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Interfacial dilational properties of model oil and chemical flooding systems by relaxation measurements

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ABSTRACT

In the present work, the influences of a model organic acid (oleic acid) on the interfacial dilational properties of different types of surfactants (anionic surfactant sodium 4,5-diheptyl-2-propylbenzene sulfonate 377 and asymmetrical anionic Gemini surfactant $C_{12}COONa\text{-}p\text{-}C_9SO_3Na$) and polymers (HPAM and HMPAM) systems were studied at decane–water interface, respectively, by means of interfacial tension relaxation measurements. The decay curves of interfacial tension were fitted by the summation of a number of exponential functions. The dilational elasticity and dilational viscosity component were calculated by Fourier transform and displayed as Cole–Cole plots (plotting ε_i or $\varepsilon_i/\varepsilon_0$ as a function of ε_r or $\varepsilon_r/\varepsilon_0$, respectively). The experimental results show that the interfacial behaviors of both surfactants are part conformance with a diffusion-controlled process and part conformance with a reorientation controlled process. In the case of partly hydrolyzed polyacrylamide Mo-4000, the nature of mixed film is controlled mainly by interaction between polymer chains and surfactant molecules in the interface. As for hydrophobically modified polyacrylamide, the film properties are controlled by the formation of mixed surfactant-hydrophobic block associations in the interface and the reorientation process resulted from exchange of associations between different regions of interface. Under our experimental conditions, the mixed adsorption films formed by oleic acid and surfactant molecules are more compact than pure surfactant films.

1. Introduction

It is well known that crude oil plays an important role in providing the energy supply of the world among various sources of energy. At the end of water flooding, almost 65–70% of OOIP is left in the reservoirs, which is believed to be in the form of ganglia and trapped in the pore structure of the rock by capillary forces. In order to recovery additional oil by a chemical flooding process, the capillary number, which determines the microscopic displacement efficiency of oil, should be increased by 3–4 orders of magnitude through reducing the interfacial tension (IFT) of oil ganglia from its value of 20–30 mN/m to 10^{-3} mN/m [1]. It has long been recognized that the IFT between crude oil and chemical flooding solutions can be reduced to lower than 10^{-2} mN/m by using an appropriate surfactant system. Moreover, surfactant-polymer flooding can expand volumetric sweep, but also improve the wash oil efficiency, which is considered one of the most commercial prospects in Enhanced Oil Recovery (EOR). In this respect, the most widespread technique is based on partly hydrolyzed polyacrylamide (HPAM), which is a low price polymer with good viscous properties, and well-known physicochemical characteristics. More recently, polyacrylamides modified with relatively low amounts of hydrophobic comonomers (HMPAM) using as aqueous viscosity modifiers have become the subject of extensively research due to their interesting solution behavior [2,3].

Fluid–fluid interfaces containing surfactants and macromolecules often exhibit interfacial rheological behavior different from that in the bulk due to the molecular orientation, interaction and packing. The orientation of these molecules, molecular complexes or structural transformations at the fluid–fluid interface can result in peculiar rheological behavior. An analysis of the rheological properties, as opposed to the static properties, such as IFT, is essential in describing the behavior of fluid interfaces where interfacial motion is involved [4]. The interfacial dilational rheological properties are believed to be very important for controlling the stability of foams and emulsions, consequently dominate the formation of oil bank during flooding process and de-emulsification process [5–8]. Some rheological studies of water/crude oil or water/model oil interfaces have been made to clarify the mechanisms involved as related to EOR [9–21]. The rheological properties of these interfaces have been found to be strongly dependent on the nature of solvent used for dilution, the oil concentration, the asphal-

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tene and resin concentrations, the resin to asphaltene ratio, and so on. However, the researches mentioned above mainly employed oscillating method, which can only provide dilational data at frequency lower than 1 Hz.

Long chain acids are the primary surface-active components in crude oil and their contribution to lowering interfacial tension of enhanced oil recovery systems has been recognized in numerous investigations of both experimental and theoretical character [22]. However, practically little attention has been drawn to the effect of the long chain acid on the viscoelastic properties of adsorption layers of the flooding systems. In the present work, the influences of a model organic acid (oleic acid) on the interfacial dilational properties of different types of surfactants (anionic surfactant sodium 4,5-diheptyl-2-propylbenzene sulfonate 377 and asymmetrical anionic Gemini surfactant $C_{12}COONa\text{-p-}C_9SO_3Na$) and polymers (HPAM and HMPAM) systems were studied, respectively, by means of interfacial tension relaxation measurements.

2. Theory

The Gibbs interfacial dilational modulus is defined by the surface tension increase after a small increase in area of a surface element:

$$\varepsilon = \frac{d\gamma}{d\ \ln A} \qquad (1)$$

It gives a measure of the interfacial resistance to changes in area. Where ε is the dilational modulus, γ is the interfacial tension and A is the interfacial area. When the interfacial area is subjected to periodic compressions and expansions at a given frequency, relaxation processes such as diffusion exchange between the surface layer and the bulk solution or molecular rearrangements within the layer may cause a phase difference (measured by the phase angle θ) between the applied area variation and the surface tension response. In that case ε is a complex number and can be decoupled into real and imaginary components ε_d and $\varepsilon_\eta = \omega\eta_d$, respectively [23,24].

$$\varepsilon = \varepsilon_d + i\omega\eta_d \qquad (2)$$

where ε_d is the dilational elasticity or storage modulus and ε_η the dilational viscosity component or loss modulus that represents a combination of internal relaxation processes and relaxation due to transport of matter between the surface and the bulk.

