Electrical Potential Oscillation in an Anionic Surfactant System with Barbitone in Octanol as an Oil Phase

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Studies were made on oscillations across a liquid membrane consisting of an oil layer, octanol containing barbitone, between two aqueous layers: one containing 8 mM SDS with alcohol and the other containing 0.1 M NaCl. The effects of various concentrations of chemical components in this system on the patterns of electrical oscillation were examined. The oscillations may be explained by the mechanism of repetitive formation and destruction of monolayer structures of the dodecyl sulfate anion at the interface between the organic and the aqueous phases, with the effect of proton penetration. This study of potential oscillation across a membrane containing a drug provides the possibility of further investigations in pharmacological activity.

INTRODUCTION

Recently, there have been considerable theoretical and experimental efforts in the investigation of the oscillatory phenomena in liquid membranes. As the need for further insight into the nature of the dynamic aspect of living organisms increases, research on liquid membrane oscillation is becoming progressively more significant [1-6]. The interest in the spontaneous fluctuation in a liquid membrane as a model of the excitation of a biological system is due to the fact that biological rhythms in health and disease can be utilized for diagnostic purposes. In addition, drugs that alter the properties of bio-membranes have an effect on the potential mode of oscillation.

Yoshikawa *et al*. [4] observed spontaneous oscillation of the electrical potential across the liquid membrane of a water/nitrobenzene/water system, which consists of two

aqueous solutions lying on top of an organic solution in a U-shaped glass tube. Most liquid membrane-oscillating systems use nitro-organic compounds as the organic medium. We used 1-octanol as an organic solvent with a specific gravity less than that of water [5] to establish a more stable membrane and oil-water (o/w) interface with high reproducibility of the shape and area of the interface. Octanol is regarded as the most important index of water- and oil-solubility of the organic compounds in the living body. We also developed a corresponding apparatus for measuring potential oscillation. The experimental set-up we designed is simple with an H-shaped cell and a pair of Pt electrodes.

In previous studies, both cationic and anionic surfactants in the water phase were found to give rise to rhythmic oscillations [6,7]. However, each of those systems requires its respective organic acid or organic base in the oil phase. A survey of literature indicated that no oscillation was observed when using an anionic surfactant in the presence of an organic acid [8]. In the present work, an octanol membrane consisting

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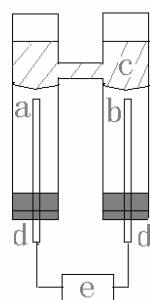* Corresponding author: E-mail: jzgao@nwnu.edu.cn

Fig. 1. Experimental set-up: (a) aqueous phase with SDS and Ethanol (w1 phase); (b) aqueous phase with electrolyte (w2 phase); (c) organic phase; (d) Pt electrode; (e) CHI-832 electrochemical analyzer.

of an octanol solution of the sedative drug barbitone (US barbital) interposed by an aqueous electrolyte solution and an

aqueous solution containing sodium dodecyl sulfate (SDS) and ethanol does display oscillation of electrical signals.

Earlier papers generally focused on the effect on the oscillating amplitude of a drug in one of the aqueous phases [5], but rarely on the effect with the drug in the oil phase. In this report, barbitone has been placed into organic phase to investigate the influence of drugs in a membrane.

