

Observation of Dynamic Molecular Behavior in a Phase Transfer Catalytic Reaction at a Liquid/Liquid Interface by Using the Time-Resolved Quasi-Elastic Laser Scattering Method

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The dynamic behavior of the phase transfer catalyst, quaternary ammonium bromide $R_4N^+Br^-$ (R: $n-C_4H_9$, $n-C_3H_7$, C_2H_5), at a water/nitrobenzene (W/NB) interface was monitored by time-resolved quasi-elastic laser scattering (QELS) measurements. The time courses of the QELS spectrum after injection of the $(n-C_4H_9)_4N^+Br^-$ phase transfer catalyst, which brings about high product yield, showed high interfacial molecular number density in the stationary state of the reaction, whereas its adsorption rate in the initial stage was almost the same as the rates of the other two. The product yield was considered to reflect the interfacial amount of the phase transfer catalyst, and the interface acted as the reaction site controlling the phase transfer catalytic reaction.

Introduction

Liquid/liquid interfaces play important roles in various processes such as phase transfer catalysis, solvent extraction, and ion-selective electrode reactions. Among them, phase transfer catalysis has attracted much attention because the catalyst activates the reaction by transferring across the liquid/liquid interface and brings about high product yield and high selectivity by the recurred cycle.^{1–5} Tetrabutylammonium bromide (TBAB, $(n-C_4H_9)_4N^+Br^-$) is a commonly used phase transfer catalyst, which behaves as a surfactant and activates organic synthesis reactions.^{6,7} It is empirically known that TBAB, whose carbon chain number is 4, brings about higher product yield than other quaternary ammonium bromides. Longer carbon chains of the quaternary ammonium bromide cause more difficult separation of product, and thus shorter carbon chains have an advantage as a phase transfer catalyst.^{8,9} However, the reason TBAB shows a higher product yield than tetrapropylammonium bromide (TPRAB, $(C_3H_7)_4N^+Br^-$) and tetraethylammonium bromide (TEAB, $(C_2H_5)_4N^+Br^-$) has not been clarified so far. Clarification by an analytical approach to the interfacial reaction as well as a conventional study using the bulk phase concentration is highly desirable.

In recent years, various spectroscopic techniques have been developed to probe liquid/liquid interfaces. Second harmonic generation (SHG) and sum frequency generation (SFG) methods have provided great insight into molecular orientation at the liquid/liquid interfaces.^{10–19} In addition to these studies on interfacial static structures, experimental approaches to the interfacial molecular density are of great significance in revealing the interfacial molecular dynamics.

We have developed a time-resolved quasi-elastic laser scattering (QELS) method and have reported on the dynamic

changes of interfacial molecular density of surfactants at the water/nitrobenzene (W/NB) interface.^{20–25} This method allows nonperturbative in situ measurement of liquid/liquid interfaces and provides insight into the interfacial mass transfer. We focused on a phase transfer catalytic reaction system with quaternary ammonium bromide, $R_4N^+Br^-$ (R: $n-C_4H_9$, $n-C_3H_7$, $n-C_2H_5$), whose reaction scheme is well-known and whose operating conditions are mild. We previously reported that the liquid/liquid interface was the reaction site for formation of ion pairs ($TBA^+C_6H_5O^-$) based on observation of one process in the phase transfer catalysis.⁷ The main aims of the present study are to clarify the dynamic molecular behavior in the phase transfer catalytic reaction and the mechanism determining the product yield. We first present time courses of the relative molecular number densities at the W/NB interface in the phase transfer catalytic reaction after injection of the phase transfer catalyst and then discuss the importance of the reaction site in the formation of ion pairs.

Experimental Section

Principle. The principle of the QELS method has already been described.^{20–27} The relationship between the capillary wave frequency f and the interfacial tension γ is expressed by Lamb's equation:²⁸

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

where ρ_w is the density of the water phase, ρ_o is the density of the organic phase, and k is the wavenumber of the capillary wave. Here, the interfacial tension γ is inversely proportional to the interfacial number density G based on the Gibbs adsorption isotherm.²³ Therefore, the relative change of the number density G can be estimated from a change in the capillary wave frequency. We have reported this previously.^{21, 22}

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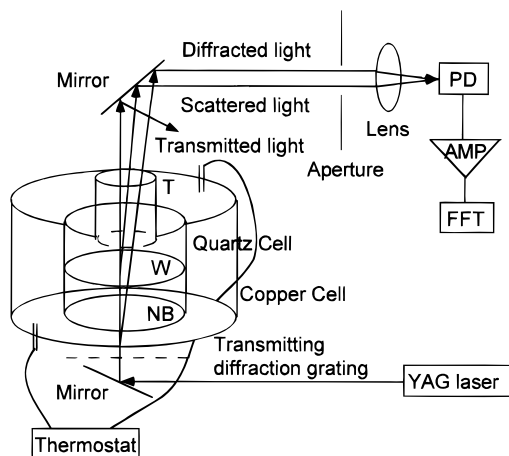


Figure 1. Schematic diagram of the experimental setup: T, glass tube; W, water phase; NB, nitrobenzene; PD, photodiode; AMP, preamplifier; FFT, FFT analyzer.

