

Density Estimation of Liquid/Liquid Interfacial Regions Using a Quasi-Elastic Laser Scattering Method

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We developed a quasi-elastic laser scattering method and applied it to the density estimation of liquid/liquid (alcohol/water, carboxylic acid/water) interfacial regions. The observed densities are smaller than the expected values in most of the cases, indicating that the interfacial densities are smaller than the bulk phase densities. Moreover, there is a marked tendency for the observed density to become smaller as the hydrophobic group in the alcohol and carboxylic acid molecules becomes larger. The results are consistent with theoretical predictions using the molecular dynamics method. The interfacial structure is discussed in connection with these results.

Introduction

The interface between two immiscible liquids is one of the most important systems of study in chemistry, since transport phenomena across the interface are fundamentally important for understanding processes such as solvent extraction, liquid chromatography, phase-transfer catalysis, etc.^{1,2} Probing the liquid/liquid interface experimentally is more difficult than examining liquid/gas interfaces because of the buried nature of the interface, and theoretical approaches to the interface are complicated by the inhomogeneous environment. Much effort has been made to overcome the difficulty in research on the liquid/liquid interface. In recent years, progress in both experimental techniques and computer simulation has contributed significantly to our understanding of the liquid/liquid interface.

Nonlinear optical techniques such as second harmonic generation (SHG) and sum frequency generation (SFG) are able to probe the liquid/liquid interface as well as liquid/gas and liquid/solid interfaces.^{3–12} These techniques have been extensively used to study molecules in the interfacial region and have provided great insight into the molecular orientation at liquid/liquid interfaces. Neutron specular reflectivity measurements have been used to study oil/water interfacial roughness and the thickness of surfactant layers at oil/water interfaces.¹³ Fluorescence anisotropy decay measurements have provided data on the relationship between the lateral diffusion coefficient and the roughness of alkane/water interfaces.^{14,15} Infrared attenuated total reflection spectroscopy has provided quantitative descriptions of the adsorption of surfactant at a liquid hydrocarbon/water interface.¹⁶ Many useful methods have been developed to probe liquid/liquid interfaces. However, only fragmental information on the interface structure has been accumulated such as orientation, roughness, etc.

On the other hand, a large number of theoretical studies on the liquid/liquid interface by computer simulation have been reported.^{17–25} Many of these reports have predicted the density profile of liquid/liquid interfacial regions by the molecular dynamics (MD) method. These predictions are based on

statistical mechanics and include assumptions on the molecular potential in the simulated model. Mass density may be a typical parameter standing for the structure. Therefore, experimental approaches to the interfacial density are of great significance.

A number of researchers have investigated liquid surfaces by measuring capillary waves generated thermally at liquid surfaces.^{26–30} Since capillary waves reflect the fundamental properties of the surface or interfacial region, much effort has been made to observe them and to analyze their spectra. We have developed a quasi-elastic laser scattering (QELS) method for measuring the interfacial capillary waves. Owing to our improvement of its time resolution, we have successfully monitored the dynamic changes of interfacial molecular number density of surfactants and have thereby provided insight into the interfacial mass transfer.^{31–34} Moreover, in the present study we have applied the QELS method to the density estimation of liquid/liquid interfacial regions. The purpose of this work is to estimate the interfacial density from the capillary wave using the QELS method. Since the density reflects the interfacial structure as discussed above, it provides insight into the molecular structure of the liquid/liquid interface. We present here our method and results for the density estimated from capillary wave frequencies in terms of macroscopic hydrodynamic theory.

Theoretical Background

Capillary waves occur spontaneously at liquid/gas or liquid/liquid interfaces due to thermal fluctuation of the bulk phases. The theoretical understanding of these waves is well established in hydrodynamics, and light scattering from the waves is widely used to monitor the interfaces.^{35,36} Since the capillary wave frequency is a function of five parameters (the interfacial tension and the interfacial densities and viscosities of both phases), the interfacial densities and viscosities can be estimated from the capillary wave frequency in principle. Here we briefly present the relevant theory for density measurements. We note that the following hydrodynamic theory assumes a macroscopic, continuous medium at the interfacial region, although it is actually composed of molecules.

