

Effects of Water-Soluble Polymers and Aqueous-Phase Viscosity on the Interfacial Tension Behavior of Reacting Oil-Alkaline Systems

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SYNOPSIS

This study presents the results of an experimental study of the effects of water-soluble polymer additives on the dynamic interfacial tension behavior of reacting oil-aqueous systems as measured by the spinning drop tensiometer. Polymer additives can exert both a direct physico-chemical effect and an indirect viscosity effect on the measured interfacial tension. This work, which complements an earlier study dealing with the effects of oil-soluble polymer additives, reveals that the nominal effects of aqueous-phase viscosity are opposite to those of oil-phase viscosity. In particular, an increase in aqueous-phase viscosity produces an increase in the rate of increase of the apparent interfacial tension after attainment of the minimum value. These differences are explained in terms of the dependence of diffusion rates and interfacial adsorption on aqueous-phase viscosity. The conclusion of principal practical interest is that although aqueous-phase viscosity exerts only a small effect on the dynamic interfacial tension at small times (i.e., prior to attainment of the minimum value) it exerts a very significant effect thereafter. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Alkaline flooding is one of the most promising methods for enhancing the recovery of heavy oil from partially depleted underground reservoirs. One of the most important features of alkaline flooding is the lowering of the oil-water interfacial tension (IFT) as a result of interfacial chemical reaction between the acids, which are naturally present in the crude oil, and the injected alkaline solution. This chemical reaction gives rise to the formation of surface-active substances that tend to adsorb at the oil-water interface and thereby reduce the IFT.

In modern applications of alkaline flooding, additional chemical components are often added to the injected alkaline solution with a view to maximizing the oil recovery.¹ The most important of these additives are water-soluble polymers (e.g., polyacrylamide), whose principal purpose is to increase the viscosity of the injected solution and thus reduce its

mobility in the reservoir rock (this increased viscosity tends to attenuate the troublesome phenomenon known as viscous fingering, in which regions of oil are bypassed by the injected solution and are consequently not recovered). It is therefore of practical importance to elucidate (i) how such polymer additives interact with the other components of the system (in particular with the surfactant being generated at the oil-water interface), and (ii) how these interactions affect the interfacial tension as measured by the laboratory instrument most commonly employed for this purpose, that is, the spinning drop tensiometer (SDT). These are the principal objectives of the present work.

It is well known that the SDT is a very useful instrument for measuring low and ultralow IFTs between immiscible or partially miscible fluids. Such low IFTs are frequently encountered in the case of oil recovery from partially depleted underground petroleum reservoirs by means of aqueous fluid injection.²⁻⁴ The SDT instrument is particularly well suited to monitoring the dynamic (transient) changes in IFT that occur when a chemical reaction is taking place at the interface, as, for example, dur-

ing the recovery of heavy oil (containing acidic components) using aqueous alkaline solutions.^{5,6} Such changes cannot be monitored on a continuous basis when using conventional equipment such as the du Nouy ring tensiometer. As the reaction progresses, surfactants are generated at the interface where they adsorb, causing a reduction in IFT. As a result of this decrease in IFT, a droplet spinning in the SDT tends to elongate and its diameter decreases accordingly. At later times the IFT begins to increase (as the reactants are used up and as the generated surfactants diffuse away from the interface), and the droplet consequently begins to contract with a corresponding increase in diameter. The traditional equation for computing the IFT from the SDT readings is⁷

$$\text{IFT} = \Omega^2 D^3 \Delta\rho / 32 \quad (1)$$

where Ω = rotational speed, D = diameter of oil droplet, and $\Delta\rho$ = density difference between the two phases. This widely quoted result represents the simplified form of a more general equation and is valid provided that the droplet length exceeds $4D$.

It should be noted that Eq. (1) is based on the assumption of an axially stationary (i.e., nonreacting, nonelongating) droplet in chemical equilibrium with the exterior aqueous phase. As discussed previously,⁸ there is an inevitable uncertainty concerning the validity of Eq. (1) when applied to a reacting system in which the length, diameter, and shape of the droplet will be changing continuously in response to the corresponding changes in IFT. In particular, as the droplet changes in shape, transient velocity profiles will become established within the two fluids and these will necessarily have a direct effect on the mass transfer rates of the various reactant and product species to and away from the interface, and hence on the computed IFT.

