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ORIGINAL CONTRIBUTION

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Effects of nonionic surfactant and associative thickener on the rheology of polyacrylamide in aqueous glycerol solutions

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Abstract The effect of a low molecular weight nonionic surfactant and an acrylic associative thickener on the rheology of polyacrylamide in aqueous glycerol solutions under steady shear was experimentally investigated. The nonionic surfactant (Tween20), associative thickener (Acrysol TT935) and polyacrylamide (Separan AP30) underwent complex molecular interactions in solution as reflected by rheological measurements. The surfactant also interacted with the glycerol solvent. The addition of surfactant in aqueous glycerol solutions reduced the surface tension, as well as the solution viscosity, at low surfactant concentration. The solution viscosity went through a minimum at certain surfactant concentration, depending on the composition of glycerol/water mixture, before increasing again. Similar behavior was found when the surfactant was added to the polyacrylamide solution, except there was an initial increase in the viscosity before the reduction. The associative thickener, Acrysol TT935 (an anionic acrylic emulsion copolymer) exhibited a strong affinity with polyacrylamide in solution, as indicated by a sharp increase in the solution viscosity. The dilute polyacrylamide solution became highly elastic in the presence of either the nonionic surfactant or the associative thickener. A three-stage model was proposed to describe the surfactant/thickener/polymer interactions.

Key words Surfactant – polyacrylamide – associative thickener – rheology – interaction

Introduction

Many industrial coating liquids contain additives such as flexible polymers, surfactants and associative thickeners. The physico-chemical properties of these mixtures have a strong effect on the performance of coating operation. Numerous studies have been carried out since the 1940s on the properties of mixtures of polymers and surfactants in aqueous solution [1]. The association of polymer/surfactant pairs of opposite charges is a result of the strong electrical force of attraction. Depending on the surfactant concentration and polymer molecular weight and structure, the surfactant may be absorbed onto the polymer in the form of individual molecules, small aggregates, or micelles. In the presence of equal numbers of opposite charges, it may result in stoichiometric precipitation from the solution. Such precipitates can be resolubilized upon the addition of excess surfactant, giving rise to the concept that a second layer of bound surfactant ions, with their ionic groups pointing "outwards", is attached to the first bound layer through association with the hydrocarbon chain of the first layer [2].

Molecular interactions between surfactant with water-soluble polymer in which one of them is uncharged have also been investigated. The early work of Jones [3] showed that two critical concentrations of surfactant T_1 and T_2 existed in a system of fixed polymer concentration with the increasing amounts of surfactant. T_1 represents the concentration at which interaction between the surfactant and the polymer first occurs, and T_2 represents the concentration at which the polymer becomes saturated with surfactant. Subsequent studies [3–5] also showed that T_1 was, in general, less than the critical micelle concentration of the surfactant (CMC). This suggests that the "aggregated" state of the surfactant with the polymer chain has a lower energy level than the surfactant molecules in the regular micellar form. Once the polymer backbones were saturated with surfactant molecules, the excess surfactant molecules would form micelles at T_2. The first critical concentration T_1 was found to be only weakly dependent on the amount of polymer present in the solution, and the "aggregate" formation was mainly a function of surfactant concentration for a particular polymer. On the other hand, the value of T_2, which represents the "saturation" of polymer, was found to be directly proportional to the polymer concentration. Recently, a considerable amount of work has been carried out by Saito and his group [6–8] on the interactions between nonionic polyethoxylated surfactants and polycarboxylic acids, or cationic polymers. They reported the existence of a minimum surfactant concentration below which no more surfactant was isolated from the agglomerates formed with the polymer. The minimum surfactant concentration was dependent on the size of the hydrophobic moiety, and independent of the polyoxyethylene chain length of the surfactants, temperature, and the type of cationic polymer present in the solution. This minimum concentration was also lower than the corresponding CMC. However, the mechanism of complex formation between the ethoxy-type nonionic surfactants with the polyacrylic acid (PAA) and with the polymethacrylic acid (PMA) appeared to be significantly different. The precipitation of complexes formed with PMA was more evident than that with PAA, and occurred at a higher temperature. With the PMA, the formation of complexes followed a two-step mechanism. Initially, the surfactant molecules were bound together as a separate entity in the form of liquid clusters, and only at a higher concentration when they began to accumulate on the polymer chain in micellar form. The critical concentration T_1 was not always lower than the CMC of the surfactant. In this case, the dependence of T_1 on the length of the polyoxyethylene part of surfactant, and on temperature appeared to be much stronger. Recently, Kientz and Holl [9] used various methods to study the surfactant/polymer interactions, including viscometry, light scattering and conductimetry measurements. A minimum solution viscosity was observed at low surfactant concentration, followed by a maximum viscosity at higher concentration before leveling off to a plateau.

