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On the mechanism of nitrobenzene liquid membrane oscillators containing hexadecyltrimethylammonium bromide

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Abstract

The oscillatory behaviour of a liquid membrane oscillator was investigated in order to contribute to the oscillation mechanism at the molecular level. The chosen system involved nitrobenzene as liquid membrane containing a constant amount of picric acid. The aqueous donor phase contained the cationic surfactant, hexadecyltrimethylammonium bromide, and ethanol. The aqueous acceptor phase was made up by sucrose solution.

It was established that the oscillations take place exclusively at the aqueous acceptor phase/membrane interface. Three stages mechanism of the oscillation (I—induction period, II—first peak formation, III—creation of the first peak) together with appropriate processes were proposed. The molecular events provoking the oscillations of electric potential difference between the two aqueous phases concern: 1) the diffusion of hexadecyltrimethylammonium bromide and ion pairs formed by cation of the surfactant and the picrate anion to the vicinity of the membrane/acceptor phase interface, 2) sudden adsorption of these ion-pairs at this interface in non-catalytic and autocatalytic steps, 3) desorption of ion pairs from the a/m interface to the acceptor phase.

It is shown by numerical simulations that the proposed mechanism may account for the observed oscillations and for the species distribution throughout the system as found experimentally.

Keywords: Liquid membrane oscillator; Cationic surfactant; Nitrobenzene; Oscillation mechanism; Liquid membrane; Numerical simulations

1. Introduction

Ion transfer through membranes accompanied by oscillations of membrane potential is closely related to the electrical excitability in living organisms. Due to the complexity of these latter, simpler models, based on artificial systems, e.g. liquid membrane oscillators, seem to be more appropriate for investigation.

Liquid membrane oscillator is composed of two aqueous phases separated by an organic phase of different density (liquid membrane). In the first aqueous phase (donor phase, d) surfactant is present which is transferred to the second aqueous phase (acceptor phase, a) through a liquid membrane containing picric acid (HPi). It was already suggested that such systems containing different substances in the acceptor phase and showing oscillations of electric potential difference between the aqueous phases might be used for molecular recognition [1,2].

The detailed mechanism of these oscillations is still the subject of controversy [3–8]. The molecular species responsible for the oscillations are not clearly identified. Even if it is generally admitted that the molecular events leading to oscillations take place at some water/membrane interface, it is still not established whether the donor phase/membrane (d/m) or the acceptor phase/membrane (a/m) interface is involved in the process. Some authors give arguments for the d/m interface [3,7], while others produce evidences in favour of the a/m interface [4–6,8].

The aim of this work is to investigate in more details an oscillator with cationic surfactant in order to contribute to the establishment of a general mechanism of oscillations of electric potential difference between the aqueous phases. For this purpose, a nitrobenzene liquid membrane oscillator containing hexadecyltrimethylammonium bromide (HTMABr) was investigated.

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2. Experimental part

Reagents: HTMABr, ethanol, nitrobenzene, nitromethane, sucrose, picric acid were commercial products of analytical grade purity (>99%). HPi was recrystallized from an ethanol–water mixture (1 : 2 v/v) and nitrobenzene or nitromethane, was distilled before use. Freshly distilled demineralised water was used in all experiments.

Experiments were performed in an apparatus with a U-shaped glass tube (12-mm inner diameter) (Fig. 1). Liquid membrane solution (m) was put at the bottom of the thermostated ($T = 25 \pm 0.1$ °C) U-tube. Above this layer aqueous donor solution (d) and aqueous acceptor solution were introduced simultaneously.

The initial composition of the three phases was the following:

- aqueous donor phase, 4 ml of 5×10^{-3} M HTMABr in ethanol (1.5M)—water mixture,
- liquid membrane, 5 ml of 1.5×10^{-3} M HPi in nitrobenzene or nitromethane,
- aqueous acceptor phase, 4 ml of 0.1 M sucrose solution.

The electric potential difference between the two aqueous phases ($\Delta E_{d1/a1}$ and $\Delta E_{d2/a2}$ in mV) was measured by using two Ag/AgCl/Cl$^-$ reference electrodes of 10 mm thickness situated at 1 cm (d_1, a_1) or 2 cm (d_2, a_2) from the interface.

