

Rheology of hydrophobic-alkali-soluble-emulsions (HASE) and the effects of surfactants

A.K.M. Lau, C. Tiu*, T. Kealy and K.C. Tam¹

Department of Chemical Engineering, Monash University, Victoria 3800, Australia

¹School of Mechanical and Production Engineering, Nanyang Technological University, Singapore

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Abstract

Steady and dynamic shear properties of two hydrophobically modified alkali soluble emulsions (HASE), NPJ1 and NPJ2, were experimentally investigated. At the same polymer concentration, NPJ1 is appreciably more viscous and elastic than NPJ2. The high hydrophobicity of NPJ1 allows hydrophobic associations and more junction sites to be created, leading to the formation of a network structure. Under shear deformation, NPJ1 exhibits shear-thinning behaviour as compared with Newtonian characteristics of NPJ2. NPJ1 and NPJ2 exhibit a very high and a low level of elasticity respectively over the frequency range tested. For NPJ1, a crossover frequency appears, which is shifted to lower frequencies and hence, longer relaxation times, as concentration increases. Three different surfactants anionic SDS, cationic CTAB, and non-ionic TX-100 were employed to examine the effects of surfactants on the rheology of HASE. Due to the different ionic behaviour of the surfactant, each type of surfactant imposed different electrostatic interactions on the two HASE polymers. In general, at low surfactant concentration, a gradual increase in viscosity is observed until a maximum is reached, beyond which a continuous reduction of viscosity ensues. Viscosity development is a combined result of HASE-surfactant interactions, accompanied by constant rearrangement of the hydrophobic associative junctions, and electrostatic interactions.

Keywords: associative polymers, rheology, hydrophobicity, surfactant addition

1. Introduction

In recent years, the potential suitability of hydrophobically modified alkali soluble emulsions (HASE) has become widely apparent in the surface coating industry for rheological manipulation. They have been introduced to improve flow and levelling in paint formulations and to provide better film build and stronger resistance to spatter. HASE are water-soluble block copolymers and are amphiphilic in nature. Each polymer consists of a hydrophobic segment that promotes interaction with latex particles or surfactants through adsorption and intermolecular association with other hydrophobes, leading to the formation of a network structure and a hydrophilic segment that allows solubility of the polymer in aqueous solution.

Typically, HASE polymers are synthesised using conventional semi-continuous emulsion polymerisation. A detailed account of the synthesis is given by Jenkins *et al.* (1996) and Tirtaatmadja *et al.* (1997). The two HASE polymers used in this study, NPJ1 and NPJ2, are synthe-

sised by emulsion polymerisation by Union-Carbide Corporation. They are long-chain acrylic polymers consisting of copolymers of methacrylic acid (MAA) and ethyl acrylate (EA), each with a macromolecule that consists of hydrophobic nonyl-phenol (C_9H_{19}) pendant groups. NPJ1 is a bi-phobe, containing two nonyl-phenol hydrophobic pendant groups while NPJ2 contains a single nonyl-phenol group. The molecular structure of the two HASE polymers is shown in Fig. 1. The number of C_9H_{19} alkyl hydrophobic groups is n ($n = 2$ and 1 for NPJ1 and NPJ2 respectively). Due to their anionic polyelectrolytic nature, upon neutralisation, the polymers become soluble in water and their backbone expands, leading to the formation of hydrophobic associations. The stiffness, steric hindrance of the polymer backbone and the hydrophobicity of the polymer system are responsible for the rheological changes in solution.

The effects of the presence of hydrophobic groups on associative polymers have been widely studied in the past, notably by Jenkins, (1990) and Tam *et al.*, (1998). These workers and others have shown that the rheology of hydrophobic associative polymer is dictated to a large extent by the significance of inter- and intra-molecular networking.

*Corresponding author: carlos.tiu@eng.monash.edu.au
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Broadly, intra-molecular associations tend to constrict coil size and reduce viscosity. Inter-molecular bonds form more intricate network structures, increasing viscosity. Analyses of the complex dynamic rheological properties for associative polymers have been reported by Annabel *et al.*, (1994) and Xu *et al.*, (1996), (1997). Ferry, (1980), has shown that the storage modulus, G climbs with increasing frequency due to the increasing inability of the polymer to dissipate stored energy. G attains an upper plateau, G_N^0 , which is an indication of the number and density of elastic junctions present.

