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Solution behavior of hydrophobically associating water-soluble block copolymers of acrylamide and *N*-benzylacrylamide

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Abstract

Hydrophobically modified water-soluble block copolymers have been prepared by an aqueous micellar copolymerization technique from acrylamide and small amounts of *N*-benzylacrylamide (2 and 3 mol%) with the objective of investigating the copolymers' rheological behavior and surface and interfacial activities under various conditions such as polymer concentration, shear rate, temperature and salinity. As expected, the block copolymers exhibit improved thickening properties due to intermolecular hydrophobic associations as the solution viscosity of the copolymers increases sharply with increasing polymer concentration. Additional evidence for intermolecular association is provided by the effect of NaCl salt on the solution viscosity, and as expected, the addition of NaCl to the polymer solution gives rise to copolymers with enhanced thickening properties. An almost shear rate independent viscosity (Newtonian plateau) is also exhibited at high shear rate and a typical non-Newtonian shear thinning behavior appears at low shear rates and high temperatures. Furthermore, the block copolymers exhibit high air–liquid surface and liquid–liquid interfacial activities as the surface and interfacial tensions (IFTs) decrease with increasing polymer concentration. This behavior is yet another evidence of polymolecular micelles formation of the copolymers in aqueous solution, and thus the high tendency to adsorb at an interface. The surface and IFTs exhibited by the copolymers were found to be relatively insensitive to the concentration of salt (NaCl). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Acrylamide block copolymers; Micellar copolymerization; Hydrophobically associating polymers

1. Introduction

Water-soluble polymers modified with a few mole percent of a hydrophobic comonomer have recently become the subject of extensive research [1–8]. In particular, the use of copolymers of acrylamide with various hydrophobic comonomers has proved to be of great interest [9–19]. Above a certain polymer concentration (CMC), the hydrophobic groups in these polymers tend to associate in aqueous solution by intermolecular hydrophobic interaction leading to the formation of polymolecular associations. As a consequence, these block copolymers exhibit thickening properties equivalent to those observed for higher molecular weight homopolymers. Thereby, these polymers exhibit particular rheological properties in solution, due to the reversible dissociation process of the physical links occurring under shear.

For instance, hydrophobically associating polymers can show interesting behavior as a function of shear rate and shear time, such as shear thinning or thixotropy. This way, it is possible to avoid the irreversible mechanical degradation which occurs for very high molecular weight polymers when subjected to high shear stresses [20]. Moreover, unlike polyelectrolytes, the aqueous solutions of these hydrophobically associating polymers are less salt sensitive [13,15]. The rheological behaviors of these compounds are of great technological importance especially in applications on water-based systems which involve a viscosity control [21].

Furthermore, in view of the amphiphilic structure (i.e. the presence of hydrophobic moieties in the mainly hydrophilic polymer chain) of most hydrophobically associating polymers, these polymers can also exhibit simultaneously high surface and interfacial activities. Amphiphilic polymers form monomolecular or polymolecular micelles in aqueous solutions [7,8,15], and thus have enhanced ability to adsorb at an interface. This can lead to a sharp reduction in the surface and interfacial tensions (IFTs) of the polymer solution. The combination of rheological behavior (i.e. thickening properties), surface and interfacial activities of these polymers can be of great technological interest, especially

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in a number of important commercial applications such as enhanced oil recovery (EOR), drag reduction, flocculation, super absorbency, latex paints, hydraulic fluids, protein separations, industrial thickeners, controlled drug release and biological/medical purposes.

As a consequence, in the past few years, there has been an increasing interest in the synthesis and solution properties of these polymers. A particularly interesting hydrophobically associating polymer is the block copolymer of acrylamide and *N*-benzylacrylamide. Interest in this polymer stems from the availability of constituting monomers and the simplicity of synthesis procedure which can be scaled up easily for large production. Moreover, it has the potential to exhibit thickening properties and surface and interfacial activities. The copolymerization process, which is used in this study, concerns essentially acrylamide-based copolymers [9–19]. The block copolymer can be prepared by micellar radical copolymerization of the hydrophobic monomer, *N*-benzylacrylamide, in an aqueous solution of acrylamide to form a water-soluble multi-block copolymer. The technique has been shown to be well suited for the preparation of high molecular weight block copolymers having improved thickening properties [17,22–25].

In this paper, we present the results of a more detailed investigation on solution properties such as rheological behavior, surface and interfacial activities of hydrophobically associating water-soluble multi-block copolymers of acrylamide and *N*-benzylacrylamide (2 and 3 mol% of *N*-benzylacrylamide as the hydrophobic monomer have been incorporated) prepared by micellar copolymerization technique. To our knowledge, the preparation and solution properties of this acrylamide/*N*-benzylacrylamide block copolymer have never been studied and reported before. The solution viscosity behavior of the polymer has been investigated with respect to the polymer concentration, shear rate, temperature and NaCl concentration. Furthermore, since very few studies have been conducted on the surface and IFT properties of this kind of polymer, a detailed investigation of the surface and IFT behavior of these polymers has been carried out with respect to the polymer concentration and NaCl concentration.

2. Experimental

2.1. Materials

The source and the purification of monomers and other reagents have been reported elsewhere [15]. *N*-decane used in the IFT measurements was supplied by BDH with purity of 99.6% and was distilled twice prior to use. Doubly distilled water was also used in the surface and IFT measurements.