$\Delta E_{d1/a1}$ values were also measured by microelectrodes (1 mm thickness). In the case of interface potentials ($\Delta E_{d1/m2}$, $\Delta E_{a1/m1}$) a home-made microelectrode was used in the liquid membrane. This latter was made up of Ag/AgCl in contact with a solution of tetrabuthylammonium chloride (1.8×10^{-4} M) in nitrobenzene.

Each experiment was repeated four–six times. The obtained oscillation characteristics for each case were similar, never exactly the same. They were very sensitive to initial conditions (the way of interface preparation, temperature, electrode distances from interface). Particularly, the oscillation characteristics depend strongly on the topology of microelectrodes [8]. Therefore, all these parameters were kept constant and equal in appropriate experiments.

The change of nitrobenzene concentrations with time in the two aqueous phases was measured by UV–VIS spectrophotometry using the π–π* band at $\lambda_{max} = 260$ nm. The bromide ion concentration was established by microcoulometry using Analyzer multi X 2000 of Analytic Jena AG firm.

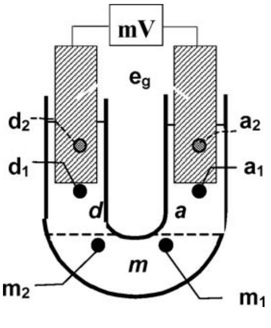

Fig. 1. Experimental set-up of liquid membrane oscillator, d_1, d_2, a_1, a_2, m_1, m_2—position of electrodes in donor and acceptor aqueous phases and liquid membrane, respectively, e_g—Ag/AgCl/Cl$^-$ electrodes.

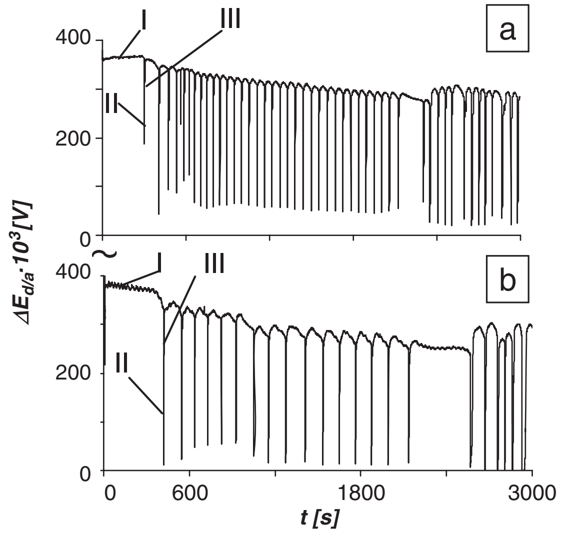

Fig. 2. Oscillation curves of $\Delta E_{d/a}$ of nitrobenzene oscillator measured by electrodes situated at a) 1 cm (d_1, a_1), b) 2 cm (d_2, a_2) from the interfaces, I, II, III—stages of proposed oscillation mechanism.

Numerical simulations were performed using Matlab programme.

3. Results and discussion

3.1. Interpretation of electric potential difference between aqueous phases ($\Delta E_{d2/a2}$)

The influence of electrode position with respect to the aqueous phase/membrane interfaces on oscillation curves of electric potential difference between aqueous phases of HTMABr oscillator is presented in Fig. 2. The $\Delta E_{d1/a1}$ and $\Delta E_{d2/a2}$ values were measured by using thick Ag/AgCl/Cl$^-$ electrodes.

The overall oscillation pattern has two regions of different frequencies (Fig. 2 a, b). After a certain induction period the first type of oscillation appears. This type of oscillation stops suddenly (at about 2100 s for the case presented on Fig. 2a). A new induction period appears which is followed by a second oscillating region. As it can be seen, the oscillation curves differ in frequency of the observed peaks and in the length of induction period. The closer the electrodes are situated to the interfaces, the shorter the induction period and more frequent peaks are noted. However, the overall pattern of oscillations is similar. These results show that the oscillation characteristics are sensitive to the electrode distance from interface. This might be due to diffusion and convection taking place between the electrodes and the interfaces.

