# Dilational Rheological Properties of Interfacial Films Containing Branch-Preformed Particle Gel and Crude Oil Fractions

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**ABSTRACT:** Dilational rheology method was used to study the interfacial rheology properties of Branch-Preformed Particle Gel (PPG) and its interaction with Shengli crude oil fractions at the kerosene/water interface. The results showed that the interfacial dilational modulus increased monotonously with increasing PPG concentration, the high values of the modulus could be due to the formation of multilayer near the interface. Study on the interaction between PPG and crude oil components showed that different crude oil components have different interactions with PPG molecules at the oil/water interface. The acidic components can adsorb onto the interface and form mixed adsorption film by replacing the PPG molecules at the interface because of their smaller molecular size and stronger interfacial activity, which results in a dramatic reduction in dilational modulus, while asphaltenes have little effect on the dilational rheological behavior of PPG solution due to their lager molecular sizes. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41337.

## INTRODUCTION

Nowadays, polymer flooding has been widely applied in enhanced oil recovery (EOR). The application of polymer flooding is essentially based on the remarkable ability of aqueous polymer solution to enlarge the swept region of aqueous solution. The major types of EOR polymers include partially hydrolyzed polyacrylamide (HPAM) and its modified products.[1] It is known that the –CONH2 groups in HPAM are easily hydrolyzed and degraded at high temperature and the viscosity of polymer solution decrease greatly at high salinity. Therefore, more and more hydrophobically modified HPAM products have been developed and studied in order to improve its performance in EOR because the associative formation can minimize the exposure of polymer to solvent and stabilize the network by hydrophobic interactions.[2–4] Here, we introduce the study of a novel derivative of HPAM, Branch-Preformed Particle Gel(PPG). PPG is synthesized by copolymerization of acrylamide and cross-linker, which is branched and partially cross-linked HPAM with a netlike structure. PPG is water soluble and will swell when dissolved in water. What's more, it is more thermally stable and aging resistant because of the introduction of cross-linked network structure. It needs higher temperature

than HPAM to destroy the structure and the increase of salinity may enhance the network structure through the increase of hydrophobic interactions. When compound with other polymers, PPG is an appropriate agent to overcome the deficiency of conventional HPAM and can make positive contribution to displacement efficiency.[5] Although it has already been putted into use, little work has been carried out to study the physicochemical properties of PPG.

Asphaltenes and acidic components are two typical surface active fractions in crude oil. The former is the heaviest and most polar faction of crude oil, and has fused aromatic ring structures surrounded by hydrocarbon tails and can form strong film at the interface, hence the adsorption of asphaltenes trends to increase the stability of crude oil emulsions.[6–9] While the later are organic acids, they can lower the interfacial tension and have great influence on the other properties responsible for better oil recovery.[10–12] Study on the interaction between PPG and this two components will help us better evaluate PPG's performance in EOR.

The dilational rheology method has been used for several decades to study the interfacial properties of different systems. Compared with conventional interfacial tension measurements,

dilational rheology method is more sensitive to the conformation of the surface active molecules, and provides important information on the adsorbed layers. To get a better knowledge of the mechanism responsible for the stability and demulsification of crude oil emulsions, numerous works have been done to investigate the dilational rheology properties of the flooding displacement systems using the dilational rheology method.[13–15]

In this article, we present studies of the interfacial dilational properties of PPG, and mixed systems containing PPG and Shengli crude oil fractions using pendant drop method. The aim of this study is to evaluate PPG's performance in polymer flooding, and how does it interact with crude oil in practical application.

