Oscillatory Phenomena in Systems with Bulk Liquid Membranes*

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Bulk liquid membrane oscillators containing ionic surfactants may be used for modelling the oscillatory behaviour of biological membranes. It has been found that the temperature variation has a strong influence on the oscillation patterns. Not only the regularity and frequency of oscillations have been changed, but also a new type of peaks appeared in the system containing nitromethane with increasing temperature. The influence of the membrane material (organic solvent) and the aqueous phase composition (concentration of surfactant and alcohol) on oscillation characteristics has been examined. No oscillations have been observed without ethanol and surfactant in the donor aqueous phase.

Liquid membranes represent an important tool in separation science [1, 2]. Their success is resulting from their high efficiency and technical simplicity (extraction and reextraction in one step). Liquid membrane technique is applied for precious metal recovery in hydrometallurgy, or for wastewater treatment in environmental protection [1, 2].

A liquid membrane system consists of three immiscible phases (organic and aqueous) in contact. There are three main types of liquid membranes: bulk, supported, and emulsion ones. Recently, for the first two types of liquid membranes nonlinear oscillations of the membrane potential in certain systems containing ionic surfactants were observed [3]. Those systems are extensively studied [4] as a useful model for simulation of the biological membranes action. As a matter of fact, the ion transport through the liquid membrane accompanied by the membrane potential oscillations is closely related to the electrical excitability in living cells. It turned out that the characteristics of these oscillations (frequency, amplitude, and phase) are rather sensitive to various physicochemical factors, *e.g.* it was shown that the addition of other substances to the aqueous phase has a great influence on the membrane oscillatory behaviour. Therefore, the liquid membrane oscillators might be applied as efficient molecular sensors [5, 6].

However, in order to reach this goal the detailed mechanism of the whole phenomenon should be known. Despite the intensive investigations, no definitive conclusions have been obtained since now. For instance, neither the detailed molecular events are completely understood, nor the very place of the oscillation occurrence is clearly established [7, 8].

In this paper, liquid membrane oscillators consisting of three phases, namely donor aqueous phase (d) containing cationic surfactant with ethanol, membrane phase (m) consisting of picric acid in nitrobenzene or nitromethane, and an acceptor aqueous phase (a), sucrose solution, are examined.

The influence of various factors, such as temperature, donor aqueous phase composition, and a nature of organic solvent, on oscillatory behaviour of these bulk liquid membrane oscillators is presented. All systems studied contained a cationic surfactant (hexadecyltrimethylammonium bromide, CTAB, or tetradecyltrimethylammonium bromide, TTAB).

EXPERIMENTAL

All reagents were anal. grade purity (≥ 99 %) commercial products. Solvents were distilled prior their use and picric acid was crystallized from ethanol—water mixture ($\varphi_r = 1 : 2$).

Experiments were performed in an apparatus consisting of a thermostated ($T \pm 0.2$ K) 12-mm inner diameter U-shaped glass tube. At the bottom, the liquid membrane was introduced. In the two branches

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of the glass tube aqueous phases were put simultaneously above the membrane layer. The composition of the three phases in each experimental run was the following:

– liquid membrane (m): 5 cm^3 of picric acid (HA, 1.5×10^{-3} mol dm^{-3}) in nitrobenzene or nitromethane;
– donor phase (d): 4 cm^3 of aqueous solution containing CTAB or TTAB ($0—5 \times 10^{-3}$ mol dm^{-3}) in ethanol (0—2.5 mol dm^{-3});
– acceptor phase (a): 4 cm^3 of aqueous solution of sucrose (0.1 mol dm^{-3}).

The electric potential difference between the two aqueous phases, E, was measured by means of two $Ag/AgCl/Cl^-$ reference electrodes connected *via* salt bridges, using a 1 MΩ input resistance voltmeter controlled by PC (sampling frequency 4 s^{-1}). Electrodes were situated 1 cm far from the aqueous phase – membrane interfaces. Each experiment was repeated at least four times. The reproducibility of oscillation characteristics was fairly good.