EXPERIMENTAL

The experimental set-up used is shown in Fig 1. The cell consisted of two glass tubes, 18 mm in diameter and 100 mm in length, and a glass tube, 4 mm in diameter and 10 mm in length. The two larger vertical tubes were connected by a smaller, horizontal one, forming an H-shaped cell. A Pt
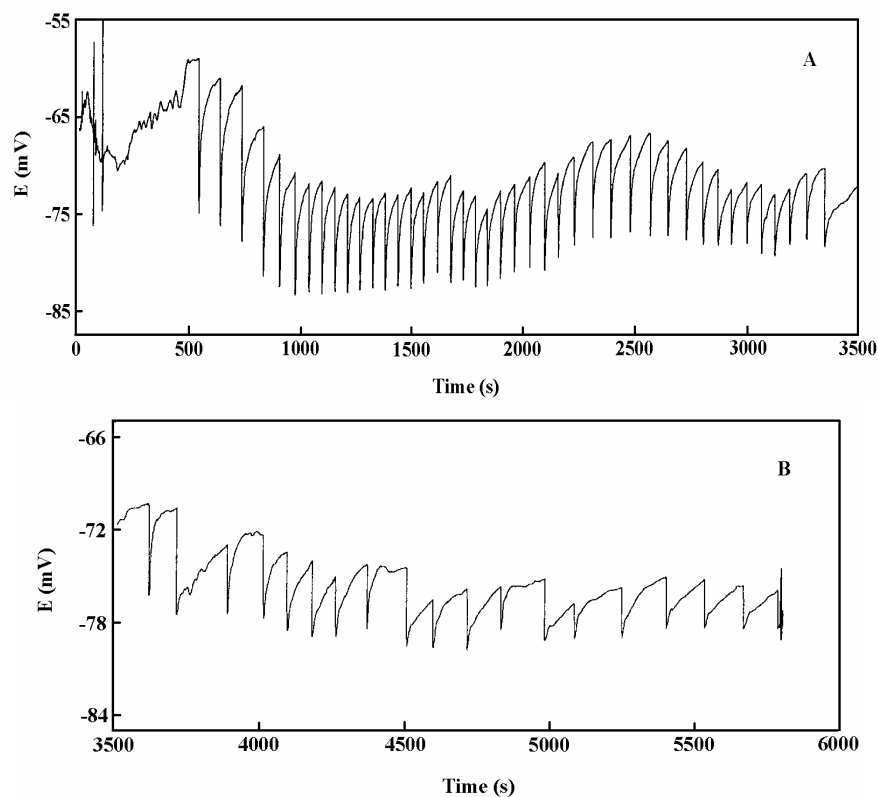

Fig. 2. Oscillations of electrical potential between the two aqueous phases: w1 and w2 (w1 = 8 mM SDS + 10% (v/v) ethanol; w2 = 0.1 M NaCl; organic phase = 10 mM barbitone in octanol). (A) High-frequency oscillation, (B) Low- frequency oscillation.

electrode was inserted into each aqueous phase to measure the electric potential.

All chemicals used were of analytical-reagent grade without further purification. Doubly distilled deionized water was used throughout.

Eight milliliters each of the aqueous solution containing sodium dodecyl sulfate and 10% (v/v) ethanol, and the aqueous solution containing 0.1 M NaCl was first introduced into the bottom of each arm of an H-shaped cell to form w1 and w2 phases. The surface of each aqueous solution was even with the lower side of the horizontal glass tube connecting the two vertical glass tubes. Eight milliliters of an octanol solution containing 10 mM barbitone was carefully layered onto the top of the aqueous solution to form an organic phase. The two Pt electrodes were connected to a CHI-832 electrochemical analyzer (Shanghai Chenhua Instrumental Company, China) to monitor the electrical potential between the two aqueous phases over time. All measurements were performed at 20 °C.

RESULTS AND DISCUSSION

Figure 2 shows the electrical oscillation across the liquid membrane. An obvious potential oscillation with pulses in the negative direction started after an induction period (from the time of the solution contact to that of the first pulse). This high-frequency oscillation was sustained for about 60 min (Fig 2a), followed by a low-frequency oscillation (Fig. 2b).

Effect of the electrode/interface distance

Different profiles of the oscillation depend on the experimental conditions, such as the boundary of the interface [9], the positions of the electrodes [10], and the electrode/interface distance. The potential oscillation across a liquid membrane is generally the simultaneous result of the oscillations at interfaces o/w1 and o/w2. The oscillation patterns with equal distances from the interface to electrode in the two aqueous phases are different from those with unequal distances [7]. Figure 2 shows the potential oscillation when both electrodes were placed 2 mm from the interfaces. The oscillation appears to have had an induction period of 500 s, and amplitude (difference between higher and lower pulse potentials) of about 10 mV. However, when the electrode in the aqueous phase without surfactant was 2 mm from the
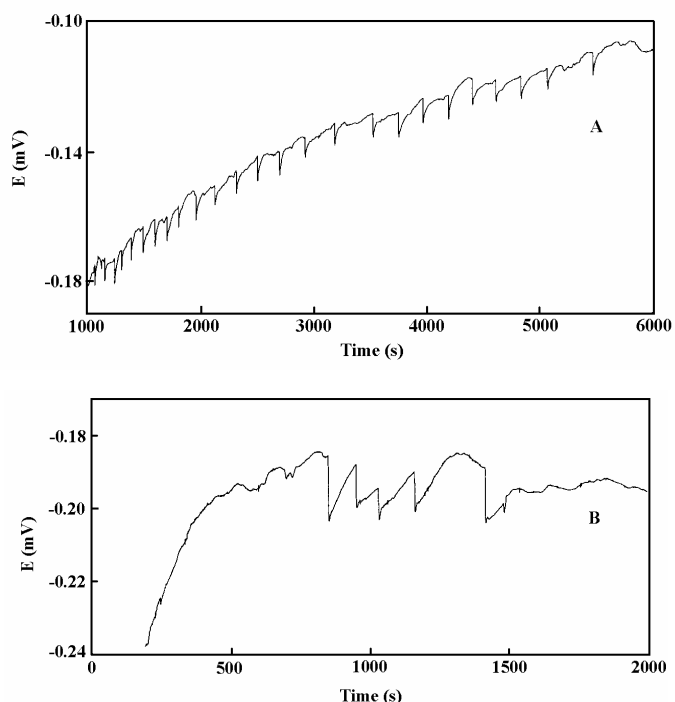