The $\Delta E_{d2/a2}$ is composed of five contributions: 1) the diffusion potential difference in donor phase, $\Delta E_{d2/d1}$, 2) the potential difference across aqueous donor phase/membrane interface, $\Delta E_{d1/m2}$, 3) the diffusion potential difference in the liquid membrane, $\Delta E_{m2/m1}$, 4) the potential difference across aqueous acceptor phase/membrane interface, $\Delta E_{\mathrm{m1/a1}}$, 5) the diffusion potential difference in the acceptor aqueous phase, $\Delta E_{\mathrm{a1/a2}}$.

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

It was already established that diffusion potentials $\Delta E_{\mathrm{d2/d1}}$, $\Delta E_{\mathrm{m2/m1}}$, $\Delta E_{\mathrm{a1/a2}}$ are close to zero during the time of experiment [3,8] and they may be safely neglected. In this case, Eq. (1) gives:

$$\Delta E_{\mathrm{d1/a1}} = \Delta E_{\mathrm{d1/m2}} - \Delta E_{\mathrm{a1/m1}} \quad (2)$$

since $\Delta E_{\mathrm{d1/a1}} = \Delta E_{\mathrm{d2/a2}}$.

The appropriate changes of ΔE ($\Delta E_{\mathrm{d1/a1}}$, $\Delta E_{\mathrm{a1/m1}}$, $\Delta E_{\mathrm{d1/m2}}$) measured by means of microelectrodes are presented in Fig. 3. As it can be seen, the $\Delta E_{\mathrm{d1/a1}}$ curve differs in pattern from that obtained for $\Delta E_{\mathrm{d1/a1}}$ values by thick electrodes (Fig. 2a). However, both curves are characterized by similar initial periods. On the other hand, the oscillation peaks are of different amplitudes and frequencies. This is a direct consequence of the fact that oscillation characteristics depend strongly on the size and topology of the electrodes used [8].

The $\Delta E_{\mathrm{d1/a1}}$ (Fig. 3a) and $\Delta E_{\mathrm{a1/m1}}$ (Fig. 3b) changes with time consist of an induction period of about 400 s and of an oscillation period (till 2400 s). The latter is characterized by irregular peaks of different amplitudes. In the case of $\Delta E_{\mathrm{a1/m1}}$ they have opposite phases to those observed for $\Delta E_{\mathrm{d1/a1}}$ (Fig. 3b). It should be noted that similar to the results of Arai et al. [4], there are no oscillations at the d/m interface and $\Delta E_{\mathrm{d1/m2}}$ values remain constant throughout the experiments (Fig. 3c).

Table 1
Components of the observed electric potential difference between the aqueous phases

t [s]	$\Delta E_{\mathrm{d1/m2}}$	$\Delta E_{\mathrm{a1/m1}}$	$\Delta E_{\mathrm{d1/a1}}$ calculated	$\Delta E_{\mathrm{d1/a1}}$ experimental
	10^3[V]			
80	320	−10	330	300
800	320	0	320	290
1600	320	−10	330	290

