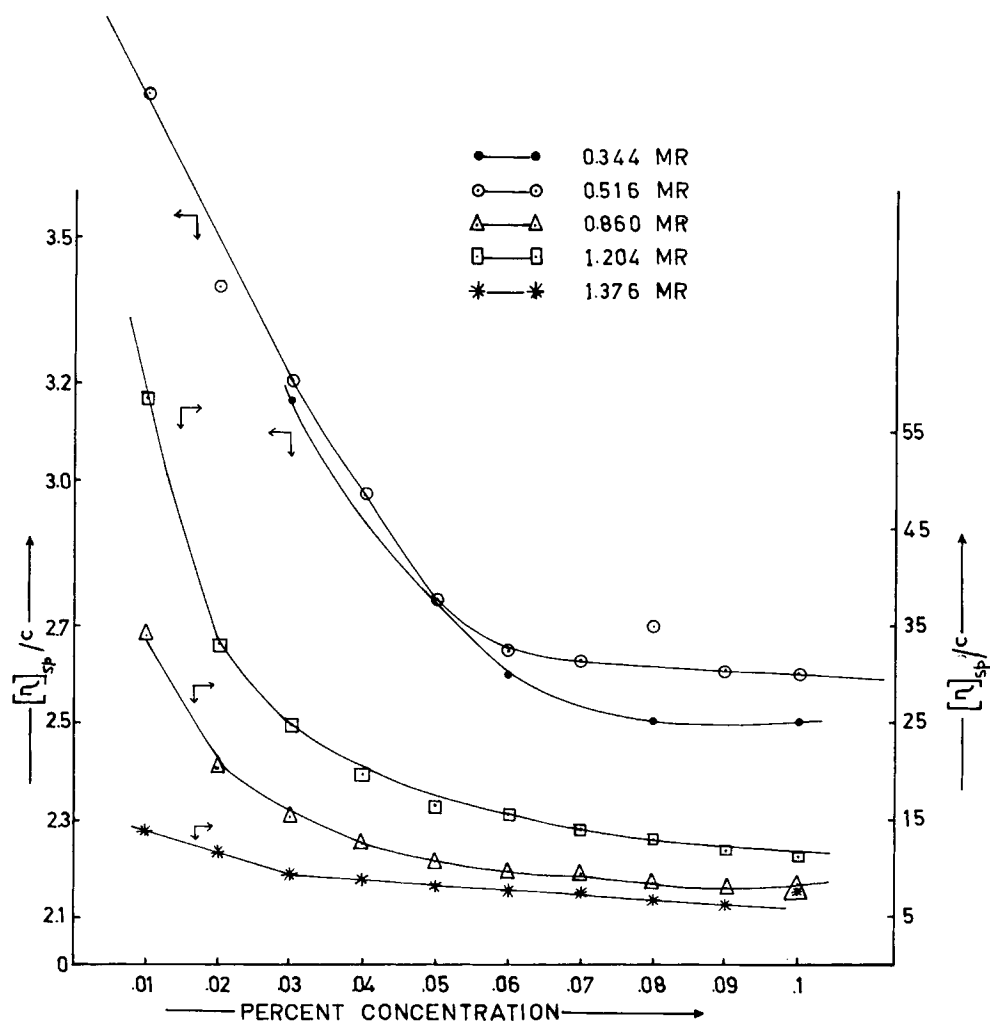
Figure 3   Effect of total dose on $[\eta]_{sp}/c$ of PAAm.

Polymerization of acrylamide was also carried out by the mutual irradiation method under identical conditions. The effect of various reaction parameters on graft copolymerization and polymerization reactions has been studied and the results are presented in Table I.

Viscosity Measurements of Starch-*g*-PAAm Composites and Polyacrylamide

The viscosities of different percent compositions of starch-*g*-PAAm composite and PAAm prepared under various reaction conditions have been determined in aqueous medium at 30 ± 0.04°C using a Ubbelohde viscometer. The specific viscosity values of each of the samples studied are presented in Ta-

bles II–IV. It is observed from Table II that the specific viscosity of starch-*g*-PAAm and PAAm prepared as a function of total dose increases with increase in percent concentration of the solution. Further, it is also observed that specific viscosity increases with increasing total dose, reaches maximum, and then decreases. Maximum viscosity is observed at a total dose of 0.86 MR for starch-*g*-PAAm composite and 1.20 MR for acrylamide.