Phase angle θ is calculated according to

$$\tan\ \theta = \frac{\varepsilon_\eta}{\varepsilon_d} \qquad (3)$$

In the absence of relaxation processes affecting the surface dilational modulus, the phase angle θ is equal to zero and the surface layer behaves as a purely elastic body.

Interfacial tension relaxation experiments are a reliable way to obtain surface dilational parameters, which uses small but fast axisymmetric trough or drop area expansion or compression to slightly disturb the monolayer equilibrium. This causes an interfacial tension jump and then the interfacial tension will decay to the equilibrium again.

For an instantaneous area change rising from $\Delta A(t) = 0$ for $t = 0$ to $\Delta A(t) = \Delta A$ for $t > 0$, the values of ε are obtained as a function of the frequency by Fourier transformation (FT) of the interfacial tension decay obtained from the experiment by the following relationship: [25–27]

$$\varepsilon(\omega) = \frac{FT\Delta\gamma(t)}{FT(\Delta A/A)(t)} = \frac{\int_0^\infty \Delta\gamma(t)\exp(-i\omega t)dt}{\int_0^\infty [\Delta A(t)/A]\exp(-i\omega t)dt} \qquad (4)$$

where ω is the angular frequency. In an ideal system that is not diffusion controlled and in which only one relaxation mechanism occurs the decay curve of γ versus t can be represented by an exponential equation.

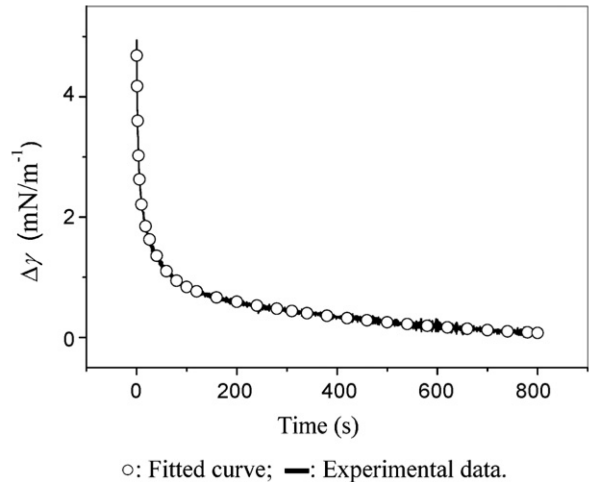

Fig. 1. Representative results for IFT decay curve and the fitted curve by exponential function. Oil phase: decane; water phase: 1×10^{-6} mol L^{-1} $C_{12}COONa\text{-p-}C_9SO_3Na$.

For a real system a number of relaxation processes may occur and the decay curve would be expressed by the summation of a number of exponential functions: [28,29]

$$\Delta\gamma = \sum_{i=1}^{n} \Delta\gamma_i\ \exp(-\tau_i t) = \sum_{i=1}^{n} \Delta\gamma_i\ \exp\left(\frac{-t}{T_i}\right) \qquad (5)$$

where τ_i and T_i are the characteristic frequency and period of the ith process, respectively; $\Delta\gamma_i$ is the fractional contribution which that relaxation process makes to restore the equilibrium; n is the total number of the relaxation processes.

For an instantaneous change in area

$$\int_0^\infty \frac{\Delta A}{A}\exp(-i\omega t)dt = \frac{\Delta A/A}{i\omega} \qquad (6)$$

With this, Eq. (4) becomes

$$\varepsilon = \frac{i\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)[\cos\ \ \omega t - i\ \sin\ \omega t]dt \qquad (7)$$

The real part of Eq. (7) is the dilational elasticity ε_d and the imaginary part is the interfacial dilational viscosity component $\omega\eta_d$: i.e.

$$\varepsilon_r(\omega) = \varepsilon_d(\omega) = \frac{\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)\sin(\omega t)dt \qquad (8)$$

$$\varepsilon_i(\omega) = \omega\eta_d(\omega) = \frac{\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)\cos(\omega t)dt \qquad (9)$$

Other parameters such as the tangent of phase angle, dilational modulus can all be obtained from these two parameters.

3. Experimental

3.1. Materials

The surfactant sodium 4,5-diheptyl-2-propylbenzene sulfonate (377) and the asymmetrical anionic Gemini surfactant $C_{12}COONa\text{-p-}C_9SO_3Na$ were synthesized by ourselves [30,31], as shown in Scheme 1. The purity of the compounds was checked by elemental analysis and ^1H NMR spectroscopy. The critical micelle concentration (CMC), which are taken as the concentration at the point of intersection of the two linear portions of the γ-log C plot, are 1.27×10^{-4} mol L^{-1} and 1.10×10^{-4} mol L^{-1} for 377 and $C_{12}COONa\text{-p-}C_9SO_3Na$, respectively. The polymer, partly