2.2. Polymerization

The comonomer, *N*-benzylacrylamide {mp 64–65°C (lit. 65.0–65.7°C)} was prepared as described in the literature [26].

Acrylamide/*N*-benzylacrylamide block copolymer containing 2 mol% of the hydrophobe was prepared as follows. An aqueous solution of acrylamide (10 g) in water (200 ml) was degassed with gentle bubbling of N_2 for 30 min in a 500 ml round bottom flask covered with a septum cap. The surfactant, CTAB (Hexadecyl trimethyl ammonium bromide) (8 g), followed by *N*-benzylacrylamide (0.463 g; 2 mol%) were added into the mixture, while stirring continued at 50°C, until a clear solution was obtained. Polymerization was then initiated by the addition of potassium persulphate solution ($K_2S_2O_8$) (1.28 g), and the reaction mixture was stirred at 50°C for 7 h. The resulting polymer was precipitated by slowly pouring the solution into constantly stirred methanol (1 l). The polymer, after filtration, was again dissolved in water (180 ml) and reprecipitated in methanol (1 l). The process was repeated four times in order to remove traces of surfactant. The polymer was then dried at 55–65°C under vacuum for approximately 8 h or until a constant weight of the polymer was obtained, and then kept in a desiccator.

The ratio of the two monomers in the copolymer was determined by ^{1}H NMR spectroscopy of the polymer samples measured in D_2O using a JEOL LA 500 MHz spectrometer. Using integration of the aromatic proton signals (around δ 7 ppm), the benzyl proton (δ 4.29 ppm) and the aliphatic proton signals (around δ 2 ppm), the ratio was found to be identical to the feed ratio. The ^{1}H NMR spectra confirmed the absence of even traces of the surfactant molecule (CTAB). The nine hydrogens belonging to the three methyl groups of hexadecyl trimethyl ammonium bromide (surfactant) appear as a large, sharp singlet at δ 3.13 ppm. The ^{1}H NMR spectrum (Fig. 1(a)) of the copolymer prepared from a feed of 2 mol% hydrophobe indicates the absence of the singlet at δ 3.13 ppm, thereby assuring complete removal of the surfactant.

The above procedure was similarly applied for the preparation of 3 mol% acrylamide/*N*-benzylacrylamide copolymer. Detailed reaction conditions and some characteristic data of the copolymers are shown in Table 1. The reaction scheme and molecular structures of monomers and the hydrophobically modified copolymer are also depicted in Fig. 1(b).

There is ample evidence in the literature that the micellar polymerization, the procedure adapted in the current work, would lead to multi-block copolymers consisting of long sequences of acrylamide separated by short sequences of the hydrophobic comonomers which occupy the micellar phase [17,25]. A chain initiated in the aqueous solution keeps on adding acrylamide units until it encounters a micelle full of the hydrophobic comonomer. The chain adds the hydrophobic monomer until all hydrophobe is exhausted form the micelle forming a short hydrophobic block. Consequently, the chain adds more acrylamide from the aqueous phase forming another block of acrylamide.

