Coupling of Oscillation with Transport Mediated by Polyoxyethylene *p*-Nonylphenyl Ether in Liquid Membrane System

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(Received June 5, 1997; CL-970427)

Oscillation coupled with transport phenomena occurred in a liquid membrane system containing polyoxyethylene *p*-nonylphenyl ether under the concentration gradient of ethyl alcohol. The solutes of ethyl alcohol and some alkaline metal salts were transported without oscillation but their transport rates were enhanced by the periodical convection synchronous with the oscillation in this system.

Oscillation has been reported in oil-water system and liquid membrane system containing an ionic surfactant.[1-5] Transport phenomena, however, have been more common than oscillation in artificial membrane systems, and the mass transfer coupled with the oscillation was well known.[6] We have investigated the transport characteristics of salt mediated by polyethylene glycol mono-(*p*-nonylphenyl) ether (POE), a nonionic surfactant, which has characteristics of an open-chain crown compound and complexes with metal ions selectively.[7] The oscillation of electric potential has been reported for the membrane system containing an ionic surfactant but we observed the oscillation in the liquid membrane containing a non-ionic surfactant, POE. In this paper, we will report the experimental conditions affecting on the oscillation and the coupling of the oscillation with the transport of solutes in this liquid membrane system.

A liquid membrane system was consisted of 1,2-dichloroethane phase (phase II) containing 100 mM POE (1 M = 1 mol L^{-1}), whose ethylene oxide unit was 20, and two water phases (phases I and III). The solution of each phase was injected by a micro syringe into a straight glass tube with an inner diameter of 1.5 mm as shown in Figure 1. The volume of membrane phase was 20 μL, and each volume of water phase was 50 μL. One of the water phases contained 5.0 M ethyl alcohol (phase I), and the other is pure water (phase III) unless otherwise stated. The potential differences between the two water phases or between one of the water phases and the membrane phase were measured using salt bridges, Ag/AgCl electrodes, and an electrometer (Toho Technical Research, 3120A). The salt bridges were saturated KCl-agar packed in a Teflon tubing with 1.25 mm outer diameter and 0.65 mm inner diameter. The amplitude and the frequency of the oscillation recorded on a recorder (Nippon Denshi Kagaku, U-226) were shown as the average values of 10 pulses at a certain time.

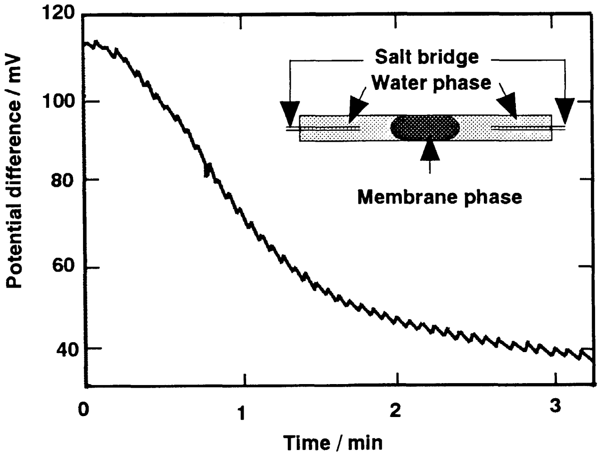

Figure 1. Experimental apparatus and typical oscillation; source phase, 5.0 M ethyl alcohol; membrane phase, 100 mM POE in 1,2-dichloroethane; receiving phase, pure water.

For the determination of the solutes in water phase, the sample solution of 20 μL was collected from the tube by a micro syringe, and the transport experiment was quitted after the sample collection. The transport experiments were carried out in a same condition simultaneously in some tubes to obtain the data of the concentration change with time. Ethyl alcohol was determined by a gas chromatograph (Shimadzu GC-9A) with 3 mm x 1 m column packed with Porapack N. The transport characteristics of some salts of alkaline metal ions were also measured by the determination of the ions in water phase using a flame emission spectrophotometer (Shimadzu AA-6700).

