Role of the Liquid/Liquid Interface in a Phase-Transfer Catalytic Reaction As Investigated by in Situ Measurements Using the Quasi-Elastic Laser Scattering Method

YoshikO Uchiyama, Takehiko Kitamori, and Tsuguo Sawada*
Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
Isao Tsuyumoto
Department of Environmental Systems Engineering, Kanazawa Institute of Technology, 7-1 Ohigayaokanonoichi, Ishikawa 921-8501, Japan

Received October 8, 1999. In Final Form: May 15, 2000

The relationship between the concentration of a phase-transfer catalyst, tetrabutylammonium bromide (TBAB), and the rate of its cyclic reaction was investigated using the quasi-elastic laser scattering (QELS) method. TBAB forms an ion pair (TBA$^+$C$_6$H$_5$O$_2^-$) with sodium phenoxydide (C$_6$H$_5$ONa) at the interface. This ion pair moves from the interface to the organic phase where it reacts with diphenylphosphoryl chloride and produces triphenyl phosphate. During this reaction, tetrabutylammonium chloride, which is generated simultaneously with the product, returns to the water phase. An increase in the concentration of the phase-transfer catalyst (TBAB) does not promote the cyclic reaction. The QELS study indicates that this is because some of the TBAB catalyst adsorbs on the interface and disturbs mass transfer of the other chemical species (TBA$^+$C$_6$H$_5$O$_2^-$). Interfacial coverage of the catalyst should be taken into account to find the optimum concentration of the catalyst. This paper shows for the first time that the interfacial catalyst promotes the reaction and at the same time disturbs mass transfer of the other chemical species.

Introduction

The liquid/liquid interface plays 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. Tetabutylammonium bromide (TBAB) is a phase-transfer catalyst, which behaves as a surfactant and activates organic synthesis reactions. For example, a 1 mM TBAB solution lowers the interfacial tension of water and nitrobenzene by 1 mN/m. The concentration of TBAB usually used in the phase-transfer catalysis is around 1 mM, which has been determined empirically. High concentrations of phase-transfer catalysts do not always bring about high product yield; i.e., they have an optimum concentration. The reason of this has not been clarified so far. To clarify the mechanism that determines the optimum concentration of the catalyst, in situ measurement of the interfacial molecular number density at various concentrations is highly desirable.

Many studies have been reported on the behavior of phase-transfer catalysts by conventional batch methods using NMR, UV-visible spectrophotometry, and gas chromatography, etc., where part of the solution is sampled from the bulk phase. These analyses of behavior have been mainly based on information from bulk phase. However, to clarify the behavior, direct measurements of the interface are essential. There are a number of studies using interfacial tension measurements that have provided useful information on the interface; in them, the interfacial tension was measured by the Wilhelmy method, the pendant drop method, etc., which perturb the interface, causing a certain amount of change in the interfacial tension. These methods are thus indirect. However, in situ measurements of liquid/liquid interfaces can provide direct information on interfacial molecular number density during the whole reaction.

We have developed a quasi-elastic laser scattering (QELS) method and have reported on the dynamics of mass transfer of surfactants at the water/nitrobenzene

10.1021/la9913295 CCC: $19.00 © 2000 American Chemical Society
Published on Web 07/14/2000
Experimental Section

Principle. The principle of the QELS method has already been described.20-24 In brief, an incident laser beam normal to the interface is scattered quasi-elastically with a Doppler shift by the capillary wave. The scattered beam is optically mixed with a local beam produced by a diffraction grating to generate an optical beat in the mixed light. The obtained beat frequency is the same as the Doppler shift, i.e., the capillary wave frequency.

Define the capillary wave frequency as

\[ f = \frac{1}{2\pi} \left( \rho_w \right)^{1/2} \frac{\gamma}{k} \]

The capillary wave frequency is approximately given by Lamb's equation, 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. The capillary wave frequency is in proportion to the square root of the interfacial tension \( \gamma \). The relative change of the number density \( \Gamma \) is inversely proportional to the interfacial tension \( \gamma \) by Gibb's equation. The relative change of the number density \( \Gamma \) can be estimated from the change in the capillary wave frequency. The error of interfacial tension and molecular number density is within 10%. This was estimated from the deviation between the conventional direct measurement and that from the QELS method. It is well-known that the interfacial tension depends on methodologies of the measurement.20-24 The accidental error of the QELS method is within 1%. We have reported previously about this.21,22

Apparatus. A schematic diagram of the experimental setup is shown in Figure 2. The beam from a YAG laser (Crystal, Laser, 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 \( \times 10^{-2} \) cm.

