

Interactions of Surfactants with Polymers in Liquid Inks

Ryszard Sprycha* and Ramasamy Krishnan*

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ABSTRACT

Interactions of acetylenic diol surfactant (Surfynol SE-F) with maleic anhydride co-polymers (SMA 1000H; SMA 3000H and SMA 1440H) and styrenated acrylic co-polymers (Joncryl 63 and Joncryl 89) have been studied using dynamic surface tension and viscosity measurements. SMA 1000H and SMA 3000H were unmodified copolymers of styrene and maleic anhydride with styrene/maleic anhydride ratios of 1:1 and 3:1, respectively, while SMA 1440H was a half ester (butoxyethanol) of SMA 1000H polymer. Polymer solutions of four different concentrations were used (1; 3; 10 and 20 % w/w). It was found that Surfynol SE-F surfactant interacted with styrenated maleic anhydride and acrylic co-polymers forming simple complexes and/or complex structures in the bulk that increased solution viscosity for high polymer concentrations and surfactant doses. The extent of interactions increased with increasing polymer hydrophobicity. Both hydrophobic and hydrogen bond interactions seem to be involved in the polymer-surfactant interactions.

INTRODUCTION

Due to regulatory limitations (VOC, toxicity of solvents, etc.) water based inks have gained a significant percentage of the liquid ink market in recent years. One of the factors important for good printability of liquid inks is low surface tension; low surface tension is indispensable for good ink spreading. Solvent borne inks have low surface tension because of the solvents used

* Sun Chemical Corporation, 631 Central Ave,
Carlstadt, New Jersey, 07072.

(e.g. toluene, alcohol, etc.). Water, on the other hand, has high surface tension ~ 72 dyne/cm, but the surface tension of water-based inks can be lowered by the addition of the appropriate surfactants. Usually non-ionic surfactants that ensure low dynamic surface tension (DST) are used for this purpose.

The minimum value of surface tension of surfactant solution is achieved when its concentration is equal to the critical micelle concentration (cmc). At the cmc the concentration of free surfactant molecules or ions reaches a maximum. Above this point association of surfactant molecules or ions in the solution is the more energetically favorable process and surfactant aggregates called micelles are formed. Micelles can form different structures depending on the total surfactant concentration. For surfactants, which do not form micelles the minimum surface tension of the surfactant solution is reached at its solubility limit. Above this concentration an excess of surfactant exists as a separate phase in the system.

The values of the cmc or solubility of many effective surfactants used in water based printing inks are of the order of 10^{-4} - 10^{-3} mol dcm⁻³ or ~ 0.1 %. On the other hand, the amount of surfactant added into the water-based inks is significantly higher than the respective cmc or solubility limit. One of the reasons for this discrepancy is the fact that surfactants can interact with other ingredients of a liquid water based ink. Water soluble or water dispersible polymers used as binders and pigment dispersants are major constituents of water based inks. Therefore, knowledge of the possible interactions between polymers and surfactants is a very important issue for ink manufacturers.

Polymer-surfactant interactions are very interesting from a theoretical point of view and very important practically due to the wide-spread applications of such systems, e.g., water-based inks, paints, coatings, detergents, rheology modifiers, to mention a few. A large number of papers deal with this subject and most of them refer to polymer-ionic surfactant systems where very strong interactions were observed (Goddard, 1993a; Goddard, 1993b; Goddard, 1994; Jones, 1967; Nahrungbauer, 1997; Kevelam et.al., 1996.). At the same time it was found that non-ionic surfactants interact with polymers (especially homopolymers) to a lesser degree than ionic surfactants (Goddard, 1993a; Goddard, 1993b; Saito, 1987; Lindman and Thalberg, 1993).

Non-ionic surfactants based on acetylenic diol chemistry represent a unique class of surfactants providing low dynamic surface tension and good defoaming and surface wetting characteristics (Dougherty, 1989; Medina and Sutovich, 1994). Despite wide applications of acetylenic diol surfactants in mixtures with polymers, to the best of our knowledge, there is no literature data available on polymer/acetylenic diol surfactant interactions.