There are two types of associative thickeners commonly used in coating and paint industry – the nonionic ethylene-based urethane block copolymers and the anionic hydrophobically modified alkali-soluble copolymers. The latter are developed from the corresponding conventional non-associative thickeners. Although nonionic associative thickeners are deemed to be better from the point of view of rheology and film quality, they are generally more difficult to handle in water and alkaline environments than the alkali-swellable anionic thickeners. Apart from their applications in latex adhesives and emulsion paint additives, associative thickeners have been used effectively for paper coating, which contains a range of polymers capable of forming liquid-liquid associations [10]. Associative thickeners have also been used to alter the rheology of polymer solutions, suspensions and emulsions [10–13].

In this study, the steady-shear properties of aqueous glycerol containing different concentrations of a nonionic surfactant, a high molecular weight polymer and an associative thickener are reported. The interactions of various additives with glycerol/water solvent are investigated. An interpretation of the interaction mechanisms of these additives in solution, based on their rheological behavior, is discussed.

Experimental

The solvent used in this study was a mixture of glycerol and water. Glycerol (technical grade), supplied by Dragon Chemicals, was diluted with distilled water to various compositions. The nonionic surfactant used was Tween20, a polyoxyethylene (20) sorbitan monolaurate, supplied by BDH Laboratory Supplies. It contains about 97–113 hydroxyl groups per molecule and has a molecular weight of 1313. The polymer additive was Separan AP30, an anionic polyacrylamide supplied by Dow Chemicals. The molecular weight of Separan AP30 is about 4 million, as given by the manufacturer. The associative thickener was Acrysol TT935, an acrylic emulsion copolymer from Rohm and Haas Co. The molecular weight of Acrysol was not given by the manufacturer, but was expected to be in the order of 10^4 based on the information in the literature given for other thickeners.

To study the effect of surfactant on aqueous glycerol solutions without the polymer and thickener, different quantities of surfactant were dissolved in the solutions containing different glycerol concentrations, ranging from 50% to 80% glycerol. In the study of the rheological behavior of Separan AP30 and Acrysol TT935 solutions with or without the presence of surfactant, the glycerol concentration in the solvent was fixed at 80%. The rheological properties measured included the steady-shear viscosity η and the first normal stress difference N_1. The rheological instruments used were Contraves Low-Shear 30 rheometer and Rheometrics Fluid Spectrometer (RFSII). The former was equipped with a bob and cup (2T/2T system), and the latter with a cone and plate (40 mm diameter, 0.4° cone) measuring system. The shear rate range covered was from 0.01 to 1000 s^{-1}. The surface tension of the test fluids was measured with a surface tensiometer (Analite). All properties were measured at 20 °C.

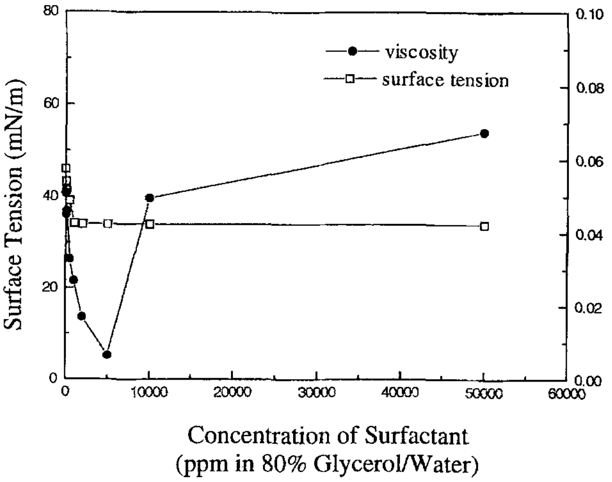


Fig. 1 Effects of surfactant concentration on surface tension and viscosity of a 80% glycerol solution

