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Effects of Alkali, Salts, and Surfactant on Rheological Behavior of Partially Hydrolyzed Polyacrylamide Solutions[†]

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The rheological behavior of a polymer solution is very important for its application in enhanced oil recovery. An experimental study was conducted to examine the effects of salts, alkali, and surfactants on the rheological properties of partially hydrolyzed polyacrylamide (PHPAM) over a wide range of parameters. The experimental results show that addition of ionic species significantly reduces the polymer viscosity by reducing the hydrodynamic size of the polymer. The power-law model was used to describe the rheological properties of the solutions. The flow behavior index, *n*, of the samples was in the range from 0.232 to 0.275, while the consistency index, *K*, ranged from (1.45 to 5.76) $\mathrm{Pa \cdot s}^n$. The variation of viscosity with temperature was also studied and found to satisfy the Arrhenius equation.

1. Introduction

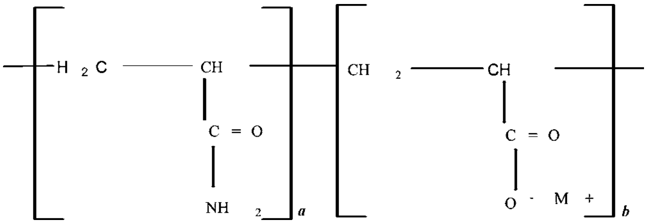
Over the last 30 years, partially hydrolyzed polyacrylamide (PHPAM) and its derivatives have attracted a great deal of attention because of their potential applications in different fields, such as enhanced oil recovery,[1,2] wastewater treatment,[3] and paper manufacturing.[4] PHPAM is widely used in oil fields and plays a very important role in tertiary oil recovery because it can be used as a viscosity modifier.[5−11]

The basic idea behind using water-soluble polymers in many oil fields' operation and various enhanced oil recovery processes is to reduce the mobility of the aqueous phase and consequently to improve the sweep efficiency. Additionally, polymer adsorption decreases the permeability to water, also reducing the mobility. There are many water-soluble polymers that can potentially be used in these applications. However, PHPAM is the most commonly employed polymer in field applications. Polymer flooding offers significant potential over the existing water-flooding method when the existing mobility ratios are poor or variation in the permeability distribution exists.

A small quantity of PHPAM can increase the viscosity of water by 2 or more orders of magnitude in the absence of added electrolytes. This phenomenon of increased viscosity results from the extremely high molecular weight of the polymers and the repulsion between the negative charges along the polymer chain.[12] However, formation fluids in the reservoir are often contaminated with different salts, naturally occurring surfactants, etc. Thus, addition of an ionic species (sodium chloride, calcium chloride, alkali, or an anionic surfactant) reduces the hydrodynamic size of the polymer molecule (physical change), changing the relationship between viscosity and shear rate.[13]

The effect of alkali on the viscosity of polymer solutions is complex, as alkali affects the polymer chain both physically (charge shielding) and chemically (hydrolysis). For alkali/polymer solutions, the viscosity is a function of the alkali type, concentration, and time after initial mixing.[14] The viscosity of alkali/polymer solutions is diminished by addition of NaCl.[15] The addition of anionic surfactants at low concentrations slightly decreases the viscosity of alkali/polymer solutions.[16−19] Because of its prominent performance, PHPAM is extensively used in mobility control of fluids in porous media.

Scheme 1. Chemical Structure of PHPAM



The interfacial rheological properties (viscosity, non-Newtonian flow behavior, constants of Ostwald's formula and the power law, temperature dependence of viscosity, activation energy of the viscous flow, etc.) are sensitive parameters for the characterization and identification of natural crude oil/water systems, and they provide valuable information for both exploration and production activities. The rheological properties of polymer solutions play an important role in determining their effectiveness. Depending on the process, polymers can encounter various chemical species, including salts, alkalis, and surfactants. The objectives of the present study are to examine the effects of salts, alkali, surfactants, and combinations of these factors on the dynamic viscosity of PHPAM over a wide range of shear rates for its application in enhanced oil recovery.

2. Experimental Section

2.1. Materials. PHPAM (Polymer Pusher 1000, SNF Floerger, France) was used as the polymer. The chemical structure of PHPAM is given in Scheme 1, where bonding of the carboxylate group with a metal ion ($M^+ = K^+$ or Na^+) is shown. The degree of hydrolysis is equal to $b/(a + b)$, where a and b are the numbers of amide and carboxylate groups, respectively. The anionic surfactant sodium dodecyl sulfate (SDS, $C_{12}H_{24}SO_4Na$, $M = 288.38 \cdot 10^{-3}\ \mathrm{kg \cdot mol^{-1}}$) was purchased from Central Drug House (P) Ltd., India. Reagent-grade sodium hydroxide (mass fraction purity 0.96) from S.D. Fine-Chem Ltd., was used as the alkali. Sodium carbonate (Na_2CO_3) and sodium

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chloride (NaCl) were purchased from Ranbaxy and Qualigens Fine Chemicals, respectively.

2.2. Preparation of PHPAM Solutions. The preparation of the polymer solution required special attention. All of the polymer solutions were prepared carefully with the minimum degree of agitation to avoid mechanical degradation of the long-chain molecules. A stock polymer solution containing $1.11 \cdot 10^{-6}$ $\text{mol} \cdot \text{kg}^{-1}$ polymer was first prepared using boiled deionized water. This solution was agitated using a magnetic stirrer for (8 to 10) h to form a consistent solution. Care was taken that the stirrer rotated at low rpm to avoid any mechanical degradation. It was then allowed to stand overnight to ensure full hydration. This process was repeated until the polymer solution was homogeneous. The polymer solution was then diluted to $5.556 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$. To remove any microgels, the $5.556 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$ solution was first filtered through a Whatman no. 1 filter by applying a pressure of $3.447 \cdot 10^{7}$ mPa across the filter. All of the polymer solutions were stored in closed containers to minimize oxygen uptake. No biocides or oxygen scavenger were added. Brines and alkali solutions were prepared from reagent-grade chemicals. All experimental runs were performed in a room in which the temperature was thermostatically controlled. The temperature was set at 301.5 K and maintained there at all times.