## THEORY

When the area of the interface is sinusoidally fluctuated at a fixed frequency and amplitude, interfacial tension also gives a sinusoilally response. The interfacial dilational modulus is determined by the changes in the interfacial tension ($\Delta\gamma$), and the interfacial area ($\Delta A$):

$$E = \Delta\gamma / (\Delta A / A) \qquad (1)$$

The interfacial dilational modulus can be considered as a measurement of the strength of the interfacial film formed at the interface. The higher value of the dilational modulus is, the stronger the interactions among the adsorbed particles at the interface, hence the higher the film strength. $E$ can be expressed as a complex quantity; it is composed of real and imaginary parts:

$$E = E_r + iE_i \qquad (2)$$

The real part and imaginary part are called the elastic modulus and viscous modulus, respectively. Elastic modulus represents dilational elasticity, where viscous modulus represents dilational viscosity. The elastic and the viscous modulus can be obtained from eqs. (3) and (4)

$$E_r = E \cos(\theta) \qquad (3)$$
$$E_i = E \sin(\theta) \qquad (4)$$

Here $\theta$ is the phase difference between the changes in interfacial tension and area. If the interfacial structure is purely elastic, the elastic modulus equals the complex modulus, the viscous modulus is zero, and the phase angle is zero. On the contrary, if the interfacial structure is purely viscous, the viscous modulus equals the complex modulus, the elastic modulus is zero and the phase angle is 90°. In most cases, interfacial structure is neither purely elastic nor purely viscous, and the phase angle is between 0° and 90°.

## EXPERIMENTAL

### Materials
PPG with a diameter of 10 micrometer was supplied by Geological Scientific Research Institute of Shengli oilfield, People's Republic of China. The typical structure of PPG is presented in Figure 1. The detail of structure can be found in our early work.[16] All aqueous solutions were prepared with redistilled water.

Kerosene was purchased from Beijing Xinhuancheng lubricating oil limited company, purified by column chromatography, the
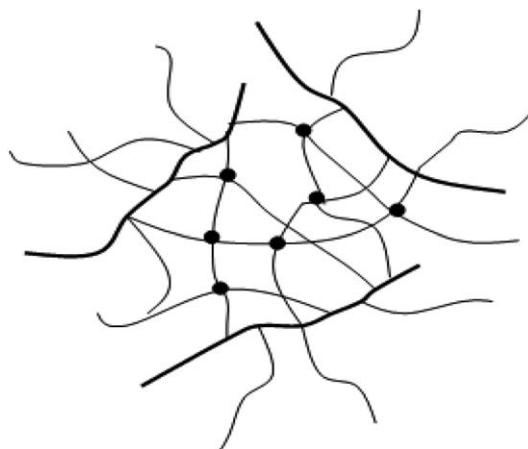


**Figure 1.** The structure of the Branch-Preformed Particle Gel (PPG).

interfacial tension of the water/kerosene interface measured by pendent drop method at 30°C was 43.5 mN/m. Shengli crude oil was obtained from Shengli Oil Field. Acidic components and asphaltenes were separated from Shengli crude oil by the method reported before.[17] After the separation, crude oil components and crude oil were dissolved in kerosene respectively, and used as oil phase.

### Interfacial Dilational Rheology
Interfacial dilational rheology was measured using the pendant drop method with oscillating drop technique (TRACKER, IT Concept Company, France). A sample of aqueous solution was added into a glass cuvette, and a drop of oil phase was formed on the end of a U-type needle immersed in the solution, and the interfacial tension of the oil/water interface was measured by analyzing the shape of the oil drop monitored by a camera. The dilational viscoelasticity data were obtained by recording the response of the interfacial tension to the periodic interface area deformation of $\Delta A/A = 10\%$ with frequency of 0.1 Hz. All the measurements were conducted at $30.0 \pm 0.1$°C using a thermostat.