It was asserted previously⁸ that Eq. (1) will provide a meaningful indication of the instantaneous IFT provided that the droplet can respond rapidly to changes in IFT, i.e., whenever the viscosities of the two phases are very low. However, when the viscosities of the oil and/or water phases are high, the rates of elongation/contraction of the droplet in response to the changes in IFT will obviously be affected, so the IFT computed from Eq. (1) should at best be regarded only as being some apparent or effective value, the value of which will depend on such variables as the oil and water viscosities, the rotational speed, and the volumetric water-oil ratio. This can constitute a very real problem in cases involving either (i) heavy crude oils or (ii) aqueous

polymer solutions, both of which have considerable relevance in practical oil recovery processes.

In the previous work⁸ the results of a study of the effects of *oil*-phase viscosity on the apparent IFT were reported, in which the viscosity was adjusted by adding small quantities of interfacially inert polystyrene polymer to the oil phase. It was observed that the oil-phase viscosity did not significantly affect the initial rate of decrease of IFT (droplet elongation), nor the magnitude of the minimum IFT attained (maximum droplet length/minimum droplet diameter), but that it did significantly affect the rate of rise of IFT (droplet contraction) after attainment of the minimum IFT. More specifically, as the oil-phase viscosity was increased, the rate of contraction of the droplet, and hence the rate of rise of apparent IFT, decreased appreciably.

The purpose of the present study is to report the findings of a complementary study of the effects of water-soluble polymer additives and *aqueous*-phase viscosity on the apparent IFT. The viscosity was adjusted by adding small quantities of polyvinyl alcohol (PVA) or polyacrylamide (PAM) to the aqueous phase. The most interesting observation is that the nominal effects of aqueous-phase viscosity are diametrically opposite to those of oil-phase viscosity, i.e., as the aqueous-phase viscosity is increased, the rate of increase of IFT after attainment of the minimum IFT actually *increases*. This possibility was not originally foreseen, as it was intuitively felt that an increased viscosity, whether it be in the oil phase or in the aqueous phase (or in both), would automatically tend to prevent the oil droplet from responding instantaneously to transient changes in the IFT. However, it is now evident that certain physico-chemical phenomena can play very significant roles and that they can even overshadow the direct (rheological) effects of aqueous-phase viscosity.

EXPERIMENTAL RESULTS

Use of Polymer Additives to Alter Aqueous-Phase Viscosity

As reported previously,⁸ whenever a chemical additive is introduced with the intention of increasing the fluid viscosity, there is always the possibility that the additive, in addition to exerting an indirect influence (via the viscosity) on the *apparent* IFT as measured by the SDT, could exert some direct physico-chemical effect on the *actual* microscopic IFT. In order to determine the magnitude of this effect we measured the IFT of *nonreacting* oil-aqueous