The number of transferred ion pairs across the W/NB interface was estimated using absorption spectrophotometry (Shimadzu UV-1600PC). Samples were withdrawn from the water phase in the equilibrated cyclic reaction.

Sample Preparation. The reaction scheme between sodium phenoxy (C6H5ONa) and diphenyolphosphoryl chloride (DPC) in the W/NB system with TBAB is shown in Figure 1. At the beginning of the reaction, TBAB reacts with C6H5ONa to form TBA\(^{+}\)C6H5O\(^{-}\) at the interface below 50 mM. This had been deduced from the results that the ratio of the equilibrium concentrations of the two reactants was not unity.2 Thus, we set the TBAB concentration below 50 mM. This ion pair moves into the organic phase where it reacts with DPC to produce triphenyl phosphate (C6H5O\(_2\)PO). During this reaction, TBA\(^{+}\)Cl\(^{-}\) is also formed and transported into the water phase to react again with C6H5ONa. TBAB activates the production of triphenyl phosphate by circulating between the two phases.

In this study, we focused on the role of the liquid/liquid interface in the phase-transfer catalytic reaction and investigated adsorption behavior of the ion pair at various concentrations of TBAB (1, 25 mM), DPC (0–100 mM), C6H5ONa (0–100 mM), and tetrabutylammonium chloride (TBAC: 0–100 mM). A liquid/liquid interface was prepared by adding 10 mL of mixed aqueous solution of TBAB (Kanto Chemical Co.), C6H5ONa (Aldrich), NaOH, and TBAC (Kanto Chemical Co.) to 10 mL of nitrobenzene containing DPC (Kanto Chemical Co.) 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

The amount of transferred ion pair TBA\(^{+}\)C6H5O\(^{-}\) was estimated from the decrease in the C6H5ONa concentration in the water phase; i.e., the difference between the initial C6H5ONa concentration and that equilibrated in the water
phase was regarded as the amount of the ion pair. The C$_6$H$_5$ONa concentration in the water phase was determined using absorption spectrophotometry. As shown in Figure 2, the amount of TBA$^+$C$_6$H$_5$O$^-$ transferred across the W/NB interface increased with increasing C$_6$H$_5$ONa concentration. On the other hand, the amount of TBA$^+$C$_6$H$_5$O$^-$ transferred was greater when the TBAB concentration was 1 mM than when it was 25 mM. This result indicates that high concentrations of the phase-transfer catalysts do not always bring about high product yield, reflecting the specificity of the liquid/liquid interface as a reaction place. To investigate details about the role of the liquid/liquid interface and the mechanism determining the optimum concentration of the catalyst, the molecular number density was investigated using the QELS method.