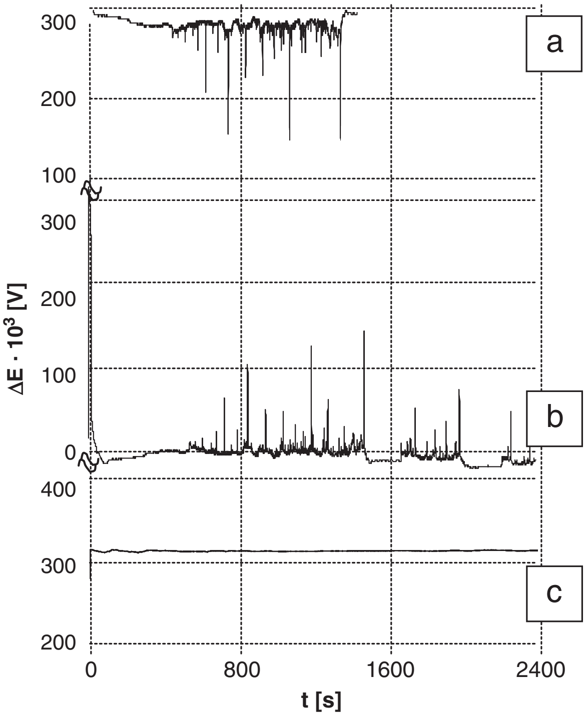

Fig. 3. ΔE changes between appropriate phases measured by microelectrodes, a) $\Delta E_{\mathrm{d1/a1}}$, b) $\Delta E_{\mathrm{a1/m1}}$, c) $\Delta E_{\mathrm{d1/m2}}$.

The obtained results show clearly that the a/m interface is responsible for the oscillation of $\Delta E_{\mathrm{d1/a1}}$ which is in accordance with the results of Arai et al. [4,6] and Maeda et al. [5] and in contradiction to the results of Yoshikawa and Matsubara [3] and Pimienta et al. [7]. It should be noted that the influence of membrane thickness favours also the a/m interface as the active site for oscillations [8]. Also visual observations of changes at the a/m interface during the creation of oscillation peak (opaque when potential suddenly diminishes and transparent after abrupt increase of potential) confirm this conclusion.

The contribution to $\Delta E_{\mathrm{d1/a1}}$ values calculated from Eq. (2) at a certain process time are presented in Table 1.

It can be seen that the calculated $\Delta E_{\mathrm{d1/a1}}$ values are in fairly good agreement with the experimental ones.

3.2. Mechanism of oscillations

In order to establish the mechanism of oscillations the influence of certain components present in donor and membrane phases on oscillation curves has been examined.

Fig. 4, obtained for nitromethane liquid membrane, shows that in absence of surfactant in the donor phase (Fig. 4b) or HPi in the membrane phase (Fig. 4c) no oscillations can be observed. On the other hand, when alcohol is absent in the donor phase only slowly decaying oscillations of small amplitude could be seen (Fig. 4a). These observations confirm previously obtained results for other surfactants (e.g. tetradecyltrimethylammonium bromide, [10]). Therefore, it is

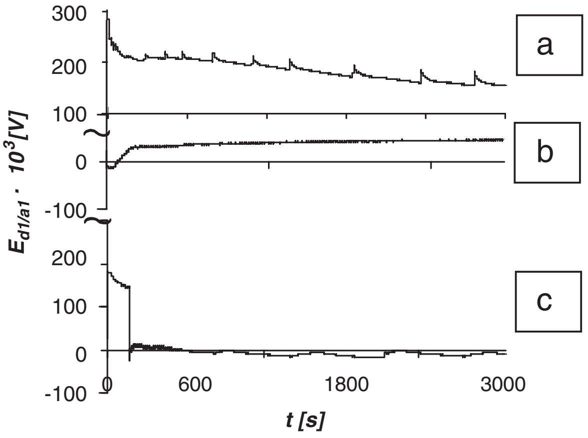

Fig. 4. $\Delta E_{\mathrm{d1/a1}}$ curves of nitromethane oscillator without a) ethanol in donor phase, b) HTMABr in donor phase, c) HPi in liquid membrane phase.

Table 2
Composition of the two aqueous phases of oscillator with HTMABr before and at the end of experiment

Substance	Concentration [M]				Process time [s]	Ref.
	Phase d		Phase a			
	Initial	Final	Initial	Final		
Nitrobenzene	0	$6.5\ (\pm 0.6)\cdot 10^{-3}$	0	$5{,}6\ (\pm 0.6)\cdot 10^{-3}$	3600	[9]
H^+	$2.5\cdot 10^{-6}$	$3.9\cdot 10^{-5}$	$2.5\cdot 10^{-6}$	$1.6\cdot 10^{-4}$	5400	[5]
Pi^-	0	$<1\cdot 10^{-6}$	0	$7.5\cdot 10^{-5}$	5400	[5]
$HTMA^+$	$1.0\cdot 10^{-2}$	$9.5\cdot 10^{-3}$	0	$<1.0\cdot 10^{-6}$	5400	[5]
	$5\cdot 10^{-3}$	**	0	$0.9\cdot 10^{-6}$	3600	This work*
Br^-	$5.0\cdot 10^{-3}$	$4.8\cdot 10^{-3}$	0	$2.0\cdot 10^{-4}$	3600	This work*

