

Noncontact and Noninvasive Monitoring of Gas Diffusion from Aqueous Solution to Aprotic Solvent Using the Optical Beam Deflection Method

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The optical beam deflection method has been applied to noncontact and noninvasive monitoring and analyzing of gas diffusion process from an aqueous solution into an aprotic solvent. Oxygen and carbon dioxide, which are in situ generated by chemical reactions in aqueous solutions above aprotic solvents, have been used as model gases. Both the model gas and the reaction heat diffuse from the aqueous solution to the aprotic solvent and thus generate a concentration gradient and a temperature gradient. Both the concentration gradient and the temperature gradient induce optical beam deflections. Since the thermal diffusion is faster than the mass diffusion, the reaction heat-induced beam deflection signal appears earlier than the concentration gradient-induced one. A simple diffusion model has been used for analyzing the diffusion process. The diffusion coefficient of the model gas in the aprotic solvent can be estimated simply from the beam deflection signal. The diffusion coefficients of O₂ in CCl₄, CH₂Cl₂, C₂H₄Cl₂, and CS₂ have been obtained. The method is expected to be particularly useful for those diffusion processes where other methods are not applicable.

Introduction

It is well-known that diffusion is a basic and fundamental problem in physical, chemical, and biochemical processes. For example, ion diffusion across cell membranes are closely connected with many cellular phenomena.^{1,2} Oxygen diffusion from atmosphere to water plays an important role in aquatic ecosystems.³ Also, diffusion of chemical species across the interface of two different phases is the basis of the separation techniques such as extraction⁴ and chromatography.⁵ Therefore, monitoring of the diffusion process is very important. Various methods have been employed for monitoring and analyzing the diffusion processes. Electrochemical methods based on electrochemical reactions on electrodes have been used to determine the diffusion coefficients of ions in aqueous solution and polymer films.^{6,7} A quartz-crystal microbalance based on mass change has been used to study the diffusion and permeation of water into organic films.^{8,9} Spectroscopic methods can also be applied for monitoring the diffusion processes, where a spectroscopic change such as absorbance change¹⁰ or fluorescence change¹¹ is accompanied. However, these methods seem to be difficult for monitoring the diffusion process of a gas such as oxygen in an aprotic solvent, since neither is the electrochemical reaction easily carried out in the aprotic solvent nor does remarkable mass change and spectroscopic change occur in the diffusion process.

The optical beam deflection (OBD) method,^{12,13} based on the mirage effect, is a well-known noncontact and noninvasive analytical method, which can be applied to a physical or chemical system where a refractive index gradient is produced. Since the refractive index of a substance is a function of temperature, it has been used for probing a temperature gradient, which is generated by either the nonradiative relaxation of photon energy absorbed by molecules^{14,15} or reaction heat released from a chemical reaction.^{16–21} It also has been used

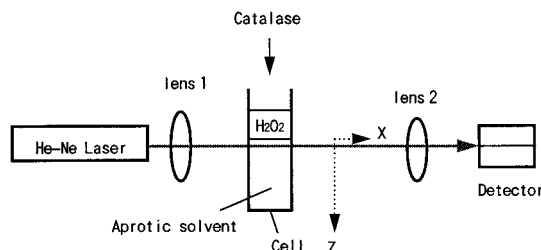


Figure 1. Illustrations of the experimental setup. The dotted arrows express the coordinate axis.

for probing a concentration gradient generated in an electrode/solution interface,^{22–26} flow injection systems,^{27–29} and capillary electrophoresis.^{30,31} The concentration gradient-induced OBD method has been used for evaluating the diffusion coefficients of some electrolytes in aqueous solutions.^{25,26} The transient signal of the concentration gradient-induced OBD has been used for separating large and small species, such as sucrose and poly(acrylic acid), since they have different diffusion coefficients.³² In this work, we have attempted to apply the OBD method for monitoring and analyzing the gas diffusion process from aqueous solution to aprotic solvents, such as carbon tetrachloride. Oxygen and carbon dioxide have been used as model samples of gas. It has been demonstrated for the first time that the diffusion process of gas from aqueous solution to organic solvent could be monitored and analyzed by the OBD method.

Experimental Section

Figure 1 illustrates the experimental setup, and it was similar to those employed in the reaction heat-induced OBD experiments.^{16–21} A He–Ne laser (wavelength 632.8 nm, output power 0.5 mW) provided the probe beam. The probe beam was focused to a cell by lens 1 (focal length 20 cm). The deflected probe beam was focused to a bicell photodiode by lens 2 (focal length 3 cm). The bicell photodiode was used as a deflection detector.³¹ The outputs of the detectors were put

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into a digital multichannel multimeter (SC7502, Iwatsu, Japan), and the data were recorded and treated in a personal computer. A glass tube (length 7 cm; i.d. 2.0 mm; o.d. 4 mm), whose one end was sealed, was used as the cell. The cell was placed on a *X-Y-Z* stage for adjusting the position at which the probe beam was passed through.