RESULTS AND DISCUSSION

The effect of temperature on the oscillation of electric potential difference between the two aqueous phases, E, of the liquid membrane oscillator containing cationic surfactant CTAB in the donor phase and nitrobenzene in the membrane is shown in Fig. 1. At low temperature (291.1 K, Fig. 1*a*), after certain induction time (about 540 s) rather regular oscillations (frequency 1.1×10^{-2} s^{-1}—0.6×10^{-2} s^{-1}) were observed up to 2600 s. At higher temperature (Fig. 1*b*), the induction time was shortened to about 300 s. Regular oscillations range from 600 s to 2100 s with the frequency 1.9×10^{-2} s^{-1} and amplitude of about 260 mV was observed. Then, after about 180 s without oscillation, new, less regular oscillation zone was found which lasted up to the end of experimental run.

Further temperature increase (303.1 K, Fig. 1*c*) had no influence on the induction time of oscillations. However, appearance of oscillation zones of higher, but irregular frequency alternating with zones without oscillations was observed.

When nitromethane was used instead of nitrobenzene as the liquid membrane (Fig. 2), the oscillation pattern was completely different. Higher frequency oscillations without induction period appeared at the beginning. Thereafter, periodic appearance of wide peaks alternating with narrower peaks (Fig. 2*a*) was

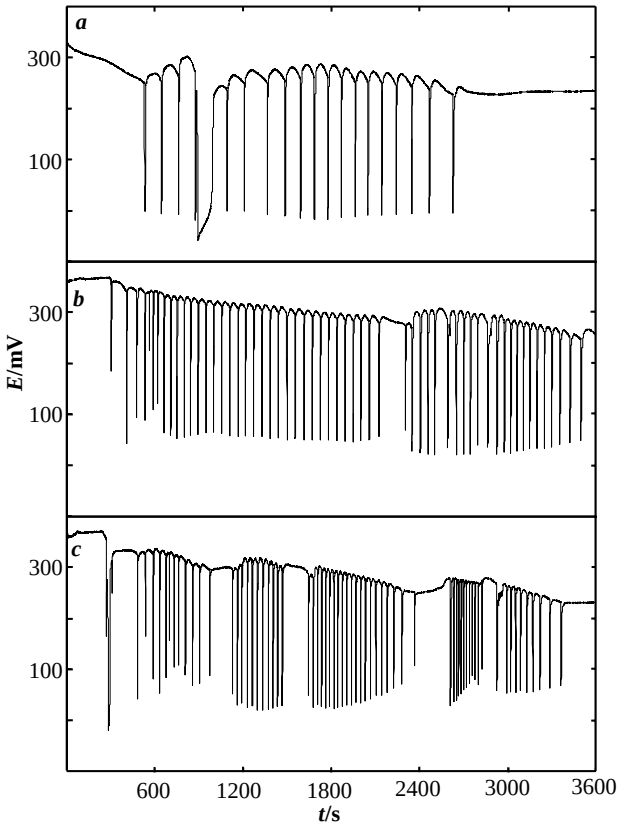

Fig. 1. Influence of temperature on the E oscillation. Membrane: picric acid (1.5×10^{-3} mol dm^{-3}) in nitrobenzene; donor aqueous phase: CTAB (5×10^{-3} mol dm^{-3}) + ethanol (1.5 mol dm^{-3}); acceptor aqueous phase: sucrose (0.1 mol dm^{-3}). *a*) T = 291.1 K; *b*) T = 298.1 K; *c*) T = 303.1 K.