Steady and dynamic shear properties are useful rheological quantities for the evaluation of the polymer interactions with surfactant, co-solvent, latex particles and for the relationship between the polymer structure and the aqueous solution rheology. The effects of the strong electrostatic forces usually present in an associative polymer-surfactant system have been studied by Petit *et al.* (1997), and Jenkins and Bassett (1993). Sarrazin-Cartalas (1984) and Loyen *et al.* (1995a) examined the role surfactant plays in rheological modification through the length of its polar group and hence its hydrophobicity. Interactions of HASE polymers and non-ionic surfactants examined by Tirta-atmadja *et al.* (1998) and Seng *et al.* (1999) showed a rise and subsequent fall in the viscosity of the polymer, induced by surfactant concentrations. Gupta *et al.* (2000) examined HASE polymers with respect to their rheological changes on interaction with capping agent, methylated β -cyclodextrin. Guo (1997), and Tam *et al.* (1998b) have recently examined the neutralisation of HASE polymers using salts. The work of English *et al.* details the rheology of HASE polymers (1996; 1997) and the influence of a non-ionic surfactant. Colby *et al.* (2001) examined the effects of surfactant addition to hydrophobically modified polyelectrolytes (HMP). They found that increasing concentrations of surfactant greater the propensity of HMP for intermolecular association until a critical concentration is reached, beyond which the solution is saturated and HMP molecules become isolated in a mixed micelle dominated by surfactant.

Since HASE polymers are frequently used together with additives such as surfactants, salt, binders, enhancers, etc., it is necessary to understand their sensitivity in the presence of these additives, which may produce beneficial or adverse effects on the rheological properties of the formulation for industrial applications. In this study, the rheological behaviours of two HASE polymers and the effect of surfactant additives are experimentally investigated and quantified through their impacts on the rheological properties of the fluids.

2. Chemical structure

Figure 1 describes the molecular structure of the two

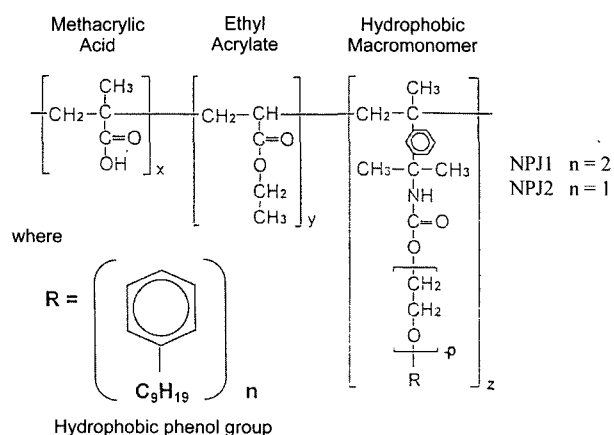


Fig. 1. Chemical structure of HASE polymers, NPJ1 and NPJ2.

HASE polymers used in this study. The polymers are structurally quite similar - each contains a long-chain hydrophobic monomer with a pendant hydrophobic phenol group. In the case of NPJ1 there are two of these groups, and one in the case of NPJ2. The extra hydrophobic pendant group of NPJ1 leads to a significant divergence between the rheological behaviours of the two polymers in solution at $\text{pH} \approx 9.0$. The concentration ranges over which these differences have been examined is 0.01-0.8 wt% NPJ1 and 0.01-2.5 wt% NPJ2.

The molecular weight, M_w , of both polymers has been determined by the static light scattering (SLS) method (Lau, 2000). SLS provides information, including weight averaged molecular weight for very dilute solutions, as well as other structural and dynamic information. M_w for NPJ2 solutions was found to be 104000 g/mol. Similar tests were performed for NPJ1, but, due to the larger amount of hydrophobic associations, all of which could not be removed by the added solvent, some inter chain aggregation occurred and a less accurate M_w for NPJ1 was achieved. M_w for NPJ1 was determined to be in the region of 100000 g/mol. This estimate is in general agreement with what one would expect given M_w for NPJ2, and serves to provide an approximate value of M_w for NPJ1.

3. Experimental methods

Steady and dynamic shear experiments captured the different rheological behaviour of the two HASE polymers in solution. The steady shear viscosity and dynamic moduli of the two HASE polymer systems with various concentrations were compared and studied. Depending on the viscosity and shear rate ranges of interest, either the Rheometrics Fluid Spectrometer (RFSII) equipped with a cone and plate measuring system, or the Contraves Low Shear 30 Sinus, with a cup and bob measuring system, was used. All measurements were conducted at 20°C.

