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ON THE MECHANISM OF OSCILLATIONS IN THREE-PHASE SYSTEM CONTAINING CATIONIC SURFACTANT AND NITROBENZENE LIQUID MEMBRANE

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ABSTRACT

Oscillations of electrochemical potential difference between donor and acceptor aqueous phases of nitrobenzene oscillator containing hexadecyltrimethylammonium bromide were observed. It was shown that this potential difference is composed of two–phase boundary potentials between a membrane and an appropriate aqueous phase. It appears that oscillations occur at an aqueous acceptor/membrane interface. They are caused by adsorption/desorption processes of surfactant ions pairs with bromide or picrate followed by their transfer to the acceptor phase. The processes taking part in three stages of oscillation mechanism were suggested.

Keywords: Liquid membrane; Membrane oscillator; Cationic surfactants; Electrochemical potential difference; Oscillation mechanism

INTRODUCTION

Liquid membrane oscillators [1-9] were suggested as artificial systems for molecular recognition which might be used for constructing the taste sensors [1,2]. They are composed of two aqueous phases separated by an immiscible organic phase (membrane). A cationic or anionic surfactant is present in the first aqueous phase (donor phase, *d*); meanwhile, the second

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aqueous phase (acceptor phase, *a*) contains a taste substance. Although it has been demonstrated that the system can attain the equilibrium in an oscillatory manner [1-7,9], there is a big controversy over the mechanism of the respective oscillations [2-6,9].

Concerning the nitrobenzene oscillator containing hexadecyltrimethylammonium bromide (HTMABr), Yoshikawa at al. [3] explained the oscillation by a mechanism of repetitive formation and abrupt destruction of a monolayer structure of $HTMA^+$ cations on the aqueous donor/membrane interface followed by the formation of inverted micelles in the organic phase. For the oscillator with dichloromethane, Pimienta et al. [4] proposed a mechanism based on Langmuir – Hinshelwood kinetics that includes the competitive adsorption of $HTMA^+$, picrate ions and buthanol at the donor/membrane interface.

On the contrary, for the Yoshikawa system [3], Arai et al. [5] have found oscillations exclusively between the liquid membrane and aqueous acceptor phase. The mechanism of oscillations described by Arai is based on an assumption that the inverted micelles of a surfactant reach the *a*/*m* interface and having attained the critical micelle concentration, they suddenly proceed to the acceptor aqueous phase. For the system with hexadecyltrimethylammonium chloride (HTMACl), Maeda [9] also claims that oscillations are induced at the *a*/*m* interface due to transfer of H^+, Pi^-, Cl^- molecules. According to this author a surfactant accumulates at the *a*/*m* interface without transferring to the acceptor phase.

From the literature quoted above [2-6,9], it can be concluded that not only the mechanism of oscillations is unclear, but also it is disputable which interface, the donor phase/membrane (*d*/*m*) or acceptor phase/membrane (*a*/*m*) one is responsible for the observed oscillations.

The purpose of the present paper is to provide further evidence to a mechanism of liquid membrane oscillators containing a cationic surfactant hexadecyltrimethylammonium bromide (HTMABr) in the donor aqueous phase and sucrose in the acceptor phase. The organic membrane phase separating the aqueous phases contained picric acid (HPi) in nitrobenzene. The molecular phenomena taking place in the system were followed by electrochemical potential difference measurements.

EXPERIMENTAL

All reagents were commercial products of analytical grade purity (>99%). Picric acid was recristallized from ethanol-water mixture (1:2). Nitrobenzene was distilled before use. Demineralized water, freshly distilled over $KMnO_4$, was used in all experiments.

At the bottom of a thermostated (T=25±0.1^o C) U-shaped glass tube (Fig.1), an liquid membrane solution (*m*) was introduced. Above this layer, an aqueous donor solution (*d*) was slowly added to the left and an aqueous acceptor solution (*a*) to the right. The initial composition of the three phases was as follows: liquid membrane – 5 ml of 1.5×10^{-3}M picric acid (HPi) in

nitrobenzene, aqueous donor phase – 4 ml of 5×10^{-3}M HTMABr in ethanol (1.5 M) - water mixture; aqueous acceptor phase – 4 ml of 0.1 M sucrose solution. The electrochemical potential difference ($\Delta E_{d/a}$ in mV) between the two aqueous phases was measured by means of two Ag/AgCl/Cl^- reference electrodes using a ~10 MΩ input resistance voltmeter controlled by a PC (sampling speed: 4-10 s^{-1}). For some experiments Ag/AgCl/Cl^- microelectrodes were also applied.