Table III represents the specific viscosity values of starch-*g*-PAAm composite and PAAm samples prepared with different monomer concentrations. Maximum specific viscosity for both starch-*g*-PAAm composite and PAAm has been obtained at [AAm] = 4.9 × 10⁻³ mol.

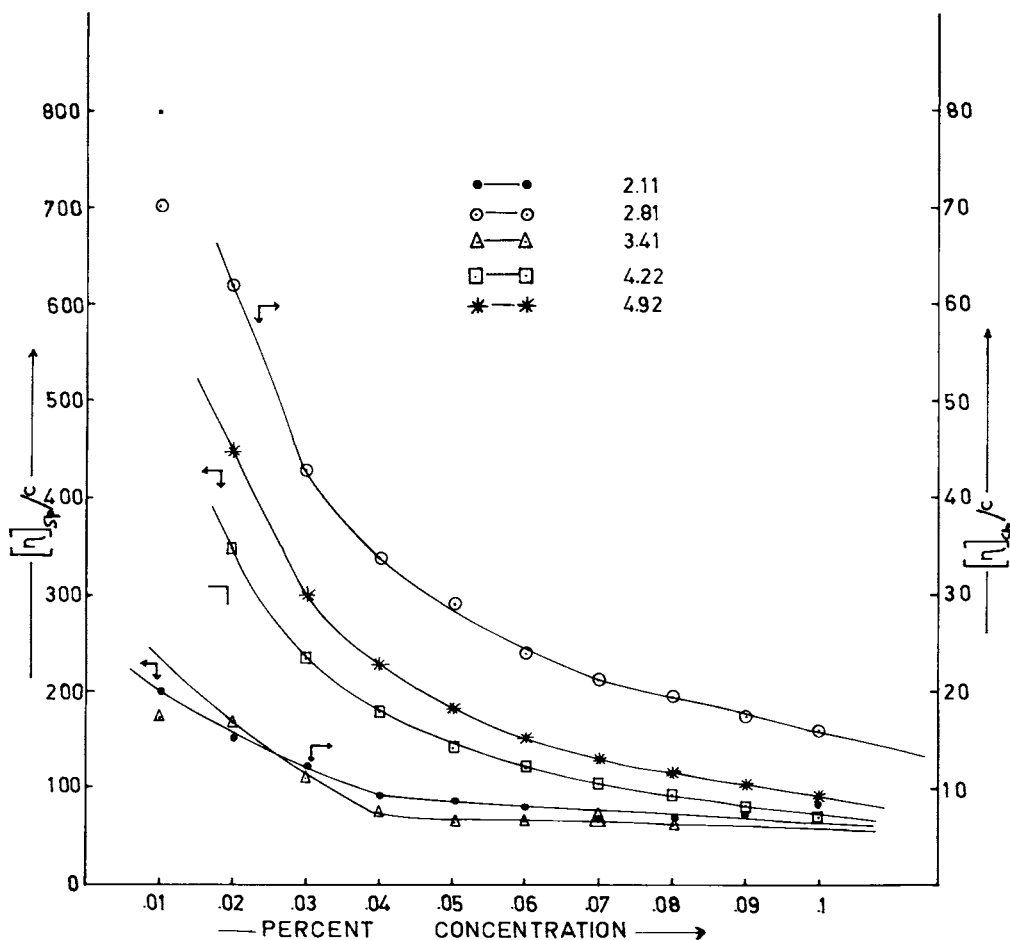The effect of the amount of water on specific viscosity of starch-*g*-PAAm composites and PAAm has

Figure 4 Effect of acrylamide concentration (mol) on $[\eta]_{sp}/c$ of starch-*g*-PAAm composite.

been studied and the results are presented in Table IV. It is observed from the table that the maximum specific viscosity for starch-*g*-PAAm composite and PAAm has been obtained using 15 mL of water.

The reduced specific viscosity of starch-*g*-PAAm composite and PAAm samples prepared as a function of total dose is plotted against different concentrations of the polymeric solutions and the results are presented in Figures 2 and 3. It is observed from Figure 2 that the effect of dilution on η_{sp}/c for the composite in water is remarkably different. The reduced viscosity increases sharply with dilution, and the increase is much higher in the case of the composite than of the homopolymer. The viscosities of the two solutions at low concentration does not increase linearly, indicating that these solutions are not true solutions. This indicates that both the composite and the homopolymer are present as gels that are highly swollen by the absorption of water.