Polymer solutions are generally classified as pseudoplastic fluids under most conditions. A pseudoplastic material is one that exhibits a smaller resistance to flow as the shear rate increases. Mathematically, the formula is known as the power-law model (eq 1):[20]

$$\tau = K\gamma^{n} \tag{1}$$

where τ is the shear stress (Pa), γ is the shear rate (s^{-1}), n is the flow behavior index (dimensionless), and K is the consistency index ($\text{Pa} \cdot \text{s}^{n}$). For pseudoplastic fluids, $n < 1.0$. It should be noted that when $n = 1$, eq 1 reduces to the Newtonian case with K equivalent to the dynamic viscosity, η.

Polymer solutions have been characterized as pseudoplastic fluids, which display a decreasing apparent viscosity with increasing shear rate. The power-law model fairly represents the flow behavior of polymers at all shear rates except the very high rates that may exist at the injection well. At these high shear rates, the polymer solution loses its pseudoplastic nature and displays an increasing apparent viscosity with increasing shear rate. Such a fluid is normally classified as dilatant.[20]

2.3. Measurements. In the present study, the rheological parameters were measured with the help of a rheometer (Physica MC1) with a cup-and-bob measuring system. The flow curves were recorded at shear rates between (10^{-1} and 10^{3}) s^{-1} with 30 measurement points and a measuring-point duration of 10 s. The measurements were conducted over the temperature range from (301.5 to 333) K. Flow and viscosity curves reveal information about the ability of polymers to flow under different shear and simulated process conditions. When the shear rate is changed to different value, there is a particular amount of time before the viscosity reaches its equilibrium value at that shear rate. For a shear-thinning fluid, when the shear rate is increased, the viscosity often is high initially and then decreases to the equilibrium viscosity as steady flow is attained; when the shear rate is decreased, the viscosity often is low initially before increasing to the equilibrium viscosity. The measurements taken as the shear rate increased were same as those taken as the shear rate decreased, indicating that the steady-state viscosity for each shear rate was measured. The zero-shear viscosity η_0 at low shear rates is an important material property that is directly proportional to the average molar mass.

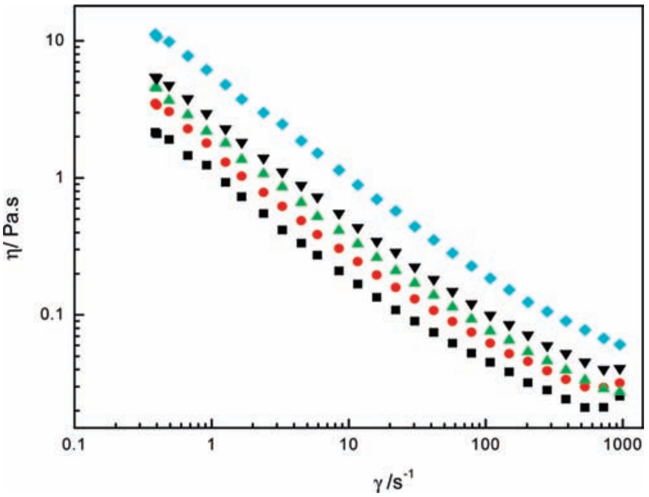

Figure 1. Viscosity (η) vs shear rate (γ) for different PHPAM solutions at 301.5 K: ■, $1.111 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ●, $1.6667 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ▲, $2.222 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ▼, $2.7778 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ◆, $5.556 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$.

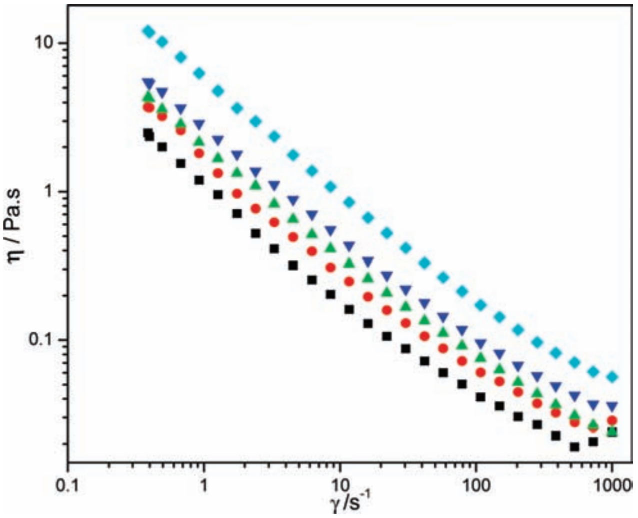

Figure 2. Viscosity (η) vs shear rate (γ) for different PHPAM solutions at 313 K: ■, $1.111 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ●, $1.6667 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ▲, $2.222 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ▼, $2.7778 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$; ◆, $5.556 \cdot 10^{-7}$ $\text{mol} \cdot \text{kg}^{-1}$.

3. Result and Discussion

3.1. Effect of Temperature on Polymer Viscosity. The flow curves for aqueous solutions of PHPAM polymer at different concentrations and temperatures are shown in Figures 1, 2, and 3. The viscosities of the solutions increased with increasing polymer concentration, as expected. As can be seen from the figures, the viscosities of all of the samples decreased with increasing shear rate, suggesting that the aqueous solutions of PHPAM exhibit non-Newtonian behavior. This is due to uncoiling and aligning of the polymer chains upon exposure to shear flow. In Figures 1, 2, and 3 for different polymer solutions, the viscosities show a plateau at low shear rates. This is the zero-shear viscosity, which can be measured by extrapolating the viscosity curve to the viscosity at zero-shear rate. At all polymer concentrations examined, the solution viscosity diminished with temperature. As temperature increases, the average speed of the molecules in a liquid increases, so the time they spend in contact with their nearest neighbors decreases. Thus, as temperature increases, the average intermolecular forces

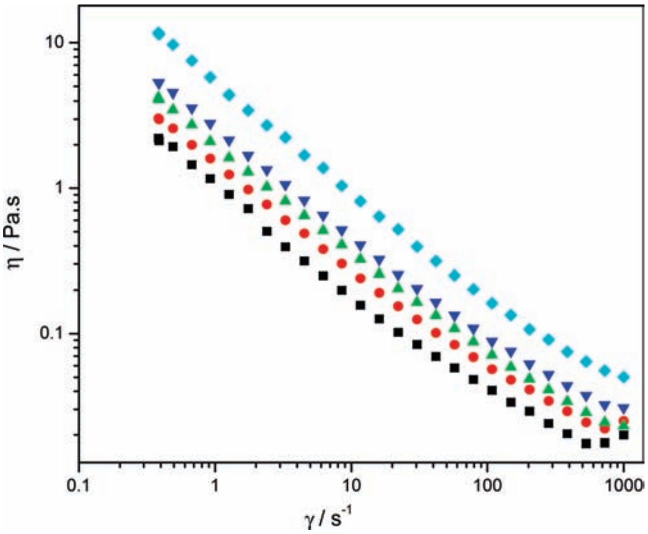

Figure 3. Viscosity (η) vs shear rate (γ) for different PHPAM solutions at 323 K: ■, 1.111·10^{-7} mol·kg^{-1}; ●, 1.6667·10^{-7} mol·kg^{-1}; ▲, 2.222·10^{-7} mol·kg^{-1}; ▼, 2.7778·10^{-7} mol·kg^{-1}; ◆, 5.556·10^{-7} mol·kg^{-1}.