The purpose of the present basic study was to investigate the interactions of acetylenic diol surfactants with polymers used in the Graphic Arts industry. Three different co-polymers, based on maleic anhydride, and two styrenated acrylic polymers were selected for investigation. Surfynol SE-F surfactant was selected among numerous acetylenic diol surfactants. The effect of polymer/surfactant interactions on the dynamic surface tension and viscosity of polymer solutions was studied. Although, surface tension methods were previously used to study polymer/surfactant interactions, the measurements were performed under equilibrium conditions (Jones, 1967; Nahrngbauer, 1997). Because printing is a very dynamic process measurements of surface tension under equilibrium conditions are not relevant to such systems.

EXPERIMENTAL

Materials

Aqueous solutions of three different resins (SMA 1000H; SMA 3000H and SMA 1440H) were obtained from Elf Atochem, Inc., USA. SMA resins are low molecular weight (MW) copolymers of styrene and maleic anhydride. They are widely used in floor polishes and as pigment dispersants in inks, paints and plastics, paper sizing, coatings etc. All the resins were made water-soluble by neutralization with ammonia. SMA 1000 (MW=1600) and SMA 3000 (MW=1900) are unmodified copolymers with styrene/maleic anhydride ratios of 1/1 and 3/1, respectively. SMA 1440 (MW=2500) is the half ester of the base resins SMA 1000 and butoxyethanol - see Fig. 1. In addition, two styrenated acrylic polymers (Joncryl 63 and Joncryl 89) were used.

Surfynol SE-F surfactant was obtained from Air Products and Chemicals, Inc., Allentown, Pennsylvania, USA. This surfactant is based on acetylenic diol (2,4,7,9-tetramethyl - 5 - decyne - 4,7 - diol) chemistry. Its easy dispersibility in water and milky appearance gave us the possibility of an independent determination of "titration end point".

Methods

Polymer solutions of four different concentrations (1%, 3%, 10% and 20% w/w solids) were prepared using de-ionized water. Titration technique was used to determine the DST of a given polymer solution as a function of titrant (Surfynol SE-F) added. Dynamic surface tension was measured using a Sensadyne 6000 tensiometer (Chemdyne Research Corp., USA), equipped with a 1-mm diameter small orifice probe. The gas flow was constant during the measurements (about 4 bubbles per second in pure water) and the measurements were performed at a constant temperature of 22° C.

