

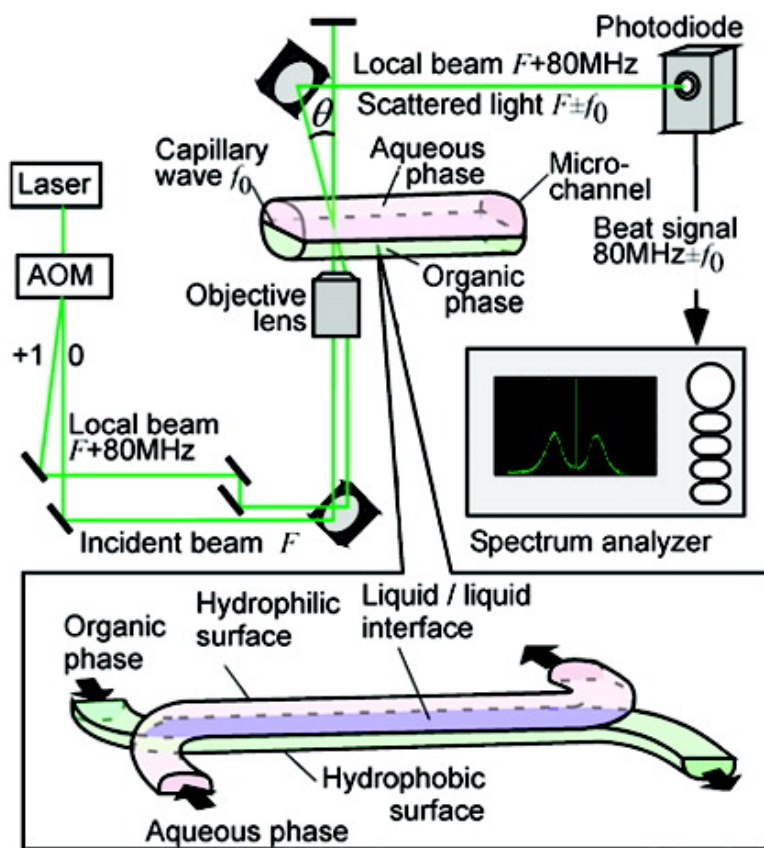
Communication

**Spectroscopic Analysis of Liquid/Liquid Interfaces in Multiphase Microflows**

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## Spectroscopic Analysis of Liquid/Liquid Interfaces in Multiphase Microflows

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Through the utilization of simple pressure-driven microflow, important chemical processes can be integrated onto a microchip.<sup>1</sup> Laminar multiphase microflow (MPMF) can be used for continuous chemical processing along a microchannel. Complex chemical operations and their applications have been demonstrated in microchips utilizing MPMF.<sup>2,3</sup> Although MPMF may be a novel tool for monitoring molecular behaviors at an aqueous/organic (A/O) interface, no quantitative analysis method for the interface has been established. Commonly, nonlinear laser spectroscopies<sup>4</sup> have been used to characterize the A/O interface. However, these methods are not suitable for dynamic process measurements such as transport phenomena.

A quasi-elastic laser scattering (QELS) method is suitable for the A/O interface analysis because of its interface-selectivity. Because the QELS method measures capillary wave, no probe molecule is necessary and the interface can be measured as it is.

Here, we report a novel microscopic quasi-elastic laser scattering ( $\mu$ QELS) method for quantitative analysis of the MPMF. A control method for MPMF guided by modification patterning<sup>5</sup> is also developed, where the modified surface holds the fluids by chemical interaction. The effectiveness of the MPMF and  $\mu$ QELS method is demonstrated by measuring the solvent extraction of a metal chelate and the mixing process of two miscible liquids.