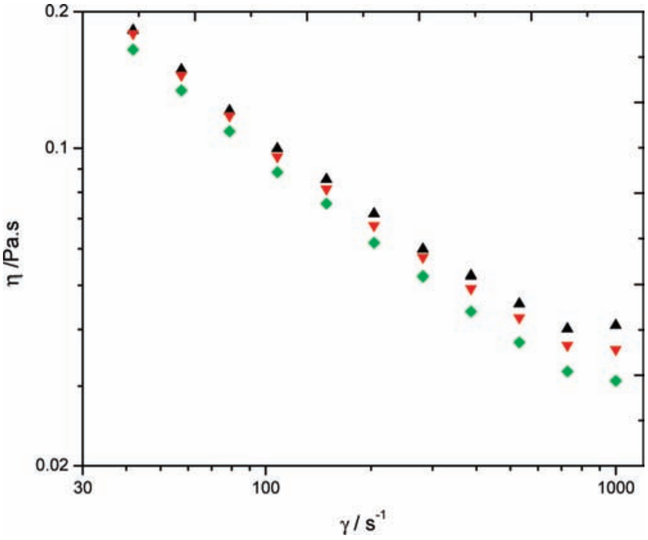

Figure 4. Viscosity (η) vs shear rate (γ) for a 2.7778·10^{-7} mol·kg^{-1} PHPAM solution at different temperatures: ◆, 301.5 K; ▼, 313 K; ▲, 323 K.

decrease. The effect of temperature on the PHPAM polymer viscosity is very complicated. As the solution temperature increases, the solvent viscosity decreases, but the degree of hydrolysis of the polymer increases.[21] As the degree of hydrolysis increases, the viscosity of the polymer in deionized water is enhanced as a result of the electrostatic repulsion between the negative charges on the polymer chain. The typical variation of viscosity with temperature is shown in Figure 4. At all polymer concentrations examined, the solution viscosity diminished with temperature. This indicates that the solution viscosity is dominant. However, the rate of decrease of the viscosity decreased with increasing shear rate because of enhanced hydrolysis of PHPAM at higher shear rates. A similar trend was observed by Nouri and Root,[22] and it implies that the viscosity of a polymer solution is a complex function of temperature. The effect of temperature on the power-law flow behavior index *n* at various polymer concentrations of PHPAM was found to be small, so *n* can be assumed to be constant over the temperature range from (301.5 to 323) K. The values are shown in Table 1.

It has been reported[23] that the relationship between the apparent viscosity of a polymer solution and temperature satisfies the Arrhenius equation (eq 2):

$$\eta = A \exp\left(\frac{\Delta E_\eta}{RT}\right) \tag{2}$$

where η is the apparent viscosity of the polymer solution, ΔE_η is the viscous activation energy, R is the gas constant, and T is the absolute temperature. According to eq 2, ln η and the reciprocal of the temperature of the polymer solution should show a straight-line relationship with a slope of $\Delta E_\eta/R$. Plots of ln η vs T^{-1} for different concentration of PHPAM are shown in Figure 5. The viscous activation energies at different concentrations were calculated from the slopes of the straight lines in Figure 5 and are plotted in Figure 6. Viscosity data were measured at an arbitrary shear rate (108 s^{-1}) where the curves were found to fit the power-law model well. The viscous activation energy is related to the dependence of the viscosity on the temperature of the polymer solution, and the higher the viscous activation energy is, the greater the influence of temperature on the viscosity.

The variation of shear stress with shear rate is shown on logarithmic scales in Figures 7 to 10. On the basis of eq 1, the values of *K* and *n* can be calculated from the intercept and slope, respectively. The *K* and *n* values for the polymer solutions under various conditions are shown in Table 1. All of the samples showed good fits to the power law, and it is obvious that all of the samples exhibit shear-thinning behavior.

3.2. Effect of Salts on Polymer Viscosity. On the basis of the rheological data, it was concluded that the polymer solution viscosity increased as the molecular weight and polymer concentration increased. The polymer solution viscosity and its

Table 1. Rheological Parameters (Consistency Index of Fluid, *K*, and Flow Behavior Index, *n*) of PHPAM Solutions at Different Concentrations (*C*) and Temperatures (*T*)

C	T		K ± SD	
mol·kg^{-1}	K	R^2	Pa·s^n	n ± SD
1.6667·10^{-7}	301.5	0.9965	1.484328 ± 0.00696	0.27574 ± 0.00770
1.6667·10^{-7}	313.0	0.9956	1.483782 ± 0.00776	0.27564 ± 0.00858
1.6667·10^{-7}	323.0	0.9982	1.459117 ± 0.00487	0.27104 ± 0.00538
2.222·10^{-7}	301.5	0.9968	2.046068 ± 0.00627	0.26170 ± 0.00693
2.222·10^{-7}	313.0	0.9981	2.000322 ± 0.00485	0.26658 ± 0.00526
2.222·10^{-7}	323.0	0.9997	1.934417 ± 0.00186	0.27428 ± 0.00206
2.7778·10^{-7}	301.5	0.9988	2.698112 ± 0.00381	0.26491 ± 0.00426
2.7778·10^{-7}	313.0	0.9990	2.674361 ± 0.00343	0.26685 ± 0.00380
2.7778·10^{-7}	323.0	0.9995	2.555465 ± 0.00222	0.25792 ± 0.00470
5.556·10^{-7}	301.5	0.9994	5.765142 ± 0.00249	0.24570 ± 0.00277
5.556·10^{-7}	313.0	0.9992	5.656268 ± 0.00279	0.23201 ± 0.00310
5.556·10^{-7}	323.0	0.9998	5.304934 ± 0.00133	0.23950 ± 0.00147