## RESULTS AND DISCUSSION

### Interfacial Dilational Properties of PPG Aqueous Solutions
**Dynamic Interfacial Dilational Properties of PPG Aqueous Solutions.** The dynamic interfacial properties of PPG solutions have been plotted in Figure 2. Figure 2(A) shows the dynamic interfacial tensions for aqueous PPG solutions at different bulk concentrations. We can see form Figure 2(A) that interfacial tension decreased as the PPG concentration increased, and was reduced to a minimum value of about 24 mN/m. Particle adsorption was accelerated at higher PPG concentration, which leaded to fasterinterfacial tension reduction. Figure 2(B) shows the evolution of dilational modulus with the age of interface. It can be noticed that at low PPG concentration, interfacial layer formed with low a dilational modulus, thendilational modulus increased gradually and reached a plateau. In the mid-concentration range, dilational modulus was almost constant since the formation of the interface. Interestingly, as the PPG concentration increased further, dilational modulus reached a
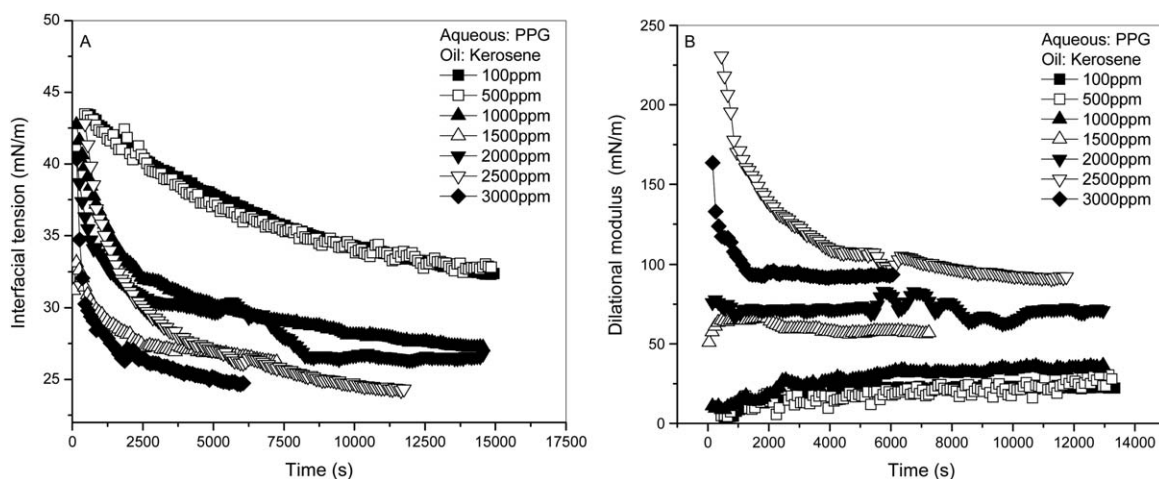
**Figure 2.** Effect of PPG concentration on the dynamic interfacial tension (A) and dilational modulus (B) of PPG aqueous solutions.

high value instantaneously in a short time, then steadily decreased over time and reached a plateau value.

To explore the characteristic of PPG adsorption film, the dependence of the dilational modulus on the interfacial pressure at different PPG concentration has been plotted in Figure 3. At low bulk concentration (<1000 ppm), dilational modulus increased slightly with increasing interfacial pressure, while for the systems in the mid-concentration range (1500 ppm and 2000 ppm), dilational modulus almost showed no change over the whole interfacial pressure region. However, when concentration was higher than 2500 ppm, dilational modulus reached a maximum value when the interfacial pressure was low, and then decreased with increasing interfacial pressure. The above experimental results indicate that the increase of interfacial PPG concentration has no effect on dilational modulus during mid-concentration range and even destroys the strength of interfacial film at higher bulk concentration.These interesting experimental results will be discussed in detail below.

**Concentration Dependence of Interfacial Dilational Properties of PPG Aqueous Solutions.** Before we try to explain the interesting and extraordinary modulus vs. interfacial pressure curves, we present the concentration dependence of dilational modulus and phase angle (Figure 4), first. Interfacial dilational modulus usually passes through a maximum value and finally decreases,[18–21] due to the enhanced diffusion-exchange process and the increasing interfacial concentration simultaneously.[18,21] However, in our study, we found that the interfacial dilational modulus monotonously increased with increasing PPG concentration. Over the concentration range 100–1000 ppm, dilational modulus increased moderately with increasing PPG concentration. Further increase of PPG concentration leaded to a sharp increase of the modulus, and the value kept in high plateau over 2500 ppm.