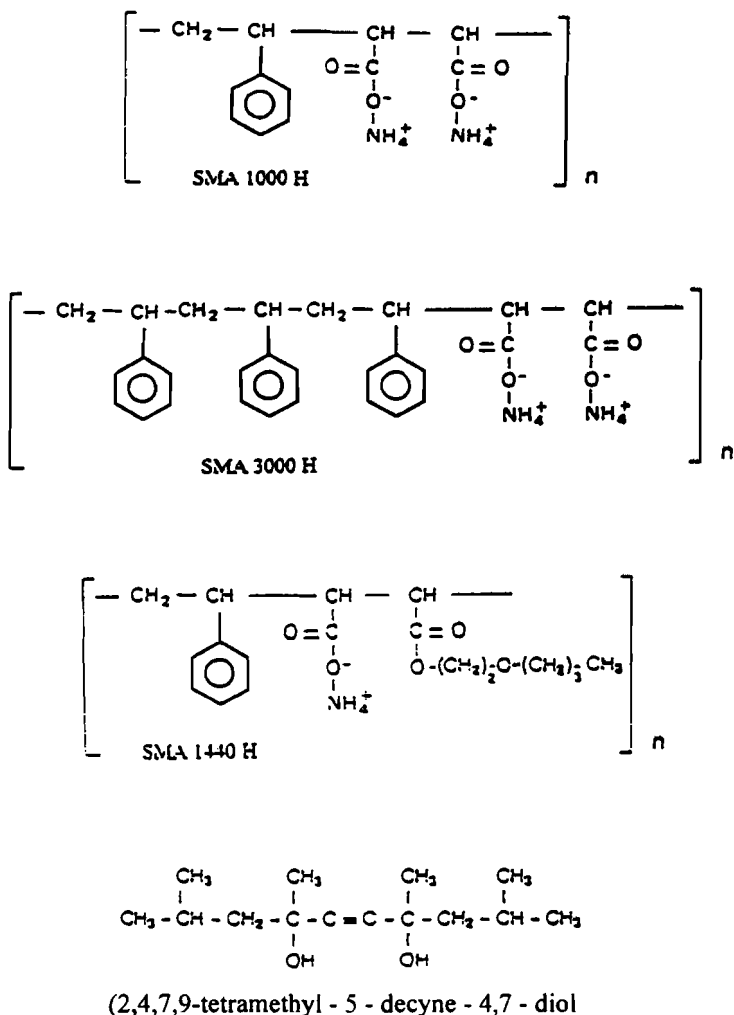


Fig.1. Structures of SMA polymers and acetylenic diol surfactant.

350g of polymer solution of a given concentration was agitated in a glass jar with a magnetic stirrer. The titrant (surfactant) was added to the polymer solutions in small portions. The time to reach "fast equilibrium" was evaluated in the separate experiments for all polymer solutions. Based on the kinetics of surfactant dissolution under different conditions it was decided to measure the

DST at 10 minutes intervals after surfactant addition. Before DST readings were taken the agitation was stopped and the solution was allowed to rest for 30-60 seconds.

The total consumption of the titrant under given experimental conditions was determined by recording the amount of Surfynol SE-F surfactant needed to observe solution cloudiness which was indicative of an excess of free surfactant in the system. The viscosity of the polymer solutions after addition of different amounts of surfactant was measured simultaneously using Shell #2 and Zahn #2 cups and the readings were subsequently converted into SI system (mPas) viscosity units.

RESULTS AND DISCUSSION

The amount of time required to dissolve a given portion of surfactant in water or polymer solution depends on surfactant affinity towards water. This time is related to the interfacial area formed between surfactant droplets (particles) and water. It was found in separate experiments that the time required to reach “fast equilibrium” for Surfynol SE-F surfactant was 10 minutes.

One factor that may effect dynamic surface tension measurements is the high viscosity of the polymer solution. To monitor whether this was the case the number of bubbles generated at constant gas flow was recorded along with the amount of surfactant added to the system. It was found that, in most cases, the viscosity of polymer solutions did not affect the bubble release from the small orifice tip. Thus, the viscosity had no negative effect on DST measurements.

Dynamic Surface Tension

The titration curves of SMA 1000H polymer with Surfynol SE-F are presented in Fig. 2 for four polymer concentrations. As observed Surfynol SE-F shows low affinity towards SMA 1000H at low polymer concentrations. Formation of polymer/surfactant complexes, less active than Surfynol SE-F surfactant, was observed for higher polymer concentrations. The interactions observed seem to be due to the presence of styrene segments in the SMA 1000H molecule. In separate experiments no interactions were found between sodium maleate solutions (concentrations $\leq 15\%$) and Surfynol SE-F surfactant

Figure 3 shows the titration curves for the SMA 3000H/Surfynol SE-F system. For this system polymer/surfactant interactions are much stronger than those observed between SMA 1000H polymer and Surfynol SE-F surfactant. The greater hydrophobicity of this polymer, due to its higher styrene content - see

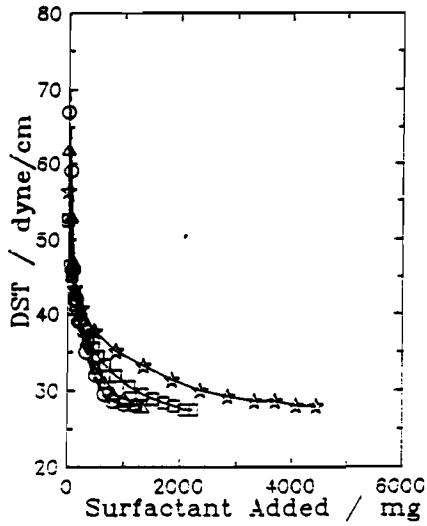


Fig.2. Dynamic surface tension vs. surfactant dose for SMA 1000H/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O , 1%; Δ , 3%; \square , 10%; \star , 20 %.