First of all, the effect of each chemical species in the reaction system on the QELS spectrum should be clarified. Capillary wave frequencies were independent of the DPC concentration. This indicates that DPC molecules are not adsorbed alone onto the interface. Capillary wave frequencies were also independent of both DPC and C$_6$H$_5$ONa concentrations. This indicates that the reaction between DPC and C$_6$H$_5$ONa does not proceed without the phase-transfer catalyst TBAB. These results agree with earlier works on the phase-transfer catalyst.$^{30,31}$ Figure 3 shows capillary wave frequencies at various concentrations of TBAB and TBAC. The frequency decreased significantly on increasing the concentration of each species and there is no difference in the frequencies between TBAB and TBAC at each concentration. This indicates that TBAB and TBAC molecules are adsorbed onto the interface and the counterion (Br$^-$ or Cl$^-$) does not affect the frequencies. Figure 4 shows calculated molecular number density based on the Lamb's equation and Gibb's equation. On the basis of these results and our previous report,$^7$ we conclude that the QELS is able to monitor adsorption dynamics of TBAB, TBAC, and TBA$^+$C$_6$H$_5$O$^-$ in solutions with different concentrations of TBAB, C$_6$H$_5$ONa, and DPC. Figure 5 shows the capillary wave frequencies for these solutions. There was a great difference in the frequencies between 1 and 25 mM TBAB. For example, when the concentration of C$_6$H$_5$ONa was 0 mM, the frequency for 1 mM TBAB was around 12.8 kHz while that for 25 mM TBAB was around 11 kHz. This showed a big difference in the interfacial molecular number density of TBAB, which was simply due to the difference in concentration of TBAB. Figures 6 and 7 show the interfacial tension and the molecular number density by using Lamb vs and Gibb’s equation, respectively. For 1 mM TBAB, the interfacial molecular number density of TBAB was 0.59 $\times$ 10$^{-10}$ mol/cm$^2$, and for 25 mM TBAB, it was 15 $\times$ 10$^{-10}$ mol/cm$^2$. On increasing the concentration of C$_6$H$_5$ONa, the frequencies for both cases (1 and 25 mM TBAB) decreased monotonically and reached equilibrium at about 50 mM C$_6$H$_5$ONa. This decrease was due to the formation of the ion pair TBA$^+$C$_6$H$_5$O$^-$, as we have reported previously.$^7$ For 1 mM TBAB, the frequency decreased from 12.8 kHz to about 12 kHz, and for 25 mM TBAB, it

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dropped from 11 to 10 kHz. These drops were approximately proportional to the amount of the formed ion pair 
\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \) at the interface. The interfacial molecular number density of 
\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \) for 1 mM TBAB was around \( 8.2 \times 10^{-10} \) mol/cm\(^2\) while that for 25 mM TBAB was around \( 11 \times 10^{-10} \) mol/cm\(^2\) from Figures 6 and 7. Thus despite the great difference in the amount of the 
TBAB adsorbed onto the interface between 1 and 25 mM TBAB, the amount of the formed ion pair 
\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \) was estimated to be almost the same. In short, the amount 
of the TBAB adsorbed onto the interface had hardly any affect on the amount of the ion pair 
\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \), which is significant in phase-transfer catalytic reaction. Combined with the results in Figure 2 that showed high 
concentrations of the catalyst did not always bring about a high product yield, we can discuss this observation 
further.

The qualitative amounts of each chemical species observed in this study are summarized in Table 1. The 
large interfacial concentration of TBAB does not result in increases in interfacial 
\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \) nor in NB phase 
\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \). This is because the liquid/liquid interface plays a double role in this reaction: it acts as the place for formation of the ion pair and as the place for selective 
mass transfer. The interfacial TBAB promotes ion pair formation and simultaneously disturbs mass transfer 
across the interface. Since reaction sites are limited at the liquid/liquid interface in the stationary state, the 
opimum concentration of the catalyst should be determined by taking into account the interfacial coverage, 
adjusting the balance between the rate for ion pair formation and the rate for mass transfer. This suggests 
the need for proposing a new reaction scheme for the liquid/liquid interface. It should be noted that an experimental 
approach to the interfacial reaction can be made only by direct measurements of the liquid/liquid interface, and 
the QELS method would be a powerful tool for such a study. Furthermore, real time monitoring of the mass 
transfer of each molecule used in the present study will give hard evidence of this conclusion and will be shown 
in the future.

In summary, the relationship between the concentration of phase-transfer catalyst, tetrabutylammonium bromide 
(TBAB), and the rate of its cyclic reaction was investigated using the quasi-elastic laser scattering (QELS) method. 
The increase in the concentration of the phase-transfer catalyst (TBAB) did not promote the cyclic reaction. The 
QELS study indicated that this was because TBAB adsorbed on the interface disturbed the mass transfer of the 
other chemical species (\( \text{TBA}^+ \cdot \text{C}_6\text{H}_5\text{O}^- \)). Interfacial coverage of the catalyst should be taken into account to 
find the optimum concentration of the catalyst. It is expected that the QELS method will contribute signifi-
cantly to the development of an interfacial reaction scheme.

LA9913295