Results of the phase angle [Figure 4(B)] showed some specificity too. Phase angle values were very small below 1000 ppm, indicating an elastic character of the adsorbed films. The value increased dramatically and reached the maximum at 1500 ppm,

then decreased as the concentration increased to 2000 ppm. The higher value is the phase angle, the more viscousis the interfacial film, dilational viscosity stems from the relaxation processes in and near the interface,[13] so the sharp increase of phase angle indicates that new relaxation process appeared at higher concentration range. When bulk concentrations are higher than 2500 ppm, the phase angle was generally on a downward trend, which indicate the relaxation processed might be hindered at high concentration.

**Frequency Dependence of Interfacial Dilational Properties of PPG Aqueous Solutions.** After the adsorption equilibrium was reached, oscillation with frequency between 0.005 and 0.1 Hz was conducted to investigate the dependences of dilational viscoelasticity on the oscillation frequency. As shown in Figure 5, increasing the oscillation frequency shifted the dilational modulus to a higher value, and phase angle values showed a decreasing trend with increasing oscillation frequency in general. This phenomenon can be explained as follows: At lower oscillation
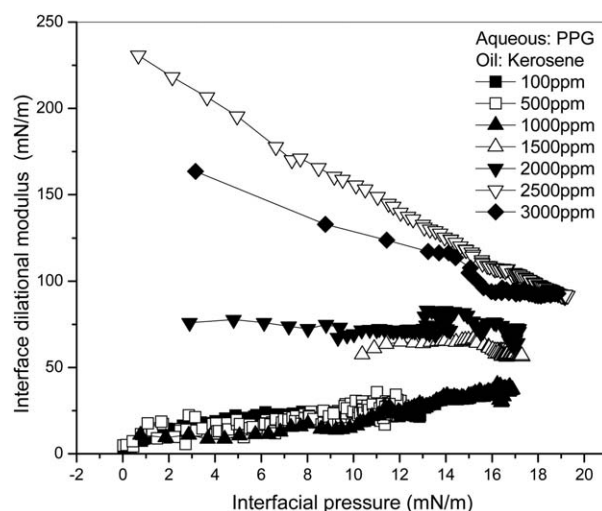


**Figure 3.** Interfacial dilational modulus versus interfacial pressure for PPG aqueous solutions of different concentrations.
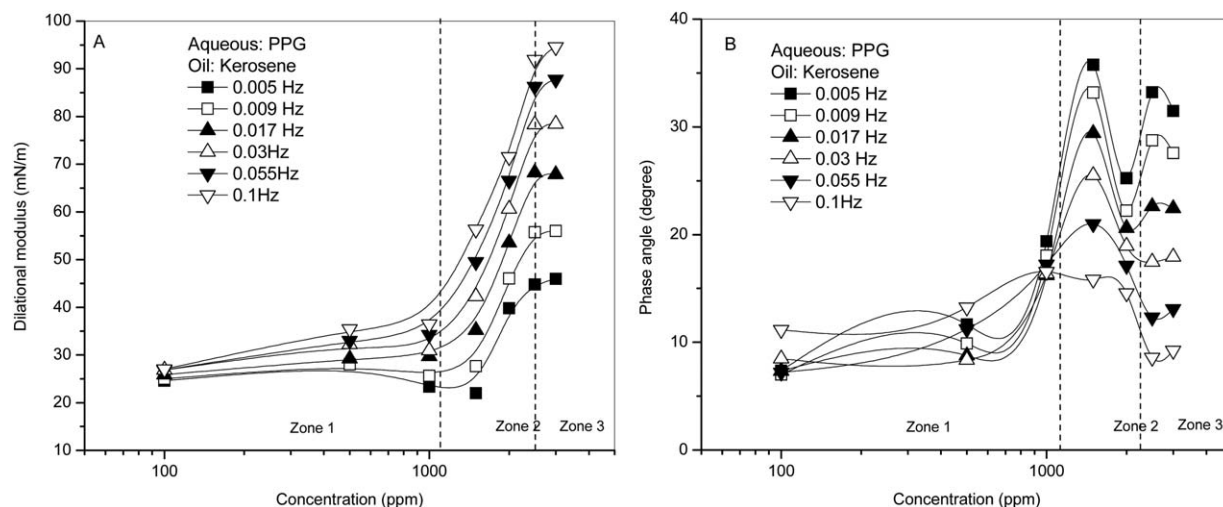
**Figure 4.** Influence of concentration on the interfacial dilational modulus (A) and phase angle (B) of PPG aqueous solution.

frequency, particles have more time to diminish the interfacial tension gradient resulting from the interfacial deformation via relaxation processes. As the oscillation frequency increases, time is too short for the restoration, therefore leads to the increase of the dilational modulus and elastic part.