Fig. 3. Oscillations of electrical potential difference between two aqueous phases: Electrode-w1/interface and electrode-w2/interface. (A) 1 cm-2 mm, (B) 2 mm-1 cm.

interface and the surfactant phase electrode was 1 cm from the interface (Fig. 3a) the oscillation began after a shorter induction period and had smaller amplitude. The potential of the base line gradually increased over time. Furthermore, when the surfactant phase electrode was 2 mm from the interface and the other electrode was 1 cm from the interface (Fig. 3b), no regular oscillation was observed.

Effect of variables concentration

To understand the roles of the surfactant, ethanol and organic substrates, the manner of electrical oscillation across the liquid membrane with variation of these chemical compounds was examined.

(1) No obvious potential oscillation could be observed without surfactant. Moreover, the regular oscillation disappeared when the SDS concentration was less than 8
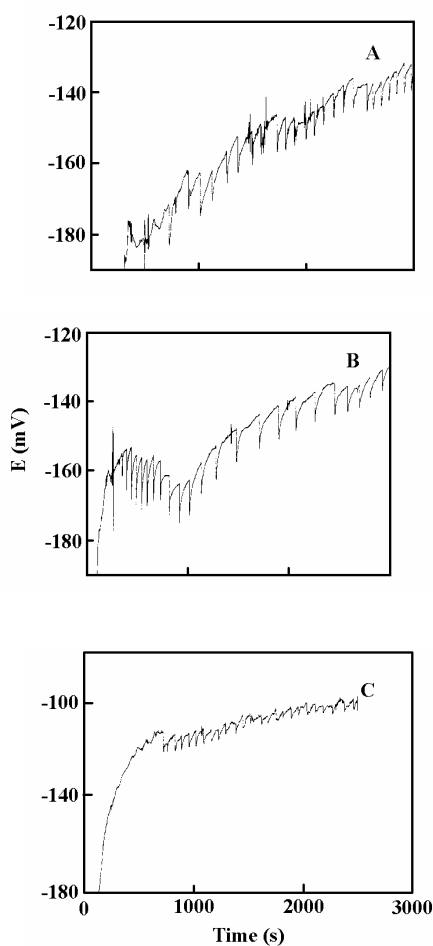
Fig. 4. Oscillations of electrical potential with   different concentrations of ethanol in the w1 phase: (A) 5% (v/v), (B) 10% (v/v), (C) 15% (v/v).

Fig. 5. Oscillations of electrical potential with different concentrations of barbitone in the organic phase: (A) 0 mM; (B) 5 mM; (C) 8 mM; (D) 10 mM.

m mol l^{-1}, which   is the critical micelle concentration (CMC) of SDS in water. When the concentration of SDS is above 8 mmol l^{-1}, the surfactant ions aggregate to form an adsorption layer at the o/w interface.