The HASE polymers, as supplied by Union Carbide

(Singapore), were dialyzed in distilled deionized water ($18 \mu\Omega \text{ cm}$) using regenerative cellulose tubular membrane (Spectra/ Por®, 2 Molecularporous Dialysis Membrane, MWCO: 12-14000). Dialysis was carried out over four weeks with a change of fresh water each week. A 3 wt% stock solution was prepared through dilution with deionized water. Various concentrations were made by further dilution. The ionic strength of the solutions were maintained at 10^{-4} M sodium chloride (NaCl) salt and the pH of the final testing fluid was adjusted in the range of 9.0 – 9.5 (measured using an Orion pH meter) by neutralization with sodium hydroxide (NaOH) or otherwise a weaker base, 2-Amino-2-Methylpropanol-1 (AMP). For aqueous polymer solutions with surfactant, different classes of surfactant were added to HASE with varying degrees of molarity of the surfactant. The anionic surfactant used was sodium dodecyl sulfate (SDS) and the cationic surfactant was cetyltrimethylammonium bromide [$\text{CH}_3 \cdot (\text{CH}_2)_{15}$] (CH_3)₃NBr (CTAB). The non-ionic surfactant employed was iso-octylphenoxypolyethoxyethanol (Triton X-100).

4. Intrinsic viscosity

The intrinsic viscosity of the polymeric solutions was determined from capillary tube measurements. It was obtained by extrapolating a plot of concentration, c , versus η_{sp}/c or $\ln(\eta_r)/c$. In either case the intercept provides the intrinsic viscosity, and the slope of the plots give the Huggins and Kraemer coefficients respectively, from the equations below:

Huggins Equation

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2 c \quad (1)$$

Kraemer Equation

$$\ln(\eta_r)/c = [\eta] + k_K[\eta]^2 c \quad (2)$$

Figure 2 shows Huggins and Kraemer plots for the estimation of the intrinsic viscosity, $[\eta]$ and the Huggins and Kraemer coefficients k_K and k_H . The corresponding $k_K = 0.191$ and 0.053 , and $k_H = 0.782$ and 0.641 for NPJ1 and NPJ2 respectively.

It is found that NPJ1 exhibits a slightly lower intrinsic viscosity, with $[\eta] = 12.07$ as compared to 13.09 dl/g for NPJ2. The smaller $[\eta]$ for NPJ1 is due to the increased density of hydrophobic pendant groups present in NPJ1, leading to more tightly coiled polymeric chains at low concentrations, where intra-molecular associations are minimal. This in turn leads to lower viscosity due to the smaller effective size of NPJ1 in solution.

The curve fits shown in Figure 2 have been achieved by linear regression analysis, a part of the Microsoft Excel spreadsheet package. The R^2 values for each fit are 0.97 and 0.77 for Huggins and Kraemer equations respectively

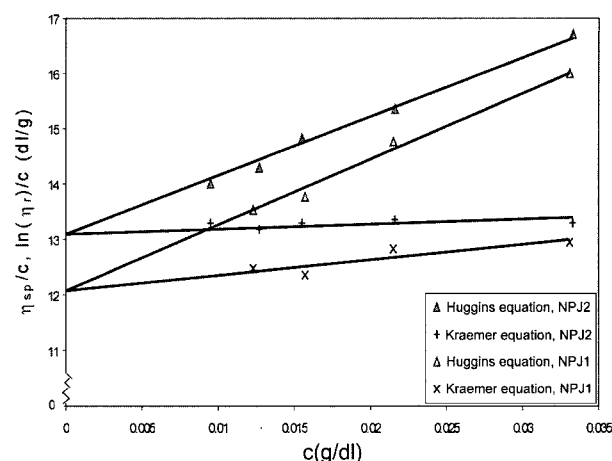


Fig. 2. Intrinsic viscosity data for NPJ1 and NPJ2 polymer solutions.

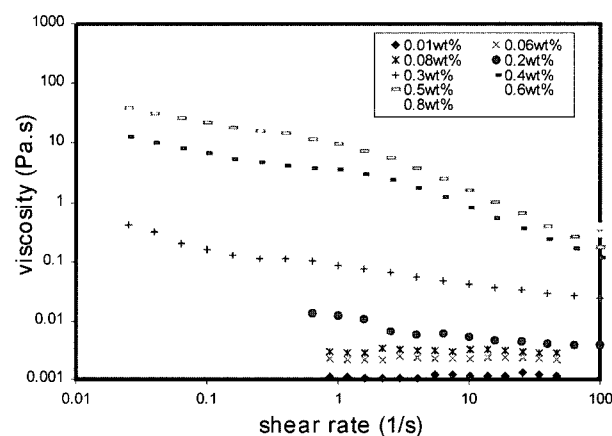


Fig. 3. Steady shear viscosity for NPJ1 solutions at different polymer concentration.

for NPJ1, and 0.99 (Huggins) and 0.97 (Kraemer) for NPJ2. As such it is noted that there is some uncertainty in the data, especially for the NPJ1, Kraemer equation correlation.