Oxygen was generated by the decomposition reaction of H_2O_2 catalyzed by enzyme catalase. Carbon dioxide was generated by the neutralization reaction between HCl and Na_2CO_3 . Catalase (activity unit 19 900 units/mg) was dissolved into phosphorus buffer (pH 7.0); its concentration was 1 mg/mL. The concentration of H_2O_2 was 0.2 mol/L. In the experiments, 150 μL of aprotic solvent such as CCl_4 , which was saturated with water beforehand, was first introduced into the cell by a syringe. Then 20 μL of water was added into the cell. The water was above the CCl_4 since it was lighter than the CCl_4 . After the baseline of the beam deflection signal was stable, 5 μL of H_2O_2 solution was introduced into the water phase above the organic solvent by a microsyringe. Finally, 2 μL of catalase solution was introduced into the water phase for catalyzing the decomposition reaction of H_2O_2 . In the introduction of the samples, both H_2O_2 and catalase solutions were strongly pushed out from the microsyringe, so that a convection was generated in the water phase to ensure the sufficient mixing of the reactants. In the experiments of the diffusion of CO_2 , 5 μL of 0.1 mol/L Na_2CO_3 solution was first added into the water phase. Then, 2 μL of 5 mol/L HCl solution was introduced into the water phase for generating CO_2 .

Catalase was from Sigma. All other chemicals were from Kantou Kagaku (Japan). Deionized water was used in the experiments. All experiments were carried out at room temperature (about 20 $^\circ\text{C}$). No special control of temperature was done in the experiments.

Results and Discussion

The concentration gradient-induced OBD signal θ is expressed as follows^{22,23}

$$\theta = (l/n)(\partial n/\partial c)(\partial c/\partial z) \quad (1)$$

where l , n , $\partial n/\partial c$, and $\partial c/\partial z$ are path length of the probe beam, refractive index of the organic solvent, concentration-dependent coefficient of the refractive index, and the concentration gradient, respectively. In a certain range of concentration, $\partial n/\partial c$ is usually approximated as a constant.^{22–26} Then, eq 1 indicates the deflection signal is proportional to $\partial n/\partial z$.

Any diffusion process will deplete and disperse a concentration gradient, and thus induce a change in OBD signal. In preliminary experiments, the baseline of the OBD signal was found to be unstable for a long time, if water was added above an aprotic solvent directly. This might be due to the diffusion of water since water dissolves a little in the aprotic solvent. Also, the initial concentrations of oxygen in water and the solvent, which are in equilibrium with the atmosphere, are different. Therefore, the contact of water and the aprotic solvent will induce their diffusion to each other. In order to investigate the diffusion of the model gases from water to the aprotic solvent, the aprotic solvent is saturated, and in equilibrium with water beforehand.

The simplest method to generate the model gases in water phase above the aprotic solvent might be the bubbling of the gases into water directly. However, the bubbling causes

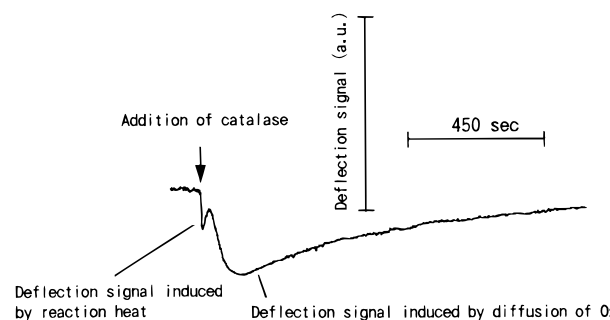


Figure 2. Typical deflection signal for the decomposition reaction of H_2O_2 occurred above a CCl_4 phase. The distance between the probe beam and the water/ CCl_4 interface was 1.5 mm.

disturbance of the water/aprotic solvent interface. Also, it is difficult to control the concentration of gas in the water. Here, chemical reaction methods are used for in situ generating the model gases. The chemical reactions for generating O_2 and CO_2 are as follows, respectively.