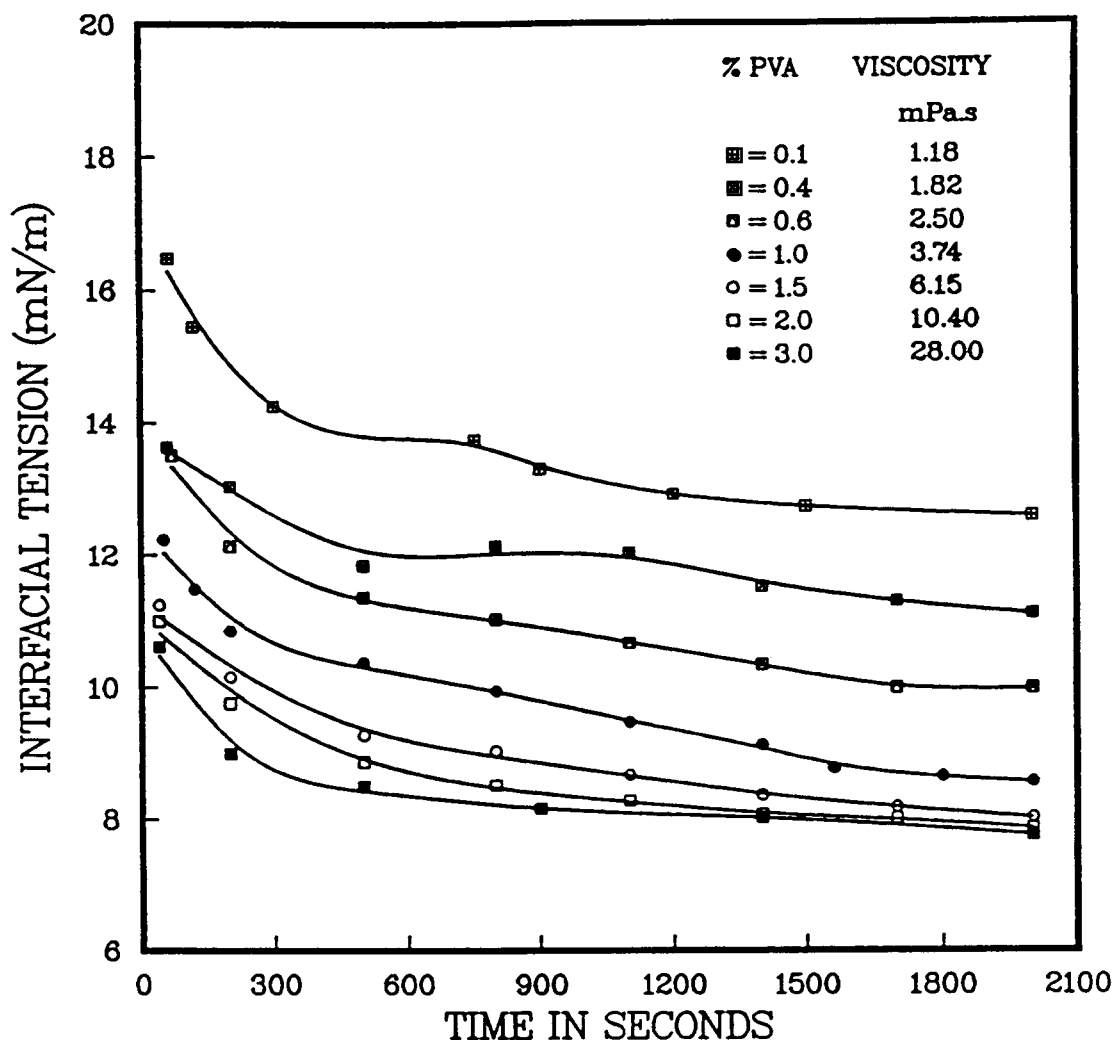


Figure 1 Effects of PVA additive on the transient IFT behavior of a 10 mM linoleic acid in paraffin oil mixture against distilled water at 25°C.

polymer solutions at various polymer concentrations using the SDT. The oil phase selected was a representative synthetic acidic oil that has been successfully used in other studies to simulate real acidic crude oils,^{9,10} namely 10 mM linoleic acid in paraffin oil. This mixture possessed a density of 839.0 kg/m³ and a viscosity of 19.77 mPa·s at 25°C. The water-soluble, oil-insoluble polymer additives employed in this work were PVA of molecular weight 115,000 and degree of hydrolysis of 87% supplied by the BDH company and a nonionic PAM of molecular weight 5,000,000 supplied by Scientific Polymer Products. As can be seen in Figures 1 and 2, the IFT decreases slightly with respect to time (approaching an essentially constant equilibrium value at large times) and decreases moderately with respect to polymer concentration for both PVA and PAM. These effects can be explained in terms of the chem-

ical nature of the polymers and their relative abilities to adsorb at the oil-water interface to form a compressed film whose spreading pressure is responsible for lowering the IFT in accordance with Gibbs law. Since it was not possible to locate an interfacially inert water-soluble polymer, it is clear that the interfacial activity of the PVA and PAM must be taken into explicit account when subsequently evaluating the transient IFT behavior of reacting oil-aqueous polymer systems.

Viscosity Effects in Reacting Systems

Figures 3 and 4 display, respectively, the effects of PVA and PAM (dissolved in the aqueous phase) on the transient IFT behavior of 10 mM linoleic acid in paraffin oil against aqueous 25 mM (0.1 wt %) NaOH solutions at 25°C as measured by the SDT.