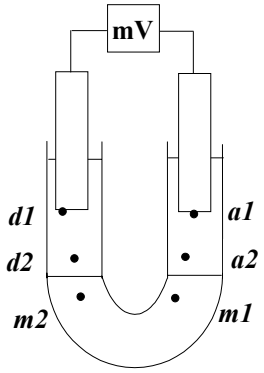

Fig. 1. Experimental set-up of liquid membrane oscillator; *d1*, *d2*, *a1*, *a2*, *m1*, *m2* – position of electrodes in donor, acceptor aqueous phases and liquid membrane, respectively, mV – milivoltmeter controlled by a PC.

Each experiment was repeated five times at least. The oscillation curves were similar in each case, but never exactly the same due to chaotic behaviour of the system.

RESULTS AND DISCUSION

The oscillations of electrochemical potential difference between the aqueous phases of nitrobenzene oscillator with HTMABr, $\Delta E_{d1/a1}$, are presented in (Fig. 2). After the induction time (350 s) the fairly regular oscillations (up to 2100 s) with amplitude of about 260 mV and frequency 1.9×10^{-2} s^{-1} were observed. Then, after about 180 s period without oscillations, new, less regular oscillation zone which lasted up to the end of the experiment was found.

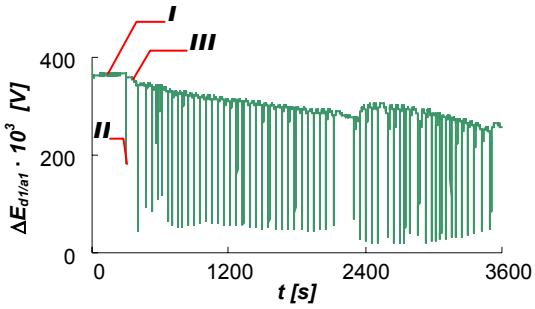

Fig. 2. Oscillations of electrochemical potential difference between aqueous phases of nitrobenzene oscillator, I, II and III represent the stages of oscillation mechanism [7].

The electrochemical potential difference between the aqueous phases, $\Delta E_{d1/a1}$, is considered as the algebraic sum of the two-phase boundary potentials on the right and left interfaces ($\Delta E_{d2/m2}$, $\Delta E_{m1/a2}$) and diffusion potentials within the organic ($\Delta E_{m2/m1}$) and aqueous phases ($\Delta E_{d1/d2}$, $\Delta E_{a2/a1}$), respectively:

$$\Delta E_{d1/a1} = \Delta E_{d1/d2} + \Delta E_{d2/m2} + \Delta E_{m2/m1} + \Delta E_{m1/a2} + \Delta E_{a2/a1} \quad (1)$$

It was found [3] that the contribution of diffusion potentials in the aqueous phases, ($\Delta E_{d1/d2}$, $\Delta E_{a2/a1}$) and in the liquid membrane ($\Delta E_{m2/m1}$) to $\Delta E_{d1/a1}$ is negligible. Therefore, Eq. (1) can be rewritten as:

$$\Delta E_{d1/a1} = \Delta E_{d2/m2} + \Delta E_{m1/a2} \quad (2)$$

or

$$\Delta E_{d1/a1} = \Delta E_{d2/m2} - \Delta E_{a2/m1} \quad (3)$$

We measured the potential difference between the aqueous and liquid membrane interfaces, $\Delta E_{d2/m2}$, $\Delta E_{a2/m1}$, respectively [7]. The values obtained in the three stages of oscillation mechanism (I, II, III) are presented in Tab.1.

The $\Delta E_{d2/m2}$ values were about 320mV and constant during experiment. No oscillations were found in this case. On the contrary, the $\Delta E_{a2/m1}$ values were very low at the beginning of process, and after certain initial time (stage I) oscillations appeared.

It can be seen from the Tab. 1 that experimental $\Delta E_{d1/a1}$ values in three stages of oscillation mechanism (last column) are in quite a good agreement with calculated ones from Eq.(3) (last but one column). It is very difficult to obtain better agreement due to chaotic behavior of the system investigated.

Tab.1. Electrochemical potential difference between appropriate points of aqueous and membrane phases of nitrobenzene oscillators in the three stages of oscillation mechanism (Fig.2).

Process time stages	$\Delta E_{d2/m2}$	$\Delta E_{a2/m1}$	$\Delta E_{d1/a1}$ calculated*	$\Delta E_{d1/a1}$ experimental**
	10^3[V]			
I	320	0	320	360
II	320	100	220	180
III	320	0	320	350

*calculated from Eq.(3),
**from Fig.1.

The concentrations of some components of the oscillator, with HTMABr or HTMACl transported during oscillation process, were established at the end of the experiment. They are presented in Tab.2, together with the initial concentrations of these species in the appropriate phases.