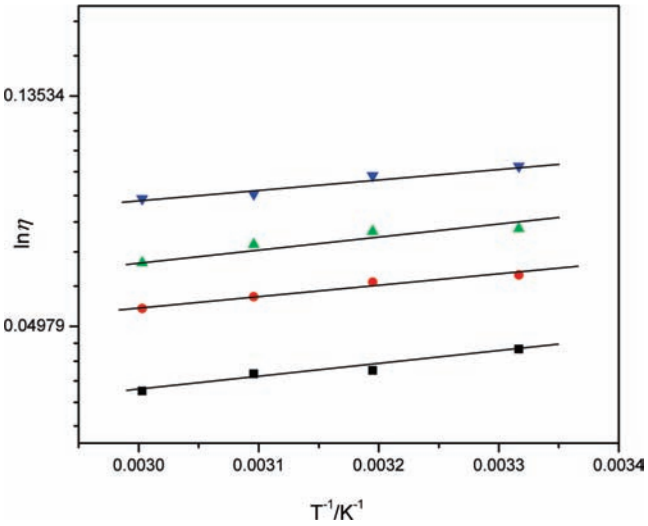

Figure 5. Variation of ln η with T^{-1} for $\gamma = 108\ \mathrm{s}^{-1}$: ■, $1.111 \cdot 10^{-7}$ mol·kg^{-1}; ●, $1.6667 \cdot 10^{-7}$ mol·kg^{-1}; ▲, $2.222 \cdot 10^{-7}$ mol·kg^{-1}; ▼, $2.7778 \cdot 10^{-7}$ mol·kg^{-1}. The solid lines are the best-fit lines through the corresponding data.

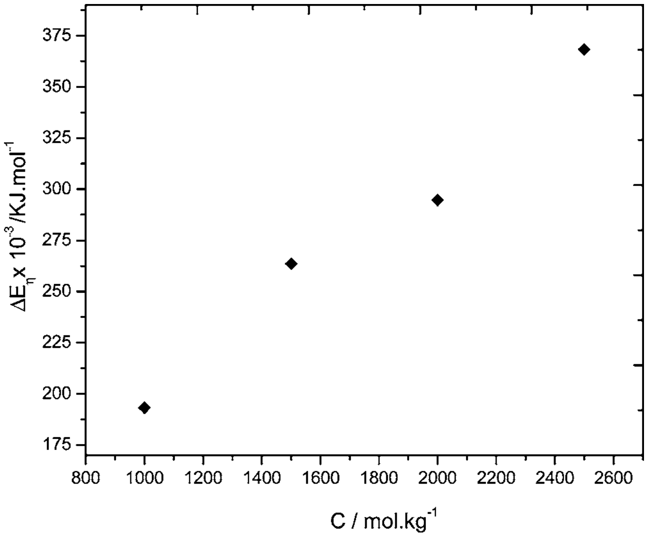

Figure 6. Variation of the viscous activation energy (ΔE_η) with concentration (C) of PHPAM solutions ($\gamma = 108\ \mathrm{s}^{-1}$).

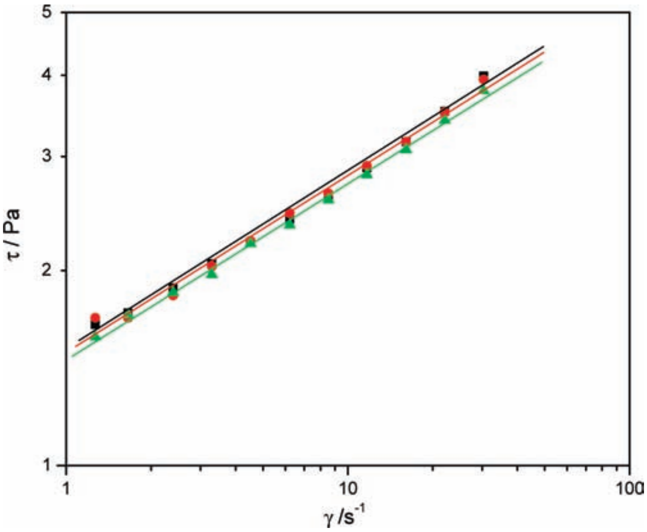

Figure 7. Shear stress (τ) vs shear rate (γ) for a $1.6667 \cdot 10^{-7}$ mol·kg^{-1} PHPAM solution at different temperatures: ■, 301.5 K; ●, 313 K; ▲, 323 K. The solid lines are best-fit lines through the corresponding data.

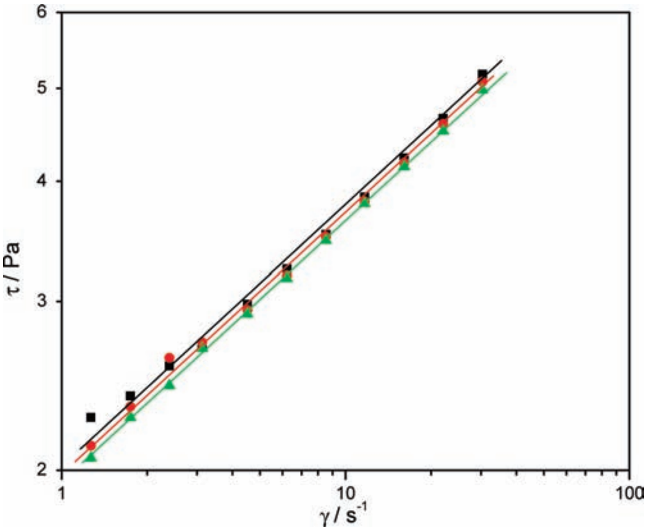

Figure 8. Shear stress (τ) vs shear rate (γ) for a $2.222 \cdot 10^{-7}$ mol·kg^{-1} PHPAM solution at different temperatures: ■, 301.5 K; ●, 313 K; ▲, 323 K. The solid lines are best-fit lines through the corresponding data.

shear dependence decreased with increasing sodium chloride concentration (Figure 11). The solution viscosity also decreased as the temperature increased.