(2) It is well known that alcohols decrease the CMC of surfactant in water because the incorporation of the alcohol into the micelle changes the manner of aggregation of the amphilic molecules. Alcohols that affect the structure of the monolayer on the interface also influence the rate of migration of DS anions from the interface to the organic phase [11]. Therefore,   oscillation   profiles   changed   with   different concentrations of ethanol in the w1 phase (Fig. 4).
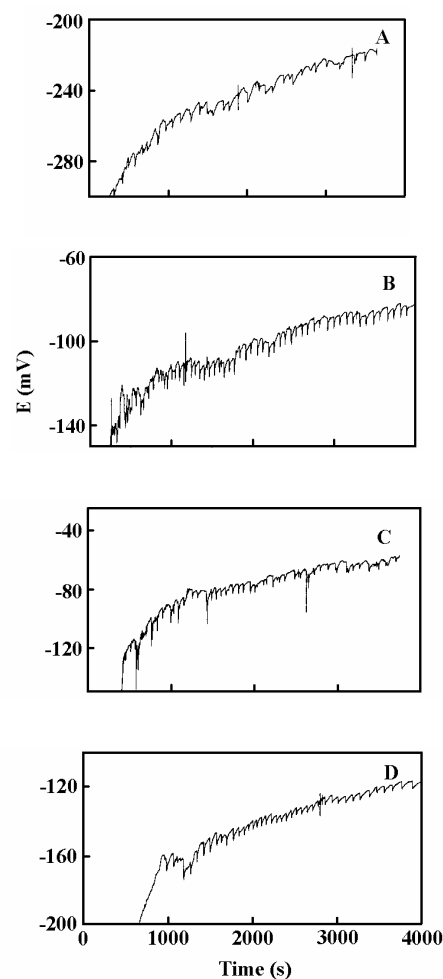
(3) Potential oscillation across the liquid membrane is ascribed to the periodic formation and destruction of the monolayer of surfactant molecules. Generally, an organic base of suitable strength is necessary for oscillations in the presence of the anionic surfactant because of their corresponding interaction. However, barbitone, a weak acid, affects the generation of oscillation in this system, which contained SDS as anionic surfactant. As shown in Fig .5, irregular potential oscillation was observed at 0 mM barbitone, but the   increase

of barbitone concentration leads to regular oscillation and an increase in amplitude and frequency.

(4) The characteristics of the oscillation, such as amplitude, frequency, induction period, change with the addition of various chemical species in the aqueous phase without surfactant. The lower and upper potential of the first oscillation were affected by the electrolyte [12]. No regular oscillation was observed without electrolyte in the w2 phase. As seen in Fig. 6, different electrolytes had different effects on the system. This indicated that the potential oscillation is the simultaneous results of both w1 and w2.

Mechanism

Yoshikawa and co-workers [6] reported the electrical oscillatory phenomena at an oil-water interface in the presence of anionic surfactant and corresponding organic base, stating that the mechanism of these phenomena is the consecutive formation and destruction of monolayer structures of the dodecyl sulfate (DS) anion at the interface between the organic and aqueous phases. The key step was the abrupt transfer of DS anions and cations from the aqueous phase to the organic phase with the formation of inverted micelles or water-in-oil microemulsions. Therefore, it seems necessary to use organic base in anionic surfactant systems to attain oscillation. However, in the present study, we observed potential oscillation with an anionic surfactant, SDS, and an organic acid, barbitone.

Shunkichi Sutou and co-workers [13] proposed that the rate of proton penetration is one of the major factors affecting the mode change of the oscillation. Kohji Maeda *et al.* [14] pointed out that the interfacial adsorption of a hydrophilic ion, which had been transferred from the membrane to the aqueous phase, and its desorption closely related to the oscillation.