The visual observation of the aqueous phases shows that the donor phase is transparent during the oscillation process whereas the acceptor phase becomes yellowish immediately after all phases get in contact. It implies that picric anions are not transferred to the donor phase contrary to the acceptor phase which is also evidenced by spectrophotometric measurements (Tab. 2).

Tab. 2. Concentration of some liquid membrane oscillator components at the beginning and at the end of oscillation experiment.

species	CONCENTRATION, [M]				Time of experim. [s]	REF.
	Donor phase, d		Acceptor phase, a			
	Beginning of the experim.	End of the experim.	Beginning of the experim.	End of the experim.		
nitrobenz.	0	$6.5\pm 0.6\times10^{-3}$	0	$5.6\pm 0.6\times10^{-3}$	3600	[8]
Pi^-	0	$<1\cdot10^{-6}$	0	$7.5\cdot10^{-5}$	5400	[9]
	0	0	0	$1.9\ 10^{-5}$	3600	[8]
H^+	$2.5\cdot10^{-6}$	$3.9\cdot10^{-5}$	$2.5\cdot10^{-6}$	$1.6\cdot10^{-4}$	5400	[9]
$HTMA^+$	$1.0\cdot10^{-2}$	$9.5\cdot10^{-3}$	0	$<1.0\cdot10^{-6}$	5400	[9]
Cl^-	$1.0\cdot10^{-2}$	$9.6\cdot10^{-3}$	0	$1.7\cdot10^{-4}$	5400	[9]

The results presented in Tab. 2 show also that, at the end of the experiment, the concentration of $HTMA^+$ ions is very small, much lower that the concentration of Cl^- ions. We also found for a similar system (nitromethane oscillator with HTMABr) [7] that the ratio of $HTMA^+/Br^-$

concentration is small and similar to the one determined by Maeda [9] for HTMACl oscillator. As it can be seen from Tab. 2 the both aqueous phases became more acidic in time of process which suggests the H^+ ions transfer to these phases.

Considering the obtained results, the following processes in three stages of oscillation mechanism in nitrobenzene liquid membrane oscillator containing HTMABr are proposed:

Stage I - phenomena during induction period.

$HTMA^+$ cations mainly present as the micelles in the aqueous donor phase move toward the *d*/*m* interface and then occupy it. HPi present in the organic phase move toward the same interface. $HTMA^+$ cations are transferred to the membrane where HTMA-Pi ion pairs are created. H^+ is dissolved in the donor phase. HTMA-Pi, HTMABr, and ethanol molecules are moving to the organic phase where the lower density layer is created near the upper wall of the U-tube. In the membrane, HTMABr reacts with HPi forming HBr. This latter is transferred to the acceptor phase in a non-oscillatory way.

During the induction period the *d*/*m* interface is fully saturated by $HTMA^+$ cations and the *a*/*m* interface is without a surfactant. As the effect of these events $\Delta E_{d1/a1}$ is equal to $\Delta E_{d2/m2}$ (Tab. 1).

Stage II - creation of the first peak (decrease of $\Delta E_{d1/a1}$).

Diffusing HTMA-Pi pairs and HTMABr molecules abruptly reach the *a*/*m* interface causing $\Delta E_{a2/m1}$ positive potential. As a result of this event, sudden decrease of $\Delta E_{d1/a1}$ values is observed (Eq.3, Tab.1).

Stage III - increase of $\Delta E_{d1/a1}$ of the first peak.

When the concentration of $HTMA^+$ at the interface reaches the critical value, they are abruptly transferred to the acceptor aqueous phase with Pi^- or Br^- ions. The $\Delta E_{a2/m1}$ values decrease to almost zero, which results in an increase of $\Delta E_{d1/a1}$ values to 320 mV (Fig. 2, Tab. 1).

The HTMA-Pi and HTMABr molecules compete for a limited and a constant total number of sites at the *a*/*m* interface. Therefore, the events taking part at the *a*/*m* interface in the stages II and III (surfactant adsorption/desorption processes) are repeated in an oscillatory way.

CONCLUSION

The results obtained show that the electrochemical potential difference oscillations in the nitrobenzene oscillator containing HTMABr surfactant occur at the aqueous acceptor/membrane interface which is contrary to Yoshikawa [3] and Pimienta [4] findings. These oscillations are caused by adsorption/desorption processes of HTMA-Pi and HTMABr molecules followed by their transfer to the acceptor phase. At *a*/*m* interface,

they compete for a limited and constant total number of sides. HBr, forming in the liquid membrane, is transferred to the aqueous acceptor phase also in a non-oscillatory way. Therefore, at the end of the experiment, Br^- (Cl^- in case of HTMACl) concentration in this aqueous phase is much higher in comparison to $HTMA^+$ concentration. The appropriate processes taking part in the three stages of the oscillation mechanism were suggested.

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