5. Steady shear viscosity data

Steady shear data were measured for both NPJ1 and NPJ2 solutions at varying concentrations. The behaviour of NPJ1 was examined at concentrations from 0.01-0.8 wt% NPJ1 and that of NPJ2 from 0.01-2.5 wt% NPJ2. Figures 3 and 4 show the results of this analysis for NPJ1 and NPJ2 respectively.

From Figure 3, NPJ1 shows Newtonian characteristics at very low concentrations, becoming increasingly shear thinning as concentration increases. At low concentrations, the number of inter-molecular junctions could be expected to be low, and one would expect that a large contribution to internal structure is made by intra-molecular bonding. As

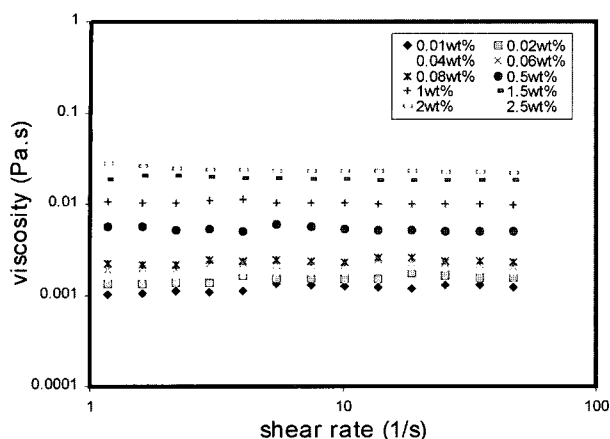


Fig. 4. Steady shear viscosity for model NPJ2 solutions at different polymer concentration.

concentration increases, the network is destroyed by shear more quickly than it is reformed. There are more inter-molecular junctions in this case as the increased concentration leads to a greater likely-hood of two or more molecules being in close proximity. As concentration rises an increasingly significant contribution to internal structure is made by the network created by inter-molecular association. A Newtonian plateau exists at low shear rates in most cases, and the point of onset of shear thinning occurs at lower shear rates as concentration increases. This serves to confirm that as the number of inter-molecular junctions increases, the stability of the network structure under steady shear is decreased.

In Figure 4, NPJ2 solutions exhibit Newtonian behaviour throughout the concentration and shear rate ranges tested. NPJ2 has only a single pendant group as compared with the two possessed by NPJ1, which reduces the ability of the polymer to provide opportunities for network building through inter-molecular attractions. It is worth noting that the viscosity of NPJ1 at very dilute (0.01 wt%) concentrations is 0.00115 Pa.s and that of NPJ2 at the same concentration is 0.00121 Pa.s. The detection range of the Contraves Low Shear LS30 system used in these experiments can detect changes with an accuracy of 2% of full scale (± 0.00004 Pa.s), therefore a viscosity difference of 0.00006 Pa.s may be detectable with this instrument, although there is considerable uncertainty regarding its exact magnitude. The lower viscosity of NPJ1, if it exists, is because it possesses a higher density of hydrophobic moieties, leading to a more tightly coiled polymer chain at low concentrations and thus a smaller effective molecular size in solution. This effect is also apparent from the lower intrinsic viscosity of NPJ1.

Figure 5 illustrates the differences in zero shear viscosity for NPJ1 and NPJ2 as the concentration of a given solution increases. In the case of NPJ1, there is a clear rapid change in slope of the plot. The change is from a slope of 0.33 to

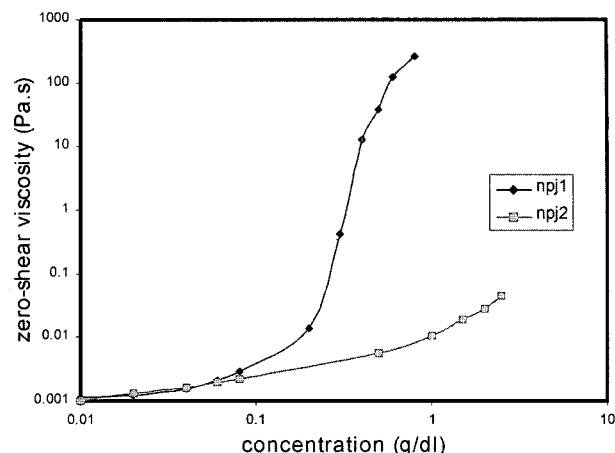


Fig. 5. Comparison of zero-shear viscosity on concentration for NPJ1 and NPJ2 solutions.

one approaching 12. This behaviour is consistent with that found by English (1997) for similar HASE solutions.

It is possible that the change in power-law behaviour results from the increased probability that inter-molecular linkages will occur at heightened concentrations of each polymer. The comparatively high activity of NPJ1 in this regard accounts for its more dramatic change. In contrast, NPJ2 is relatively inert, and remains close to Newtonian throughout the concentration profile, indicating that there are few inter-molecular bond sites, and as a result, little change in its η_0 -concentration profile.