Similar behavior was also observed by Taylor and Bagley[10] for starch–polyacrylonitrile graft copolymers. It is observed from Figure 3 that PAAm solutions also show similar behavior as that of the starch-*g*-PAAm composite, indicating that gel formation also occurs in PAAm solutions.

The reduced specific viscosity for starch-*g*-PAAm composites and PAAm prepared with different monomer concentrations are plotted against different concentrations of the polymeric solution and the results are presented in Figures 4 and 5. It is important to observe from Figures 4 and 5 that the shape of the curve of the composite and the homopolymer is markedly different when 2.1×10^{-3} mol of monomer was used for the preparation of the composite or the homopolymer. The reduced viscosity does not significantly vary with dilution and the curve is almost linear, indicating that when a particular concentration of acrylamide is used (2.1
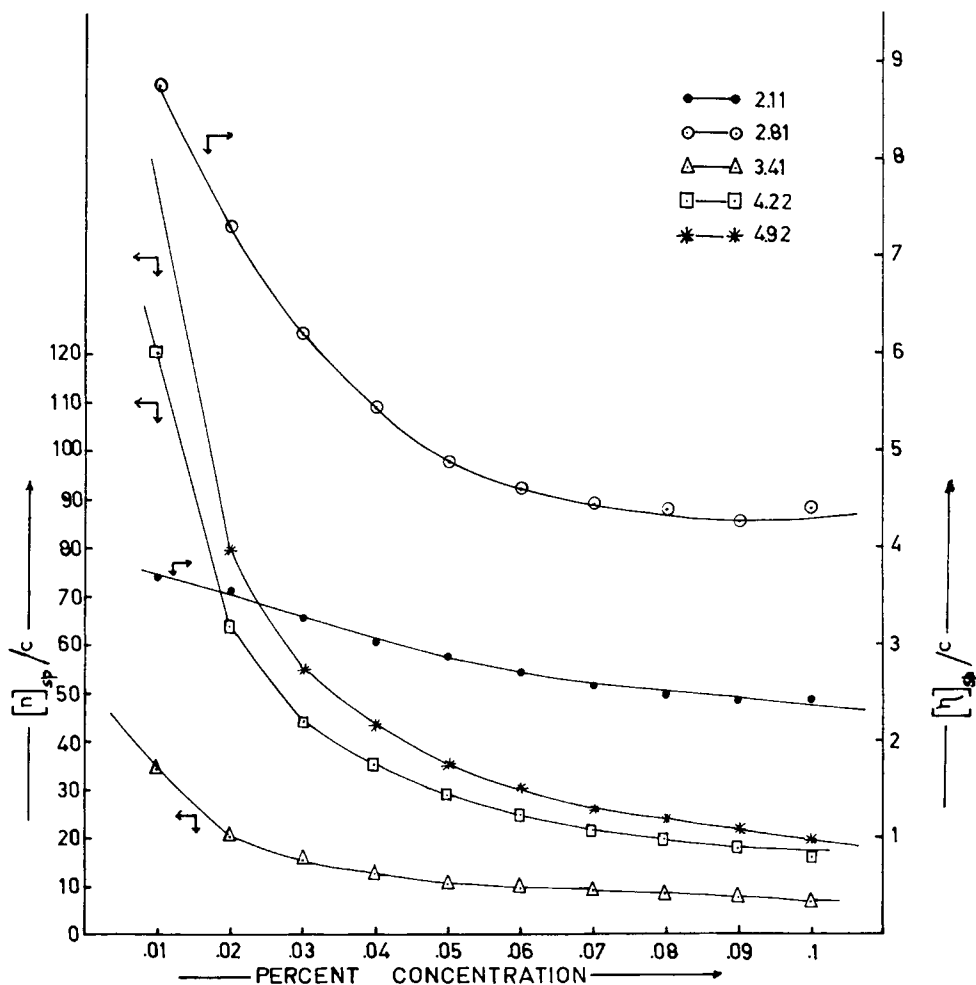
Figure 5 Effect of acrylamide concentration (mol) on $[\eta]_{sp}/c$ of PAAm.

$\times 10^{-3}$ mol) gel formation does not occur and the polymer behaves as a neutral polymer.