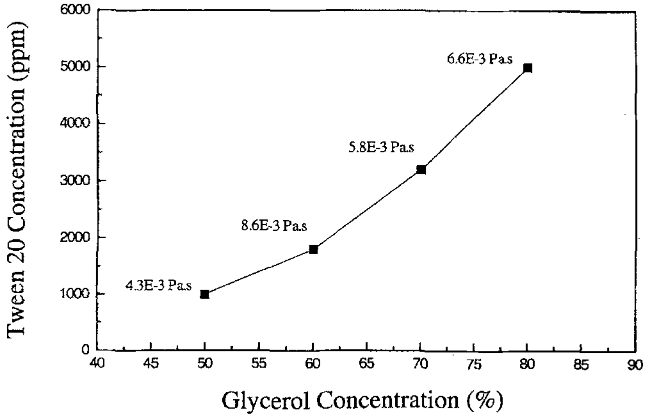


Fig. 2 Critical surfactant concentration which yields minimum viscosity as a function of glycerol concentration

Results and discussion

Interaction of nonionic surfactant with glycerol

The glycerol/water solvents behaved as Newtonian liquids at all compositions. The Newtonian behavior was retained with the addition of the nonionic surfactant, Tween20, in the concentration range from 10 ppm to 50000 ppm (5.0 wt%). However, significant change in the viscosity and surface tension were observed, depending on the surfactant and glycerol concentration, suggesting molecular interactions between Tween20 and glycerol. As seen in Fig. 1, addition of 10 ppm Tween20 into the 80% aqueous glycerol solution resulted in a 20% reduction in the surface tension from its original value of 0.058 N/m. This concentration is in the vicinity of the critical micelle concentration (CMC) of Tween20. The rate of decrease in the surface tension slowed down considerably after the CMC, until the concentration reached about 1000 ppm. The surface tension leveled off to about 0.035 N/m at high surfactant concentration. The addition of surfactant also resulted in a decrease in viscosity in the lower concentration region. A minimum viscosity was reached at a certain surfactant concentration depending on the surfactant concentration. In the case of the 80% glycerol solution, the minimum viscosity occurred at a Tween20 concentration of about 5000 ppm, where the corresponding viscosity was about 6.5 mPa.s (about 12% of the viscosity of the 80% glycerol solution without the surfactant). Beyond the critical surfactant concentration, the solution became more viscous with increasing surfactant concentration. At 5.0% surfactant concentration, the viscosity exceeded that of the original solution with no surfactant by about 20%.

The minimum viscosity was also observed when Tween20 was added to other mixtures of glycerol/water of different compositions. Figure 2 shows the critical surfactant concentration, which yields the minimum viscosity, as a function of the glycerol concentration. The minimum viscosity value for each concentration is shown on the figure. From 50% to 80% glycerol concentrations, the critical surfactant concentration increased with glycerol concentration. The nonlinear relationship suggests that in addition to the surfactant-glycerol interactions, self-micellization of surfactant molecules in water environment is also taking place. This is further supported in that for pure glycerol, the critical surfactant concentration was found to be 1000 ppm, the same level as that of the 50% solution.

The dependence of the critical surfactant concentration on the glycerol concentration indicates a strong molecular interaction occurring between surfactant and glycerol molecules. A small amount of surfactant may be sufficient to cause micelle formation with glycerol molecules. The hydrophilic groups in the surfactant may surround and

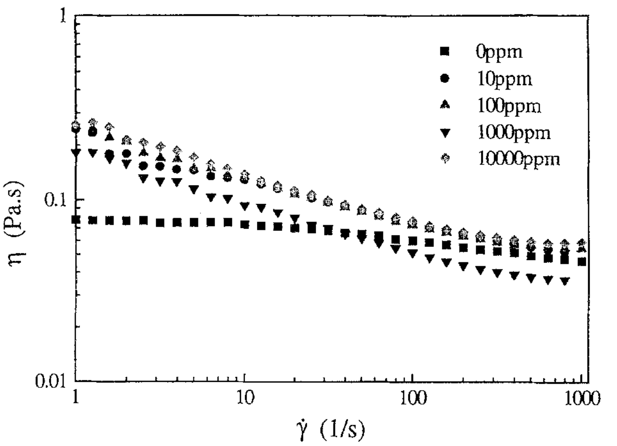


Fig. 3 Viscosity curves of 50 ppm Separan AP30 solutions with different amounts of Tween20