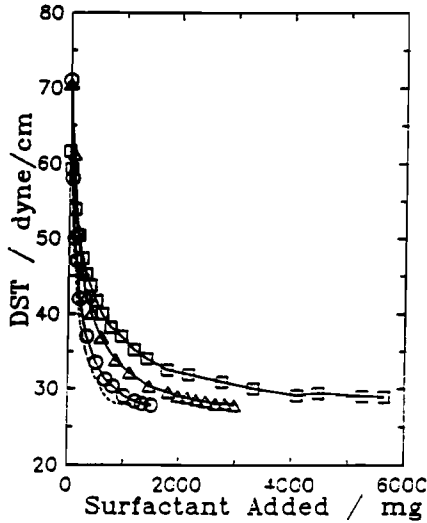


Fig.3. Dynamic surface tension vs. surfactant dose for SMA 3000H/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O , 1%; Δ , 3%; \square , 10%.

Fig.1 - seems to be responsible for stronger polymer/surfactant interactions in this system. Usually hydrophilic nonionic polymers show no evidence of interactions with polyoxyethylenated non -ionic surfactants. However, hydrophobic polymers can interact strongly with nonionic surfactants (Saito, 1987).

DSTs of the polymer solutions as a function of the amount of surfactant added for the SMA 1440H/Surfynol SE-F are presented in Fig. 4. As noted from Fig. 4 the interactions between Surfynol SE-F and SMA 1440H polymer are much stronger than those observed between SMA 1000H and Surfynol SE-F (Fig. 2), and similar to those observed for the SMA 3000H/Surfynol SE-F system. The strong interactions between Surfynol SE-F and SMA 1440H seem to be due to the presence of styrene segments and ester groups in the polymer molecule. As shown in Fig. 1 there is one butoxyethanol group per polymer segment, while the rest of the structure of SMA 1440H is exactly the same as that for SMA 1000H polymer. The presence of ethylene oxide in the structure of Surfynol SE-F and an ester group in the SMA 1440H polymer molecule are responsible for strong interactions between these species. In addition to polymer/surfactant interactions due to the presence of hydrophobic segments in the polymer structure, the presence of ether oxygen in the butoxyethanol chain of SMA 1440H may generate additional hydrogen bonding interactions with surfactant hydroxyl groups

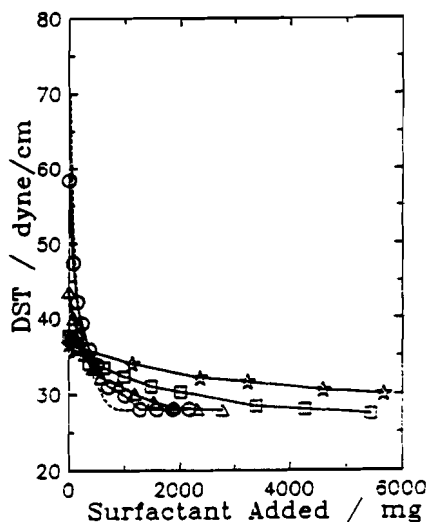


Fig.4. Dynamic surface tension vs. surfactant dose for SMA 1440H/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O , 1%; Δ, 3%; □ , 10%; ☆ , 15%.

According to Goddard (Goddard, 1994) the simple indicator of polymer affinity towards surfactants is surface activity of the polymer solution itself. As seen from Figs. 2 - 4 the SMA 1440H polymer solution showed the highest dynamic surface activity (the lowest surface tension) but the extent of its interactions with Surfynol SE-F surfactant was similar to that observed for SMA 3000H resin - Figs 3 and 4. The low surface tension of SMA 1440H polymer solutions seems to be mainly due to the presence of free butoxyethanol in the commercial sample and possible ester hydrolysis in an aqueous environment.

Though complexes formed between polymer and surfactant can adsorb at the water/air interface their performance under dynamic conditions can be much worse than that for Surfynol surfactants. This may result from the fact that the complexes are much bigger than the acetylenic diol molecules. Therefore, they diffuse much slower to the water/air interface than molecules of Surfynol surfactants. At sufficiently high concentrations, however, they can compete successfully with surfactant molecules and adsorb at the interface. Such a phenomenon has been observed previously with other polymer/surfactant systems (Chari and Hossain, 1991).