The A/O interface thickness is usually defined as thermal fluctuation amplitude, which is about 1 nm. Because a quasi-elastic laser scattering (QELS) method measures the capillary wave due to the thermal fluctuation and interfacial tension at the A/O interface, it can measure the interface characteristics selectively.<sup>6,7</sup> When an incident beam irradiates the interface, the capillary wave having a wavenumber  $k$  scatters the beam, where the relationship of  $k = K \sin \theta$  is required from momentum conservation.  $K$  is the wavenumber of the laser light, and  $\theta$  is the scattering angle. In the scattering process, the incident light frequency  $F$  is modulated by the capillary wave having a frequency of  $f_0$ , and, then, the scattered light has a frequency of  $F + f_0$ . By mixing the local beam having a frequency of  $F$  with the scattered light, we could measure the capillary wave frequency  $f_0$  as a beat frequency. The observed beat frequency  $f_0$  can be related to the wavenumber  $k$  and interfacial tension  $\gamma$  as<sup>8</sup>

$$f_0 = \frac{1}{2\pi} \left( \frac{\gamma k^3}{\rho_A + \rho_O} \right)^{1/2} \quad (1)$$

where  $\rho_A$  and  $\rho_O$  are densities of aqueous and organic phases, respectively.

To realize  $\mu$ QELS for MPMF, two technical problems should be solved. First, low-frequency noise due to flow, which disrupts

QELS measurement, should be avoided. Second, scattering angle determination is very difficult because the diffraction grating method in the conventional QELS method<sup>9</sup> cannot be applied when a microscope objective lens is used. A block diagram of our  $\mu$ QELS method is shown in Figure 1. To avoid low-frequency noise, the center frequency of measurement is shifted to 80 MHz from 0 Hz by utilizing the frequency offset of the local beam induced by the acousto-optic modulator (AOM).<sup>10</sup> Next, to determine the scattering angle, the numerical aperture of the lens is utilized. The incident and local beams are aligned parallel, focused with an objective lens, and crossed at the liquid surface in the microchannel. The local beam containing scattered light of the incident beam is fed into a photodiode. The optical beat signal is monitored by a spectrum analyzer. The inset of Figure 1 illustrates MPMF, in which the top and bottom plates are modified with hydrophilic and hydrophobic groups, respectively.<sup>5</sup> The microchannel has a width of 300  $\mu\text{m}$ , a depth of 200  $\mu\text{m}$ , and a length of 20 mm.

A typical  $\mu$ QELS spectrum in the microchannel is shown in Figure 2a, where the water/toluene interface was measured ( $k = 0.59 \times 10^6 \text{ m}^{-1}$ ). The spectrum power intensity depends on the difference of the refractive indices between two fluids  $\Delta n$ , and we estimated the limit of detection as  $\Delta n \approx 0.02$ . Flow velocity of the water and toluene was set to 2 mm/s. The solid line indicates fitted results of the theoretical spectrum, and the beat frequency  $f_0 = 0.317 \pm 0.002 \text{ MHz}$  was fitted. From the fitted  $f_0$ , the interfacial tension of 35.3 mN/m was obtained (literature value: 36.3 mN/m). By comparing the literature and experimental values for various interfaces, we confirmed the validity of the  $\mu$ QELS method.

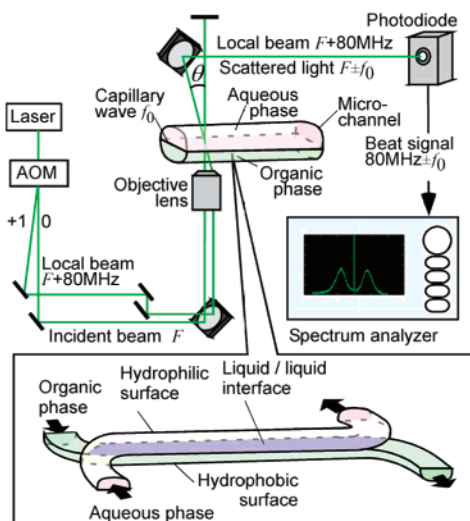
One of the most important applications of the  $\mu$ QELS is transport characterization through the A/O interface in the MPMF. To demonstrate effectiveness and usefulness, the solvent extraction process of Co-2-nitroso-5-dimethylaminophenol (Co-DMAP) at the water/toluene interface was measured. Figure 2b shows a time-course of the beat frequency during the extraction process. The minimum beat frequency around 2 s corresponded to the minimum interfacial tension due to Co-DMAP adsorption where a decrease of the interfacial tension corresponds to an increase of interfacial density. Interfacial density of Co-DMAP increased until 2 s. The interfacial density then decreased until 10 s to achieve an equilibrium density. As we demonstrated here, the  $\mu$ QELS method is very powerful for molecular transport analysis at the micro liquid interface.

