

# Observation of One Process in a Phase Transfer Catalytic Reaction at a Liquid/Liquid Interface by Using the Quasi-Elastic Laser Scattering Method

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The interfacial behavior of a phase transfer catalyst, tetrabutylammonium bromide (TBAB), was investigated by the quasi-elastic laser scattering (QELS) method. TBAB forms an ion pair ( $\text{TBA}^+\text{C}_6\text{H}_5\text{O}^-$ ) with sodium phenoxide ( $\text{C}_6\text{H}_5\text{ONa}$ ) in a water phase. This ion pair moves from the water phase to the organic phase where it reacts with diphenylphosphoryl chloride (DPPC). This one process in the phase transfer catalytic reaction at a water/nitrobenzene (W/NB) interface was investigated by the QELS method. When the TBAB concentration was above 50 mM, the ratio of TBAB concentration to  $\text{C}_6\text{H}_5\text{ONa}$  in equilibrium at the W/NB interface was unity. On the other hand, when the TBAB concentration was below 50 mM, the ratio was below unity. These results suggested that the reaction place between TBAB and  $\text{C}_6\text{H}_5\text{ONa}$  changed with TBAB concentration; the reaction place was in the water phase above 50 mM, whereas it was at the interface below 50 mM.

## Introduction

The liquid/liquid interface holds important roles in various processes such as phase transfer catalysis, solvent extraction, and ion-selective electrode operation. Among them, phase transfer catalysis has attracted much attention because a reaction is promoted by transfer across the liquid/liquid interface to get high product yield and high selectivity.<sup>1–5</sup> Tetrabutylammonium bromide (TBAB), a well-known surfactant, is a phase transfer catalyst, which circulates between the two phases across the interface. Therefore, the investigation of the behavior of TBAB at the liquid/liquid interface is essential to understand the overall catalytic reaction.

Many studies have been reported on the behavior of a phase transfer catalyst based on conventional batch methods using NMR, UV–vis spectrophotometry, and gas chromatography, etc., by taking out part of the solution from the bulk phase.<sup>6–13</sup> Thus, the behavior of the phase transfer catalyst has been mainly analyzed by information from the bulk phase. However, for better understanding, direct measurement of the interface is essential. There are a number of studies that measure interfacial tension to provide useful information on the interface. In these studies, the interfacial tension was measured by the Wilhelmy method, drop method, etc., which perturbs the interface and causes a certain amount of change in the interfacial tension.<sup>14–17</sup> These techniques cannot be adapted to precise measurements of interfacial behavior of the phase transfer catalyst. Thus, the behavior of a phase transfer catalyst at the liquid/liquid interface has not been directly measured so far, and the reaction rate and field of its elementary processes such as adsorption, desorption, and reaction between the two chemical species still remain unclarified. In situ measurements of liquid/liquid interfaces should provide great insight into interfacial molecular behavior of phase transfer catalyst.

We have developed a quasi-elastic laser scattering (QELS) method and have reported on the dynamics of mass transfer of surfactants at a water/nitrobenzene (W/NB) interface.<sup>18–22</sup> We demonstrated that the QELS method is a useful spectroscopic

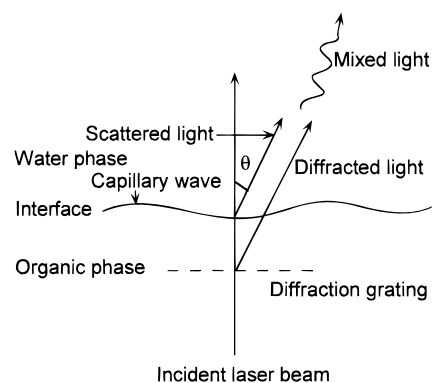


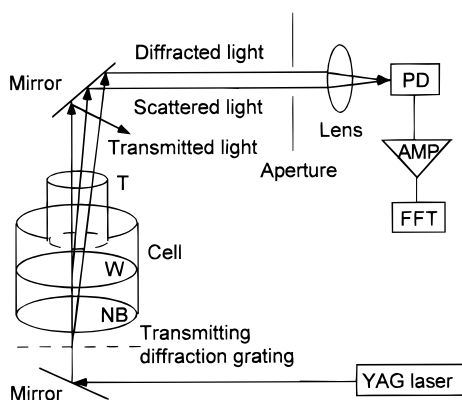
Figure 1. Principle of the quasi-elastic laser scattering method.

technique for nonperturbative in situ measurements of liquid/liquid interface.