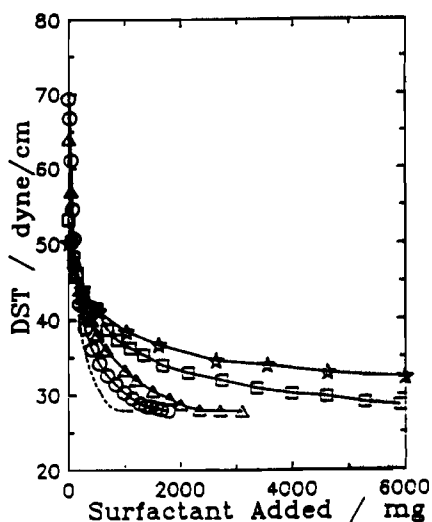


Fig.5. Dynamic surface tension vs. surfactant dose for Joncryl 63/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O , 1%; Δ, 3%; □ , 10%; ☆ , 20 %.

The titration curves for Joncryl 63 (solution) and Joncryl 89 (dispersion) styrenated acrylic polymers are presented in Figs 5 and 6, respectively. The

curves have a similar shapes to those for maleic anhydride co-polymers. The strongest interactions between surfactant and polymer were again observed for higher polymer concentrations and higher doses of surfactant. For a given polymer concentration more surfactant was consumed by Joncryl 63 than by Joncryl 89, which is because of a different number of polymer segments being exposed to interactions with surfactant. Joncryl 63 is water-soluble thus, all segments can interact with surfactant molecules. On the other hand, for Joncryl 89 (dispersion of solid particles) only polymer segments that extend into the solution phase can interact with surfactant molecules. The interactions observed between styrenated acrylics and Surfynol SE-F seem to be due to the presence of styrene segments in the polymer structure. In separate experiments no interactions were found between sodium acrylate and sodium polyacrylates and Surfynol SE-F surfactant (concentrations $\leq 20\%$ and molecular weight from 1, 200 to 30, 000).

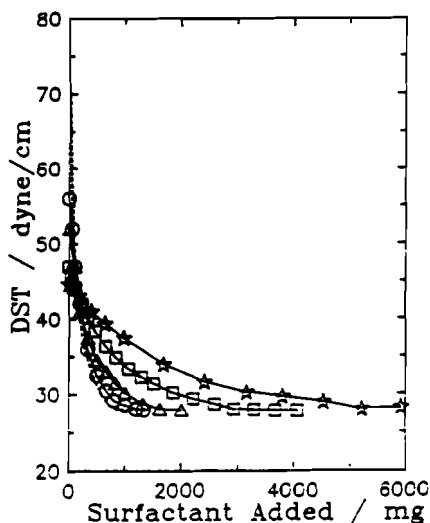


Fig.6. Dynamic surface tension vs. surfactant dose for Joncryl 89/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O, 1%; Δ , 3%; \square , 10%; \star , 20%.

If there were no interactions between surfactant and polymer molecules the titration curves for different polymer concentrations should almost coincide with the reference curve i.e. titration in pure water. As seen from Fig. 2 for increasing polymer concentration titration curves deviate more and more from

the reference curve. This deviation is a measure of polymer/surfactant interactions. The higher the difference the stronger the interactions. In other words, more surfactant has to be added to the polymer solution compared to pure water to reach the same value of DST.

Viscosity

Viscosity of the polymer solution depends on the conformation of its hydrocarbon chains and possible interactions with other solution ingredients. Flexible uncharged polymer molecules will adopt a random-coil configuration in solution. Charged polymers (polyelectrolytes), however, will tend to be linear because of strong electrostatic repulsion between the charged groups on the hydrocarbon chain. This will promote an increase in viscosity. Uncharged polymers may acquire charge by interactions with charged species, for instance ionic surfactants, and thus increase in viscosity. Indeed, such behavior was observed for the polyethylene oxide/sodium dodecyl sulphate system (Jones, 1967). The rheological behavior of such systems can be very complex depending on the extent of polymer/surfactant interactions and may be affected by polymer concentration, presence of other electrolytes, pH, surfactant concentration and type of binding. In some cases cross-linking can be also