The plots of η_{sp}/c vs. concentration of the composite and PAAm prepared by using different amounts of water are presented in Figures 6 and 7. It is observed from the figures that when 15 mL of water is used both acrylamide and the composite show maximum values for specific (Table III) and reduced specific viscosities. This may indicate that when 15 mL of water is used maximum polymerization of acrylamide occurs both in the absence and presence of starch. The shapes of the curves (Figs. 6 and 7) of PAAm and the composite are, however, different from those discussed above. PAAm shows almost linear behavior up to a 0.03% solution, and upon further dilution, departure from linearity is observed. Such behavior is not shown by the com-

posite. This may indicate that under these conditions the polymeric solution is behaving as a neutral solution. Under similar conditions, the composite showed (Fig. 8) nonlinear behavior, which suggests that the composite shows polyelectrolytic behavior in which this stretching of the polymer takes place on dilution, thereby increasing the reduced specific viscosity.

Thus, it is clear from the above discussion that both PAAm and the starch-g-PAAm composite behave in aqueous solution as a polyelectrolyte, the latter being more efficient than the former. The differences in viscometric behavior of polymeric solutions reflecting the dependence of viscosity on polymer concentration reveal that dilution produces continuous changes in the nature of the electrostatic environments of individual polyions, leading to major changes in both intra- and interpolyion inter-
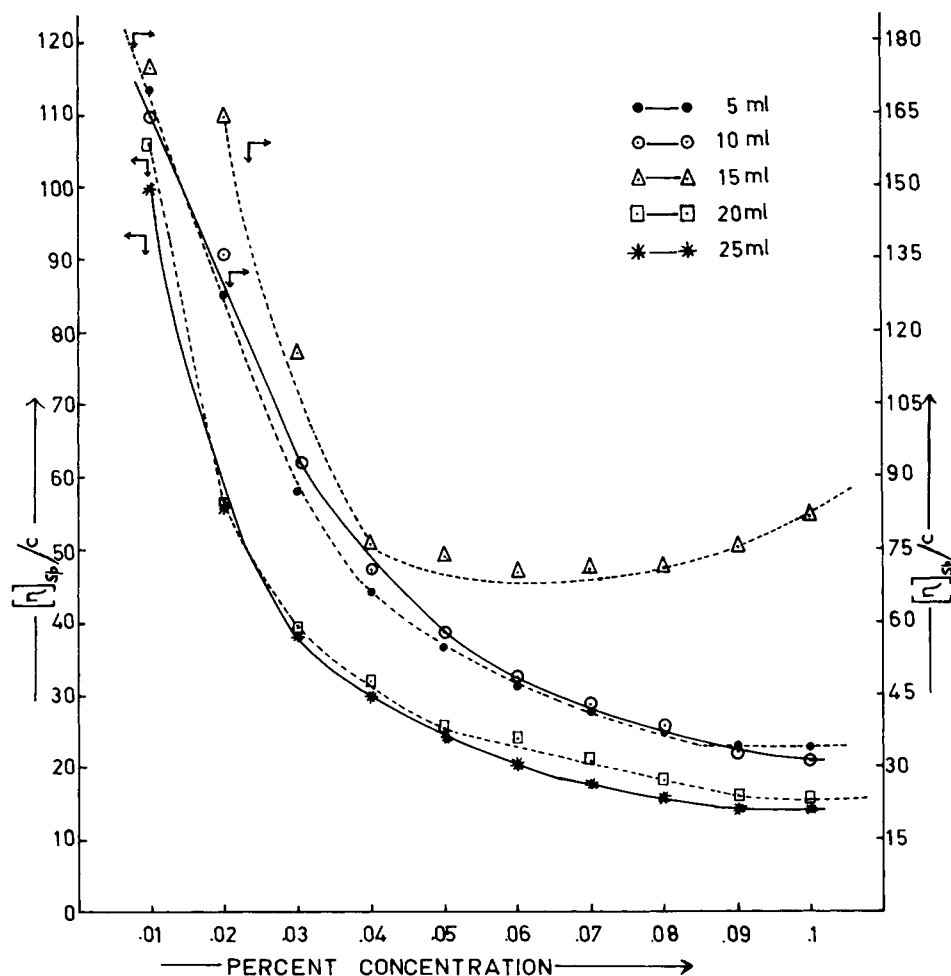
Figure 6   Effect of amount of water on $[\eta]_{sp}/c$ of starch-g-PAAm composite.