interact with the hydroxyl groups of glycerol, resulting in the hydrophobic parts pointing outward to form the first layer of micelles. The homogeneity of the solution suggests that vesicles (bi-layer micelles) are formed by the approaching of hydrophobic "tails" between the surfactant/glycerol micelles and the excess surfactant present in the solution. When more vesicles are formed and dispersed in the solution, the solution viscosity decreases until a minimum value is reached. By increasing the surfactant concentration above its critical value, the hydrophobic ethyoxy-groups of the "excess" surfactants tend to occupy the interior of the vesicles, and even interact with other hydrophobic groups to form surfactant complexes. Hence, the solution viscosity is expected to increase at higher surfactant concentration.

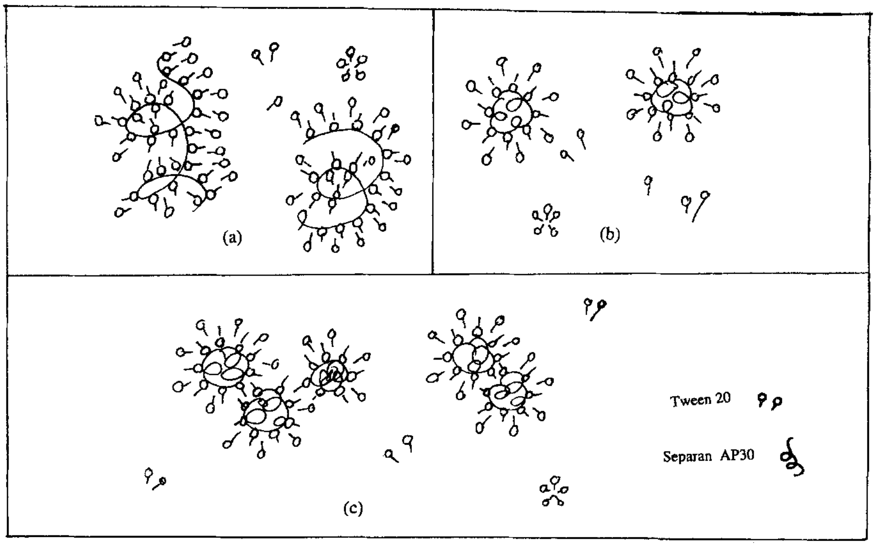
Nonionic surfactant in polyacrylamide/glycerol aqueous solution

The interaction between the surfactant hydrophilic groups and the carboxylic acid groups of linear long-chain polymer may result in the formation of hydrogen bond pendant on the polymer backbone. A small number of hydrogen bond surfactant molecules is sufficient to cause a dramatic change in the rheological behavior of the polymer solution. This phenomenon was investigated rheologically by measuring the steady-shear properties of 500 ppm Separan AP30 in 80% aqueous glycerine solutions containing different amounts of Tween20.

Figure 3 shows the viscosity curves for the 500 ppm Separan AP30 in 80% glycerol solutions with various concentrations of Tween20 over the range of shear rate($\dot{\gamma}$) from about 1 to 1000 s^{-1}. Without any surfactant, the viscosity curve of the Separan AP30 solution is almost flat, indicating a Newtonian behavior at low shear rate and slightly shear-thinning at high shear rate. With the addition of a small quantity of Tween20, even as low as 10 ppm, the viscosity increases dramatically in the low shear rate region, and also exhibits a strong shear-thinning characteristic. As in the case of Tween20 in glycerol/water solutions, the solution viscosity does not always increase with increasing surfactant concentration, but goes through a minimum before increasing again.