The addition of Na^+ could effectively neutralize the negative charge, resulting in shrinkage of the molecule chains and a decrease in the hydrodynamic radius. Because of the increase in ionic strength produced by adding aqueous NaCl solution, the double electrical layers on the PHPAM molecular chains were compressed, and the electrostatic repulsion among the anions was shielded. For the flow curves obtained with deionized water, a Newtonian behavior was observed at low shear rates for NaCl concentrations $\geq 3.418 \cdot 10^{-2}$ mol·kg^{-1}. At a given shear rate, the apparent viscosity diminished as the NaCl concentration increased, especially at low shear rates. The critical shear rate, at which there is a transition from Newtonian to shear-thinning behavior, increased with NaCl concentration. The PHPAM chain is stretched in deionized water because of the repulsive forces between the negative charges (carboxylate groups) on the chain. This means that the hydrodynamic radius of the polymer chain is large in deionized water, and consequently, the viscosity of the polymer solution is high. As the concentration of the sodium ion in solution is increased, the repulsive forces within the polymer chain decrease as a result of charge-screening effects, and the chain coils up. This change in the polymer conformation causes the hydrodynamic radius of the chain to decrease and the degree of polymer chain entanglement to diminish. Both factors cause the viscosity of the polymer solution to decrease. Also, the reduction in the polymer chain size due to charge shielding would increase the critical shear rate. Hence, the Newtonian behavior can be seen over a wider range of shear rates as the salt concentration increases.

The electrolytes NaCl and $CaCl_2$ were shown to suppress the viscosity and the pseudoplasticity, with the latter suppressing it to a greater extent because of the doubly charged cations (Figure 12). Carboxylic acid groups are ionized in aqueous solution, and the electrostatic repulsion among the anions causes the molecule chains to expand. For PHPAM, the reaction mechanisms for different metal ions and the carboxylic groups of the molecule chains were also different. Monovalent cations (Na^+) can effectively produce an electrolyte charge-shielding effect, which results in shrinking of the molecule chains, thereby

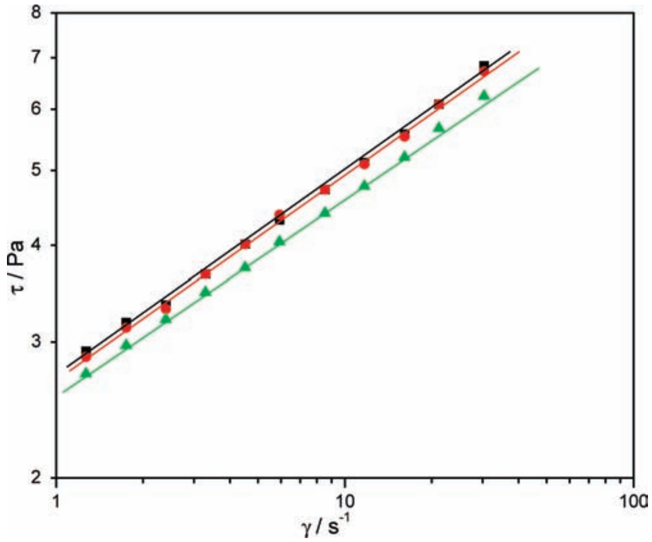

Figure 9. Shear stress (τ) vs shear rate (γ) for a 2.7778·10^{-7} mol·kg^{-1} PHPAM solution at different temperatures: ■, 301.5 K; ●, 313 K; ▲, 323 K. The solid lines are best-fit lines through the corresponding data.

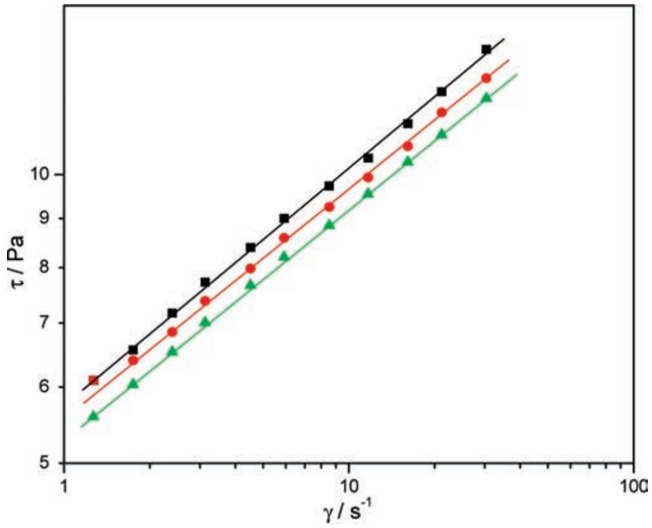

Figure 10. Shear stress (τ) vs shear rate (γ) for a 5.556·10^{-7} mol·kg^{-1} PHPAM solution at different temperatures: ■, 301.5 K; ●, 313 K; ▲, 323 K. The solid lines are best-fit lines through the corresponding data.

increasing the flexibility and decreasing the hydrodynamic radius. However, the reaction between bivalent cations (Ca^{2+}) and acid groups is more complex, because the bivalent cations can act as a cross-linking agent to interconnect the PHPAM chains and further influence the conformation and rheological behavior of PHPAM.

The decrease in the viscosity with shear rate is mainly related to the orientation of macromolecules along the streamline of flow and to the disentanglement of macromolecules with increasing shear force. In general, while in the solution of a good solvent, ionic polymers exist in the maximum possible expanded state in order to minimize the repulsive interactions between the ionic groups of the same macroion bearing a similar charge. Addition of an electrolyte to the ionic polymer solution induces an increase in the solution ionic strength and screens the electrostatic charges. The macromolecule conformation then reduces to the statistical coil conformation.

3.3. Effect of Alkali on Polymer Viscosity. Alkali can modify the viscosity of a PHPAM solution in two ways. First, alkali provides cations in the polymer solution. These cations can reduce the polymer viscosity (Figure 13) through the charge-shielding mechanism explained earlier. Second, alkali can hydrolyze the amide groups on the polymer chain (base hydrolysis). This process can increase the polymer solution viscosity. Obviously, the net effect of alkali on the polymer solution viscosity depends on the relative extent of these two factors. To examine the effect of alkali on polymer viscosity, the viscosities of polymer solutions were measured as a function of shear rate at various alkali concentrations. This process was repeated on the same solutions 1 week and 4 weeks after initial mixing (Figure 14). The variation of the low-shear (9.6 s^{-1}) relative viscosity was observed for different sodium hydroxide concentrations at a polymer concentration of 1.11·10^{-7} mol·kg^{-1} and temperature of 301.5 K. Approximately 1 h after initial mixing, the low-shear relative viscosity decreased with sodium hydroxide concentration to a limiting value. This is similar to the trend previously observed with sodium chloride and is due to the shielding effect of the sodium ions. The influence of sodium hydroxide on the low-shear viscosity

