Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Colloids and Surfaces A: Physicochem. Eng. Aspects 289 (2006) 53–59
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Fibrous crystals: Relaxation processes and dilational properties at oil–water interface

Lixin Xia[a,b,*], Yiyang Wang[c], Lan Luo[c], Lu Zhang[c], Guoying Cao[b], Sui Zhao[c], Shiwei Lu[b], Quan Liu[a], Jiayong Yu[c]

[a] *Institute of Chemical Science and Engineering, Liaoning University, 66 Chongshan Middle Road, Huanggu District, Shenyang 110036, PR China*
[b] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China*
[c] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 3 Datun Road, Beijing 100101, PR China*

Received 6 August 2005; received in revised form 25 March 2006; accepted 4 April 2006

Abstract

The dilational viscoelastic properties of interfacial films containing fibrous crystals were investigated by means of two methods: the interfacial tension response to sinusoidal area variations and the relaxation of an applied stress. The results obtained show that fibrous crystals (length > 50 μm) could increase the dilational modulus of interfacial films on a jet kerosene/water interface. The dilational modulus increased with time due to the increase of sedimenting quantities and decreased with concentration after 15 h of pre-equilibrium time due to the enhancement of particle exchange between the bulk and the interface. The nature of films containing solid particles strongly depends on their shape. The ethyl metal phosphates, which are short and rigid, may pack tightly at the interface and form long-range ordered structure. As a result, interfacial films containing ethyl metal phosphates had higher dilational modulus and showed more elastic behaviour. The results obtained by interfacial tension relaxation measurements show that there exist two main relaxation processes in all films: the fast relaxation process with a characteristic relaxation time of several seconds, which may correspond to the exchange of alkyl metal phosphates between the bulk and the interface, and the slower relaxation process with a characteristic relaxation time of several tens of seconds, which may correspond to the interparticle interaction. However, only the films containing ethyl metal phosphates have the third relaxation process, which is the slowest process with a characteristic time of several hundreds of seconds. This slowest process may correspond to the reorganization of whole interfacial film. Our results may be used to account for the ability of solid particles in stabilizing emulsions.

Keywords: Dilational modulus; Phase angle; Interface; Relaxation process; Fibrous crystal

1. Introduction

According to Bancroft [1], the stability of an emulsion is largely due to the nature of the interfacial film. The stability of the film depends strongly on adsorption/desorption kinetics and solubility of the surface-active fractions, as well as on its interfacial rheological properties [2]. Bonfillon and Langevin [3] have proved that the stability of a sodium dodecanol sulfate foams was improved by adding a small amount of dodecanol due to an increase of the dilational elasticity. Interfacial dilational viscoelasticity seems to play a significant role in many domains such as foam and emulsion stability [4]. Its microscopic basis is the relaxation processes in the interface and near the interface. The study of dilational viscoelasticity properties can provide a basis of understanding the stability of emulsion and the mechanism of demulsification.

Finely divided insoluble particles play an important role in stabilizing emulsions [5]. The effectiveness of these particles depends on factors such as particle size, interparticle interactions, and the wettability of the particles. Solid-stabilized emulsions are commonly encountered during the production of crude oil and it is necessary that these emulsions be treated before any refining can take place. Clint and Taylor [6] have studied the physical characteristics of spreading monolayers of small hydrophobic particles (diameter < 0.5 μm) of overbased calcium detergents by using Langmuir film balances. Information on particle size, particle/particle interaction forces and contact angles of the particles on the water surface could be obtained in a rela-

---

[*] Corresponding author. Tel.: +86 24 86813935; fax: +86 24 62202380.
E-mail address: lixinxia@lnu.edu.cn (L. Xia).

0927-7757/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2006.04.006

tively straightforward manner using simple geometric considerations. Tambe and Sharma [7] have reported that solid particles could stabilize emulsions both by providing steric hindrance to drop–drop coalescence and by modifying the rheological properties of the interfacial region. Similar results have been reported by Neuhausler et al. [8] Later, Tambe and Sharma [9] used the pulse drop method to study the dilational viscoelastic properties of a decane/distilled water interface loaded with graphitic carbon or polystyrene particles (diameter = 0.5 or 1 μm).