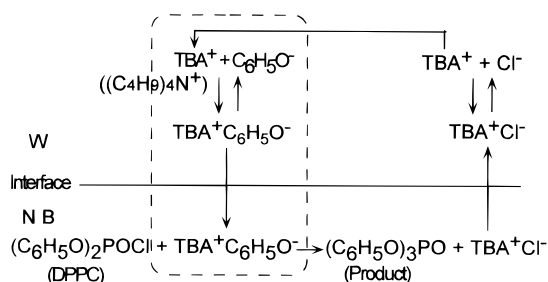
In this study, we investigated a phase transfer catalytic reaction system with TBAB, whose reaction scheme is well-known and the operating conditions are mild. We focused on the behavior of TBAB at the W/NB interface in one simple process of phase transfer catalytic reaction.<sup>23,24</sup> Our aims are to obtain direct information about the interface from in situ measurements and to clarify the reaction place around the interface from the interfacial molecular behavior. We present here the results for in situ measurements of interfacial adsorption behavior, which suggest the reaction place changes with the concentration.

## Experimental Section

**Principle.** The principle of the QELS method has already been described previously.<sup>18–22</sup> In brief, an incident laser beam normal to the interface is scattered quasi-elastically with a Doppler shift by the capillary wave (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.



**Figure 2.** Schematic diagram of the experimental setup: T, glass tube; W, water phase; NB, nitrobenzene; PD, photodiode; AMP, preamplifier; FFT, FFT analyzer.



**Figure 3.** Scheme of the reaction between  $C_6H_5ONa$  and DPPC in the W/NB system. The part surrounded by the dashed line is the process investigated in this study.

The obtained beat frequency is the same as the Doppler shift, i.e., the capillary wave frequency.

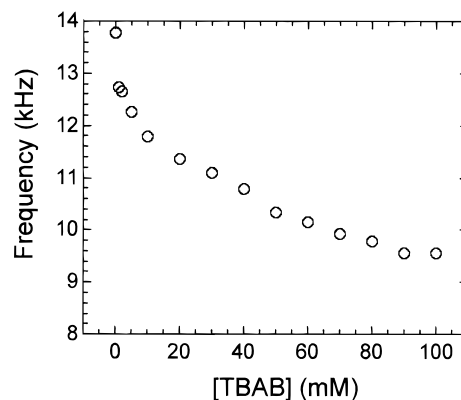
The capillary wave frequency  $f$  is approximately expressed by Lamb's equation,<sup>25</sup>

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

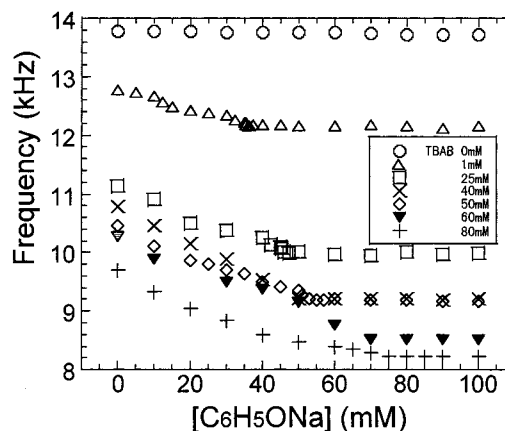
where  $\rho_w$  is the density of the water phase,  $\rho_o$  is the density of the organic phase, and  $k$  is the wavenumber of the capillary wave. Because the interfacial number density  $\Gamma$  of a surfactant monolayer is approximately inversely proportional to the interfacial tension  $\gamma$ , the relative change of the number density  $\Gamma$  can be estimated from the capillary wave frequency.