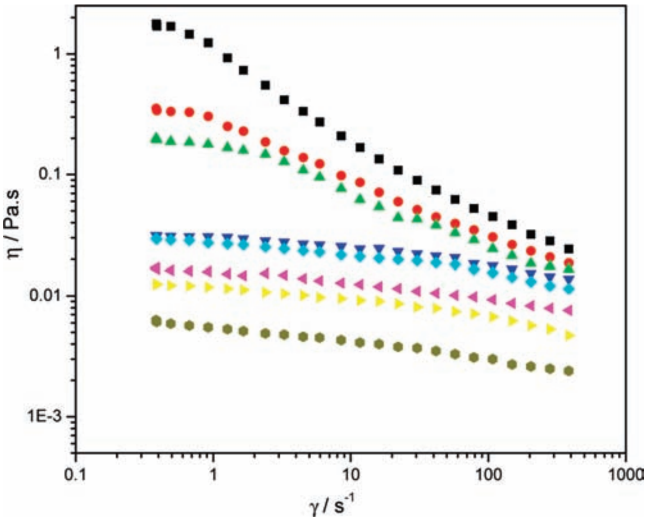

Figure 11. Effect of NaCl on the rheology of a 1.111·10^{-7} mol·kg^{-1} PHPAM solution at 301.5 K: ■, 0 mol·kg^{-1} NaCl; ●, 8.547·10^{-3} mol·kg^{-1} NaCl; ▲, 3.4188·10^{-2} mol·kg^{-1} NaCl; ▼, 8.547·10^{-2} mol·kg^{-1} NaCl; ◆, 17.098·10^{-2} mol·kg^{-1} NaCl; left-pointing triangles, 25.641·10^{-2} mol·kg^{-1} NaCl; right-pointing triangles, 85.4701·10^{-2} mol·kg^{-1} NaCl; ⬢, 136.7521·10^{-2} mol·kg^{-1} NaCl.

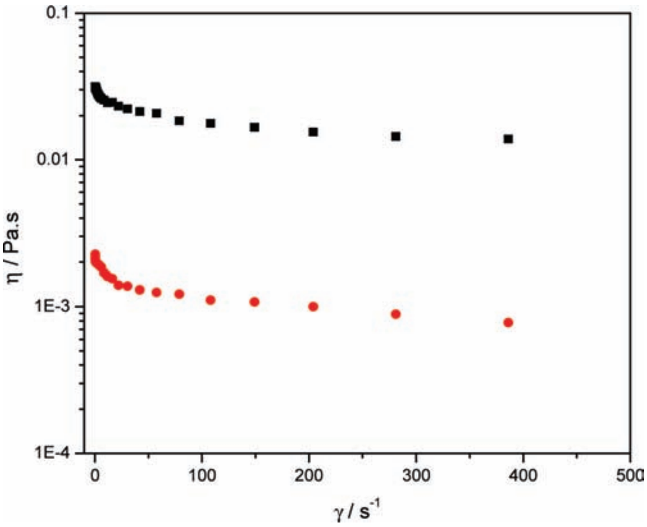

Figure 12. Effects of addition of NaCl and $CaCl_2$ to 1.111·10^{-7} mol·kg^{-1} PHPAM solutions at 301.5 K: ■, 8.547·10^{-2} mol·kg^{-1} NaCl; ●, 4.5045·10^{-2} mol·kg^{-1} $CaCl_2$.

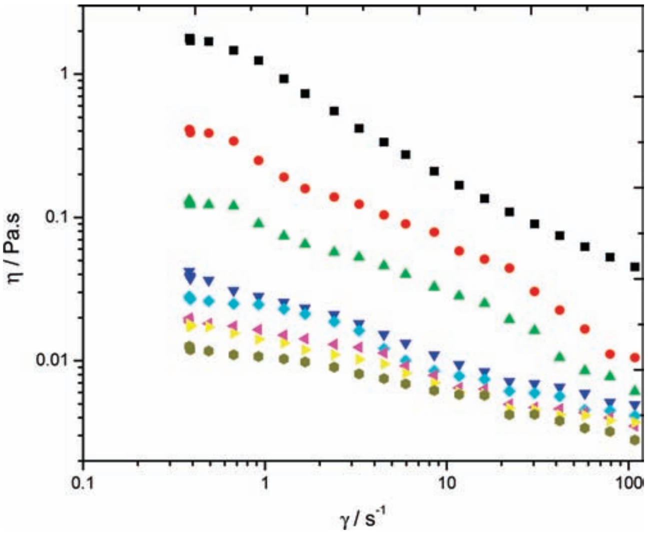

Figure 13. Effect of NaOH concentration on a $1.111 \cdot 10^{-7}$ mol·kg^{-1} PHPAM solution at 301.5 K: ■, 0 mol·kg^{-1} NaOH; ●, $2.5 \cdot 10^{-3}$ mol·kg^{-1} NaOH; ▲, $1.25 \cdot 10^{-2}$ mol·kg^{-1} NaOH; ▼, $12.5 \cdot 10^{-2}$ mol·kg^{-1} NaOH; ◆, $25 \cdot 10^{-2}$ mol·kg^{-1} NaOH; left-pointing triangles, $37.5 \cdot 10^{-2}$ mol·kg^{-1} NaOH; right-pointing triangles, $125 \cdot 10^{-2}$ mol·kg^{-1} NaOH; ⬢, $200 \cdot 10^{-2}$ mol·kg^{-1} NaOH.

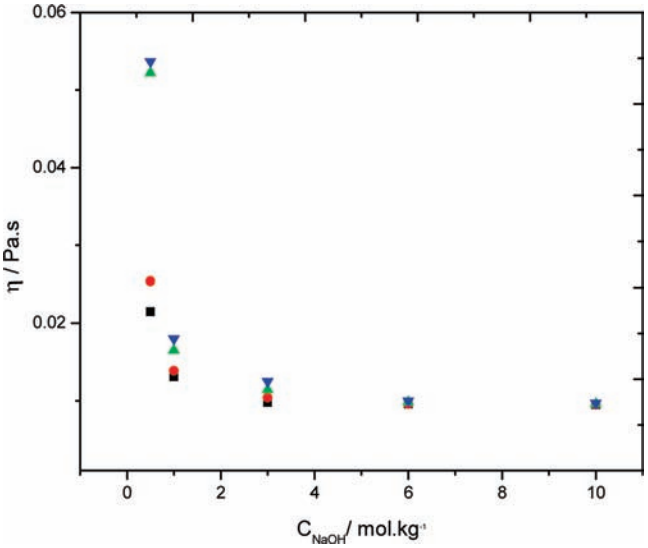

Figure 14. Effect of NaOH and aging on the low-shear viscosity (η) of a $1.111 \cdot 10^{-7}$ mol·kg^{-1} PHPAM solution at 301.5 K ($\gamma = 9.6$ s^{-1}): ■, 1 h; ●, 24 h; ▲, 1 week; ▼, 4 weeks.