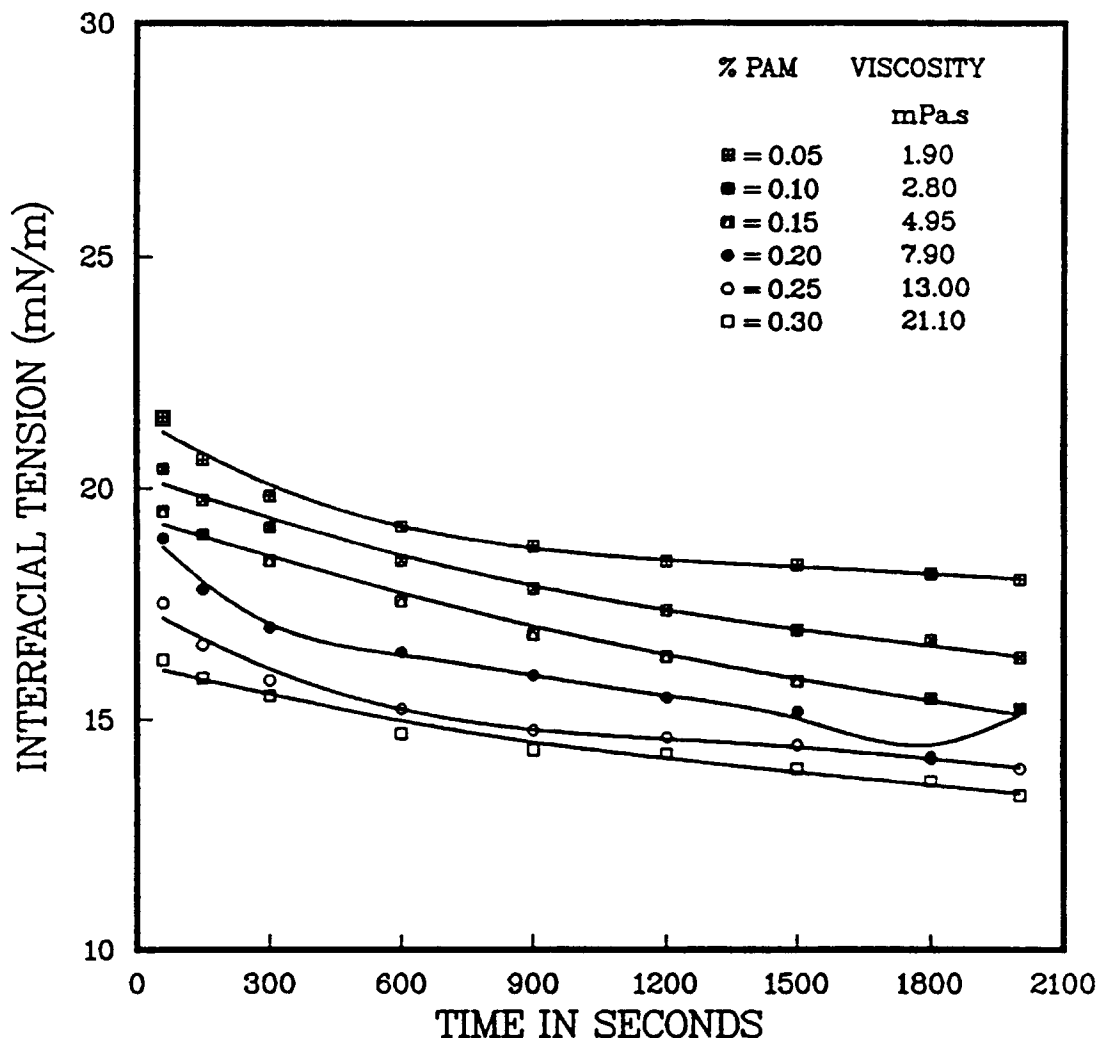


Figure 2 Effects of PAM additive on the transient IFT behavior of a 10 mM linoleic acid in paraffin oil mixture against distilled water at 25°C.

Very similar trends are observed for other NaOH concentrations within the working range 2.5–250 mM. All IFT measurements were conducted at 25°C and a rotational speed of 7500 rpm, and all data points represent the average values of two replicate runs. The errors in the IFT measurements for identical systems were generally less than 5%, which compares favorably with the findings of previous workers. The viscosities of all PVA and PAM solutions employed in this work were measured using a Brookfield Synchro-lectric viscometer and were found to exhibit slight to moderate degrees of pseudoplasticity (the viscosity data reported in Figs. 1–4 correspond to the specific viscometer operating speed of 12 rpm).

The general transient IFT behavior exhibited in Figures 3 and 4 is typical of most acidic oil-alkaline systems.^{6,11} Thus, at short times after initial contact

the apparent IFT drops sharply on account of the sudden initial generation of surfactant(s) by reaction at the droplet surface. Shortly thereafter, a minimum IFT is attained, followed by a steady increase in IFT as the acid in the oil phase and the alkali in the aqueous phase are gradually depleted by reaction. The overall process is extremely complicated, and the relative rates of IFT decrease and increase depend to a great extent on the initial acid and alkali concentrations, as well as on the relative rates of diffusion (which are viscosity dependent) of the reactants and products to and away from the droplet surface. As noted by Rubin and Radke,¹² the lower the IFT minimum, the later it generally appears. It should be noted that meaningful data cannot generally be recorded for contact times less than about 50 s since a finite time is necessarily required to introduce the oil droplet into the SDT. It is evi-