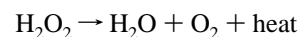


Figure 2 shows a typical OBD signal for the decomposition reaction of H_2O_2 occurring above a CCl_4 phase. Two peaks appear in the deflection signal. The first is the deflection signal induced by the reaction heat,^{16–20} which has been analyzed elsewhere.²¹ The second is induced by the concentration gradient of O_2 . When the decomposition reaction of H_2O_2 is carried out, reaction heat and O_2 are released simultaneously. A part of them diffuse into the CCl_4 phase, and thus a temperature gradient and concentration gradient are generated in the organic solvent phase. Both the temperature gradient and the concentration gradient induce the refractive index gradients, and in turn induce the deflections of the probe beam. Since the rate of heat diffusion is faster than that of O_2 diffusion, the reaction heat-induced OBD signal is observed earlier than the concentration gradient-induced one. The decomposition reaction of H_2O_2 is a relatively fast reaction, it ends in a few seconds. The slow decay of the beam deflection signals reflects the diffusion processes of heat and O_2 . Therefore, monitoring of the diffusion process is possible by the OBD method.

Furthermore, the diffusion process of the O_2 is analyzed with a simple diffusion model. Here, the decomposition reaction in the water phase is assumed to occur instantaneously and homogeneously, since the reaction rate is much faster than the diffusion rate of O_2 . The heights of the water phase and organic phase were calculated to be about 8.6 and 47.8 mm respectively, which are much larger than the distance between the probe beam and the water/organic solvent interface (0.8–1.5 mm). It is further assumed that the water phase and the organic phase are semiinfinite for the duration of measurements. Then, the diffusion equations of O_2 in water phase and organic phase after the reaction ended are presented as follows:

$$\begin{aligned} \partial C_{\text{wa}}(z,t)/\partial t &= D_{\text{wa}}(\partial^2 C_{\text{wa}}(z,t)/\partial z^2) \\ \partial C_{\text{or}}(z,t)/\partial t &= D_{\text{or}}(\partial^2 C_{\text{or}}(z,t)/\partial z^2) \end{aligned} \quad (2)$$

where t is time and z is coordinate axis as shown in Figure 1; $C_{\text{wa}}(z,t)$ and $C_{\text{or}}(z,t)$ are concentrations of O_2 in water and organic solvent, respectively; and D_{wa} and D_{or} are diffusion coefficients

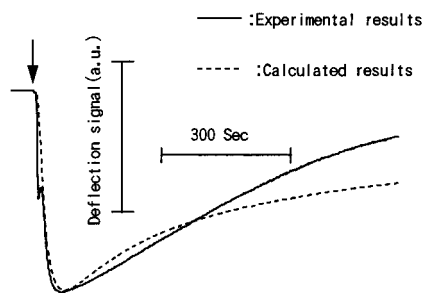


Figure 3. Comparison of the calculated and detected beam deflection signals. The distance z_0 between the probe beam and the interface was 0.9 mm, and the diffusion coefficient D_{or} used in the calculation was $4.5 \times 10^{-5} \text{ cm}^2/\text{s}$.

of O_2 in water and organic solvent, respectively. The initial and boundary conditions are expressed as follows:

$$\begin{aligned} C_{wa}(z, t) &= C_1 & \text{at } t = 0 \\ C_{or}(z, t) &= C_2 & \text{at } t = 0 \end{aligned} \quad (3)$$

and

$$\begin{aligned} k &= C_{wa}(z, t)/C_{or}(z, t) & \text{at } z = 0 \\ D_{wa}(\partial C_{wa}(z, t)/\partial z) &= D_{or}(\partial C_{or}(z, t)/\partial z) & \text{at } z = 0 \end{aligned} \quad (4)$$

where C_1 and C_2 are the initial concentrations of O_2 in the water and organic solvent phases, respectively, and k is the distribution constant of O_2 between the water and organic solvent. The initial concentration C_1 of O_2 in the water phase is the sum of the O_2 dissolved in the water and produced by the decomposition reaction. This diffusion model has been investigated well,³² and the concentration gradient of O_2 in the organic solvent is

$$\partial C_{or}/\partial z = K(D_{or}t)^{-1/2} \exp[-z^2/(4D_{or}t)] \quad (5)$$

where K is a constant determined by such factors as the initial concentrations, diffusion coefficients, and distribution constant. Substituting eq 5 into eq 1, the deflection signal at z_0 (z_0 is the distance between the probe beam and the water/aprotic solvent interface) is expressed as

$$\theta(z_0, t) = K'(D_{or}t)^{-1/2} \exp[-z_0^2/(4D_{or}t)] \quad (6)$$

where K' is also a constant. Equation 6 shows that the shape of the time decay curve of the deflection signal depends on the D_{or} and z_0 .

