A Modified Method to Detect Surface Rheological Behavior of Mixed Partially Hydrolyzed Polyacrylamide (HPAM)/Surfactant Systems

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ABSTRACT: The visualization of monolayers at the air/water interface by Brewster Angle Microscope (BAM) was used to watch the movement of the domains of surfactant or surface-active complexes without any adscititious probe materials, and to examine the changes in surface rheology of partially hydrolyzed polyacrylamide (HPAM)/surfactant systems. Clear indications of rheological properties at the air/water interface are obtained over substantial concentration regions of the HPAM/Sodium Dodecyl Benzene Sulfonate (SDBS) and HPAM/Triton X-100/SDBS systems, respectively. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 704–706, 2000

Key words: visualization; surface rheology; Brewster angle microscope; HPAM; surfactant

INTRODUCTION

An insight into the interactions between partially hydrolyzed polyacrylamide (HPAM) and various surfactants is fundamental to enhanced oil recovery. From our previous investigation, the physicochemical change occurring in bulk water upon addition of surfactant to HPAM solution was interpreted in terms of the formation of polymer/ surfactant complexes.^{1, 2}

Interface rheology is a sensitive indicator of interface structure development. Regismond et. al.³ reported a method to determine if interfacial association structures are present in mixed polycation/anionic surfactant systems based on a simple talc particle test of the surface rheology of a solution developed by Winnik and Goddard. Talc

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is an inert material, and the talc test is a good enough method for surface viscoelasticity. But there is trouble with the talc test—talc particles will sink when the concentration is higher than the cmc of the surfactants, and the surface flow properties are difficult to watch. Fortunately, a visualization of monolayers at the air/water interface by a Brewster Angle Microscope (BAM) has been developed in several laboratories.⁴⁻⁶ The reflectivity at the Brewster angle is strongly dependent on the interfacial properties. In other words, using the BAM we can watch the domains of surfactant or surface-active complexes of a polymer/surfactant and check the changes of the interface in the absence of any adscititious probe materials. This method can be applied to the study of various polymer/surfactant systems.

In this article, the two-dimensional flow properties are reported for mixed HPAM/surfactants solution of varying concentrations without talc, but watching for the domain movement of complexes directly under a home-made BAM.

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Figure 1 BAM images of domains of HPAM/SDBS complexes.

MATERIALS

Triton X-100 (TX-100) is a commercial product of Union Carbide Co., USA. Sodium Dodecyl Benzene Sulfonate(SDBS) is a chemical reagent grade (Beijing Donghuan Chemical Engineering Factory, Beijing), and was purified by recrystallizing with a 5 : 1 mixture of methanol and ethanol three times and then drying. Its purity was established by the complete absence of a minimum in the surface tension-concentration curve. Partially hydrolyzed polyacrylamide (the degree of hydrolysis is 26–28%) was a commercial product of Pfizer Co., USA. Its molecular weight is stated to be $(15–17) \times 10^6$ Da. The polymer was exhaustively dialyzed against distilled water before use. All water used was doubly distilled.

EXPERIMENTAL METHODS

Stock solutions of HPAM were prepared by dissolving the polymer in water and allowing it to equilibrate for 24 h. Mixed HPAM/surfactant solutions were allowed to stand in Petri dishes 10 cm in diameter for at least 30 min. Without sprinkling the talc powder, a gentle current of air was directed tangentially at the solutions for a second or two and then removed. A Brewster Angle Microscope (BAM) system, composed of a *p*-polarized He-Ne laser, a CCD camera, video recorders and a monitor, were used to observe the movement of the domains of complexes along the surface.

Figure 1 shows the BAM images of domains of the HPAM/SDBS complexes. The following qualitative characterizations of the interface were made (where F denotes fluid; V, viscous; VE, viscoelastic). While in category VE, both a net movement of the domain is observed, together with some recovery upon removing the air current. In category V, a net (slow) movement of the domain is observed, with no recovery upon removing the air current. On category F, the BAM images of domains formed from surfactant molecules, HPAM/surfactant aggregate,¹ and some defectiveness of film, for example, tiny bubbles, can be observed.

RESULTS AND DISCUSSION

The phase maps representing mixtures of HPAM/ SDBS and HPAM/TX-100/SDBS are shown in Figures 2 and 3, respectively. Surface rheology was indicated clearly even above the cmc of the surfactants.

Referring to Figure 2, the surface viscoelasticity occurs on the left-hand side of the phase diagram, i.e., in the regions of relatively low SDBS concentration, which is similar to the results of mixed polymer JR400/SDS system in Regismond's work.³

Figure 3 represents the surface-phase map as the function of TX-100 and SDBS concentrations



Figure 2 Surface-phase map of the HPAM/SDBS system (VE denotes vicsoelastic; V, viscous; F, fluid).



Figure 3 Surface-phase map of the HPAM/TX-100/ SDBX system.

at a fixed HPAM concentration of 0.1 g/L. One notices that the system exhibits flow properties of the HPAM/SDBS solution alone at low a TX-100 concentration. That is, the surface is viscoelastic, viscous, then fluid, with increasing SDBS concentration. Another observation is that the addition of traces of TX-100 transforms the surface region to one exhibiting VE behavior.

The concentrations of polymer and surfactants used in enhanced oil recovery correspond to the VE region of Figure 3. In this area, we may envisage that the formation of polymer/surfactants "complexes" on the surface is responsible for the marked synergism in surface tension lowering¹ and for registering surface viscoelasticity. From the surface-rheology map of the mixture, we can probe the feasible mechanism of adsorption and aggregation process at the air/water interface.

CONCLUSIONS

While to some extent it lacks the rigor of other complicated techniques, our data suggest that this method has the credentials to develop into a powerful, yet simple measurement to detect polymer/surfactant interactions on the surface. It can be applied to study a wide range of polymer/surfactant systems.

REFERENCES

- Zhang, J. Y.; Zhang, L. P.; Tang, J. A.; Jiang, J. Colloids Surfaces A Physicochem Eng Aspects 1994, 88, 33.
- Zhang, J. Y.; Wang, X. P.; Liu, H. Y.; Tang, J. A.; Jiang, L. Colloids Surfaces A Physicochem Eng Aspects 1998, 132, 9.
- Regismond, S. T. A.; Winnik, F. M.; Goddard, E. D. Colloids Surfaces A Physicochem Eng Aspects 1996, 119, 221.
- Henon, S.; Meunier, J. Thin Solid Films 1992, 210/ 211, 121.
- 5. Honig, D.; Mobius, D. J Phys Chem 1991, 95, 4590.
- Li, B.-F.; Song, Y.-C.; LI, J.-R.; Tang, J.-A.; Jiang, L. Colloid Surfaces B Biointerface 1995 3, 317.