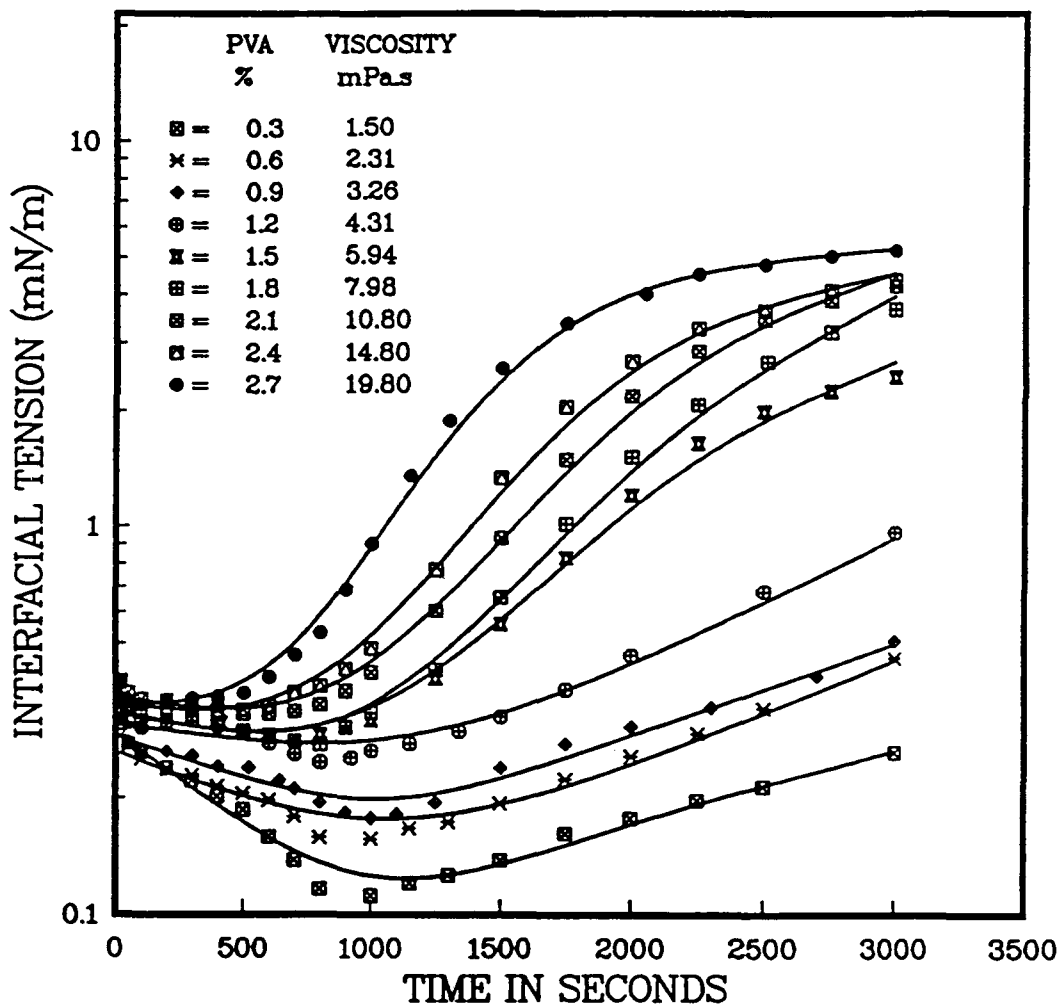


Figure 3 Effects of PVA additive on the transient IFT behavior of a 10 mM linoleic acid in paraffin oil mixture against aqueous 25 mM NaOH solutions at 25°C.

dent from Figures 3 and 4 that the aqueous-phase viscosity has relatively little effect on the apparent IFT before attainment of the minimum IFT, but that it exerts a very significant effect thereon after attainment of the minimum IFT. These latter effects are quite pronounced even at low PVA-PAM concentrations, where a small increase in concentration, although producing only a small increase in viscosity, produces a relatively large increase in the apparent IFT.

For comparison purposes, Figure 5 has been included to show the transient IFT behavior for one representative case in which the oil-phase viscosity is altered by addition of polystyrene. The data in Figure 5 correspond to a similar oil phase (i.e., 10 mM linoleic acid in *toluene*) and the same NaOH concentration (i.e., 25 mM) as in Figures 3 and 4. Toluene was employed instead of paraffin oil in this case since polystyrene is insoluble in the latter. It

should be noted that the polystyrene is interfacially inert and that the oil-polystyrene mixtures remain essentially Newtonian. Although the general appearance of Figure 5 is superficially the same as Figures 3 and 4, closer inspection reveals that the apparent IFT *decreases* with increasing oil-phase viscosity, whereas it *increases* with increasing aqueous-phase viscosity. The effects of oil-phase viscosity on the apparent IFT have been discussed in more detail elsewhere,⁸ and Figure 5 has been included here solely to afford a convenient qualitative comparison with the results of the present aqueous-phase viscosity study.