Such results are in contrast with conventional flexible polymers in which the change of slope from dilute to concentrated regimes is from 1.0 to 3.4 (Bicerano, 1996). The change in slope occurs at a critical concentration, c^{**} , where $c^{**} = 1/[\eta]$. For NPJ1 $c^{**} = 0.083$ wt%. The location of c^{**} , the cluster overlap concentration, indicates the concentration at which individual clusters begin to associate, ie the point at which inter-molecular association begins to play a role in the fluid internal structure. As inter-molecular interaction increases, the inter-molecular network becomes more intricate and the slope steepens. For NPJ2, $c^{**} = 0.076$ wt%, and the change in slope (from approximately 0.33 to 0.7) is much less dramatic. These results illustrate the importance of the availability of sites for cross-linking, as evidenced by the higher activity of NPJ1 compared with conventional polymeric materials, and the relative inactivity of NPJ2.

6. Dynamic behaviour

Figures 6 and 7 show the dependence of the dynamic moduli on frequency for model NPJ1 and NPJ2 solutions respectively.

Figure 6 shows that at low to moderate polymer concentrations of NPJ1 solutions, minimal interaction occurs

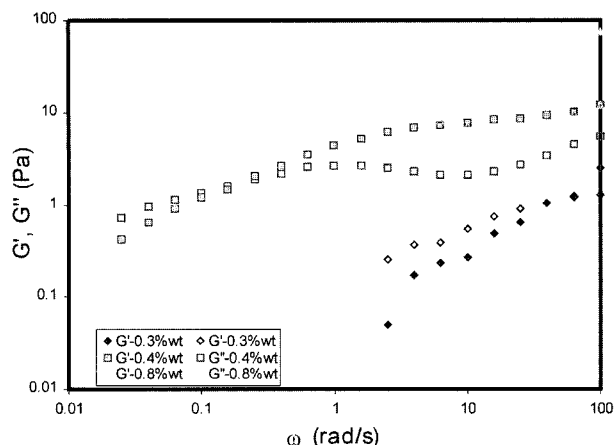


Fig. 6. Dynamic moduli versus frequency for model NPJ1 solutions.

between polymer chains, resulting in a low level of network formation. This is illustrated by the fact that G'' is of higher magnitude than G' at low NPJ1 concentration over the frequency range tested. With increasing concentration, a crossover frequency becomes apparent, whereby the magnitude of G' becomes larger than that of G'' , indicating the increasing dominance of inter-molecular associations and more intricate network structure. At 0.8 wt% NPJ1, a gel-like structure is formed, indicating extensive inter-molecular associations. As this effect would imply, the crossover frequency is shifted to lower frequency as concentration increases. This frequency was not detected in the range measured, but is to be expected from the trends exhibited in the plots in Figure 6. At low concentrations of NPJ1, $G' \propto \omega^2$ as manifested by many conventional flexible polymers.

At high frequency, based on the theory of Green and Tobolsky (1946) the plateau modulus is related to the strength of the network. The storage modulus, G' , indicates the mechanically active junction densities in the transient network system. Thus, as concentration increases, the junction density and hydrophobic aggregate size increase, leading to a stronger network structure. The frequency at which the loss modulus, G'' , curve intersects the G' curve is referred to as the crossover frequency, ω_c . The inverse of this frequency is termed the relaxation time. As expected, the relaxation time increases with NPJ1 concentration.

NPJ2 exhibits only weakly elastic behaviour with the magnitude of G'' greater than G' for the frequency range tested. No crossover of G' and G'' is observed, suggesting that relaxation times of NPJ2 solutions are extremely short. This would indicate that there is a tendency for NPJ1 to have a higher degree of inter- and intra-molecular bonding because of the extra hydrophobic group at its tail which can randomly provide either inter- or intra-molecular interaction opportunities for each hydrophobic moiety.

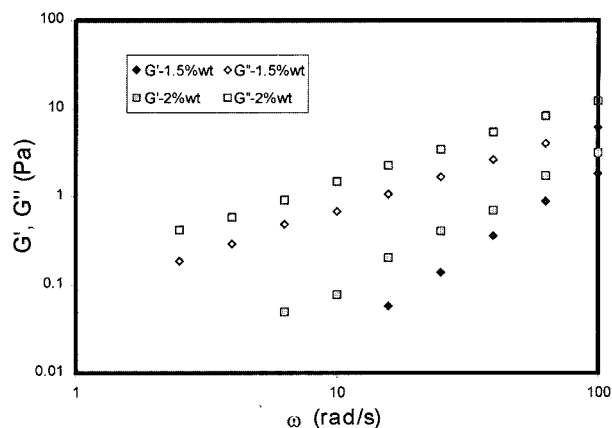


Fig. 7. Dynamic moduli versus frequency for model NPJ2 solutions.