The thermally excited displacement $\xi(\mathbf{r}, t)$ of the free surface

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of a liquid from the equilibrium position normal to the surface can be Fourier decomposed into a complete set of surface modes as

$$\xi(\mathbf{r}, t) = \xi_0 \sum_k \exp[i\mathbf{k} \cdot \mathbf{r} + \Omega t] \quad (1)$$

The complex wave frequency ($=i_0\omega_0 - \Gamma$) is related to \mathbf{k} via a dispersion relation.

For an inviscid liquid, Lamb's equation is well-known as a classical approximation for the dispersion relation³⁷

$$f = \frac{1}{2\pi} \left(\frac{\gamma}{\rho_U + \rho_L} \right)^{1/2} k^{3/2} \quad (2)$$

where f is the capillary wave frequency, γ the interfacial tension, ρ_U the density of the upper phase, ρ_L the density of the lower phase, and k the wavenumber of the capillary wave. This equation is valid for both liquid surfaces and liquid/liquid interfaces. For capillary waves at a liquid surface, ρ_U is regarded as zero in eq 2. In this equation, only the normal component of the interfacial tension is considered to act as a restoring force on the thermally excited displacement (\mathbf{r}, t). Although this equation neglects the effect of surface viscosity, it gives a good fit to the observed relation between the frequency and wave-number of capillary waves at a liquid surface such as ethanol, anisol, or water.^{29,38}

For the surface of a low-viscosity liquid, Levich³⁹ has derived the following dispersion relation:

$$D(S) = (S + 1)^2 + y - (2S + 1)^{1/2} = 0 \quad (3)$$

where $S = \Omega/2\nu k^2$ and $y = \sigma/4\rho\nu^2 k$. Here ν is the kinematic viscosity ($\nu = \eta/\rho$, where η is the viscosity of the liquid). In this equation, both the normal components of the surface tension and the viscous stress contribute to the restoring force on the displacement (\mathbf{r}, t). Based on this equation, a heterodyne power spectrum of the capillary wave in the frequency domain becomes a Lorentzian profile centered at

$$\omega_0 = 2\pi f = |\text{Im}(\Omega)| \quad (4)$$

having the full width at half-maximum (fwhm)

$$\pi\Delta f = |\text{Re}(\Omega)| \quad (5)$$

Under the condition that the effect of the viscosity is negligible, eq 3 is simplified to

$$f = \frac{1}{2\pi} \left(\frac{\gamma}{\rho} \right)^{1/2} k^{3/2} \quad (6)$$

and

$$\Delta f = 2\nu k^2/\pi \quad (7)$$

Equation 6 is the same as Lamb's classical approximation (2).

Since Levich's eq 3 was derived only for a liquid surface, some researchers have extended the equation to a liquid/liquid interface.⁴⁰ Jon et al.⁴¹ have proposed the analysis of liquid/liquid interfacial spectra using a dispersion relation similar to eq 3. In their case ρ is taken as the sum of the densities of both phases and as the sum of the viscosities of both phases, that is, $\rho = \rho_L + \rho_U$ and $\nu = (\eta_L + \eta_U)/(\rho_L + \rho_U)$ are substituted into eq 3. Here ρ_L and ρ_U are the densities of the lower and the upper phases, and η_L and η_U the viscosities of the lower and the upper phases, respectively. In the present study, we

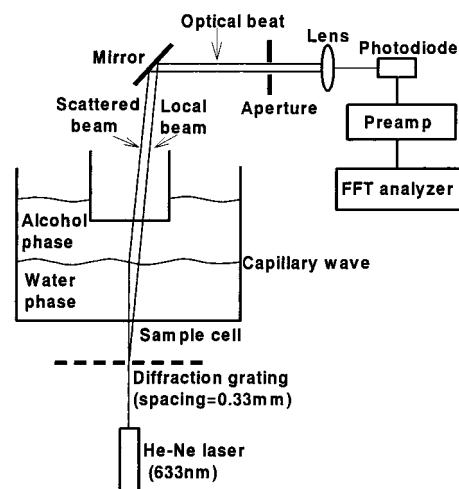


Figure 1. Schematic diagram of the experimental setup for the QELS method. A glass cylinder with an optically flat bottom is immersed in the alcohol phase to avoid the observation of surface capillary waves.

adopted this equation for the analysis of the liquid/liquid interfacial spectra.