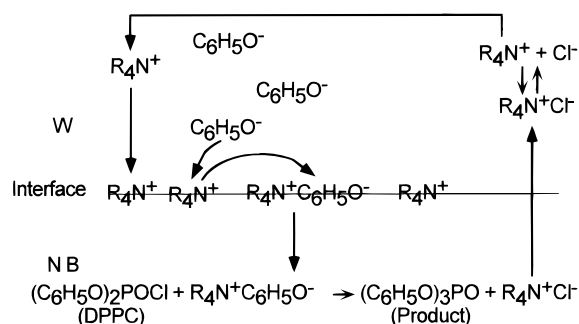


Figure 2. The phase transfer catalytic reaction scheme between C_6H_5ONa and DPPC in the W/NB system.

Apparatus. A schematic diagram of the experimental setup is shown in Figure 1. 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 is 6.6×10^{-2} mm. The quartz cell is placed inside a copper cell that has a thermostat (Tokyo Rikakikai Co., UA-110) to keep the measurement temperature at 283 K because the W/NB interface is most stable at that value.

Sample Preparation. The reaction scheme between sodium phenoxide (C_6H_5ONa) and diphenylphosphoryl chloride (DPPC) in the W/NB system with quaternary ammonium bromide, $R_4N^+Br^-$ (R: *n*- C_4H_9 , *n*- C_3H_7 , C_2H_5), is shown in Figure 2. At the beginning of the reaction, $R_4N^+Br^-$ reacts with C_6H_5ONa to form $R_4N^+C_6H_5O^-$ at the interface.⁷ This ion pair moves into the organic phase, where it reacts with DPPC to produce triphenyl phosphate ($(C_6H_5O)_3PO$). During this reaction, $R_4N^+Cl^-$ is also formed and is transported into the water phase to react again with C_6H_5ONa . $R_4N^+Br^-$ activates the production of triphenyl phosphate by circulating between the two phases.

In this study, we focused on the liquid/liquid interface in the phase transfer catalytic reaction and investigated the dynamic behavior of the ion pair ($R_4N^+Cl^-$, $R_4N^+C_6H_5O^-$) formed in the presence of $R_4N^+Br^-$ (1 mM), DPPC (1 mM), and C_6H_5ONa (70 mM). We used three kinds of quaternary ammonium

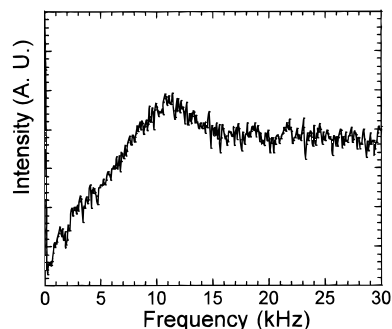


Figure 3. Power spectra for capillary waves excited at the W/NB interface (283 K).

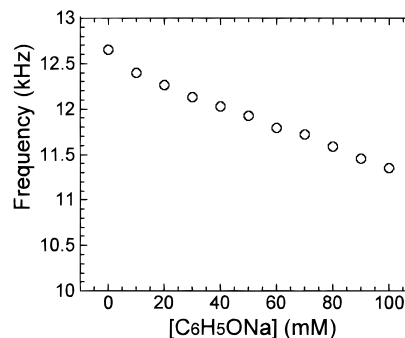


Figure 4. Capillary wave frequency dependence on the concentrations of C_6H_5ONa (283 K).

bromides, $R_4N^+Br^-$: tetrabutylammonium bromide (TBAB), $(C_4H_9)_4N^+Br^-$; tetrapropylammonium bromide (TPRAB), $(C_3H_7)_4N^+Br^-$; and tetraethylammonium bromide (TEAB), $(C_2H_5)_4N^+Br^-$. A liquid/liquid interface was prepared by adding 9.8 mL of an aqueous solution of C_6H_5ONa (Aldrich) and NaOH (Kanto Chemical Co.) to 10 mL of nitrobenzene containing DPPC (Kanto Chemical Co.) in the quartz cell. After 0.2 mL of $R_4N^+Br^-$ (Kanto Chemical Co.) was injected in the water phase with a microsyringe, the power spectrum was obtained every 1 s. 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 were used without further purification.