measured 2 weeks after initial mixing was more dramatic. Low-shear viscosity measurements after 4 weeks were very similar to those obtained after 2 weeks. The effects of hydrolysis on polymer viscosity are shown in Figure 15. As the polymer is hydrolyzed, the number of carboxylate groups (i.e., the number of negative charges) on the polymer chain increases. Consequently, the electrostatic repulsion increases, causing the chain size to increase. This increase in the polymer chain size enhances the viscosity of the polymer solution in deionized water. The viscosity enhancement due to polymer hydrolysis depends on the type and concentration of the cations present. Figure 16 shows that the viscosity of the polymer solution decreased with increasing concentration of alkali because of the dominating effect of charge shielding over hydrolysis, but the rate of decrease gradually decreases. It was also found that the inhibiting effect of sodium carbonate on viscosity is weaker than that of sodium hydroxide, as the latter is a stronger alkali than the former. The variation of viscosity with shear rate at different alkali concentrations is shown in Figure 17.

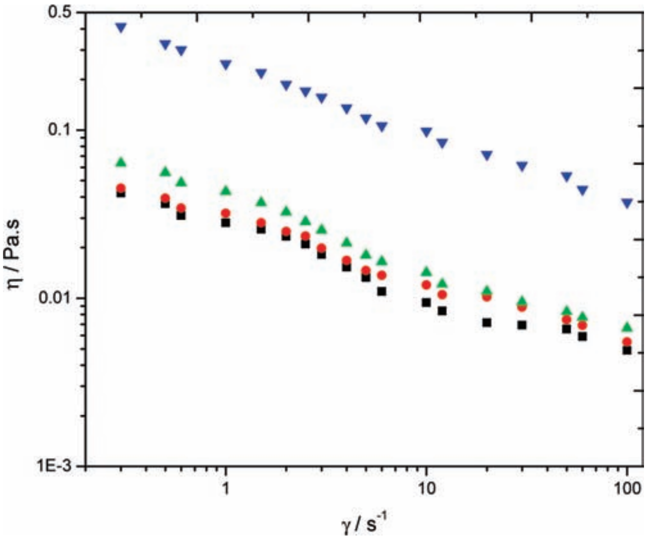

Figure 15. Effect of hydrolysis on the flow curve of a solution containing $1.111 \cdot 10^{-7}$ mol·kg^{-1} PHPAM and $1.25 \cdot 10^{-2}$ mol·kg^{-1} NaOH at 301.5 K: ■, 1 h; ●, 24 h; ▲, 150 h; ▼, 450 h.

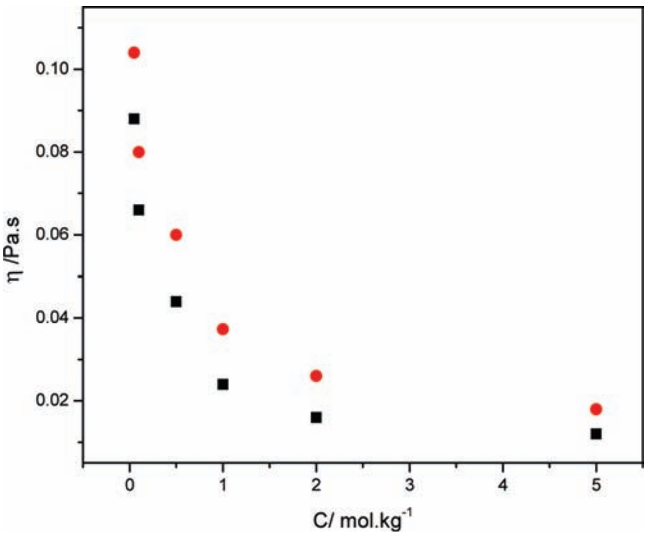

Figure 16. Effect of alkali type and concentration (C) on a $1.111 \cdot 10^{-7}$ mol·kg^{-1} PHPAM solution at 301.5 K ($\gamma = 9.6$ s^{-1}): ■, NaOH; ●, Na_2CO_3.

3.4. Effect of Surfactants on Polymer Viscosity. Surfactant slugs are frequently used in enhanced oil recovery processes to mobilize residual oil by changing the rock wettability or reducing the interfacial tension. To increase the efficiency of such processes, polymers can be either coinjected with the surfactant slug or injected after it (i.e., as a chase). In such cases, there is every chance of mixing of surfactant with polymer. Thus, the effects of SDS (an anionic surfactant) on the viscosity of PHPAM solutions were examined. Figure 18 shows the effect of SDS concentration on the apparent viscosity of a $1.11 \cdot 10^{-7}$ mol·kg^{-1} PHPAM polymer solution. Increasing the SDS concentration to 0.27742 mol·kg^{-1} had a significant effect on the apparent viscosity of the polymer solution. The apparent viscosity of polymer decreases with an increase in the surfactant concentration. These results indicate that SDS reacts physically as well as chemically with the polymer chain in deionized water. This trend is similar to that observed by Shupe[24] and suggests that the anionic surfactant affects the viscosity behavior of the polyacrylamide through the charge-shielding mechanism.

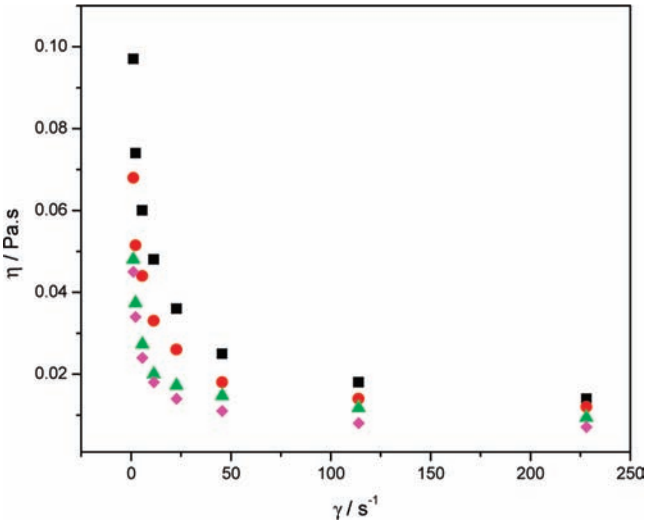

Figure 17. Variation of viscosity (η) with shear rate (γ) for a $1.111 \cdot 10^{-7}$ mol·kg^{-1} PHPAM solution at 301.5 K and different alkali types and concentrations: ■, $4.717 \cdot 10^{-2}$ mol·kg^{-1} Na_2CO_3; ●, $12.5 \cdot 10^{-2}$ mol·kg^{-1} NaOH; ▲, $9.434 \cdot 10^{-2}$ mol·kg^{-1} Na_2CO_3; ◆, $25 \cdot 10^{-2}$ mol·kg^{-1} NaOH.