DISCUSSION

Whereas the presence of polystyrene in the oil phase has no appreciable physico-chemical effect on the

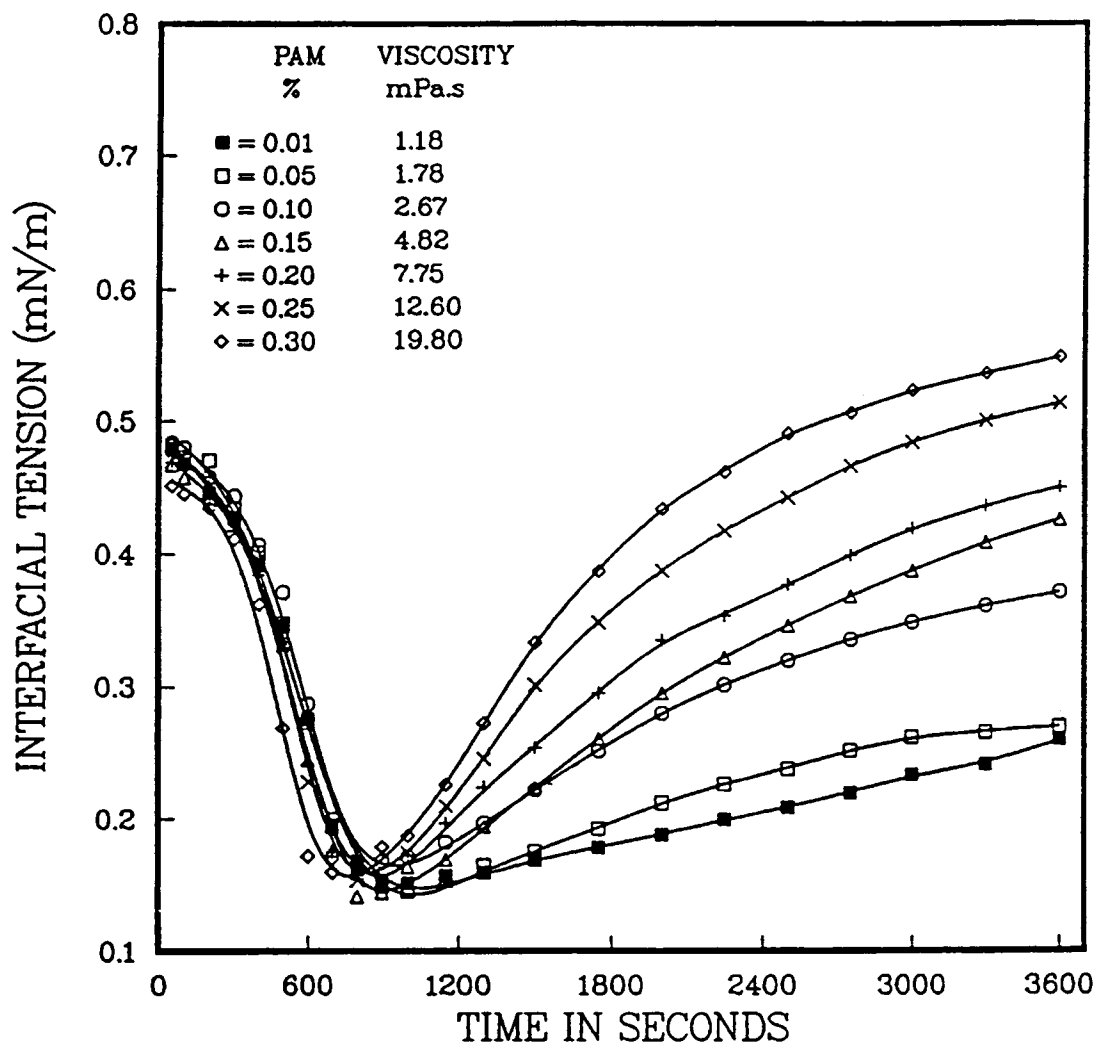


Figure 4 Effects of PAM additive on the transient IFT behavior of a 10 mM linoleic acid in paraffin oil mixture against aqueous 25 mM NaOH solutions at 25°C.