If we draw a curve represent $\log E$ as a function of $\log\omega$, the $\log E$–$\log\omega$ curves are linear in the concentration range we investigate.[22,23] The slops of the $\log E$–$\log\omega$ curve of PPG solutions with different concentration are listed in Table I. Slops of the $\log E$–$\log\omega$ curve reflect the dependence of dilational modulus upon frequency. The higher the value is, the higher degree of dependence, which means the more viscous the film appears.[24] From the slops of $\log E$–$\log\omega$ curves we can find some regularity: The slop of the $\log E$–$\log\omega$ curve rose along with the bulk concentration until it reached the peak (1500 ppm), at which point it dipped somewhat. So we can conclude that at a certain concentration range, the viscous character of the adsorption film increased with the bulk concentration, when the bulk concentration was higher than 1500 ppm, the

elastic character of the adsorption film increased slightly. The concentration dependence is similar to that of phase angle.

**Mechanisms Responsible for the formation of PPG Film at the Interface.** To sum up, according to the interesting experimental results of dynamic interfacialdilational data and concentration dependence of steady dilational properties we discussed above, we suggest a mechanism scheme for the formation of PPG film at the interface (Figure 6).

We speculate that when PPG concentration was below 1000 ppm, particles in the bulk were not high enough to saturate the interface. At the beginning of the formation of interface, there were little PPG particles adsorbed at the interface, so a loose monolayer was formed at the interface. As more particles adsorbed onto the interface, the film was strengthened and the value of dilational modulus reached a plateau after the adsorption equilibrium was reached [shown in Figure 6(A)]. At the same time, interfacial tension continuously decreased to a steady value. During this stage, the increase of bulk
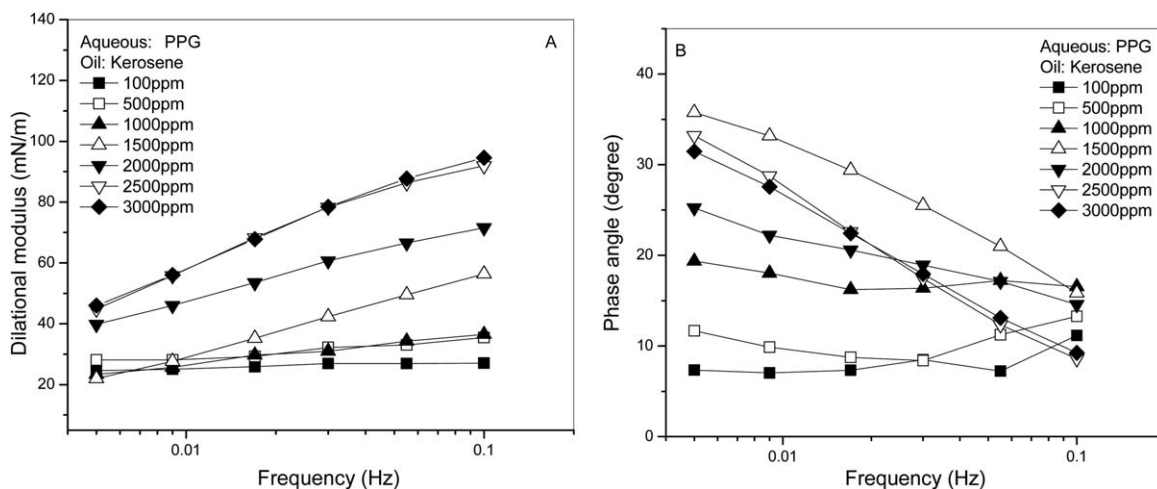