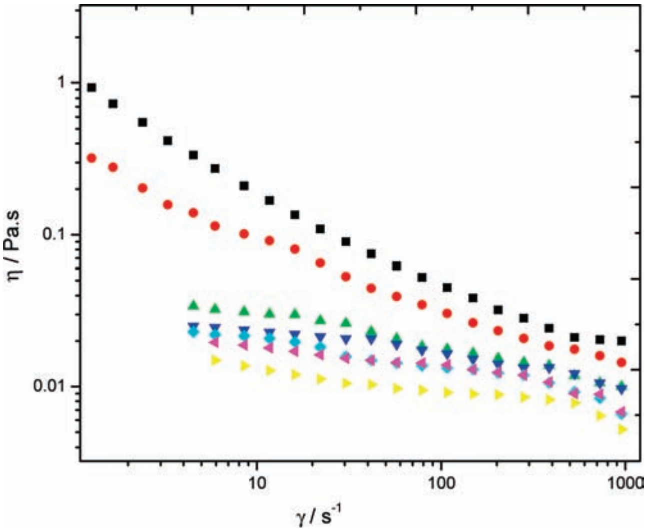

Figure 18. Effect of SDS on the relationship between viscosity (η) and shear rate (γ) at 301.5 K: ■, 0 mol·kg^{-1} SDS; ●, $1.734 \cdot 10^{-3}$ mol·kg^{-1} SDS; ▲, $17.338 \cdot 10^{-3}$ mol·kg^{-1} SDS; ▼, $34.676 \cdot 10^{-3}$ mol·kg^{-1} SDS; ◆, $52.015 \cdot 10^{-3}$ mol·kg^{-1} SDS; left-pointing triangles, $173.382 \cdot 10^{-3}$ mol·kg^{-1} SDS; right-pointing triangles, $277.412 \cdot 10^{-3}$ mol·kg^{-1} SDS.

3.5. Simultaneous Effect of Surfactant and Alkali on Polymer Viscosity. Similar to alkali slugs, coinjection of polymer with surfactant/alkali slugs improves the mobility of the slugs and increases the oil recovery. The effects of a strong alkali (e.g., sodium hydroxide) and an anionic surfactant (e.g., SDS) on the dynamic viscosity of PHPAM were dramatic. Therefore, it was of interest to examine how adding both species would affect the flow curve of this polymer (Figure 19). It was found that the presence of the anionic surfactant (SDS) further reduced the viscosity of alkaline PHPAM solutions, which would have a detrimental effect on mobility control of the polymer slug. On the other hand, adding both alkali and the anionic surfactant would reduce the interfacial tension between oil and water,[25] which would increase the enhanced recovery of oil by injection of ann alkali−surfactant−polymer (ASP) slug during flooding.

Conclusion

The rheological behavior of PHPAM aqueous solutions is significantly influenced by the presence of salts, alkali, and anionic surfactants. The viscosity of the polymer solutions decreased with temperature because of self-aggregation of the polymer chains. The experimental results on the viscosity−temperature relationship were found to satisfy the Arrhenius equation. The variation of shear stress with shear rate under different conditions indicated that the power-law model is very much applicable in explaining the rheological behavior of the polymer. At a given shear rate, the apparent viscosity is diminished with an increase in salt concentration. It was also found that the viscosity and pseudoplasticity of PHPAM polymer are suppressed more by divalent cations (Ca^{2+}) than monovalent cations (Na^{+}) under similar conditions because of the greater shielding effect of the former. The viscosity of PHPAM polymer in presence of alkali is very complex in nature. Alkali can modify the viscosity of the polymer solution in two different ways: reducing the viscosity by providing cations in the solution and increasing the viscosity by increasing the hydrolysis of PHPAM in aqueous solution. Anionic surfactant (SDS) reduced the viscosity of PHPAM solution by hindering its hydrolysis in aqueous solution. These investigations are very important for the application of PHPAM as a mobility controller in enhanced oil recovery.

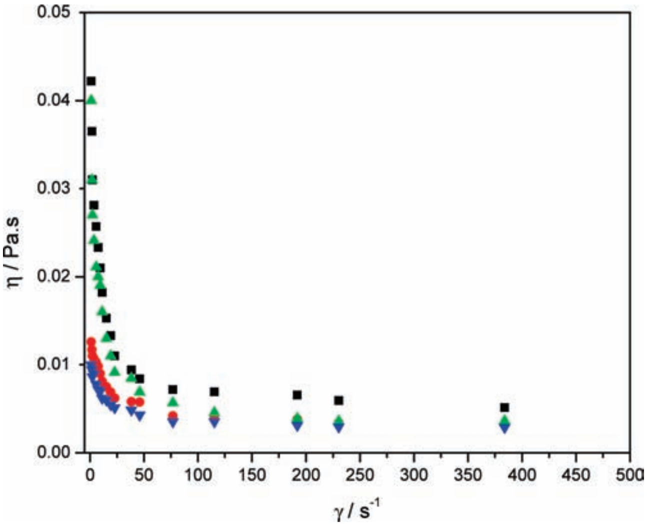

Figure 19. Effect of SDS and NaOH on the relationship between viscosity (η) and shear rate (γ) at 301.5 K: ■, $12.5 \cdot 10^{-2}$ mol·kg^{-1} NaOH; ●, $200 \cdot 10^{-2}$ mol·kg^{-1} NaOH; ▲, $12.5 \cdot 10^{-2}$ mol·kg^{-1} NaOH + $17.338 \cdot 10^{-3}$ mol·kg^{-1} SDS; ▼, $200 \cdot 10^{-2}$ mol·kg^{-1} NaOH + $17.338 \cdot 10^{-3}$ mol·kg^{-1} SDS.

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