Experimental Section

Method. The principle of the QELS method has already been described previously.^{33,34} In brief, an incident laser beam normal to the interface is scattered quasi-elastically with a Doppler shift by the capillary waves (Figure 1). The scattered beam is optically mixed with a local beam produced by a diffraction grating to generate an optical beat in the mixed light.⁴² The obtained beat frequency is the Doppler shift, i.e., the capillary wave frequency. The generated optical beat is measured by a photodiode, and the signals are Fourier transformed by a digital spectrum analyzer. In the present study, we observed capillary waves having a wavelength of 1.1×10^{-2} cm.

Sample Preparation. 1-Hexanol, 1-heptanol, 1-octanol, 1-decanol, hexanoic acid, heptanoic acid, octanoic acid, and nonanoic acid (all analytical grade, Kanto Chemical Co.) were used without further purification. Purified water from a Millipore Milli-Q system was used. Liquid/liquid interfaces were prepared by adding the alcohol or the carboxylic acid to the water in a quartz cell. The samples were left for more than 48 h before measurement so that equilibrium is established between the two phases.

Results and Discussion

A typical power spectrum obtained by the QELS method is shown in Figure 2. The broad peak centered at 2.0 kHz is due to the capillary wave at the 1-decanol/water interface having a wavelength of 1.1×10^{-2} cm. The detected signals are somewhat noisy because of the transmitting optical configuration employed in the present study. The width of the spectrum is determined by the instrumental function as well as the interfacial viscosity. The asymmetric shape of the spectrum is considered to be intrinsic to the capillary waves of low frequencies, and further theoretical investigation is needed to elucidate the shape. In the present case, only the peak frequency is used for the analysis. Table 1 shows the peak frequencies of capillary waves at each interface along with the number of carbon atoms.

The densities of the liquid/liquid interfacial regions are estimated from the peak frequencies of capillary waves using eq 3. By substituting the capillary wave frequency, the kinematic viscosity and the interfacial tension in the literature^{43,44}

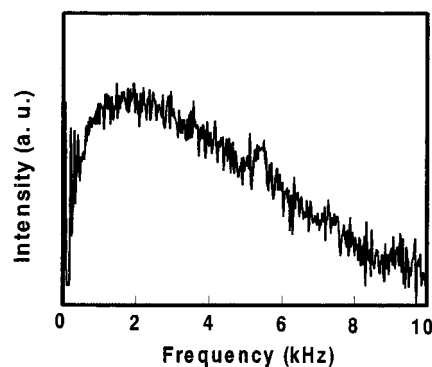


Figure 2. A typical power spectrum for the capillary wave at the 1-decanol/water interface.

TABLE 1: Peak Frequency (kHz) of the Capillary Wave at Studied Water/Alcohol and Water/Carboxylic Acid Interfaces at 25 °C^a

sample	peak freq	sample	peak freq
1-hexanol/water	2.59	hexanoic acid/water	2.48
1-heptanol/water	2.80	heptanoic acid/water	2.80
1-octanol/water	2.68	octanoic acid/water	3.05
1-decanol/water	2.01	nonanoic acid/water	1.78

^aThe wavelength of each capillary wave is 1.1×10^{-2} cm.

into the equation, we obtain the sum of the interfacial densities of the upper and lower phases.