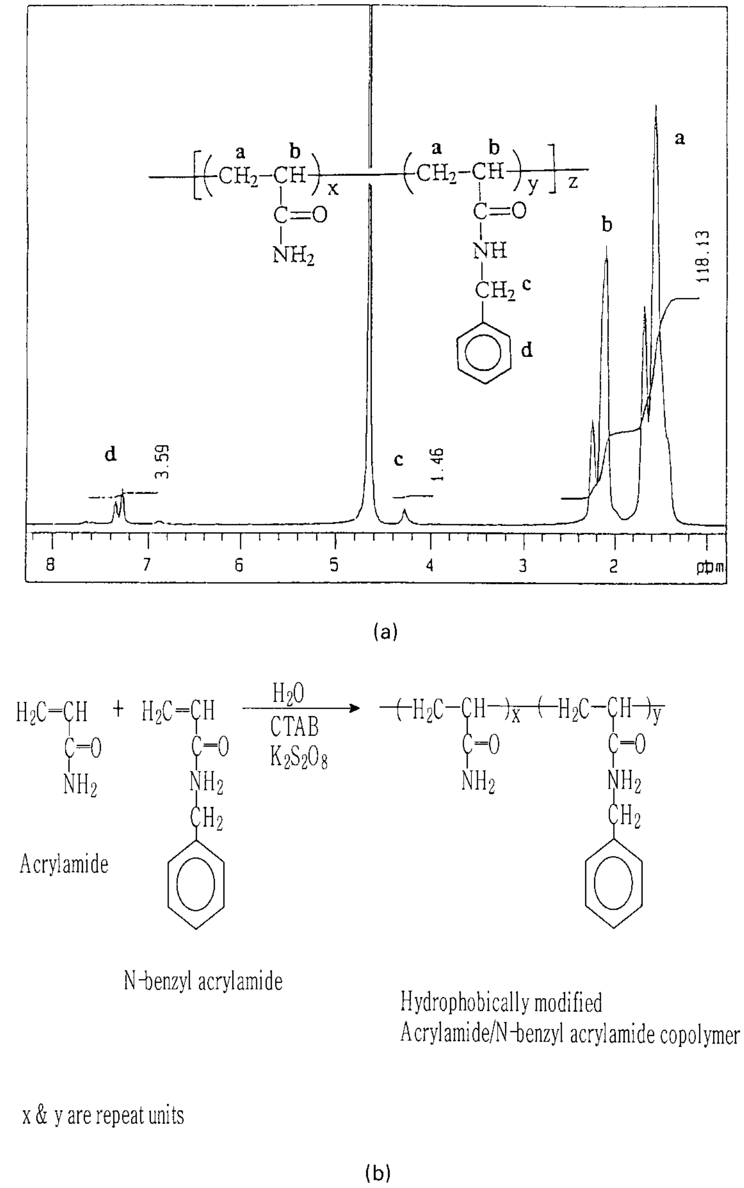

Fig. 1. (a) ^{1}H NMR spectrum for a copolymer containing 2 mol% hydrophobe. (b) Reaction scheme and molecular structures of monomers and hydrophobically modified multi-block copolymer.

The process is repeated many times to form a multi-block copolymer.

2.3. Experimental measurements of viscosity, surface and interfacial tensions

The solution properties of the block copolymers such as viscosity, surface and IFTs were investigated with respect to the polymer concentration, shear rate, temperature and salinity. In this study, concentrated stock solutions were prepared at least 24 h prior to the measurements. The dissolution processes lasted for 2–3 days. Final solutions of the desired composition were obtained by dilution of the appropriate stock solution with distilled water. Saline solutions

Table 1
Reaction conditions and some characteristic data of the copolymers (CM = comonomer (*N*-benzylacrylamide); AA = acrylamide; CTAB = (hexadecyl triethyl ammonium bromide) surfactant; PPS = potassium per sulphate ($K_2S_2O_8$); RT = reaction time)

CM (mol %)	AA (g)	CM (g)	H_2O (ml)	CTAB (g)	CTAB/AA (w/w)%	PPS/AA (w/w)%	RT (h)	Yield (g)	Yield (%)
2	10	0.463	200	8	80	12.8	7	8.74	83.6
3	10	0.701	200	8	80	12.8	7	9.93	92.8

were prepared by dissolving an appropriate amount of solid NaCl in the diluted polymer solution.

The solution viscosities of the block copolymers (2 and 3 mol% copolymers of acrylamide and *N*-benzylacrylamide) were measured for different polymer concentrations and salinities using a digital Brookfield rotational viscometer with SC4-18 spindle accessory at shear rate ranging from 0.4 to 79.4 s^{-1} and for temperature ranging from 25 to 95°C.

The air–liquid surface tensions (STs) of the copolymers were determined for different polymer concentrations (for 3 mol% copolymer of acrylamide and *N*-benzylacrylamide) using the plate method of the Processor tensiometer K12 (Kruss). The oil (*n*-decane)–aqueous solution IFTs of the copolymers were determined for different polymer concentrations (for 3 mol% copolymer of acrylamide and *N*-benzylacrylamide) using the ring method of the same tensiometer used for ST measurement. *N*-decane was used as the oil phase. The IFTs of the *n*-decane–aqueous polymer solution were measured for a polymer concentration of 2.0 wt% (for 2 mol% copolymer of acrylamide and *N*-benzylacrylamide) with NaCl salt concentration ranging from 0.1 to 9.0 wt%. All surface and IFT measurements were performed at 25°C.

All the measurements were carried out at least twice and sometimes thrice and the results were reproducible to ±5% and reported (Figs. 2–10) as the average value of these measurements with a standard deviation of ±5%.

3. Results and discussion

The solution properties of hydrophobically associating water-soluble acrylamide/*N*-benzylacrylamide block copolymers were studied under different conditions as part of a continuing research program to investigate the relationship between polymer structures and their solution viscosity behaviors, and air–liquid and liquid–liquid interfacial activities. These were investigated with the objective of designing polymers with optimized structure for high solution viscosity, and simultaneously high surface and interfacial activities that could be applied in such areas as EOR, drag reduction and industrial thickeners.

3.1. Viscosity behavior of the copolymers

Figs. 2–6 depict the dependencies of polymer concentration, shear rate and temperature on the solution viscosity of hydrophobically modified 3 mol% block copolymer of acrylamide and *N*-benzylacrylamide. Fig. 7 shows NaCl concentration dependence of the solution viscosity for 2 mol% acrylamide/*N*-benzylacrylamide copolymer.

As shown in Fig. 2 for shear rates of 0.4, 0.8 and 2.0 s^{-1}, the hydrophobically associating polymer exhibits a sharp increase in viscosity with increasing polymer concentration for all the shear rates considered. This observation is similar to that frequently observed for hydrophobically modified associative polymers [3,5,6,9,13–16,19,25]. This behavior is caused by the strong interchain associations forming large aggregates (a network structure of polymer chains) as the polymer concentration increases (greater than a certain level). At low polymer concentration, hydrophobic chains have little chance of interacting intermolecularly with each other, thus leading to the formation of small aggregates with a small hydrodynamic volume. Intramolecular associations are dominant compared to intermolecular associations in this dilute solution, thus the hydrophobic interactions produce a decrease in the hydrodynamic radius of the copolymer coil. However, as the copolymer concentration is increased (above a critical level), hydrophobic intermolecular associations are more probable, giving rise to a network structure of polymer chains (large aggregates) with large hydrodynamic volumes and, consequently, high solution viscosity. These network structures contribute significantly to the thickening behavior of this associative polymer.