A pictorial representation of the proposed surfactant/polymer interaction is shown in Fig. 4. The initial increase in viscosity could be attributed to an increase in the polymer effective volume by the surfactant occupation of the free volume within the polymer chains. Other surfactant hydrophilic groups may form hydrogen bonding with polymer carboxylic acid groups (see Fig. 4a). When more

Fig. 4 Mechanisms of surfactant/polymer interactions



surfactant is added, in excess of the required amount to form complexes with polymer molecules, the surfactant molecules will surround the polymer macromolecules and reduce the strength between the ions of the polymer (note that Separan AP30 is an anionic polyelectrolyte). Hence, the polymer/solvent affinity (or the polymer molecular expansion factor) is reduced towards the θ-condition, resulting in a decrease in the viscosity. At this stage, the surfactant/polymer micelles have the lowest energy level (see Fig. 4b). Kienz and Holl [9] also observed a similar phenomenon and suggested that for nonionic surfactants, the attraction occurring between the ethylene oxide segments was perhaps through hydrogen bonding involving water molecules. The decrease in the solution viscosity could also be partly due to the surfactant/glycerol interaction. As seen in Fig. 1, the 1000 ppm Tween20 in the 80% glycerol solution without the polymer also exhibits a substantial reduction in the solution viscosity. The subsequent increase in the solution viscosity at higher surfactant concentration is a result of intermolecular attraction between the hydrophobic groups of the excess surfactant in the solution (see Fig. 4c).

Polyacrylamide solutions with surfactant also exhibited highly shear-thinning characteristics. At high shear rates, the viscosity of all solutions, except the 1000 ppm solution, approached that of Separan AP30 solution without the surfactant. This could be attributed to the breakup of surfactant/polymer complexes under high shear conditions. It is observed that the viscosity curve for the 1000 ppm solution crosses over the Separan AP30 curve at a shear rate of about 40 s^{-1}, giving a viscosity that is actually lower than the one without the surfactant in the high shear rate region. In this region, the large surfactant/polymer complexes could have been broken under high shear. The lowering of viscosity could primarily be due to the surfactant/solvent interaction as discussed earlier.

Figure 5 shows the first normal stress difference (N_1) as a function of shear rate for the four surfactant/polymer solutions. For the 500 ppm Separan AP30 solution free of surfactant, no measurable N_1 was detected with the Rheometric (RFSII) instrument, suggesting a very low level of elasticity, if any, existed for this solution. A substantial increase in elasticity becomes evident with added surfactant. Similar to the viscosity results, the N_1 data also increase initially at lower concentration of Tween20, and then decrease at higher concentration. Unlike the behavior of most aqueous polymer solutions which exhibit a monotonic increase in N_1 with increasing shear rate, the present results indicate that they are relatively insensitive to shear rate over the range $1 < \dot{\gamma} < 400\ s^{-1}$, except the one with 1000 ppm Tween20 which shows a dramatic increase in N_1 at $\dot{\gamma} > 20\ s^{-1}$. This behavior is closer to those commonly observed for food gels or emulsions [14].

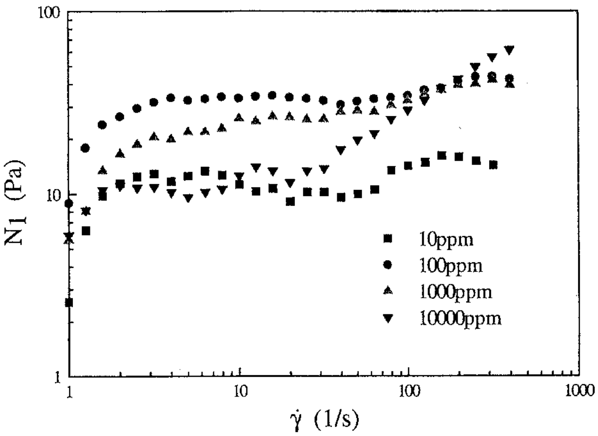


Fig. 5 First normal stress difference curves of 50 ppm Separan AP30 solutions with different amounts of Tween20

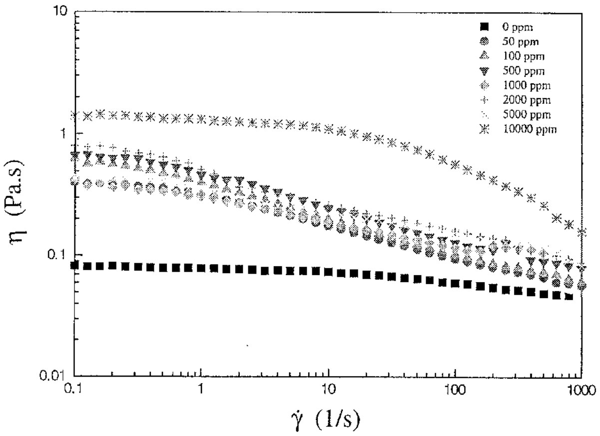


Fig. 6 Viscosity curves of 50 ppm Separan AP30 solutions with different amounts of Acrysol TT935