The  $\mu$ QELS method is useful not only for dynamic analysis of interfaces between two immiscible solvents but also for those between miscible solvents. Generally, we implicitly assume immiscible interfaces when we use the word liquid-liquid interface. However, two miscible liquids also have interfaces before they mix. Very few studies have been made on direct measurements of the mixing process.<sup>11,12</sup> In these papers, critical consolute phenomena of aniline/cyclohexane or water/isobutyric acid were utilized to

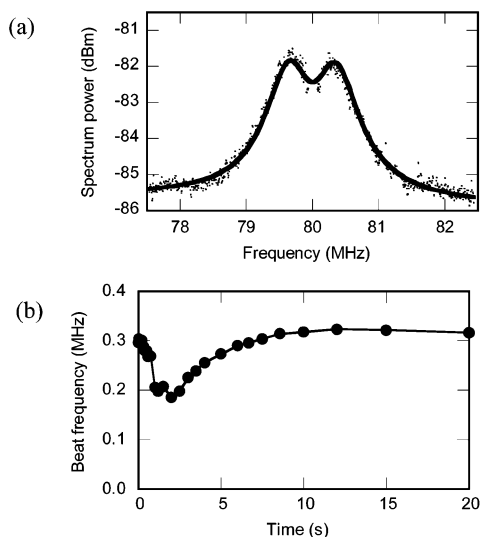
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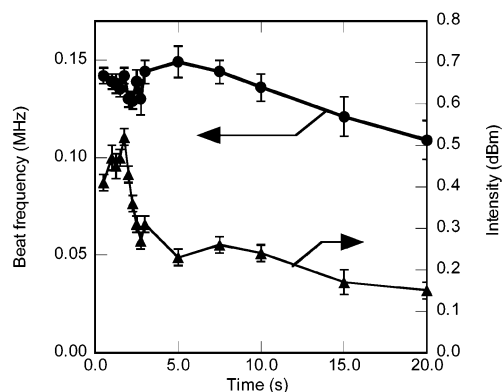
**Figure 1.** Block diagram of  $\mu$ QELS apparatus. The inset illustrates multiphase microflow (MPMF) utilizing the hydrophilic/hydrophobic modification patterning.



**Figure 2.** (a)  $\mu$ QELS spectrum of the water/toluene interface in the microchannel. The solid line shows the fitted result. (b) Beat frequency during the extraction process of Co-DMAP through the water/toluene interface. The initial concentration of Co-DMAP was  $1 \mu\text{M}$ .

measure the miscible liquids, where a slight temperature change induced two-phase mixing under stable conditions. Obviously, this method can be applied to only limited combinations of solvents and to measuring very slow mixing processes. In contrast, our method utilizing  $\mu$ QELS and MPMF has wide applicability for dynamical measurements of miscible interfaces.