Rheological properties are the main characteristics of the dynamic properties of a film. The measurements of dynamic dilational viscoelasticity can be used to study the single chemical and physical process in the system and provide more information of the dynamics of polymer chains and their interaction with surfactant molecules at interface [10]. The dilational viscoelasticity of both insoluble polymer monolayer and adsorbed polymer film at the water surface have been studied more and more in the past decade [11]. Recently the dynamic surface viscoelasticities of adsorbed non-ionic homopolymer films and polyelectrolyte films at the liquid–gas interface and the liquid–liquid interface were measured in broad frequency and concentration ranges [11–13].

2. Experimental

2.1. Materials

Oil phase: Silica gel (particle size 120–200 mesh) was heated for 10 h at 110 °C in a muffled oven, then cooled in a desiccator. A jet kerosene was processed by flash chromatography to remove the aromatic hydrocarbons.

Aqueous phase: Double distilled water.

Fibrous crystal: Alkyl metal phosphates, a kind of hydrophobic particles produced utilizing hydrothermal synthesis by Dalian Institute of Chemical Physics, Chinese Academy of Sciences. The particles were fibrous in shape. They do not contain any other surfactants. The density of the ethyl metal phosphates was 1.3 g cm^{-3}, their lengths were from 50 to 300 μm, and diameters were from 3 to 30 μm. The density of butyl metal phosphates was 1.1 g cm^{-3}, their lengths were from 50 to 500 μm, and diameters were also from 3 to 30 μm.

2.2. Interfacial dilational viscoelasticity measurements [14–16]

The dilational rheology gives a measure of the interfacial resistance to changes in area. The interfacial dilational modulus ε at a particular frequency is characterized by its absolute value ε and by a phase angle θ describing the phase difference between dynamic interfacial tension variation and interfacial area variation:

$$\varepsilon \equiv \frac{\mathrm{d}\gamma}{\mathrm{d}\ \ln A} = |\varepsilon| \exp(i\theta) \tag{1}$$

where ε is the dilational modulus, γ the interfacial tension, θ the phase angle and A is the area of the interface. When a relaxation process takes place in or near the interface as a result of a disturbance, the interface will exhibit viscoelastic rather than pure elastic behavior. Dilational modulus can also be expressed as the summation of elastic and viscosity contribution:

$$\varepsilon = \varepsilon_{\mathrm{d}} + i\omega\eta_{\mathrm{d}} \tag{2}$$

where the real part (storage modulus) represents the elastic energy stored in the interface and is known as the dilational elasticity ε_{d}, and the imaginary part (loss modulus) may be expressed in terms of the interfacial dilatonal viscosity η_{d} because it accounts for the energy dissipated in the relaxation process.

In order to probe the dilational viscoelasticity of the interfacial film, the Langmuir trough–Wilhelmy plate technique, which is most convenient and suitable for working at air–liquid and liquid–liquid interface, was employed. The interface area can be changed on sine oscillation (0.01–0.1 Hz) mode by the horizontal slide of the barriers. The dynamic interfacial tension was measured by the Wilhelmy plate method, using a PTFE plate suspended in the middle of the trough area from a sensitive force transducer.

2.3. Interfacial tension relaxation measurements [17–20]

Moving barriers can be used to produce a little change in interfacial area in a short period of time. The film is able to come to equilibrium before any disturbance was applied. The method allows one to convert any kind of interfacial tension change into the interfacial dilational modulus and its component parts, provided that the form of the area change applied is known.

For an instantaneous area change rising from $\Delta A(t) = 0$ for $t \le 0$ 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:

$$\varepsilon(\omega) = \frac{\mathrm{FT}\,\Delta\gamma(t)}{\mathrm{FT}(\Delta A/A)(t)} = \frac{\int_0^\infty \Delta\gamma(t)\exp(-i\omega t)\mathrm{d}t}{\int_0^\infty [\Delta A(t)/A]\exp(-i\omega t)\mathrm{d}t} \tag{3}$$

where ω is the angular frequency.

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:

$$\Delta\gamma(t) = \sum_{i=1}^{n} A_i \exp(-B_i t) \tag{4}$$

where B_i is the characteristic frequency of the ith process; A_i the fractional contribution that relaxation process makes to restore the equilibrium; and n is the total number of the relaxation processes.

For an instantaneous change in area

$$\int_0^\infty \frac{\Delta A}{A}\exp(-i\omega t)\mathrm{d}t = \frac{\Delta A/A}{i\omega} \tag{5}$$

With this, Eq. (3) becomes

$$\varepsilon = \frac{i\omega}{\Delta A/A}\int_0^\infty \Delta\gamma(t)[\cos\omega t - i\ \sin\omega t]\mathrm{d}t \tag{6}$$