*For nitromethane liquid membrane, **not examined.

expected that alcohol cannot be responsible for the observed oscillations. It is quite likely that it's role is rather the creation of an appropriate medium for the transport processes across the liquid membrane. By increasing the polarity of the membrane phase it facilitates dissolution and diffusion of ion pairs in the membrane. This is confirmed by visual observation of the system during the experiment. Since the three phases are not saturated mutually the solvent components penetrate (alcohol) also into the membrane phase. Alcohol can diffuse even to the acceptor phase. It can be observed visually that the diffusing alcohol rich layers become deep yellow in contrast to the very slight yellow colour of the membrane. This is due to the fact that the presence of alcohol increases the solubility of both picric acid and picrate containing ion pairs.

The chemical composition of the two aqueous phases was also measured at the end of the experiments (at $t = 3600$ s). The results obtained are presented in Table 2 together with literature data. Nitrobenzene concentration was established from its $\pi-\pi^*$ band. This latter obeys the Lambert–Beer's law and has a molar extinction coefficient of $\varepsilon_{max} = 14{,}000 \pm 100\ M^{-1}\ cm^{-1}$ (correlation coefficient = 0.999) [9].

As it can be seen from the Table 2, the final compositions of the two aqueous phases are different from their initial values. At $t = 0$ the donor phase contains $HTMA^+$, Br^-, ethanol and water molecules. At the end of the process nitrobenzene is also present. This phase becomes more acidic as shown by the increase of H^+ concentration. On the other hand, the $HTMA^+$ and Br^- concentrations decrease. Traces of Pi^- in this phase were detected by Maeda et al. [5]. On the contrary, we did not find by spectrophotometry any Pi^- concentration in donor phase after 3600 s.

At the beginning of the oscillation process the acceptor phase is made up from aqueous sucrose solution. Table 2 shows that at the end of the process each component of the donor and membrane phase can be detected in the acceptor phase.

It should be noted that nitrobenzene is transferred to the aqueous phases mainly in the first 180 s of the process (2.0 ± 0.2 M in the d phase, 2.1 ± 0.2 M in the a phase). After 1800 s its concentration is settled. This suggests that nitrobenzene cannot play an active role in the observed oscillations.

It should be noted also that the concentration of $HTMA^+$ in the acceptor phase is almost 50 times lower than that of Br^-.

We produced evidences (see above) that oscillations take place at a/m interface. For the oscillation mechanism we propose three stages (Fig. 2): stage I—induction period, stage II—first peak formation (decrease of $\Delta E_{d1/a1}$ values), stage III—creation of the first peak (increase of $\Delta E_{d1/a1}$ values). Stages II and III are repeated at regular intervals giving rise to the observed oscillation peaks.

The following molecular events take part in these stages:

Stage I. Interface d/m is saturated with $HTMA^+$ cations forming a monolayer. As a consequence, very high and time independent $\Delta E_{d1/m2}$ values are observed. $HTMA^+$ cations are exchanged at this interface with H^+ cations from the liquid membrane making the donor phase more acidic. $HTMAPi_{id}$ and $HTMABr_{id}$ diffuse across the membrane from the proximity of d/m interface (id) to the vicinity of a/m interface

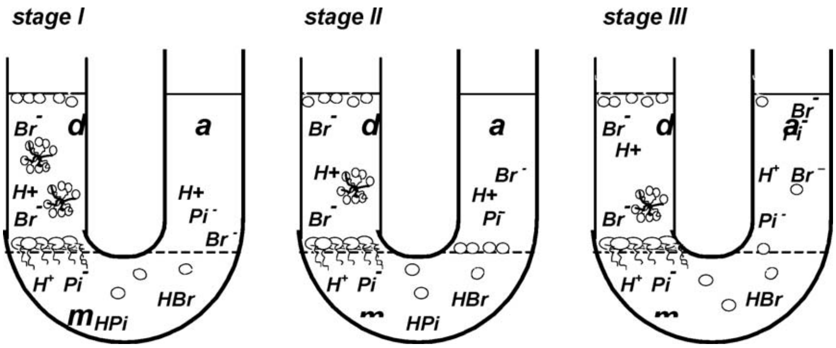

Fig. 5. Oscillation mechanism in the nitrobenzene oscillator containing HTMABr.