**Apparatus.** A schematic diagram of the experimental setup is shown in Figure 2. The beam from a YAG laser (CrystaLaser, model GCL-025S, 532 nm, 20 mW) passes through a transmitting diffraction grating in front of the cell. The cell is made of quartz glass and has an optically flat bottom. After passing through the sample, one of the diffracted beams, which is mixed with the scattered light, is selected by the aperture in front of the photodiode (Hamamatsu Photonics S1290). Signals from the photodiode are Fourier transformed and saved by a digital spectrum analyzer (Sony Tektronix Co., model 3056). In the present study, the wavelength of the observed capillary wave was  $6.6 \times 10^{-3}$  cm.

**Sample Preparation.** The scheme of the reaction between sodium phenoxide ( $C_6H_5ONa$ ) and diphenylphosphoryl chloride (DPPC) in a W/NB system by TBAB is shown in Figure 3. At the beginning of the reaction, TBAB reacts with  $C_6H_5ONa$  to form  $TBA^+C_6H_5O^-$ . This ion pair is transported into the organic phase where it reacts with DPPC to produce triphenyl phosphate ( $(C_6H_5O)_3PO$ ). During this reaction,  $TBA^+Cl^-$  is also formed and transported into the water phase to react again with  $C_6H_5-$



**Figure 4.** Capillary wave frequency dependence on TBAB concentration.



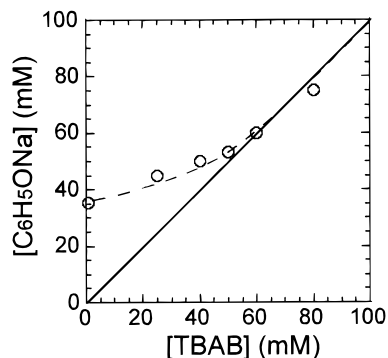
**Figure 5.** Capillary wave frequency dependence on the concentrations of TBAB and  $C_6H_5ONa$ .

ONa. TBAB activates the production of triphenyl phosphate by circulating between the two phases.

In this study, we focused on one transfer process in which the formed ion pair is transferred from the water phase to the nitrobenzene phase. Thus, we investigated the adsorption behavior of the ion pair at various concentrations of TBAB (0–80 mM) and  $C_6H_5ONa$  (0–100 mM). A liquid/liquid interface was prepared by adding 10 mL of mixed aqueous solution of TBAB (Kanto Chemical Co.),  $C_6H_5ONa$  (Aldrich), and NaOH (Kanto Chemical Co.) to 10 mL of nitrobenzene in a quartz cell. Ultrapure water (from Millipore Milli-Q system) was used for all sample preparations. NaOH was added to adjust the ionic strength to 0.2 and to prevent the production of phenol or benzoic acid. All chemicals were reagent grade and used without further purification.

## Results and Discussion

Capillary wave frequencies at various concentrations of TBAB alone are shown in Figure 4. The frequency decreased significantly with increasing TBAB concentration and became constant at about 100 mM. This indicated that interfacial tension was decreased by the interfacial adsorption of TBAB, and the interfacial adsorption became saturated at about 100 mM. Capillary wave frequencies at various concentrations of TBAB and  $C_6H_5ONa$  are shown in Figure 5. When  $C_6H_5ONa$  alone was in the water phase, the frequency was independent of the  $C_6H_5ONa$  concentration. On the other hand, when both  $C_6H_5ONa$  and TBAB were present, the frequency decreased gradually and only slightly with increasing  $C_6H_5ONa$  concentration and then became constant at a certain  $C_6H_5ONa$  concentration. These