Associative thickener in polyacrylamide/glycerol solution

Figure 6 shows the steady shear viscosity as a function of shear rate for several 500 ppm Separan AP30/80% glycerol aqueous solutions containing different concentrations of Acrysol TT935. Acrysol TT935 is an acrylic copolymer which is insoluble in water in acidic environment. When the pH is adjusted above 8, the weakly hydrophilic groups are completely water-soluble. The greatly expanded hydrodynamic volume of the neutralised acrylic polymer molecules provides an extensive chain overlap and entanglement with polyacrylamide molecules, resulting in an increase in both viscosity and elasticity. The solutions also exhibit more shear-thinning. The associative thickener Acrysol TT935 is also considered as a polymeric surfactant and is expected to behave similarly to Tween20

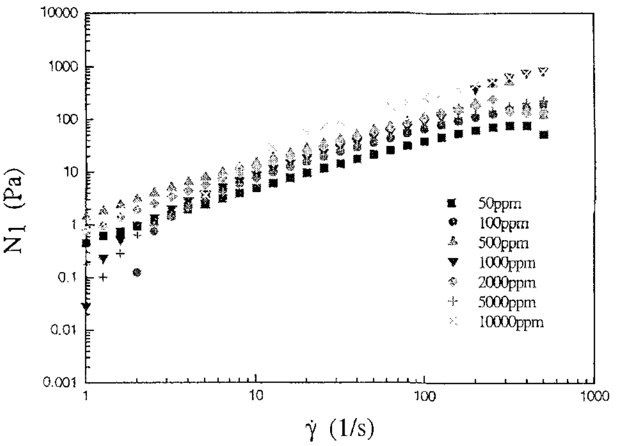


Fig. 7 First normal stress difference curves of 50 ppm Separan AP30 solutions with different amounts of Acrysol TT935

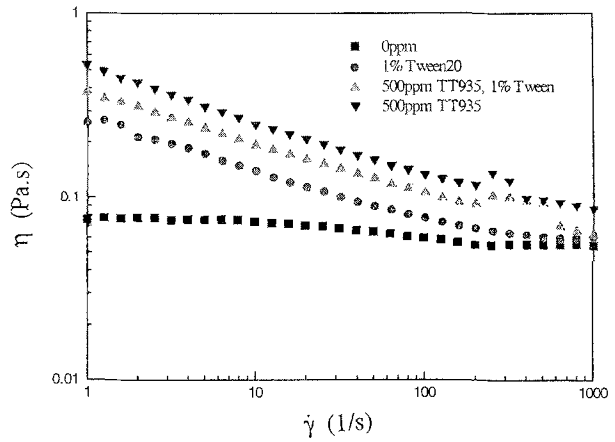


Fig. 8 Comparisons of various viscosity curves of 50 ppm Separan AP30 solutions with and without surfactant and/or associative thickener

when in contact with Separan AP30. However, due to its larger molecular size, it increases the probability of extended overlapping and entanglement with polymer chains, resulting in an enhancement of viscosity, over and above that of the Tween20. The viscosity in the low shear rate region reaches a maximum at a TT935 concentration of about 500 ppm and decreases to a minimum at about 1000 ppm before increasing again. It is interesting to note that the 500 and 1000 ppm solutions exhibit shear-thickening behavior at a shear rate of about 200 s^{-1}. The dilatant behavior of dilute solutions of polyacrylamide has also been reported in the literature [15–17]. There is a diversity of opinion as to whether the manifestation of shear-thickening behavior in dilute polymer solutions is due to some physical or chemical changes of polymer macromolecules during deformation, or is a result of flow instability or instrument artifacts [18].