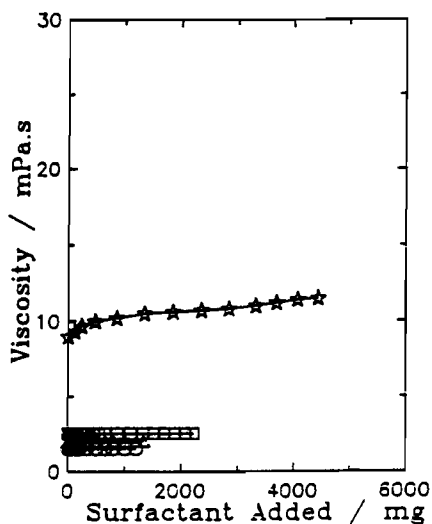


Fig. 7. Viscosity of polymer solution vs. surfactant dose for SMA 1000H/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O, 1%; Δ, 3%; □, 10%; ☆, 20%.

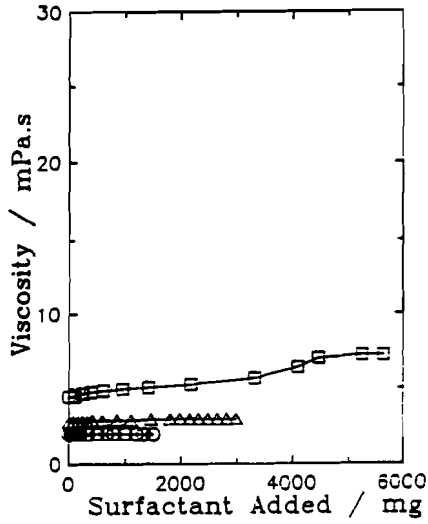


Fig. 8. Viscosity of polymer solution vs. surfactant dose for SMA 3000H/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O, 1%, Δ , 3%; \square , 10%.

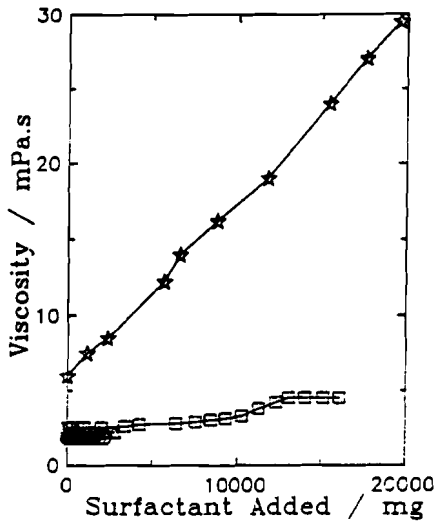


Fig. 9. Viscosity of polymer solution vs. surfactant dose for SMA 1440H/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O, 1%, Δ , 3%; \square , 10%; \star , 15%.

observed leading to gelling. A viscosity increase, due to polymer/surfactant interactions, may be a desirable or unwanted phenomenon and if desired may find many practical applications (Goddard, 1993c).

The viscosity of polymer solutions as a function of Surfynol SE-F surfactant dose, for different polymer concentrations, is presented in Figs 7 - 9 for SMA 1000H, SMA 3000H and SMA 1440H polymers, respectively. For SMA 1000H polymer the surfactant had no effect on solution viscosity at low polymer concentrations ($\leq 10\%$); a slight increase (~ 2 mPas) in viscosity for 20 % SMA 1000H solution was observed for higher doses of Surfynol SE-F surfactant. For SMA 3000H polymer an increase in the viscosity of polymer solution, upon addition of surfactant was noticed only for 10 % (w/w) polymer solution concentration.

Similar viscosities vs. surfactant dose plots were obtained for SMA 1440H. However, for 15 % solution a dramatic increase in polymer solution viscosity was observed - Fig. 9. The results presented in Figs 7-9 are in agreement with the DST measurements presented in Figs. 2-4. The stronger the interactions between surfactant and polymer the more surfactant is needed to reach a given value of DST and the higher the viscosity of the polymer solution. Increases in viscosity are related to the polymer chain conformation in the solution as well as formation of networked structures due to bridging (cross-linking).