actions, and, hence, gives rise to reduced viscosity curves that differ fundamentally from those of nonionic polymers. Fuoss and Strauss[11] in 1948 reported that the reduced viscosity, η_{sp}/c, of solutions containing a pure highly charged linear polyelectrolyte increased sharply and continuously with dilution at very low concentration. These authors proposed that the observed sharp rise in η_{sp}/c with dilution was due primarily to polyion expansion. It was also argued that dilution would promote increased counterion dissociation, thus augmenting the intrapolyion repulsive forces that act to dilate the polyion dimensions. In complete absence of ionic impurities, it is probable that η_{sp}/c for pure electrolytes would increase with dilution without limit. Since this behavior is characteristic of simple electrolytes that increase the viscosity of water, it would be interesting to examine the reduced specific viscosities of

solutions containing multiply charged electrolytes. For flexible polyelectrolytes, the observed increase in η_{sp}/c with dilution is not only due to swelling of individual polyion, but must also reflect the increased hydrodynamic resistance to flow arising from increased interactions between the bulkier dilated polyions; these interactions would be expected to become very significant at high dilutions owing to the enormous expansion of polyion atmospheres at a very low ionic strength.

It is apparent from the foregoing discussion that the composites show a much higher increase in reduced specific viscosity at low concentrations as compared to PAAm. The starch-g-polycrylamide composite, therefore, possesses all desirable properties to act as an excellent EOR reagent for recovery of residual oil after primary and secondary recovery processes are exhausted.
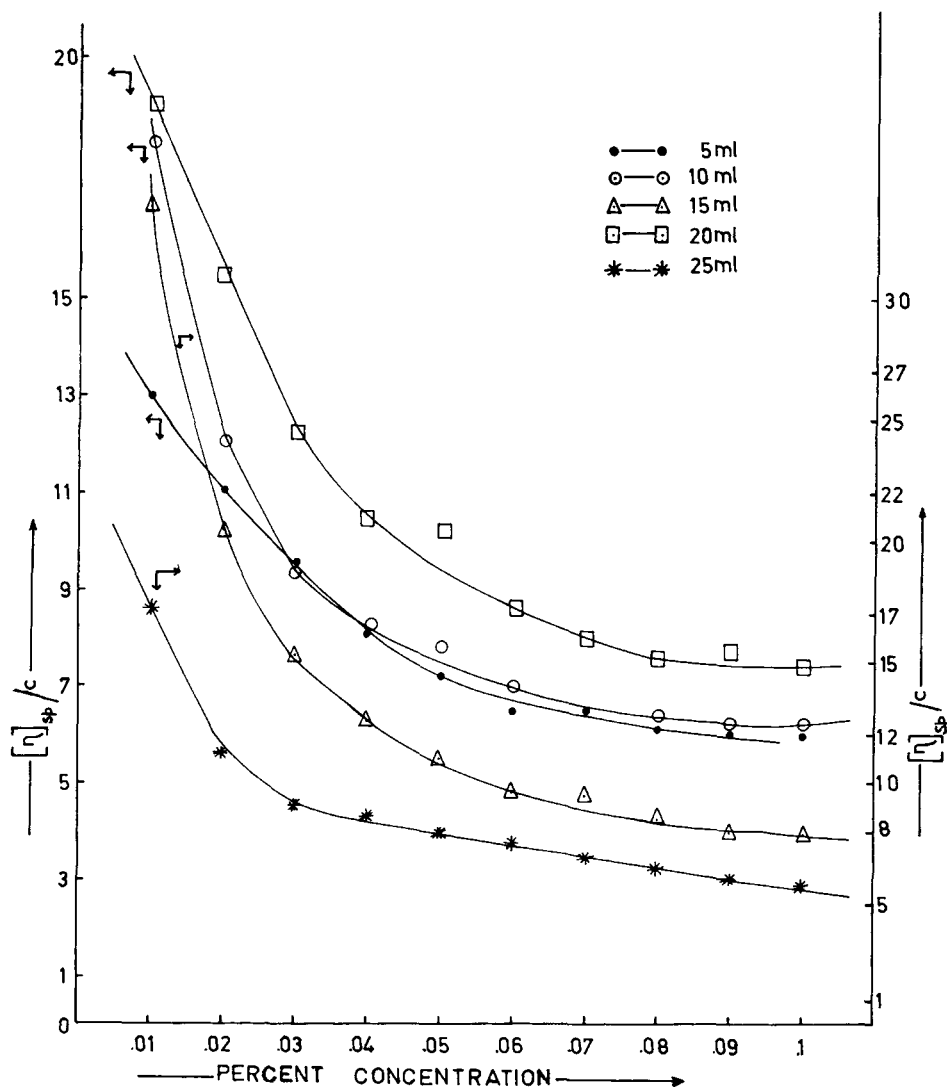
Figure 7 Effect of amount of water on $[\eta]_{sp}/c$ of PAAm.

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