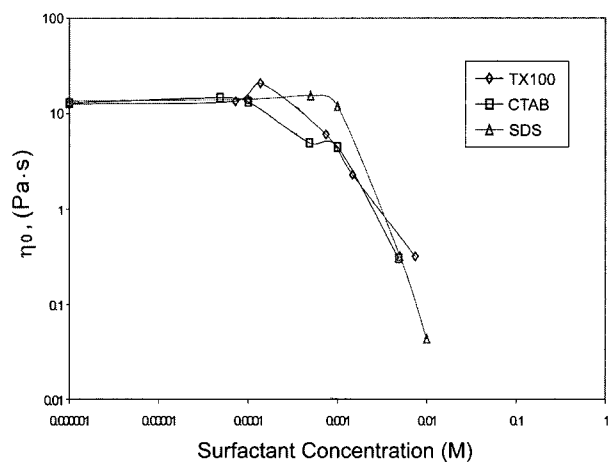


Fig. 8. Influence of surfactant concentration on η_0 for 0.4 wt% NPJ1.

7. Rheological effect of surfactant

It is expected that appropriate surfactant addition to HASE polymers will improve coating performance through modification of rheological properties. This modification occurs through the interaction of the surfactant with the hydrophobic group. The effects of anionic (SDS), non-ionic (TX-100), and cationic (CTAB) surfactants were examined.

Figures 8, 9 and 10 illustrate the effects of additives on the performance of increasingly concentrated HASE polymers through changes in zero-shear viscosity, η_0 , and elastic modulus, G' . Dynamic data are available for NPJ1 only, as NPJ2 solutions exhibit very low levels of elastic behaviour as discussed earlier. The 0.4 wt% NPJ1 and 1.5 wt% NPJ2 solutions were used. To examine the effect of surfactants, dynamic data was arbitrarily collected at 4 rad/s.

For NPJ1, Figure 8 shows a similar trend for each surfactant. There is a marginal increase in the magnitude of

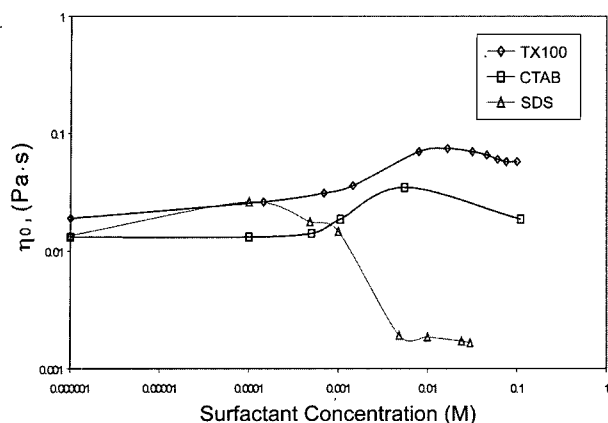


Fig. 9. Influence of surfactant concentration on η_0 for 1.5 wt% NPJ2.

η_0 , followed by a rapid fall as surfactant concentration increases beyond a critical concentration, c^*_s . c^*_s occurs first for CTAB at $c^*_s = 0.00005\text{M}$, followed by TX-100, $c^*_s = 0.000155$ and then SDS at $c^*_s = 0.001\text{M}$. The change of η_0 is the most rapid for SDS with concentration beyond c^*_s .

Intuitively, one would expect this pattern to emerge since NPJ1 is highly active in terms of its elevated concentration of hydrophobic pendants on a negatively charged polymer chain. The interactions of NPJ1 alone are therefore mainly of a hydrophobic nature. Negatively charged SDS, having the same charge as the NPJ1 backbone, encourages hydrodynamic expansion of the polymer chains, leading to viscosity increases, until c^*_s is reached. Thereafter, SDS neutralises charged pendant sites, effectively shielding them from cross-linking, resulting in rapid viscosity reduction as increasing numbers of available junction sites are occupied by surfactant rather than by other polymer chains. On the other hand, the polymer backbone is neutralised by the presence of the positively charged CTAB ions. This reduces the ability of the polymer backbone to interact with pendant groups, and form a network structure. At c^*_s , this effect becomes dominant, leading to rapid reduction in network intricacy with increasing surfactant concentration. This reduction in network density leads to a similarly rapid drop in viscosity.