The potential differences were measured between one of the two water phases and the membrane phase and compared to each other. The oscillation occurred at the interface between phase I and II, and a convective flow synchronizing with the oscillation also occurred in the phase I adjacent to the membrane phase. The periodical movement of the membrane interface was reported to be synchronous with the oscillation.[8] The oscillation occurred without POE in liquid membrane, although it became periodical by the addition of POE in the membrane phase. It was reported that the electrical double layer formed at the interface of the liquid membrane containing some surfactant was disordered periodically by Marangoni effect.[2-4] The oscillation did not occur without ethyl alcohol or some other organic solvent in the source phase. The amplitude and the frequency depended on ethyl alcohol and POE concentrations. A typical

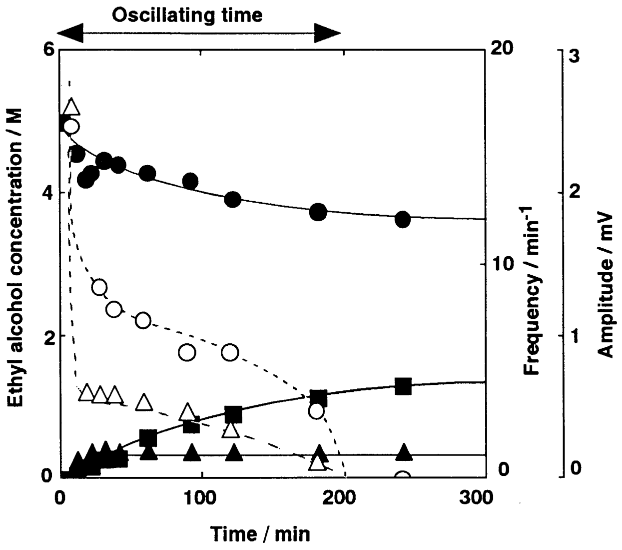

Figure 2. Amplitude (△) and frequency (○) of potential oscillation and ethyl alcohol concentration change in source phase (●), membrane phase (▲), and receiving phase (■); source phase, 5.0 M ethyl alcohol; membrane phase, 100 mM POE in 1,2-dichloroethane; receiving phase, pure water.

oscillation measured between the two water phases was shown in Figure 1. The reproducibility of the oscillation was higher in the straight glass tube with a small inner diameter than that in U-shaped glass tube used commonly in the oscillation experiment because of the decreasing interface area.[9]

Ethyl alcohol was transported in this oscillation system from phase I to phase III across membrane phase as shown in Figure 2. The concentration change was large and the oscillation was vigorous at the initial period of this experiment. After about 200 min in this condition, the oscillation finished, although there was no concentration equilibrium between two water phases and the transport of ethyl alcohol continued. The flux of ethyl alcohol was large in the duration of the oscillation.

It was reported that alkaline metal ions were selectively transported by POE[7] and then, the effect of the oscillation on the salt transport was investigated. Figure 3 shows the effect of the receiving phase concentration of ethyl alcohol on the transported amounts of potassium chloride and ethyl alcohol and the duration of the oscillation. In this experiment, the initial composition of the source phase was the same to each other, and the amplitude and the frequency did not depend on the concentration in the receiving phase, although the duration of the oscillation decreased with the decrease of the concentration difference between the source phase and the receiving phase. The transported amount of not only ethyl alcohol but also potassium chloride decreased with decreasing the duration. When ethyl alcohol concentration in the receiving phase was 5 M, ethyl alcohol was transported in the opposite direction for the salting out effect, although there was no concentration difference of ethyl alcohol. In this system, there was no mechanical stirring, and the diffusion rate was very slow. The flux of potassium chloride was over three times larger in the duration of the oscillation than that after the duration. The enhancement of the transport was caused by the periodical convection which was synchronous with the oscillation.

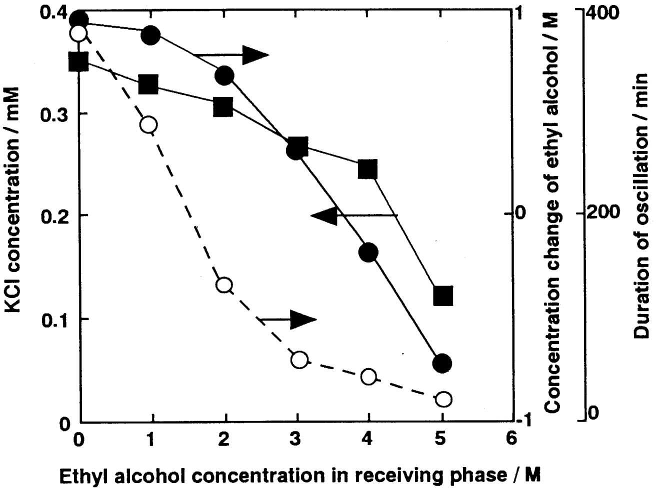

Figure 3. KCl concentration (■) and concentration change of ethyl alcohol (●) in receiving phase after transport experiment of 200 min and duration of oscillation (○) vs. ethyl alcohol concentration in receiving phase; source phase, 0.1 M KCl and 5.0 M ethyl alcohol; membrane phase, 100 mM POE in 1,2-dichloroethane; receiving phase, pure water.

It is ascertained that the solute was transported without oscillation but its transport rate increased during the duration of oscillation.

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