actual microscopic IFT, the same cannot be said regarding the presence of PVA and PAM in the aqueous phase, as is clearly evident from Figures 1 and 2. However, it is important to note from Figures 1 and 2 that the presence of PVA or PAM in non-reacting systems tends to *decrease* the actual IFT, whereas Figures 3 and 4 indicate that the presence of PVA or PAM in reacting systems tends to *increase* the apparent IFT as measured by the SDT. In other words, the effects of polymer concentration on the apparent IFT in Figures 3 and 4 must be real effects and not artifacts of the physico-chemical effects of PVA and PAM on the actual microscopic IFT. One may therefore conclude that the aqueous-phase viscosity does exert (directly and/or indirectly) a significant effect on the apparent IFT as measured by the SDT, especially at larger times after attainment of the minimum value. However, it is less straight-

forward to explain exactly why the apparent IFT increases with increasing aqueous-phase viscosity. The explanation with regard to oil-phase viscosity has already been presented in the introduction of this study and in the earlier article,⁸ and it relates primarily to the retarding effect that a high oil-phase viscosity has on the rates of elongation/contraction of the oil droplet in response to transient changes in the actual IFT. In addition, an increased oil-phase viscosity would also tend to reduce the rate of diffusion of the chemically generated surfactant molecules from the interface into the oil phase, which would tend to further slow down the rate of increase of apparent IFT after attainment of the minimum value (Fig. 5).

Although it might be felt that a similar explanation to that presented in the previous paragraph could be adduced to explain the effects of aqueous-