**Figure 5.** Frequency dependences of interfacial dilational modulus (A) and phase angle (B) of PPG aqueous solutions.

**Table I.** The Slops of log $E \sim$ log $\omega$ Curves for PPG Solutions with Different Concentrations

| $C_{PPG}$ (ppm) | Slop |
|---|---|
| 100 | 0.04 |
| 500 | 0.08 |
| 1000 | 0.15 |
| 1500 | 0.32 |
| 2000 | 0.20 |
| 2500 | 0.24 |
| 3000 | 0.24 |

concentration will enlarge interfacial PPG concentration and result in slowly increasing modulus value. Moreover, formation of the loose adsorption film was determined mainly by diffusion exchange process, therefore the film show almost elastic nature due to the slow diffusion speed of macromolecule.

When the bulk concentration increased to 1500 ppm, the high interfacial dilational modulus of PPG solutions can be attributed to the formation of amore complicated structure at the sub-layer near the interface. Similar structure has been reported for hydrophobically modified polyacrylamide.[25] Note that PPG molecule has a three-dimensional structure with cross-links and alkyl residues, so it is reasonable to assume that the alkyl resi-

dues of PPG particles will interact with each other and form a high strength film at the sub-phase. When interface was formed, PPG concentration on the interface was still low, but they piled up at the sub-layer and formed a condensed structure. During this stage, the rheological properties of adsorption film were mainly controlled by the sub-layer, while the interfacial tension was determined by interfacial PPG concentration. As time went by, exchange took place between both the interface and sub-layer, and the sub-layer and the bulk. That is to say, PPG molecule at the bulk phase replenished the sub-layer via diffusion process, so the sub-layer structure did not change much as the film continued to grow at the interface [Figure 6(B)]. Therefore, dilational modulus kept constant with aging time while interfacial tension was lowered. Moreover, the sub-layer became more compact with increasing bulk concentration and dilational modulus increased sharply. On the other hand, the appearing of new process such as exchange among the interface, sub-layer, and bulk will enhance the viscous part of film and improve the value of phase angle sharply. However, the sub-layer becomes more compact with further increasing concentration and results in the increase of elastic part and the weakness of exchange processes, which can explain the maximum of phase angle in Zone 2 (see Figure 4).

At the third concentration range, PPG concentration near the interface was high enough to adopt acondensed multilayer sub-layer structure at the beginning of the interfacial adsorption,
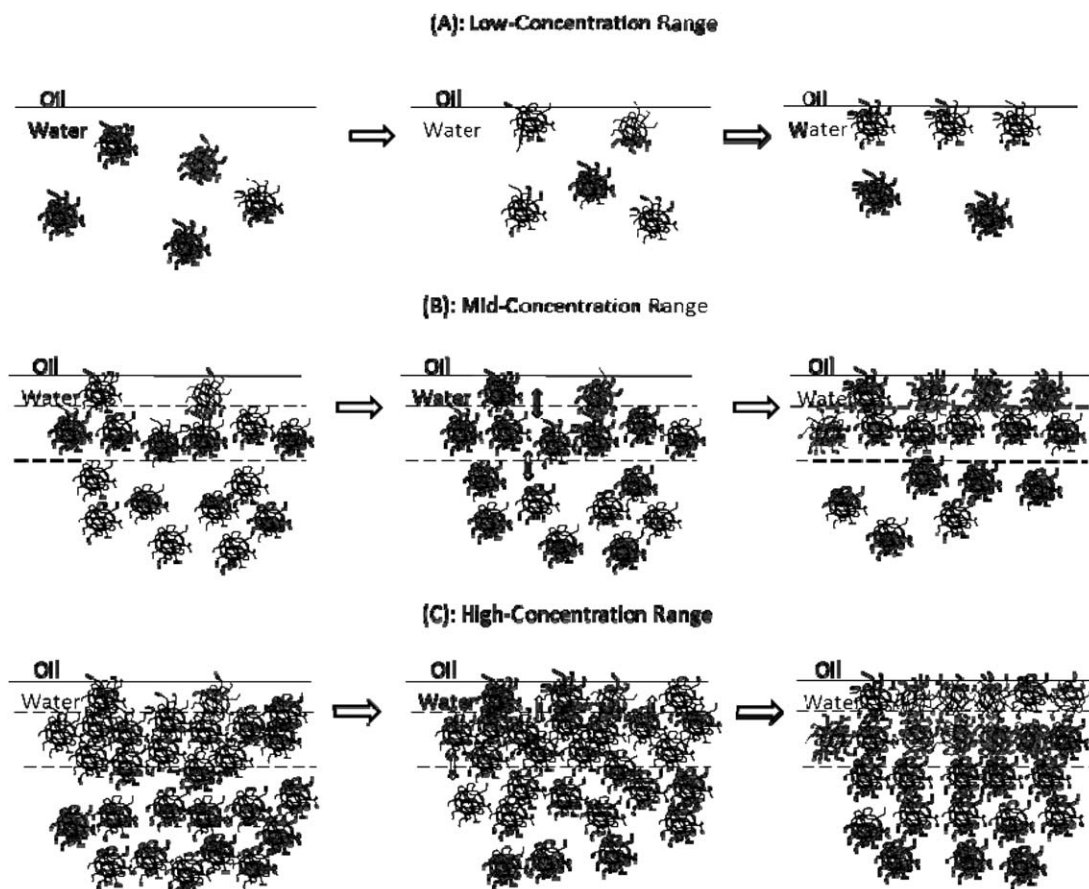