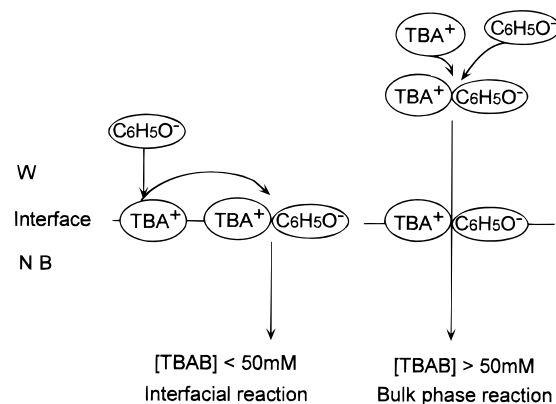
**Figure 6.** Relationship between the TBAB and  $C_6H_5ONa$  concentrations in equilibrium.

facts indicated that  $C_6H_5ONa$  molecules did not adsorb onto the interface alone, and the adsorption of  $C_6H_5ONa$  molecules was promoted in the presence of TBAB. Therefore, the decrease of frequency indicated that TBAB formed an ion pair with  $C_6H_5ONa$ , such as  $TBA^+C_6H_5O^-$ , and these ion pairs adsorbed at the interface. The constant frequency above a certain concentration indicated that the number of interfacial adsorptions of ion pairs that occurred became constant. This suggested that the reaction between  $C_6H_5ONa$  and TBAB was in equilibrium, and the number of ion pairs that occurred became constant. This stable formation brought about the saturated interface. The formation of ion pairs corresponded to findings in other reports.<sup>23,24</sup> However, saturation of the interfacial adsorption above a certain concentration of  $C_6H_5ONa$  has not been reported so far, and this provided significant information on the reaction between TBAB and  $C_6H_5ONa$ .

Furthermore, interestingly, the equilibrium concentration of  $C_6H_5ONa$  above which the adsorption was saturated depended on the TBAB concentration. We used these equilibrium concentrations to analyze the reaction between the two reactants, assuming that at these concentrations the reaction proceeds without residue and deficiency. The relationship between this  $C_6H_5ONa$  concentration and the TBAB concentration is shown in Figure 6. We noted that the ratio of the TBAB concentration to the  $C_6H_5ONa$  concentration deviated from the line for 1:1 below 50 mM. When the TBAB concentration was above 50 mM, the ratio of the TBAB concentration to the  $C_6H_5ONa$  concentration at the W/NB interface was unity. On the other hand, when the TBAB concentration was below 50 mM, the ratio of the  $C_6H_5ONa$  concentration to the TBAB concentration was more than unity.

In general, the formation of an ion pair  $TBA^+C_6H_5O^-$  occurs by the reaction between one TBAB molecule and one  $C_6H_5ONa$  molecule in the water phase. This can be empirically deduced from studies on the bulk phase concentrations.<sup>6-13</sup> Thus, the ratio of the  $C_6H_5ONa$  concentration to the TBAB concentration should be unity if we assume the reaction occurs in the water phase. The behavior above 50 mM can be simply explained by the reaction in the water phase between one TBAB molecule and one  $C_6H_5ONa$  molecule because the ratio is unity. However, the behavior below 50 mM cannot be explained by the simple water phase reaction. This result suggests that the reaction place is not in the water phase. It is generally said that the concentration or activity at the interface is different from that in the water phase. Thus, if we assume the ratio of the two concentrations at the interface is unity and the reaction between the TBAB molecules and the  $C_6H_5ONa$  molecules occurs at the interface, the deviation from the line of 1:1 can be explained.

As shown in Figure 7, our results suggested that below 50 mM the reaction of the formation of the ion pair occurred at



**Figure 7.** Model of the reaction between TBAB and  $C_6H_5ONa$ .

the interface while above 50 mM the reaction occurred in the water phase.

Our results reflected interfacial specificity for a chemical reaction and mass transfer. We successfully observed the molecular behavior reflecting the interfacial specificity focusing on one process of the phase transfer catalyst system using the QELS method. In future studies the advantages of the QELS method can be used to provide details on interfacial specificity for chemical processes by nonperturbative measurements.

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