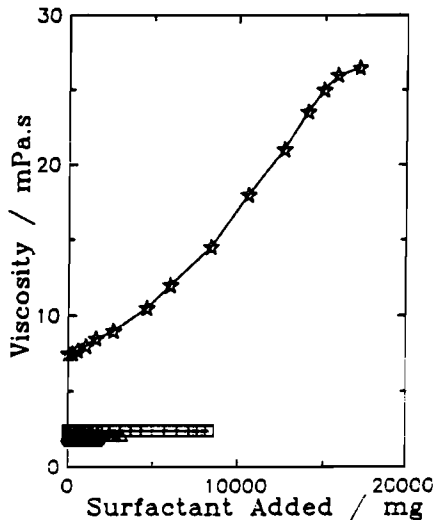


Fig.10. Viscosity of polymer solution vs. surfactant dose for Joncryl 63/Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O, 1%; Δ, 3%; □, 10%; ☆, 20 %

The plots of viscosity vs. surfactant dose for styrenated acrylic co-polymers are presented in Figs 10 and 11 for Joncryl 63 and Joncryl 89, respectively. No effect of the surfactant dose on the viscosity of Joncryl 89 dispersion was

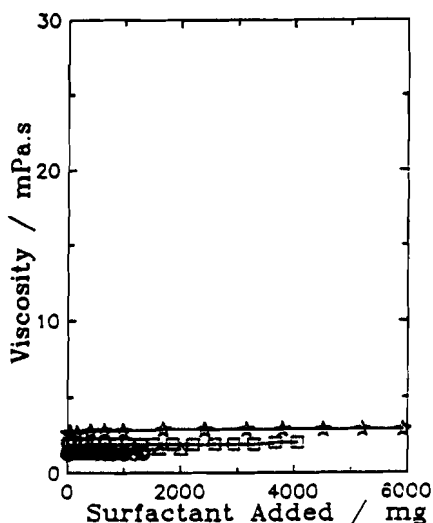


Fig. 11. Viscosity of polymer solution vs. surfactant dose for Joncryl 89 /Surfynol SE-F system. Polymer concentrations: dashed line, 0%; O , 1%, Δ , 3%; \square , 10%; \star , 20 %.

observed over the entire concentration range studied - Fig.11. The same behavior was observed for Joncryl 63 for lower polymer concentrations (up to 10 %). For a 20 % polymer solution a significant increase in solution viscosity was observed, with increasing amounts of surfactant added to the system - Fig.10. The difference between the data presented in Figs. 10 and 11 can be again explained by the lower amount of polymer segments available for polymer/surfactant interactions for Joncryl 89 (polymer dispersion) compared to Joncryl 63 (polymer solution).

CONCLUSIONS

Polymer (styrenated maleic anhydride and acrylic co-polymers)/Surfynol SE-F surfactant (acetylenic diol type) interactions were studied using dynamic surface tension and viscosity measurements. It was shown that polymer/surfactant interactions are an important issue for ink manufacturers. Knowledge of the interactions between a particular polymer and surfactant allows for a better understanding of the system and optimization of its properties. Correct selection of polymer and surfactant during ink formulation can help to minimize the

amount of surfactant (sometimes very expensive) required for good ink performance and improved product quality. Such studies can also help to change the existing situation where a large number of commercial products, containing polymer and surfactant mixtures, are formulated on an empirical trial-and-error basis only. The findings in the present paper may be summarized as follows:

1. Nonionic acetylenic diol surfactants interact with anionic polymers forming less surface active species than the surfactant.
2. The extent of interactions increased with increasing hydrophobicity of the polymer.
3. Hydrophobic as well as hydrogen bond interactions seem to be involved in the polymer/surfactant interactions.
4. For higher polymer concentrations (SMA 3000H, SMA 1440H and Joncryl (63) and higher doses of Surfynol SE-F surfactant an increase in solution viscosity was observed due to polymer/surfactant complex structures formed in the bulk of the solution.
5. The mechanism of polymer/surfactant interactions seems to be very complex. Knowledge of these interactions is very important for ink makers.

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