For the hydrophobically associating polymer, an almost shear rate independent viscosity (Newtonian plateau) is observed at high shear rates, as depicted in Fig. 3 for polymer concentrations of 0.5, 1.0 and 2.0 wt% and in Fig. 4 for temperature ranging from 25 to 85°C. However, a sharp decrease in viscosity with shear rate (a typical shear thinning behavior) appears at low shear rates as shown in the same figures. The shear thinning behavior can be attributed to the disorientation and disentanglement of the macromolecular chains under shear, which corresponds to the progressive rupture of the intermolecular associations upon increasing the shear rate. The development of viscosity behavior for associative polymers like the one under investigation relies on an increase in the apparent macromolecular aggregation among hydrophobic groups (moieties) with increasing polymer concentration. Under high shear condition, the hydrophobic interactions can be disrupted, giving rise to a decrease in the apparent molecular weight, and hence a decrease in the solution viscosity. However, under low shear conditions the hydrophobic interchain associations will reform, restoring the high solution viscosity [6,9,15–17,19,25]. A similar relationship between viscosity and temperature is observed in Fig. 4. At low temperatures, a sharp decrease in viscosity is initially observed at low shear rates, which indicates that intermolecular assemblies formed at low temperatures are disturbed by the high shear. Increasing the temperature results in rupture of the intermolecular aggregates because of the higher mobility of chains, which leads to the less pronounced effect of the shear rate observed at high temperature on the viscosity.

Figs. 5 and 6 display the effect of temperature on the solution viscosity of the polymer for different polymer concentrations and shear rates, respectively. As expected, a sharp decrease in viscosity is observed with increasing temperature, especially for high polymer concentration and for all the shear rates considered. The decline in viscosity with temperature is less pronounced for low polymer

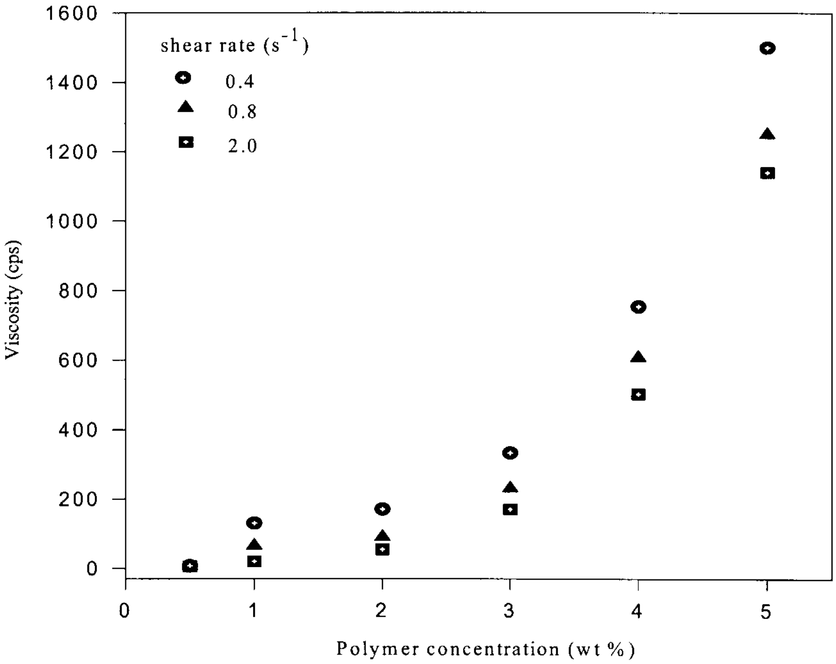

Fig. 2. Effect of polymer concentration on the viscosity of 3 mol% acrylamide/*N*-benzylacrylamide copolymer for three different shear rates at 25°C.

concentration. The lowering of the solution viscosity with increasing temperature has been reported for aqueous solutions of hydrophobically associating water-soluble polymers [6,8,9,15,19]. This effect could be attributed to the weakening of the hydrophobic effect at elevated temperatures due to the increased mobility of the polymer chains (as a result of decrease in solvent viscosity), which gives rise to loss of interchain liaisons and/or an increase in copolymer solubility as the temperature increases. The influence of temperature is more pronounced at higher polymer concentration where intermolecular association is more common compared to low polymer concentration.