Results and Discussion

First, a typical power spectrum of capillary waves excited at the W/NB interface is shown in Figure 3. The signal-to-noise ratio of the present system was improved by increasing the data acquisition frequency from 4 Hz to 20 Hz and integrating the data every 1 s. The errors on the values of the capillary wave frequency were 0.1 kHz obtained as the standard deviation of 10 repeated measurements.

Capillary wave frequency dependence on C_6H_5ONa is shown in Figure 4. The frequency decreased significantly with increasing C_6H_5ONa concentration. This indicated that interfacial tension was decreased by the interfacial adsorption of C_6H_5ONa .

To examine the dynamic molecular behavior in the phase transfer catalytic reaction, we investigated the time courses of the capillary wave frequencies after the injection of the TEAB, TPRAB, and TBAB solutions into the water phase. These curves were obtained with good reproducibility. The time just prior to the injection was regarded as 0 s, and the power spectrum was obtained every 1 s. Capillary wave frequencies after the injection of the TEAB, TPRAB, and TBAB solutions are plotted as a

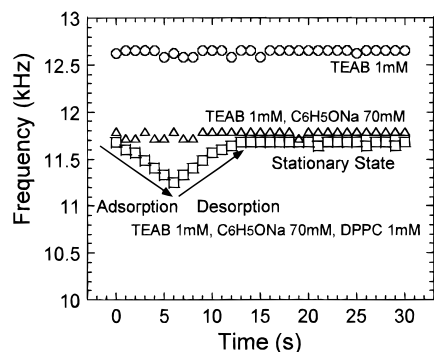


Figure 5. Time courses of capillary wave frequency after an injection of TEAB solution (1mM) at 283 K.

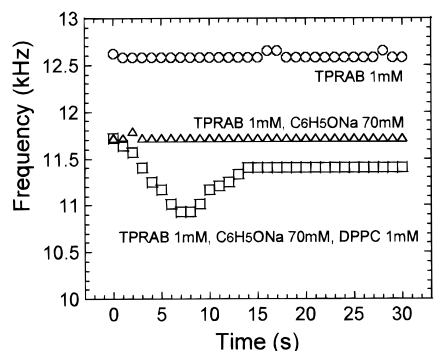


Figure 6. Time courses of capillary wave frequency after an injection of TPRAB solution (1mM) at 283 K.

function of time in Figures 5, 6, and 7, respectively. In these figures, no changes in capillary wave frequencies were observed. This indicated that $R_4N^+Br^-$ molecules were not adsorbed alone onto the interface. Our measurements showed that C_6H_5ONa molecules were present at the interface, whereas $R_4N^+Br^-$ molecules were in the bulk phase at 283 K.

Capillary wave frequencies after the injection of the TEAB, TPRAB, and TBAB solutions into the water phase containing C_6H_5ONa are also plotted in Figures 5, 6, and 7, respectively. No changes in the frequencies after the injection were observed. This suggests the two following possibilities. One is that interfacial C_6H_5ONa does not react with $R_4N^+Br^-$ under such conditions. The other is that interfacial C_6H_5ONa reacts with $R_4N^+Br^-$ and forms ion pairs $R_4N^+C_6H_5O^-$ at the interface, but this formation of ion pairs does not affect the capillary wave frequency.

As shown at 0 s in Figures 5, 6, and 7, the capillary wave frequencies at the interface between the W phase containing C_6H_5ONa and the NB phase containing DPPC were the same as those at the interface between the W phase containing C_6H_5ONa and the NB phase without DPPC. This indicates that the DPPC molecules were not adsorbed at the interface and the reaction between C_6H_5ONa and DPPC did not proceed without the phase transfer catalyst. On the other hand, when the phase transfer catalyst ($R_4N^+Br^-$) was injected into the interface between the W containing C_6H_5ONa and the NB containing DPPC, the capillary wave frequencies decreased gradually. After attaining their minimum, they increased gradually and then became constant after 8–15 s. As shown within the dotted line rectangle of Figure 8, the decrease in frequency corresponded to the adsorption of $R_4N^+Cl^-$ onto the interface and the increase corresponded to the desorption from the interface, because the change in frequency was observed only when DPPC was added. The times when the frequencies attained their minimum and became constant are summarized in Table 1. The time of the