Figure 3 shows an example of comparison of the experimental result with the theoretical one, which is calculated according to eq 6. In the calculation, D_{or} was also approximated as a constant. The experimental result coincides with the calculated one at the beginning of the diffusion process, and then decays faster than the calculated one. This might be due to the one-dimensional semiinfinite approximation of the two phases (especially for the water phase), and the approximation that the decomposition reaction occurred instantaneously and homogeneously in the calculation model. In practice, the two phases are not semiinfinite. Also, the decomposition reaction could not be an instantaneous and homogeneous reaction, since no rapid stirring operation was added in the cell. Moreover, O_2 produced in the water phase diffused not only to the organic phase but also to air. The diffusion of the O_2 to air would decrease the concentration of O_2 in water phase. Therefore, the practical diffusion of O_2 to organic solvent is faster than the calculated one, where the concentration is assumed to

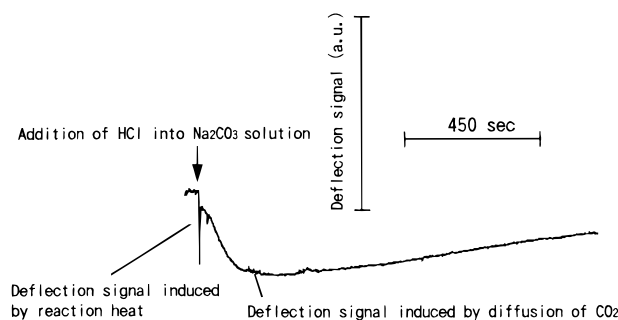


Figure 4. Beam deflection signal for the neutralization reaction between HCl and Na_2CO_3 .

TABLE 1: Diffusion Coefficients of O_2 in Aprotic Solvents

org solvent	diffusion coeff ($\times 10^{-5} \text{ cm}^2/\text{s}$)
CCl_4	4.0–4.5
CS_2	5.1–5.5
$\text{C}_2\text{H}_4\text{Cl}_2$	2.9–3.4
CH_2Cl_2	1.3–1.7

constant and homogeneous. Another factors contributing to the discrepancies between the calculated and experimental results might be the convection in the organic phase, which is also induced by the introduction of the catalase solution.

Time t_{max} , at which the maximum deflection signal appears, is related to the diffusion coefficient as follows:

$$t_{\text{max}} = z_0^2/(2D_{or}) \quad (7)$$

Therefore, the diffusion coefficient D_{or} can be estimated by eq 7.

Diffusion of O_2 from water to other aprotic solvents such as CS_2 , $\text{C}_2\text{H}_4\text{Cl}_2$, and CH_2Cl_2 is also monitored by the method. The time decay curves of the OBD signals in CS_2 , $\text{C}_2\text{H}_4\text{Cl}_2$, and CH_2Cl_2 are similar to that in CCl_4 except that their t_{max} are different. The diffusion coefficients of O_2 in these solvents are calculated, and the results are shown in Table 1. Furthermore, the monitoring of the diffusion of O_2 from water to the aprotic solvents is also carried out for different distance z_0 between the probe beam and the water/organic solvent interface (z_0 is adjusted from 0.8 to 1.2 mm). Nearly the same diffusion coefficients are obtained for the different z_0 . It seems that the diffusion coefficient is largest in CS_2 and smallest in CH_2Cl_2 , for the four organic solvents. The diffusion coefficient of O_2 in CCl_4 is reported as $3.71 \times 10^{-5} \text{ cm}^2/\text{s}$ (at 25°C).³³ The method shows that the diffusion coefficient of O_2 in CCl_4 is $(4.0\text{--}4.5) \times 10^{-5} \text{ cm}^2/\text{s}$ (at about 20°C) (Table 1). Although the diffusion coefficient obtained in the experiments is a little larger than the reported one, it is an appropriate value considering the experimental errors for different methods.

Change in temperature is expected to affect the diffusion coefficient. Since the temperature change in the water phase caused by the reaction heat is very small (about 1°C), its effect on the diffusion process is ignored in the work. In order to obtain more accurate value of diffusion coefficient, improvements in the experimental setup such as speeding up the mixing in the water phase, and use of a more accurate diffusion model in the calculation, are required.

The method is also applicable to other gases. Figure 4 shows an example of the monitoring of the diffusion process of CO_2 from water to CCl_4 . It seems that the diffusion of CO_2 from water to CCl_4 is slower than that of O_2 . Its diffusion coefficient is estimated to be on the level of $2.4 \times 10^{-5} \text{ cm}^2/\text{s}$.

In conclusion, the concentration gradient-induced OBD method is an useful tool for monitoring the diffusion process

of a gas from one liquid phase to another liquid phase. The sensitivity of the method depends on the concentration-dependent coefficient $\partial n/\partial c$, which usually increases with the molecule weight of the sample.³¹ Oxygen and CO₂ used in the experiments belong to small molecular species. Therefore, in principle the method could be applicable to almost all gas samples, as long as the samples and organic solvents would not absorb all of the probe beam. It is expected to be particularly useful for monitoring those diffusion processes, where other methods are not applicable.

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