Figure 3 shows results of QELS measurements for the water/methanol interface. The beat frequency and signal intensity dependence on time was clearly observed. Because the single intensity of  $\mu$ QELS depends on the contrast of refractive index at the interface, the time-course of the intensity reflects the thickness of mixing. The intensity had a maximum because the mixing layer thickness increased while the layer's contrast decreased. In contrast, the beat frequency may reflect the thermodynamic state of the mixing layer. Cahn and Hilliard<sup>13</sup> proposed the interfacial free energy as  $\gamma \propto \int_x (dc/dx)^2 dx$ , where  $c$  is local composition and  $x$  is the axis across the interface. By using eq 1, the frequency was converted to the interfacial free energy which ranged from 1.71 mN/m (5 s) to 0.92 mN/m (20 s). This is the first report on the



**Figure 3.** Beat frequency and signal intensity measured at the water/methanol interface.

interfacial energy of the water/methanol interface during the mixing process. A particle image velocimetry investigation on miscible two-phase flow suggested an anomalous imbalance in shear stress at the interface.<sup>14</sup> For understanding chemical and physical mechanisms of solution and mixing, water–alcohol mixtures have been intensively studied,<sup>15</sup> and our approach will contribute to the fundamental chemistry of solution.

In conclusion, we have demonstrated a novel method to analyze interfacial phenomena in microchannels, such as the transport of a Co chelate through the A/O interface and the mixing process of two miscible solvents. Our method will be a very important tool for monitoring transport phenomena in microfluidic devices, for fundamental research on solution and mixing, and even for direct measurement of syntheses at the liquid/liquid interfaces.

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**Supporting Information Available:** Principle and instruments of QELS and  $\mu$ QELS (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Kopp, M. U.; de Mello, A. J.; Manz, A. *Science* **1998**, *280*, 1046–1048. (b) Weigl, B. H.; Yager, P. *Science* **1999**, *283*, 346–347. (c) Kenis, P. J. A.; Ismagilov, R. F.; Whitesides, G. M. *Science* **1999**, *285*, 83–85.
- (2) (a) Tokeshi, M.; Minagawa, T.; Uchiyama, K.; Hibara, A.; Sato, K.; Hisamoto, H.; Kitamori, T. *Anal. Chem.* **2002**, *74*, 1565–1571. (b) Surmeian, M.; Slyadnev, M. N.; Hisamoto, H.; Hibara, A.; Uchiyama, K.; Kitamori, T. *Anal. Chem.* **2002**, *74*, 2014–2020.
- (3) Kuban, P.; Dasgupta, P. K.; Morris, K. A. *Anal. Chem.* **2002**, *74*, 5667–5675.
- (4) (a) Richmond, G. L. *Chem. Rev.* **2002**, *102*, 2693–2724. (b) Eisenthal, K. B. *Chem. Rev.* **1996**, *96*, 1343–1360.
- (5) Hibara, A.; Nonaka, M.; Hisamoto, H.; Uchiyama, K.; Kikutani, Y.; Tokeshi, M.; Kitamori, T. *Anal. Chem.* **2002**, *74*, 1724–1728.
- (6) Katyl, R. H.; Ingerd, U. *Phys. Rev. Lett.* **1967**, *19*, 64–66.
- (7) *Light Scattering by Liquid Surfaces and Complementary Techniques*; Langevin, D., Ed.; Marcel Dekker: New York, 1992.
- (8) Lamb, H. *Hydrodynamics*, 6th ed.; Cambridge University Press: Cambridge, 1932.
- (9) Zhang, Z.-H.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *J. Phys. Chem. B* **1998**, *102*, 10284–10287.
- (10) Sakai, K.; Choi, P.-K.; Tanaka, H.; Takagi, K. *Rev. Sci. Instrum.* **1991**, *62*, 1192–1195.
- (11) Vailati, A.; Giglio, M. *Nature* **1997**, *390*, 262–265.
- (12) May, S. E.; Maher, J. V. *Phys. Rev. Lett.* **1991**, *67*, 2013–2016.
- (13) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1958**, *28*, 258–267.
- (14) Sugii, Y.; Okamoto, K.; Hibara, A.; Tokeshi, M.; Kitamori, unpublished.
- (15) Dixit, S.; Crain, J.; Poon, W. C.; Finney, J. L.; Sopper, A. K. *Nature* **2002**, *416*, 829–832.

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