Finally, for the case of non-ionic TX-100, surfactant addition effects can be observed unclouded by the electrostatic interactions between the surfactants and HASE head groups or polymer chains. The NPJ1 - TX-100 system exhibits a sharp rise in η_0 , at c^*_s , after which a gradual decrease in viscosity occurs. The high value of η_0 , indicates the importance of electrostatic interactions in the binding of ionic surfactant molecules to NPJ1 as in the SDS and CTAB systems. TX-100 does not inhibit the interaction between the pendant groups and the polymer chains, allowing structural build-up, as evident by higher viscosity

values. The similarity between the magnitudes of this peak and the zero-shear viscosity, around 20 Pa·s, of a similar surfactant-free system (see Figure 5) implies that the surfactant is not interfering with the actions of the pendant groups, allowing good access to the polymer chains. Therefore one would expect that the structure of the NPJ1-TX-100 system would be more intricate, and the change of η_0 with surfactant concentration is due primarily to hydrophobic interaction.

Similar effects are illustrated for NPJ2 in Figure 9. Both SDS and CTAB exhibit lower η_0 than TX-100. CTAB and SDS hinder network structure development through shielding effects on either the polymer chain or the pendant group, the absence of these electrostatic effects increases availability of network junctions and hence the magnitude of η_0 is greater for the TX-100 system. The rate and magnitude of viscosity reduction is greatest for SDS as increasing surfactant concentration quickly shields the active sites and network structure becomes negligible. The shielding effect on the pendant group is much more pronounced than that on the polymer backbone due to the already low concentration of hydrophobic junction sites on NPJ2. This might also explain why c^*_s is lower for SDS relative to both CTAB and TX-100 for NPJ2. This is in contrast to the effects noted for NPJ1, where c^*_s for SDS occurred at the highest surfactant concentration. This comparison implies that the presence of increased numbers of hydrophobic sites allows more consistent rheological performance, with catastrophic structural collapse at c^*_s .

For NPJ2, the effects of shielding the polymer backbone are less pronounced. A maximum is reached at c^*_s for CTAB, followed by a gradual decrease in viscosity. In contrast with NPJ1 solutions, intra-molecular attractions normally dominate the structure of NPJ2 solutions. The maximum may be due to the fact that, at low concentrations, CTAB does not neutralise all junction sites, allowing some polymer intra- and inter-molecular bonding to occur. As increasing numbers of sites on all polymer molecules become saturated with CTAB, further inter- and intra-molecular linkings are inhibited for the polymer molecules, and viscosity decreases. The relatively low rate of change of viscosity is likely to be due to the similarity in the viscosities of CTAB and the NPJ2 solution, and, the effects of further addition of CTAB to the solution counteracting the gradual neutralisation of increasing numbers of negatively charged bonding sites. This contrasts with the case of NPJ1, where η_0 is several orders of magnitude higher (due to increased inter-molecular activity), and viscosity increases due to increasing concentrations of CTAB have negligible impact on the overall viscosity.

These results compare qualitatively with those of Colby *et al.* (2001) for hydrophobically modified polyelectrolyte (HMP) molecules with similarly charged surfactant. They discovered that HMP molecules are at first encouraged to

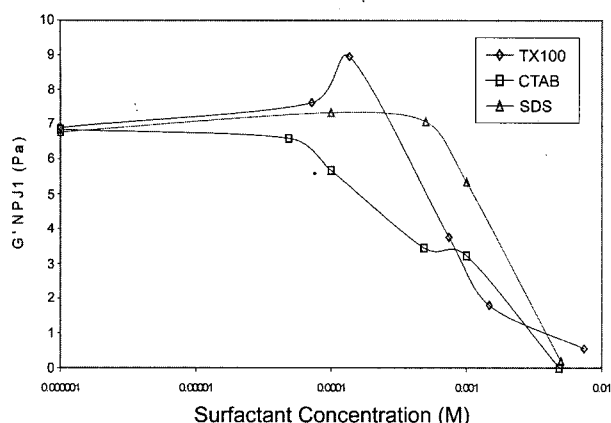


Fig. 10. Influence of surfactant concentration on G' for 0.4 wt% NPJ1.

form intermolecular associations in the presence of surfactant, but are subsequently prevented from doing so at a critical concentration due to their isolation in a surfactant saturated micelle.

Figure 10 shows the influence of surfactant concentration on the dynamic performance of 0.4 wt% NPJ1. Similar trends to those exhibited for η_0 are evident. A slight rise in G' occurs until a critical concentration is attained after which G' drops significantly with rising concentration. c^* is lowest for CTAB and highest for SDS. A sharp peak is evident for the TX-100-NPJ1 system, this was not observed for the other solutions. It is interesting to note that this peak occurs at the same c^* , as did the peak in η_0 for the TX-100 system (Figure 8).