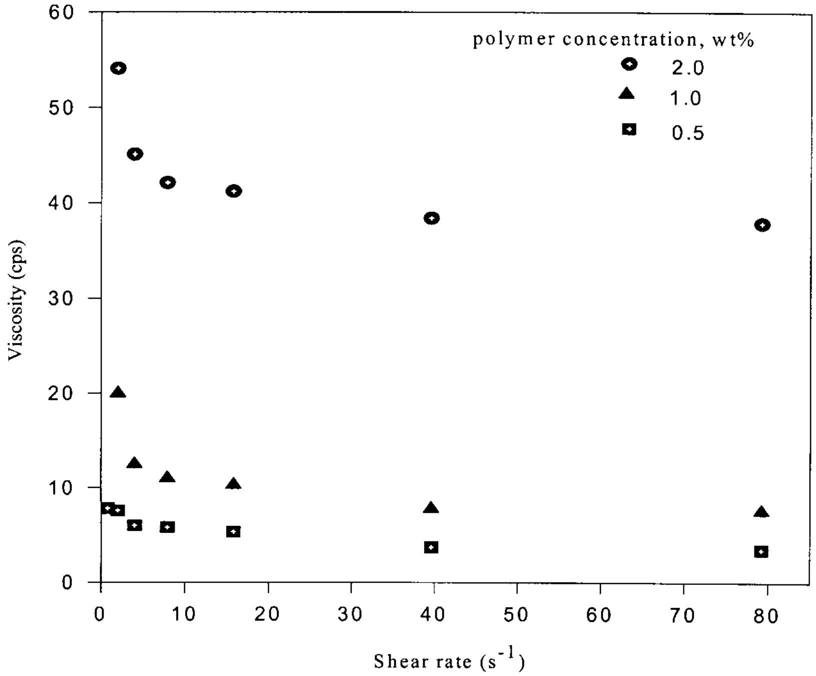

Fig. 3. Variations of viscosity of 3 mol% acrylamide/*N*-benzylacrylamide copolymer with shear rate for three different polymer concentrations at 25°C.

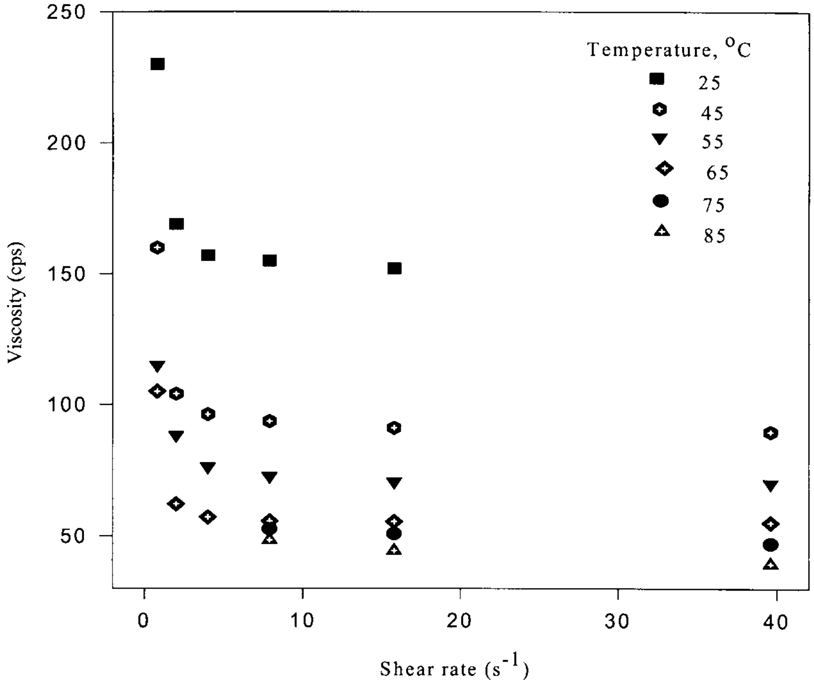

Fig. 4. Variations of viscosity of 3 mol% acrylamide/*N*-benzylacrylamide copolymer with shear rate for various temperatures and for polymer concentration of 3.0 wt%.

Additional evidence for intermolecular association is provided by the effects on the solution viscosity of 2 mol% copolymer of acrylamide and *N*-benzylacrylamide by the addition of NaCl salt, shown for different shear rates in Fig. 7. As depicted, the viscosity of the copolymer solution increases appreciably with increasing NaCl concentration especially at lower shear rates (2.0 s^{-1}). These results suggest that intermolecular association is favored by the addition of salt. The addition of salt makes the aqueous environment more hostile for the hydrophobic blocks causing them to favor association with each other, and hence promoting the formation of large macromolecular aggregates [19]. Salt reduces the quality of the solvent because many of the water molecules are consumed in

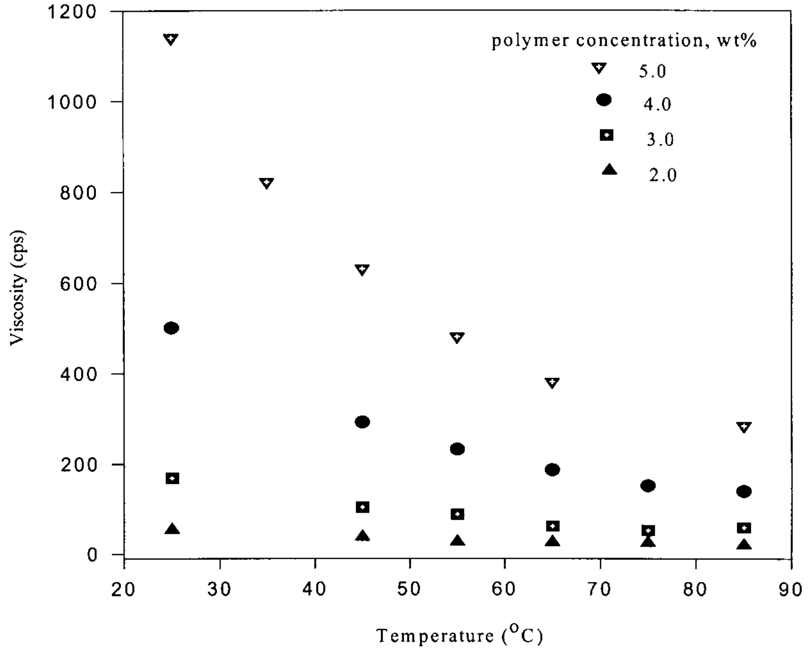

Fig. 5. Effect on the viscosity of 3 mol% acrylamide/*N*-benzylacrylamide copolymer of temperature for various polymer concentrations at shear rate of 2.0 s^{-1}.