(ia) (Eqs. (3) and (4)).

$$\mathrm{HTMAPi}_{id} \xrightarrow{k_1} \mathrm{HTMAPi}_{ia} \tag{3}$$

$$\mathrm{HTMABr}_{id} \xrightarrow{k_2} \mathrm{HTMABr}_{ia} \tag{4}$$

No surfactant molecules are present on a/m interface ($\Delta E_{\mathrm{a1/m1}}=0$) therefore, $\Delta E_{\mathrm{d1/a1}}=\Delta E_{\mathrm{d1/m2}}$ (Eq. (2)).

Stage II. $\mathrm{HTMAPi_{ia}}$ and $\mathrm{HTMABr_{ia}}$ ion pairs being in the vicinity of the a/m interface suddenly adsorb to this interface occupying free sites (I) ($\Delta E_{\mathrm{a1/m1}}>0$):

$$\mathrm{HTMAPi}_{ia} + \mathrm{I} \xrightarrow{k_3} \mathrm{HTMA^+I} + \mathrm{Pi}_a^- \tag{5}$$

$$\mathrm{HTMABr_{ia}} + \mathrm{I} \xrightarrow{k_6} \mathrm{HTMA^+I} + \mathrm{Br}_a^- \tag{6}$$

This sudden adsorption may be also catalyzed by surfactant molecules already present in the interface. We suppose that the contribution of this autocatalytic step is more efficient in case of the more concentrated species:

$$\mathrm{HTMAPi}_{ia} + \mathrm{I} + \mathrm{HTMA^+I} \xrightarrow{k_5} 2\mathrm{HTMA^+I} + \mathrm{Pi}_a^- \tag{7}$$

The role of reaction (8) is to maintain the excess of $\mathrm{HTMAPi_{ia}}$ and to produce an excess of HBr in the aqueous acceptor phase (see Table 2):

$$\mathrm{HTMABr}_{ia} + \mathrm{HPi}_m \xrightarrow{k_6} \mathrm{HBr}_a + \mathrm{HTMAPi}_{ia} \tag{8}$$

Stage III. $\mathrm{HTMA^+I}$ desorbs to the acceptor phase ($\Delta E_{\mathrm{a1/m1}}\sim 0$):

$$\mathrm{HTMA^+I} \xrightarrow{k_7} \mathrm{HTMA}_a^+ + \mathrm{I} \tag{9}$$

This process leads to an increase of $\Delta E_{\mathrm{d1/a1}}$ values.

All these events are shown in Fig. 5.

The proposed mechanism suggests that the sudden adsorption and desorption of surfactant molecules at a/m interface reinforced by the continuous feeding by diffusion is responsible for the observed oscillations. The present model considers only a limited number of species and steps which are indispensable for explaining the oscillatory behaviour and the material balance. Using only a minimum number of species allows to simplify considerably the mathematical analysis. For this reason also the reverse reactions of each step are neglected.

The time evolution of the various chemical species involved in the mechanism can be represented by the following system of differential equations:

$$\begin{aligned}\frac{\mathrm{d[HTMAPia]}}{\mathrm{dt}} &= k_1[\mathrm{HTMAPi_{id}}] - k_3[\mathrm{HTMAPi_{ia}}][\mathrm{I}] \\ &\quad - k_5[\mathrm{HTMAPi_{ia}}][\mathrm{I}][\mathrm{HTMA^+I}] \\ &\quad + k_6[\mathrm{HTMABr_{ia}}][\mathrm{HPi_m}]\end{aligned} \tag{10}$$