The effect of surfactant concentration on G' may be explained in a similar manner to that of concentration on η_0 . For SDS, the surfactant monomers bind to the NPJ1 hydrophobic junctions, stabilising them and creating SDS-NPJ1 aggregates, which have structural strength and enhance network structure, increasing G' . Subsequent addition of SDS hinders network development through the shielding effect high concentrations of SDS have on the hydrophobic junctions.

For CTAB-NPJ1 systems, as in the case of the η_0 analysis, the polymeric backbone becomes increasingly neutralised, due to the strong electrostatic attraction between itself and CTAB ions. This reduces the ability of the polymer pendant group to interact with a polymer backbone and form a network structure, especially at c^* , and thereafter, when a rapid reduction in interaction between polymer molecules occurs with increasing surfactant concentration. This reduction leads to a rapid reduction in G' .

For the TX-100 HASE system, electrostatic interactions are absent, which increases the availability of hydrophobic junction sites and so enhances the ability of the polymer to create a network. However, as surfactant concentration becomes prohibitively high it disrupts the hydrophobic

domains and destroys the network. Again the extent of this increased structural build-up is apparent through the magnitude of G' .

8. Conclusions

The two HASE polymers examined (NPJ1 and NPJ2) which have similar molecular weights and similar chemical structure, exhibit different rheological behaviour due primarily to the number of hydrophobic groups at the tail of the side chain along the polymer backbone. As a result, the intrinsic viscosity of NPJ1 is slightly lower than that of NPJ2 under these conditions. On the other hand, the increase in zero shear viscosity at critical concentration for NPJ1 is significantly greater than that for NPJ2.

NPJ1 and NPJ2 exhibit a very high and a low level of elasticity respectively over the frequency range tested. In the case of NPJ1, the number of mechanically active sites increases with polymer concentration. At the crossover point, where G' becomes of larger magnitude than G'' , intermolecular association begins to dominate rheologically as network structure becomes more extensive. The heightened activity of NPJ1 through its extra pendant group is responsible for this improved ability to create an intermolecular network structure.

A critical concentration exists, beyond which η_0 decreases dramatically for both HASE solutions mixed with different surfactants.

For NPJ1, fluid structure tends to be dominated by associative inter-molecular attractions, driven by the extra hydrophobes present in the system. For this fluid, in solution with SDS, there is an initial η_0 increase due to the hydrodynamic expansion of the polymer backbone. Thereafter, as surfactant molecules increasingly occupy hydrophobic sites, the ability of individual polymer molecules to cross-link is reduced. η_0 drops sharply after the critical concentration. On the other hand, CTAB is attracted to the long chain backbone of the polymer, progressively, preferentially neutralising it, and prohibiting further access to its charged sites, preventing intermolecular structural build-up. Finally, TX-100 removes the effects of electrostatic forces due to surfactant-polymer interaction. For NPJ1 in the presence of increasing concentrations of TX-100 a high value of η_0 , indicates that ionic surfactant-polymer interactions play an important part in binding surfactant molecules to NPJ1. Their absence enable the structure of the TX-100 system to be more intricate, increasing the maximum η_0 in comparison with the ionic surfactant systems.

The proposed interaction mechanisms are further supported by the dynamic data for NPJ1-surfactant systems. The extent of the enhanced structural build-up is evident from the magnitude of G' .

In the case of NPJ2, structural change has been shown to be due predominantly to electrostatic interaction. Addition

of SDS causes hydrodynamic expansion of the chains through electrostatic repulsion, followed by an occupation of the pendant sites, leading to reduced viscosity through less intra- (and inter-) molecular bonding. Intra-molecular bonding dominates the structure of NPJ2 solutions, so, CTAB introduction is less conspicuous than that of SDS, it does not cause initial expansion, nor does it prevent all intra- and inter-molecular linkage until extremely high concentrations are reached, when viscosity decreases. It does, however occupy some charged sites on the polymer chain, hence reducing the extent of structural build-up in comparison with that achieved by TX-100, which has no interaction with either chain or pendant group, allowing the charged sites to interact freely.

The results presented emphasise the importance of allowing intermolecular associations through the liberation of potential junction sites. Surfactant addition can have a significant impact on the rheological performance of HASE polymers. The concentration of the additive must be closely controlled if a successful outcome in terms of physical property control is to be achieved.

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Nomenclature

c^{**}	Cluster overlap concentration, g/dl
c^*	Critical concentration, g/dl
η_0	Zero shear rate viscosity, Pa.s
λ	Relaxation time, s
$[\eta]$	Intrinsic viscosity, Pa.s
$G(\omega)$	Storage modulus, Pa
$G''(\omega)$	Loss modulus, Pa
G_N^0	Plateau modulus, Pa

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