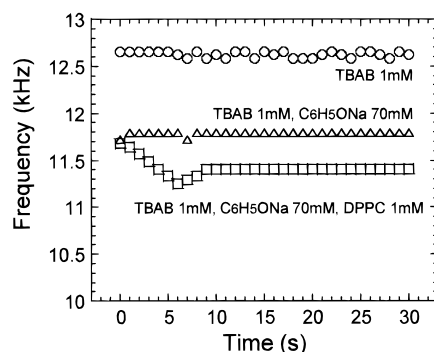


Figure 7. Time courses of capillary wave frequency after injection of TBAB solution (1mM) at 283 K.

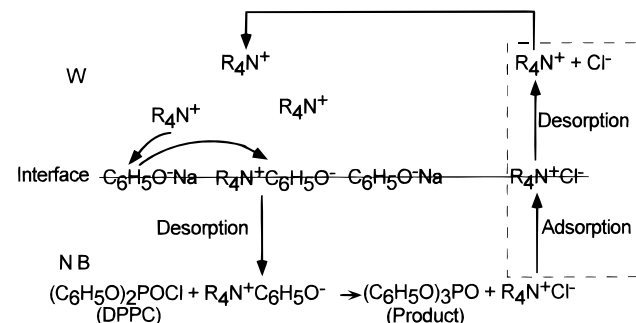


Figure 8. Reaction scheme that corresponds to the decrease and increase in capillary frequency.

TABLE 1: Time of the Minimum and Stationary State Frequencies and the Change of Frequency of $R_4N^+Br^-$ Estimated in This Study

	TEAB	TPRAB	TBAB
time of minimum frequency	6 s	7 s	6 s
time of stationary state frequency	13 s	14 s	9 s
Δf (adsorption) (kHz)	0.43	0.78	0.43
Δf (desorption) (kHz)	0.43	0.47	0.16
ratio of adsorption onto the interface of stationary state (%) (Δf (adsorption) – Δf (desorption))/ Δf (adsorption)	0	40	64

minimum frequency was almost the same regardless of the phase transfer catalyst, whereas the frequency of TBAB became constant much faster than the other two. This meant that the adsorption rates of $R_4N^+Cl^-$ were almost the same for the three phase transfer catalysts, whereas the desorption behavior of the TBAB ion pair differed from that of the other two. This suggested that the desorption rate of the TBAB ion pair was very low and the stationary state could be established quickly at high interfacial molecular density. Furthermore, the ratio of interfacial adsorption of the stationary state is defined and summarized in Table 1. This parameter reflects the amount of interfacial adsorbate of the stationary state. This result indicated that the interface accommodated the most adsorbate in the cyclic reaction of TBAB. In short, the TBAB ion pairs were difficult to desorb from the interface to the W phase, and thus many interfacial adsorbate molecules were present for the stationary state. This behavior of TBAB was considered to be related to the high product yield as a phase transfer catalyst.

Based on the experimental fact that the high interfacial molecular density of TBAB ion pair was related to the high product yield, we considered that the interface was the reaction site controlling the phase transfer catalytic reaction. Thus, we proposed a model for the phase transfer catalytic reaction in the stationary state. It is shown within the dotted line rectangle of Figure 9. This model is a further explanation for our previous

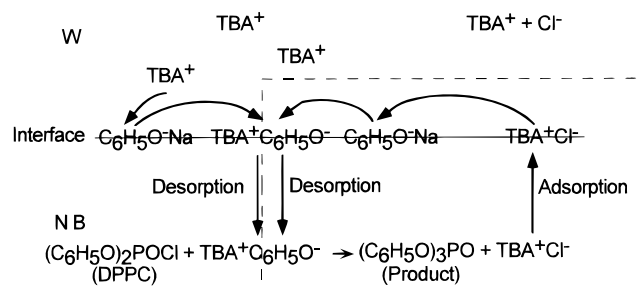


Figure 9. Model of the phase transfer catalytic reaction in the stationary state. Reaction proceeds between the adsorbed chemical species at the interface after adsorption from the water phase.

study, which demonstrated the interfacial reaction of TBAB below 50 mM.⁷

Our results reflected an interfacial specificity for a chemical reaction and mass transfer. We successfully observed dynamic molecular behavior reflecting the interfacial specificity by focusing on the phase transfer catalyst system using the time-resolved QELS method. We expect the QELS method will contribute significantly to the development of an interfacial reaction scheme by molecular dynamics at liquid/liquid interfaces.

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