In this report, protons formed by the dissociation of barbitone in the octanol phase play an important role in this oscillatory system. The possible mechanism for the potential oscillation is as follows: at first, the DS anions, which are present in the w1 phase as micelles, resulting from hydrophobic interaction, gradually align with the o/w1 interface and form a monolayer causing an increase in concentration at the interface. In terms of Langmuir-Hinshelwood kinetics, DS$^-$ adsorb to the free sites (I) of the o/w1 interface, which can be assumed to be a
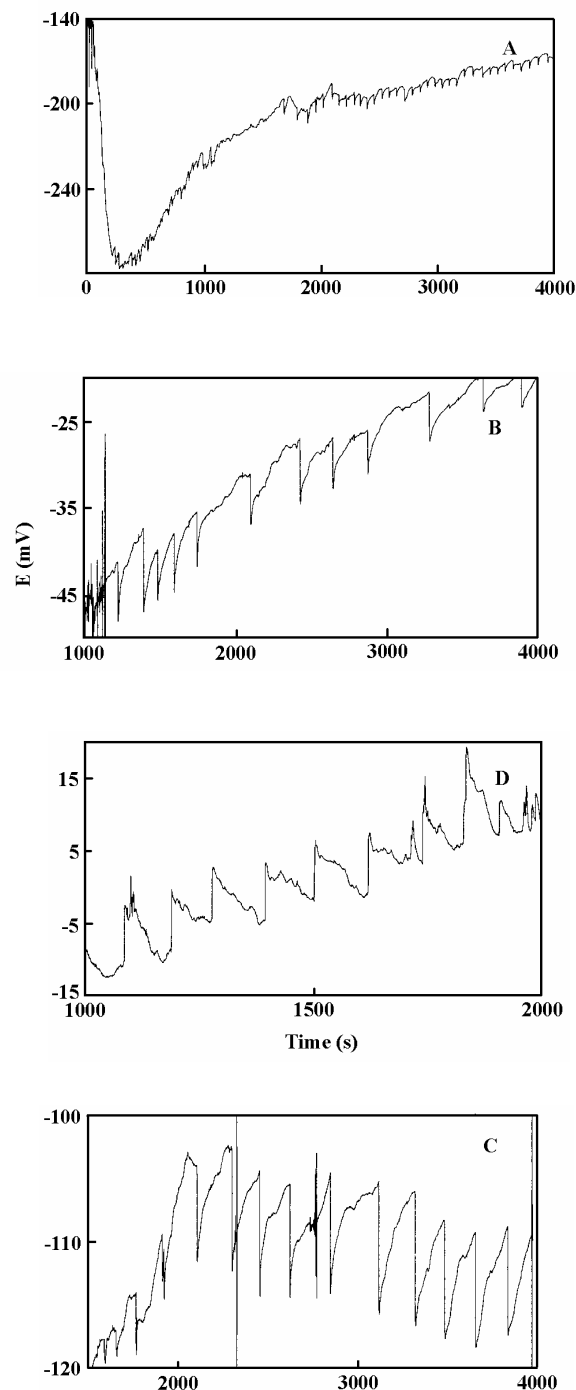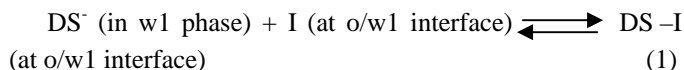

Fig. 6. Oscillations of electrical potential with different electrolytes in the w2 phase: (A) no electrolyte, (B) NaF (0.1 M); (C) KBr (0.1 M); (D) NaI (0.1 M).

diffusion-controlled transport of the surfactant:

DS⁻ (in w1 phase) + I (at o/w1 interface) ⇌ DS –I (at o/w1 interface)   (1)

Considering the similar effect of alcohol molecules tending to intercalate between surfactant molecules that are adsorbed at the oil/water interface [15], ethanol in the w1 phase can affect step 1.

At the same time, barbitone (BH) coming from the organic phase arrives at the vacant sites of the interface forming B-I and H⁺:

BH (in organic phase) + I (at o/w1 interface) ⇌ B-I (at o/w1 interface) + H⁺   (2)
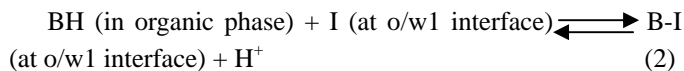
Protons formed by the dissociation of barbitone easily penetrate into the aqueous phases, especially into w1 due to the formation of ion pairs of DS anions and hydrogen:

DS–I (at o/w1 interface) + H⁺ ⇌ DS-H (ion pair compounds) + I (at o/w1 interface)   (3)
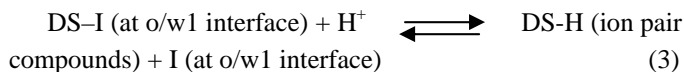
On reaching a critical concentration, ion pair compounds are suddenly transferred to the organic phase where they form inverted micelles. The process obviously repeats itself due to interfacial instability (Marangoni effect: the interfacial flow can be governed by gradients in the interfacial tension driven by local concentrations resulting from mass transfer) between liquid and liquid phases in systems that are far from equilibrium.

A study on the self-oscillatory phenomena in oil-water systems is an extension of nonlinear dynamics, from a theoretical point of view. To gain further understanding of the nature of oscillatory behavior, several mechanisms and kinetic models have been proposed [16,17].

Theoretical considerations on the oscillation of the liquid membrane system hold the promise of increasing understanding of chemical sensors mimicking the sensing mechanism in bio-membranes, and the theory of vacant sites at the interface may be used to develop the selection of various chemical-sensing systems.

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