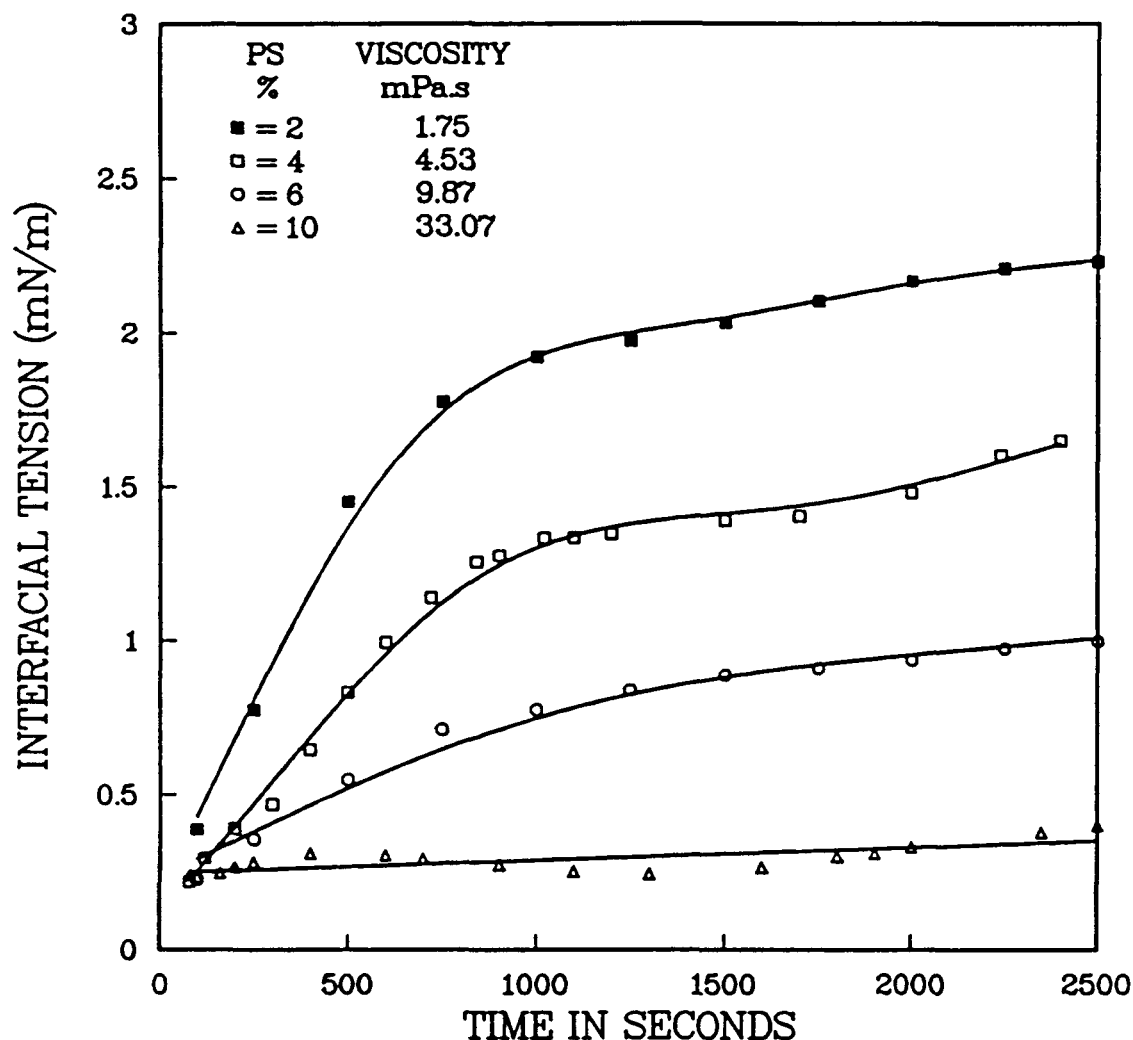


Figure 5 Effects of polystyrene (PS) additive on the transient IFT behavior of a 10 *mM* linoleic acid in toluene mixture against aqueous 25 *mM* NaOH solutions at 25°C.

phase viscosity, a modified or different explanation must be sought since an increase in aqueous-phase viscosity actually tends to promote the rate of contraction (i.e., the rate of increase of apparent IFT) of the droplet in the SDT after attainment of the minimum IFT. The most plausible explanation is that although the same basic rheological mechanisms discussed above are still present, they are overshadowed by various physico-chemical effects. The situation is, of course, complicated by the fact that in the present study involving aqueous-phase viscosity there will always be a mixture of interfacially active species present at the interface, namely the moderately active PVA (or PAM) polymer additive and the highly active surfactant generated by the chemical reaction, and the polymer molecules will necessarily be in competition with the generated surfactant molecules for the changing number of

adsorption sites at the expanding/contracting interface (Note that in the earlier study involving oil-phase viscosity the polystyrene polymer additive was interfacially inert and therefore it did not compete with the surfactant for adsorption sites).

When the interface is initially created (at time zero) it is reasonable to assume that the occupied adsorption sites at the interface will be filled exclusively with the polymer molecules. As the chemical reaction proceeds, the generated surfactant molecules will preferentially adsorb at the interface and progressively displace the adsorbed polymer molecules. After some time a minimum IFT is reached that in absolute terms tends to increase slightly with increasing polymer concentration (Fig. 3). This behavior is to be expected since the degree of polymer adsorption at the interface increases as the aqueous-phase polymer concentration increases, thereby

making it more difficult for the highly active surfactant molecules to replace the less active polymer molecules at the interface. Beyond the minimum IFT, the polymer molecules continue to compete with the generated surfactant molecules for the steadily decreasing number of adsorption sites as the droplet in the SDT contracts. A constant IFT situation, corresponding to an axially stationary (i.e., noncontracting, nonelongating) droplet, is eventually reached in which an equilibrium exists between the adsorbed surfactant and polymer molecules at the interface.

The formation of new surfactant at the interface is diffusion controlled, and therefore decreases with increasing aqueous phase viscosity (i.e., with increasing polymer concentration). At the same time, the degree of surfactant adsorption at the interface decreases with increasing polymer concentration as the supply of polymer to the interface becomes more plentiful. Furthermore, since surfactants are known to be capable of binding with polymers in aqueous media, the presence of polymer in the aqueous phase will tend to reduce the chemical potential of the surfactant in that phase, thereby increasing the driving force responsible for diffusion of the generated surfactant from the interface into the aqueous phase. In other words there are three distinct but interrelated phenomena that come into play, namely (i) a lower rate of diffusion-controlled surfactant generation at higher aqueous-phase viscosities, (ii) a lower degree of surfactant adsorption at the interface at higher polymer concentrations (i.e., at higher aqueous-phase viscosities), and (iii) a higher rate of diffusion of surfactant away from the interface at higher polymer concentrations (i.e., at higher aqueous-phase viscosities). Each of these three factors tends to *increase* the rate of increase of apparent IFT after attainment of the minimum value and, when acting in unison, they completely mask the direct rheological effects of viscosity that were dominant in the previous oil-phase viscosity study (see Fig. 5).

In conclusion, although the nominal effects of aqueous-phase viscosity on the dynamic IFT as measured by the SDT are opposite to those of oil-phase viscosity, the results of the present study do confirm the general validity of the conclusions of the earlier study,⁸ namely (i) that the SDT is ca-

pable of providing a meaningful measurement of the dynamic IFT behavior of reacting oil-alkaline systems at small times (i.e., prior to attainment of the minimum IFT) and (ii) that IFT results obtained at larger times must be interpreted with caution and with due consideration being given to the relative interfacial activities of, and interaction effects between, the various polymer and surfactant species present. These conclusions should be of general interest to all users of the spinning drop tensiometer, and of particular interest to those involved in the design of viscosity-enhanced polymer-alkaline systems for practical oil recovery operations.

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