Figure 7 shows the results of the first normal difference N_1 for the same solutions. The associative thickener (Acrysol TT935) is also a polymeric surfactant, its normal stress behavior was expected to be similar to that of Tween20. The value of N_1 first increased with increasing concentration of TT935, reached a maximum, and decreased to a minimum before another increase at higher thickener concentration. The difference was that with Acrysol TT935, the dependence of N_1 on $\dot{\gamma}$ appeared to be much stronger than with Tween20. It is interesting to note that stress jump was also observed in the N_1 results for the same two solutions at the same shear rate range as the shear-thickening phenomenon encountered in the viscosity measurement. This observation appears to support that shear-thickening of dilute polymer solutions is a real phenomenon, not an instrument artifact.

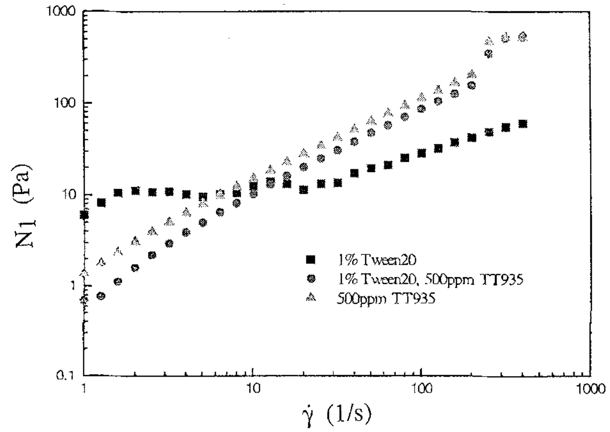


Fig. 9 Comparisons of various normal stress curves of 50 ppm Separan AP30 solutions with and without surfactant and/or associative thickener

Tween20/Acrysol TT935/Separan AP30 in 80% Glycerol Solutions

Many industrial coating liquids contain additives such as polymers, thickeners and surfactants to enhance their shear and extensional viscosities, and liquid elasticity for specific applications. Figures 8 and 9 compare the viscosity and normal stress results of different 500 ppm Separan AP30 in 80% glycerine solutions with or without the addition of surfactant or/and associative thickener. The data for the AP30 solutions without the additives, and with surfactant or with thickener addition have already been presented and discussed earlier. It is interesting to observe that adding together both surfactant and thickener into the AP30 solution yielded a viscosity curve intermediate to the two curves representing each additive alone. A possible explanation is that the presence of surfactant increased the probability of forming surfactant-enclosed complexes with the thickener/polymer aggregates. The resulting complexes became more dispersed in solution, which inhibited further entanglements between the AcrysolTT935 and Separan AP30 molecules. Consequently, a reduction of the solution viscosity from the one with TT935 in AP30 alone at the same thickener concentration was experienced.

The normal stress results shown in Fig. 9 are larger for the Tween20 in polyacrylamide solution at lower shear rates, but smaller at higher shear rates compared to the other two mixtures. Values of N_1 for the polymer solution containing both surfactant and thickener are slightly lower and follow the same trend as those of the Acrysol TT935/Separan AP30 solution without Tween20. This suggests that the solution elasticity is predominantly controlled by the high molecular weight thickener even in the presence of surfactant.

Conclusions

The study showed that rheological measurements of solution properties could provide useful information regarding molecular interactions of various solutes in solution. The addition of a nonionic surfactant in aqueous glycerol solutions with or without the presence of polymer and thickener reduced not only the surface tension of the solution, but also resulted in a complex rheological behavior, particularly with those solutions containing high molecular weight polymer and thickener additives. The solutions containing surfactant and polymeric additives were more viscous and elastic, as well as more shear-thinning. The solution viscosity increased initially with increasing surfactant concentration to a maximum, followed by a decrease to a minimum, and then increased again monotonically at very high surfactant concentration. Based on the rheological behavior, a three-stage molecular interaction mechanism was proposed – the initial formation of surfactant/polymer hydrogen bonds, resulting in an increase in viscosity; the formation of polymer/surfactant vesicles by the surrounding surfactant molecules, resulting in a reduction of viscosity; and the aggregation of polymer/surfactant complexes, forming a more viscous solution. The nonionic surfactant also interacted with the glycerol solvent. The interaction mechanism of the associative thickener with polyacrylamide was similar to that of the nonionic surfactant with polyacrylamide, but more pronounced as a result of larger complex molecules formed in the solution.

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