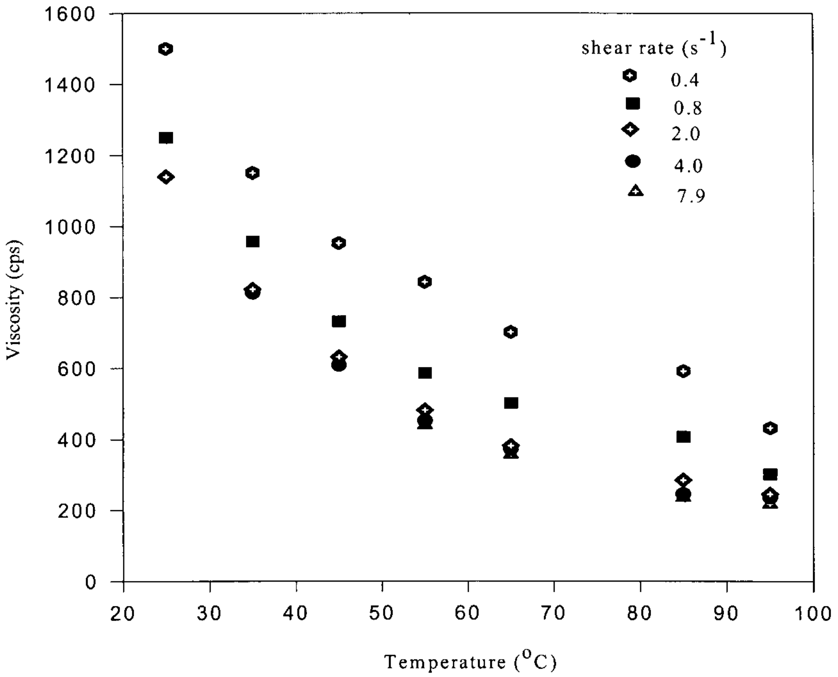

Fig. 6. Effect on the viscosity of 3 mol% acrylamide/*N*-benzylacrylamide copolymer of temperature for various shear rates and for polymer concentration of 5.0 wt%.

dissolving the salt ions and consequently, less water molecules are available for dissolving the copolymer molecules. This forces the copolymer molecules to favor interacting with each other over interacting with the solvent molecules, and consequently they tend to form intermolecular aggregates through the hydrophobic blocks at lower copolymer concentrations. At the low shear rate of 2.0 s^{-1}, a sharp increase in viscosity is observed above salt concentration of 5%. This sharp increase is similar to that associated with the onset of hydrophobic association upon increase of copolymer concentration. The sharp increase in viscosity is not observed at higher shear rates as a consequence of

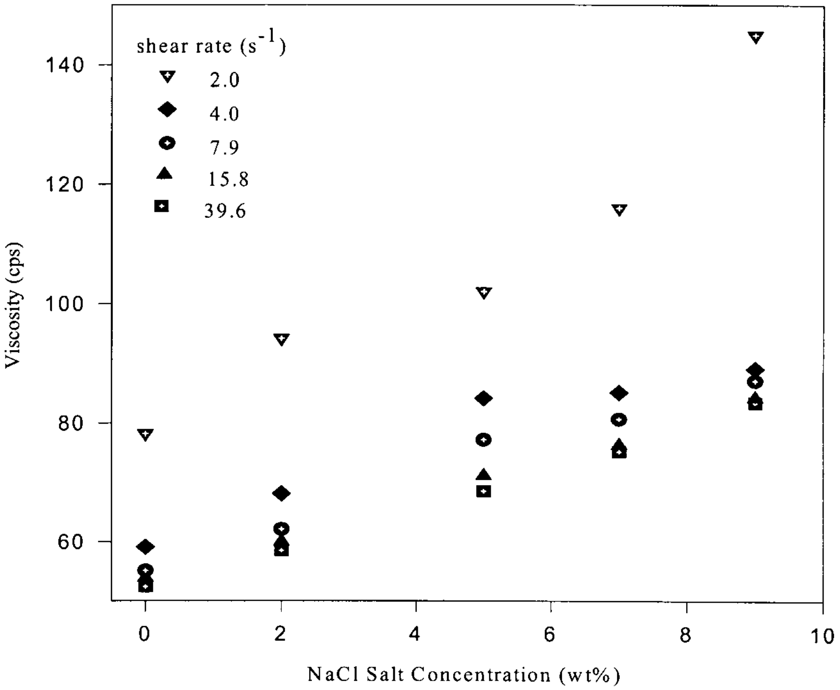

Fig. 7. Effect on the viscosity of 2 mol% acrylamide/*N*-benzylacrylamide copolymer of NaCl salt concentration for various shear rates at 25°C.