The kinematic viscosity and the density should be determined independently by nature. Some researchers have reported the surface viscosity as determined from the width of the capillary wave spectra.^{26,35,45,46} In the present study, however, the instrumental function was undetermined because of the transmitting optical configuration employed for the observation of the interface, and the width could not be used for the analysis. Regarding the reported results, the interfacial viscosity was difficult to determine even for liquid surfaces, and Langevin²⁶ has reported that a highly viscous surface region does not exist on the water surface. Thus, we assume this result also applies to water surfaces in the interfacial region and therefore that the kinematic viscosity of the interfacial region can be related to the bulk phase viscosities as described above. In addition, the change in viscosity hardly affects the capillary wave frequency whereas the change in density strongly affects the frequency. This suggests that the large deviation of the frequency from the theoretical value is owing to the change in density.

The experimentally estimated densities ($\rho = \rho_L + \rho_U$ of eq 3) of the alcohol/water and carboxylic acid/water interfacial regions are shown in Figure 3. These values are lower than the calculated bulk $\rho_L + \rho_U$ values except for the hexanoic acid/water and heptanoic acid/water interfaces, and there is a marked decrease in the interfacial density as the hydrophobic group of the alcohol molecule becomes larger. While this difference between the experimental and the calculated $\rho_L + \rho_U$ values may mean that the interfacial mass density is actually lower than the bulk phases, it could also indicate that Levich's equation, which assumes a continuous medium at the interfacial region, cannot be applied to microscopic interfacial regions. However, a number of reports have indicated the validity of Levich's equation for liquid surfaces.^{26,29,46} By analogy, we interpret our results assuming the validity of Levich's equation at liquid/liquid interfaces. We conclude that alcohol/water interfacial regions have smaller densities than the bulk phases and that the hydrophobic groups in both alcohol and carboxylic acid molecules cause some porosity in the interfacial regions.

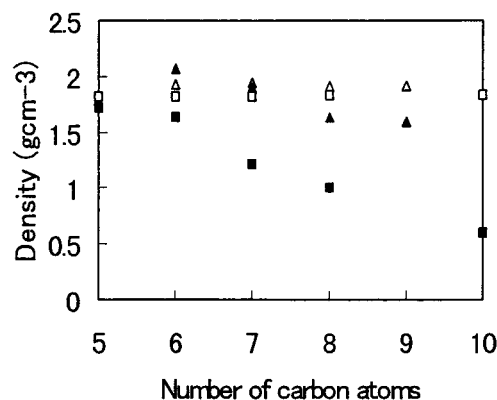


Figure 3. Relationship between the total density (the sum of the upper phase and the lower phase, $\rho_L + \rho_U$) and the number of carbon atoms in the hydrophobic group. The experimentally estimated interfacial densities are shown as ■ and ▲ for alcohol and carboxylic acid, respectively. The calculated bulk phase densities are shown as □ and △ for alcohol and carboxylic acid, respectively.

Our results are consistent with these obtained from other theoretical and experimental studies.^{47–49} Michael and Benjamin⁴⁷ have reported MD simulations that show the density of the water/1-nonane interface to be smaller than that of water/“spherical” nonane, and Benjamin⁴⁸ has indicated that the total density of the water/1-octanol interface is smaller than that of the bulk phase. Moreover, Conboy⁴⁹ et al. have observed a significant degree of molecular ordering at alkane/water interfaces using the SHG method. It may be reasonable to think that the alcohol molecules are also ordered at the liquid/liquid interfacial region, directing a hydrophobic group to the alcohol phase and a hydrophilic group to the water phase. Thus, we might hypothesize from these results and say that the orientation of the hydrophobic group at the interfacial region causes the interfacial porosity.

Our experimental results have been interpreted on the basis of the macroscopic continuous medium model of hydrodynamic theory. In this model the two phases are separated discontinuously by a dividing line having no width, and the microscopic interfacial region is also regarded as a continuous medium. The interfacial region, however, is actually composed of molecules, and the two phases are considered to be mixed at the interfacial region. For a more precise discussion on microscopic interfacial regions, a molecular theoretical interpretation of capillary waves based on statistical mechanics will be necessary. Such a theory would make the QELS method a more powerful tool for the study of liquid surfaces or liquid/liquid interfaces.

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