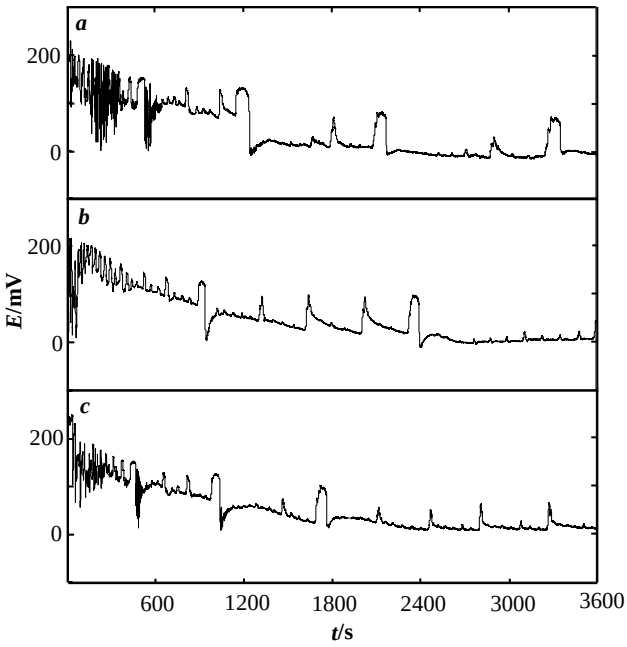

Fig. 2. Influence of temperature on the E oscillation. Membrane: picric acid (1.5×10^{-3} mol dm^{-3}) in nitromethane; donor aqueous phase: CTAB (5×10^{-3} mol dm^{-3}) + ethanol (1.5 mol dm^{-3}); acceptor aqueous phase: sucrose (0.1 mol dm^{-3}). *a*) T = 291.1 K; *b*) T = 298.1 K; *c*) T = 303.1 K.

found. The number of these small peaks increased at $T = 298.1$ K (Fig. 2*b*). At the highest temperature applied during this experiment (303.1 K, Fig. 2*c*), only this type of peaks was observed after 2100 s.

Independently of the liquid membrane oscillatory system studied (nitrobenzene or nitromethane), the temperature variation brought about a significant change in the system oscillatory behaviour. However, the temperature effect for the two systems studied differed due to the different mechanism of surfactant transfer from (d) to (a) aqueous phases.

The oscillatory pattern depended also on the donor aqueous phase composition. Without surfactant in (d) phase no oscillations were observed during the measurement (Fig. 3*a*). Stable, but rather low E value of about 35 mV was found. When 1×10^{-3} mol dm^{-3} CTAB was added to (d) aqueous phase (Fig. 3*b*), the initial electric potential difference E increased to the value of 150 mV and only some perturbations were observed at the beginning of the experimental run. Increasing the CTAB concentration five times, concentration much higher than the critical micelle concentration (CMC; for CTAB in ethanol (1.5 mol dm^{-3}) —water mixture the value 1.1×10^{-3} mol dm^{-3} was found [9]), resulted in oscillations of the membrane potential (Fig. 3*c*). This oscillatory pattern consisted of two different regions. It could be concluded that the surfactant concentration must be well above CMC in order to obtain oscillations of the surfactant transport between (d) and (a) aqueous phases.

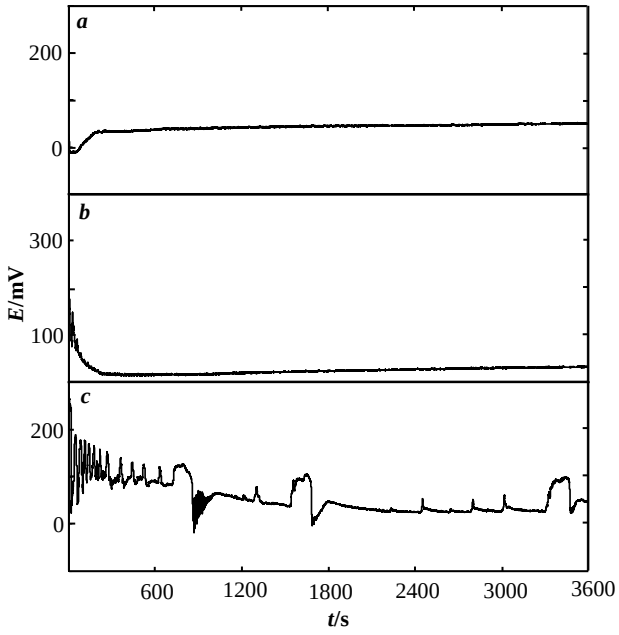

Fig. 3. Influence of CTAB concentration on the E oscillation. Membrane: picric acid (1.5×10^{-3} mol dm^{-3}) in nitromethane; acceptor aqueous phase: sucrose (0.1 mol dm^{-3}); donor aqueous phase: ethanol (1.5 mol dm^{-3}) + CTAB, concentration of CTAB: *a*) 0 mol dm^{-3}; *b*) 1×10^{-3} mol dm^{-3}; *c*) 5×10^{-3} mol dm^{-3}.