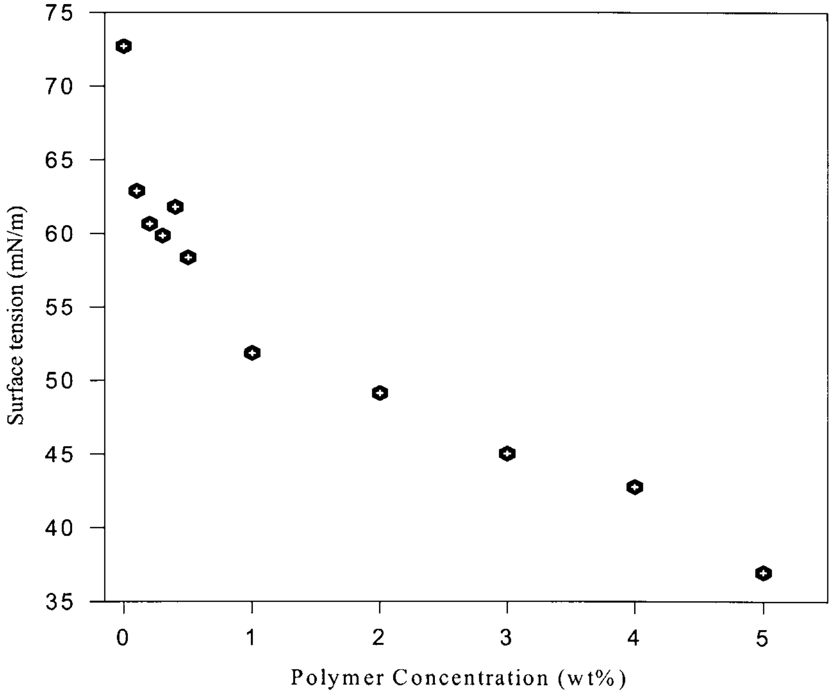

Fig. 8. Surface tension (ST) versus polymer concentration for 3 mol% acrylamide/*N*-benzylacrylamide copolymer at 25°C.

the rupture of intermolecular aggregates under higher shear. A similar effect has been reported in many previous studies of this kind [6,8,15,16].

The pseudoplasticity, the salt tolerance, and the relatively favorable viscosity–temperature profiles are some of the attractive features of these hydrophobically associating block copolymers that could make them of potential interest in oil recovery or drilling applications.

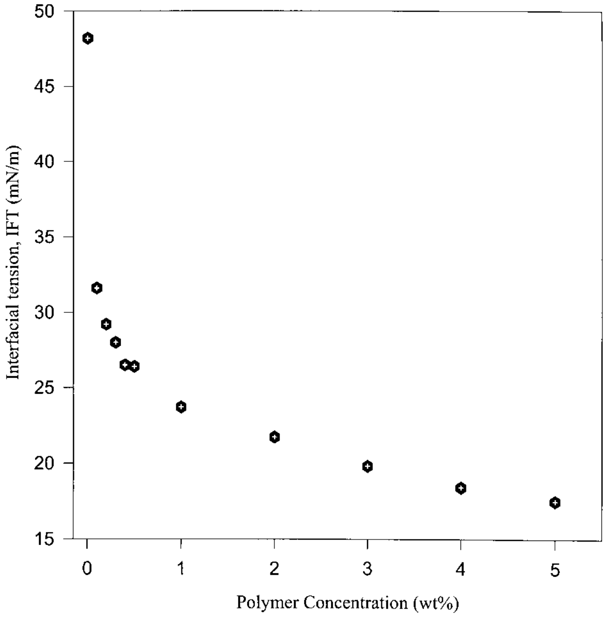

Fig. 9. Interfacial tension (IFT) versus polymer concentration for 3 mol% acrylamide/*N*-benzylacrylamide copolymer at 25°C.

3.2. *Surface and interfacial tension properties of the copolymers*

Another interesting feature, which has rarely been investigated [7,8,15], concerns the surface and interfacial activities of the hydrophobically modified block copolymers. Thus, Figs. 8–10 show the dependence of polymer concentration and NaCl salt concentration on air–liquid surface and *n*-decane–aqueous polymer solution IFTs of the copolymers.

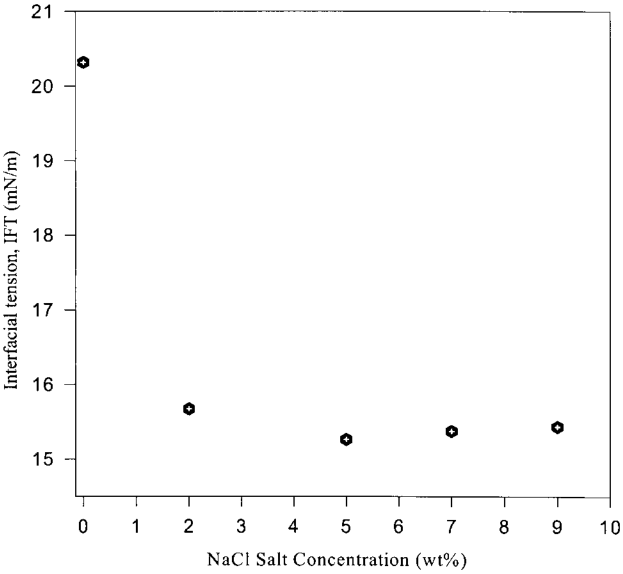

Fig. 10. Effect on the IFT of 2 mol% acrylamide/*N*-benzylacrylamide copolymer of NaCl salt concentration for polymer concentration of 2.0 wt% at 25°C.