**Figure 6.** Schematic of dynamic adsorption behaviors for PPG at the water/oil interface at different bulk concentration ranges.
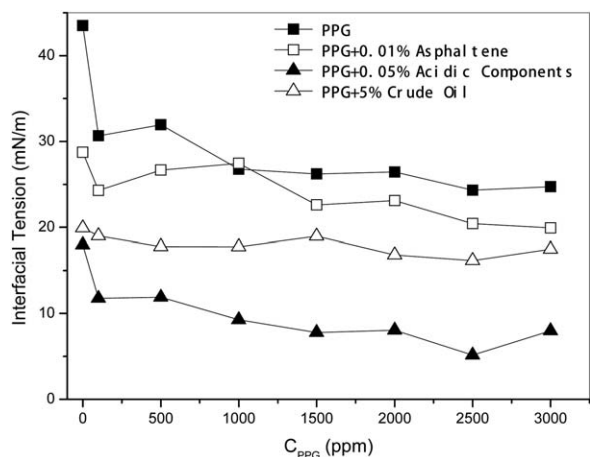
**Figure 7.** Effect of petroleum surface-active components on interfacial tensions between kerosene and PPG solutions.

which leads to a higher modulus value at short time. As time went by, PPG molecules adsorbed to the interface from the sub-layer and lowered the interfacial tension. At the same time, the multilayer structure of sub-layer converted to a more organized-structure, which helped to release the high pressure of the sub phase, thus the interfacial dilational modulus reduced with the course of time. Further more, at this concentration range, the diffusion of the particles was hindered by the more compact structure near the interface; therefore dilational modulus didn't decrease with increasing concentration as usual. It is also very interesting to point out that the arrangement of condensed multilayer sub-layer structure is very slow, so the interfacial film shows more elastic at higher frequency and phase angle decreases with increasing bulk concentration. However, with the decrease of frequency, arrangement process works and phase angle increases with increasing bulk concentration.

By the mechanism we suggest above, the paradoxical and interesting experimental results of dynamic interfacial tension, dynamic dilaitonal modulus, concentration dependences of modulus and phase angle, and frequency dependences of dilational properties can be explained well.

**Interaction Between PPG and Surface-Active Components of Crude Oil at the Water/Oil Interface**

The adsorption of asphaltenes and acidic components can dramatically change the properties of interfacial film between oil phase and the aqueous bulk. In this paper, we studied the interaction between PPG and asphaltenes/acidic components at the oil/water interface by dilational rheological measurements. For the sake of comparison, the influence of diluted crude oil has also been studied.