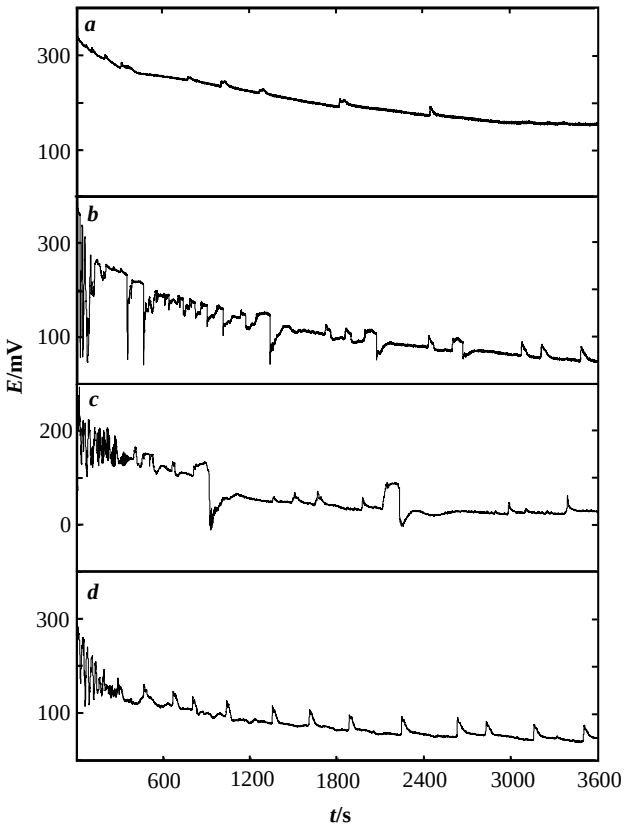

Fig. 4. Ethanol concentration effect on the oscillation characteristics of the liquid membrane oscillator. Membrane phase: picric acid (1.5×10^{-3} mol dm^{-3}) in nitromethane; acceptor aqueous phase: sucrose (0.1 mol dm^{-3}); donor aqueous phase: TTAB (5×10^{-3} mol dm^{-3}) + ethanol (concentration of ethanol: *a*) 0 mol dm^{-3}; *b*) 0.5 mol dm^{-3}; *c*) 1.5 mol dm^{-3}; *d*) 2.5 mol dm^{-3}).

The ethanol concentration has also important influence on the oscillatory pattern. When cationic surfactant TTAB was used (from the original one, CTAB, it differs only in the chain length), no oscillations were observed without ethanol in (d) phase (Fig. 4*a*). If the ethanol concentration 0.5 mol dm^{-3} was used (Fig. 4*b*), irregular oscillations occurred during the whole range of experiment. With increasing the ethanol concentration (Fig. 4*c*) two different oscillatory regions can be distinguished: higher frequency damped oscillations (up to about 500 s) followed by the two wide peaks. Further addition of ethanol to the donor aqueous phase (2.5 mol dm^{-3}, Fig. 4*d*) provoked a dramatic change in the oscillation pattern. The fast oscillation region found at the beginning of the run was followed by a periodic appearance of peaks of smaller amplitude (30—45 mV). On the other hand, wide peaks observed for lower ethanol concentrations (see Figs. 4*b* and *c*) disappeared. The above results showed that the alcohol molecules were necessary for the surfactant transport from (d) to (a) phase through

the liquid membrane.

The present study showed the high sensitivity of the liquid membrane oscillators to various physicochemical factors. Temperature has strong influence on the oscillatory patterns, especially in the case when nitrobenzene is used as the liquid membrane. The composition of aqueous phases as well as the aqueous phase—membrane interface structure seems also to play an important role. Furthermore, comparison of Figs. 1 and 2 representing systems with different liquid membranes (nitrobenzene or nitromethane) showed the intrinsic effect of the membrane material on the system oscillatory characteristics. Three types of oscillations were observed when nitromethane was used as a membrane material, meanwhile only one type of peaks appeared for the systems comprising nitrobenzene as the liquid membrane.

Further work is in progress to elucidate the molecular mechanism of the observed phenomenon.

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