As shown in Fig. 8 for the copolymer of 3 mol% acrylamide/*N*-benzylacrylamide, a sharp decrease in ST is observed up to a polymer concentration of 0.3 wt% followed by a slight increase in ST up to a polymer concentration of 0.4 wt%, after which a dramatic decrease is observed with increasing polymer concentration. The decrease in the ST could be attributed to the increased adsorption of the available copolymer molecules at the air–aqueous solution interface as the copolymer concentration increases leading to interfacial excess of the copolymer. At low copolymer concentrations, the copolymer molecules absorb at the interface so that the hydrophobic blocks can avoid the unfavorable aqueous environment and escape to the air phase because of the in-availability of enough polymer molecules to form intermolecular aggregates. As a result, a sharp decrease in ST is observed at low copolymer concentration. At higher copolymer concentrations, the interface becomes saturated with copolymer molecules and the intermolecular aggregates start providing a favorable environment for the hydrophobes. Consequently, a less pronounced decrease in ST is observed at higher polymer concentration.

Fig. 9 depicts the effect of polymer concentration on the IFT of the same copolymer shown in Fig. 8. As expected, the IFT decreases as the polymer concentration increases. A minimum is observed at 0.3 wt% polymer concentration and a maximum at 0.4 wt%. The decrease in the IFT with polymer concentration could also be attributed to the same reason given for decrease in ST as shown in Fig. 8. The small peak observed in ST and IFT (i.e. Figs. 8 and 9, respectively) at 0.4 wt% polymer concentration can be attributed to the migration of the hydrophobic segments from the interface to the bulk of the solution to participate in forming macromolecular aggregates. Increasing polymer concentration further results in the availability of more hydrophobe at the interface after the intermolecular aggregates have been formed, thus resulting in the observed decrease in ST and IFT at higher polymer concentrations.

As shown in Fig. 10 for the copolymer of 2 mol% acrylamide/*N*-benzylacrylamide, a sharp decrease in IFT is observed up to 2.0 wt% NaCl concentration followed by an almost NaCl concentration independent IFT (relatively insensitive to salt) with increasing NaCl salt concentration. A similar salt tolerance behavior is observed for ST as the salt concentration increases. This behavior is unusual for non-ionic polymers like the ones under investigation as they usually exhibit little change in surface activity with salt. However, this behavior corresponds with the effect of salt on viscosity. Adding salt to the copolymer solution causes less water molecules to be available for dissolving the copolymer molecules. As salt is added to the copolymer solution, the copolymer becomes less soluble in the bulk and is pushed to the interface where the hydrophobic blocks of the copolymer molecules can avoid the increased hydrophilicity of the environment causing the observed decrease in ST and IFT. Once the copolymer is absorbed at the interface, it is no longer influenced by the increased salt concentration and hence the plateau in salt effect is observed at higher salt concentrations. Another possible cause of the decrease in IFT with increased salt may be the change of conformation of the copolymer molecules at the interface. The reduced quality of the solvent with salt addition can cause the polymer molecules to contract or aggregate at the interface leaving space for more copolymer molecules at the interface and leading to higher interfacial excess and thus lower IFT. However, the copolymer solution can still be considered salt tolerant as the interfacial properties remain constant after the initial drop. This salt tolerant behavior of surface and interfacial activities at high salt concentration is also one of the attractive features of these hydrophobically associating copolymers that could make them of potential interest in oil recovery or drilling applications.

4. Conclusions

The solution properties of hydrophobically associating water-soluble acrylamide/*N*-benzylacrylamide block copolymers were studied under different conditions as part of a continuing research program to investigate the relationship between polymer structures and their solution viscosity behaviors, and air–liquid and liquid–liquid interfacial activities. These were investigated with the objective of designing polymers with optimized structure for high solution viscosity, and simultaneously high surface and interfacial activities for possible application in such areas as EOR. Because of the unique structural features of the copolymers, which are characterized by hydrophobic moieties (amphiphilic) that promote intermolecular hydrophobic associations and the formation of polymolecular micelles, the copolymers have been found to exhibit improved thickening properties and high air–liquid surface and liquid–liquid interfacial activities, especially with increasing polymer and NaCl concentrations. A relatively high salt tolerance, typical of non-ionic polymers, is also exhibited by the copolymers. Furthermore, an almost shear rate independent viscosity (Newtonian plateau) is exhibited at high shear rate and a typical non-Newtonian shear thinning behavior appears at low shear rates and high temperatures. The pseudoplasticity, the salt tolerance, and the relatively favorable viscosity–temperature profiles are some of the attractive features of these hydrophobically associating copolymers that may make them of potential technological interest in oil recovery or drilling applications and other important commercial applications.

Acknowledgements

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