In this section, oil phases were prepared by dissolving asphaltenes, acidic components, and crude oil in kerosene with the concentration of 0.01%, 0.05%, 5% (w.t.), respectively. Comparing the influence on the interfacial behavior when acidic components, asphaltenes, and crude oil were added, significant differenceswere observed between these mixture systems. Influences on the interfacial tension by different crude oil components are illustrated in Figure 7. It can be seen that addition of

acidic components reduced the interfacial tension to <10 mN/m, and crude oil to ∼20 mN/m, while asphaltenes only reduced the interfacial tension by 3∼4 mN/m.

When 0.01% asphaltenes were added to the system, the dilational modulus variations were relatively small, which may result from the lower interfacial activity and larger molecular size. On the other hand, the influence of acidic components was much more noticeable. As shown in Figure 8, the dilatoinal modulus was dramatically loweredwhen 0.05% acidic components were added, especially above 1000 ppm PPG concentration. One plausible explanation is that acidic components have a much smaller molecule size, so they are able to diffuse and adsorb onto the interface more promptly, displacing PPG molecules and forming mixed adsorption film, which reduces the interfacial dilational modulus. The concentration dependence of dilational modulus for PPG/crude oil mixture systems is similar to that of asphaltenes system, but the values of moduli are slightly smaller, which shows the effect of asphaltenes and petroleum acids both.

## CONCLUSIONS

On the basis of interfacial dilational rheological data of PPG systems we discussed above, it can be concluded that PPG represents interesting interfacial behavior at the kerosene/water interface. The molecules first adsorbed onto the interface with an almost two-dimensional loose conformation. As the bulk concentration increases, PPG formed a compact adsorbed monolayer with a more condensed structure near the interface (sub-layer). The interfacial tension is determined by the amount of PPG molecules on interface, while the dilational properties are controlled by the characteristic of whole interfacial layer, especially by the sub-layer. A higher amount of PPG molecules reached the sub-layer of the interface and then transferred to the interface, and the interface became saturated, in the meanwhile, exchange took place between the sub-layer and the bulk phase, which resulted in a constant value of interfacial dilational modulus. Subsequent increase of the bulk concentration leaded to the transition from two-dimensional structure to a more
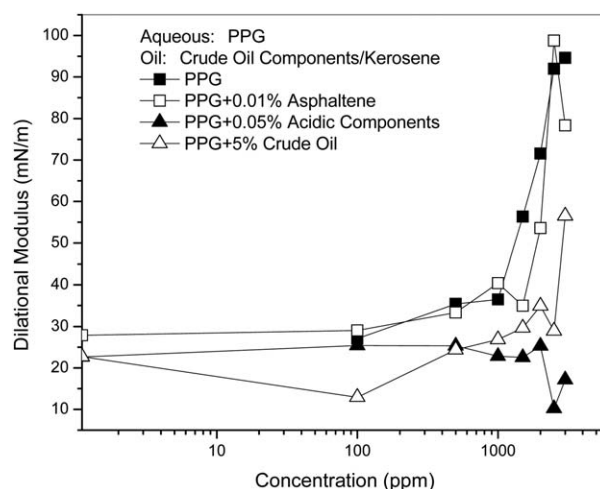


**Figure 8.** Effect of petroleum surface-active components on dilational modulus at kerosene/PPG interfaces (frequency 0.1 Hz).

disorganized and rigid multilayer structure near the interface, exchange between the sub-layer and the bulk phase are not fast enough to compensate the exchange between the interface and the sub-layer, so the interfacial tension and the dilational modulus values were both lowered in the course of time.

Study on the interaction of PPG and crude oil components showed that the dilatoinal modulus was lower than that of the individual PPG when acidic components or crude oil were added,while variations are relatively small for asphaltenes/PPG systems. The results demonstrated that different crude oil components have different interaction scenarios with PPG molecules at the kerosene/oil interface, which may be attributed to the different molecular structure and interfacial activity of the crude oil components. The acidic components can adsorb to the interface and replace the PPG molecules at the interface because of their smaller molecular structure and stronger interfacial activity, which result in a dramatic reduction of interfacial dilational modulus.

## ACKNOWLEDGMENTS

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