$$\begin{aligned}\frac{\mathrm{d[HTMABr_{ia}]}}{\mathrm{dt}} &= k_2[\mathrm{HTMABr_{id}}] - k_4[\mathrm{HTMABr_{ia}}][\mathrm{I}] \\ &\quad - k_6[\mathrm{HTMABr_{ia}}][\mathrm{HPi_m}]\end{aligned} \tag{11}$$

$$\begin{aligned}\frac{\mathrm{d[HTMA^+I]}}{\mathrm{dt}} &= k_3[\mathrm{HTMAPi_{ia}}][\mathrm{I}] + k_4[\mathrm{HTMABr_{ia}}][\mathrm{I}] \\ &\quad + k_5[\mathrm{HTMAPi_{ia}}][\mathrm{I}][\mathrm{HTMA^+I}] \\ &\quad - k_7[\mathrm{HTMA^+I}]\end{aligned} \tag{12}$$

$$\begin{aligned}\frac{\mathrm{d[I]}}{\mathrm{d}t} &= -k_3[\mathrm{HTMAPi_{ia}}][\mathrm{I}] - k_4[\mathrm{HTMABr_{ia}}][\mathrm{I}] \\ &\quad - k_5[\mathrm{HTMAPi_{ia}}][\mathrm{I}][\mathrm{HTMA^+I}] + k_7[\mathrm{HTMA^+I}]\end{aligned} \tag{13}$$

They are nonlinear equations having unknown rate constants and concentrations of different species.

These equations have been used to verify the possibility of oscillations. All the mathematical simulations were realized using Matlab programme (see Experimental part). The species $\mathrm{HTMAPi_{id}}$ and $\mathrm{HTMABr_{id}}$ are considered to be in steady state. Therefore, their initial concentrations were taken at the constant

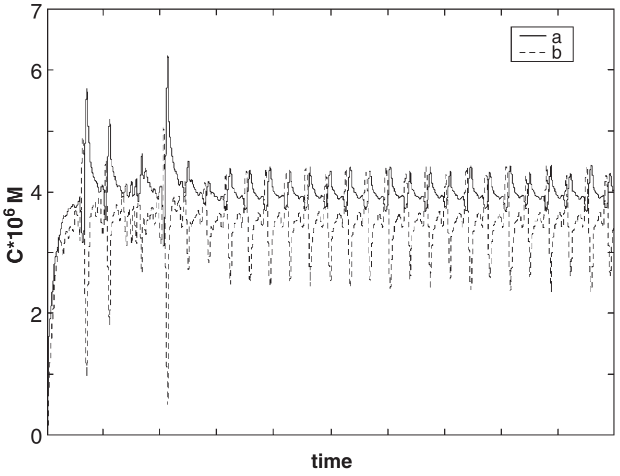

Fig. 6. Numerical simulation of oscillatory behaviour of the concentrations of $\mathrm{HTMAPi_{ia}}$ (curve a) and of $\mathrm{HTMA^+}$ I (curve b).

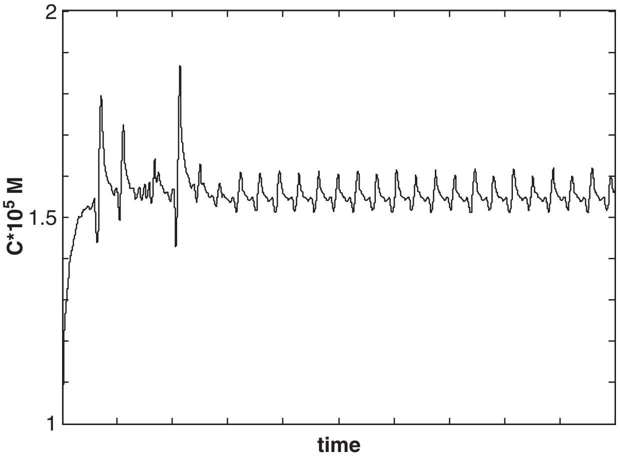

Fig. 7. Time evolution of the concentration of the sum of four oscillating species: $\mathrm{HTMAPi_{ia}}+\mathrm{HTMABr_{ia}}+\mathrm{HTMA^+}$ I+I.

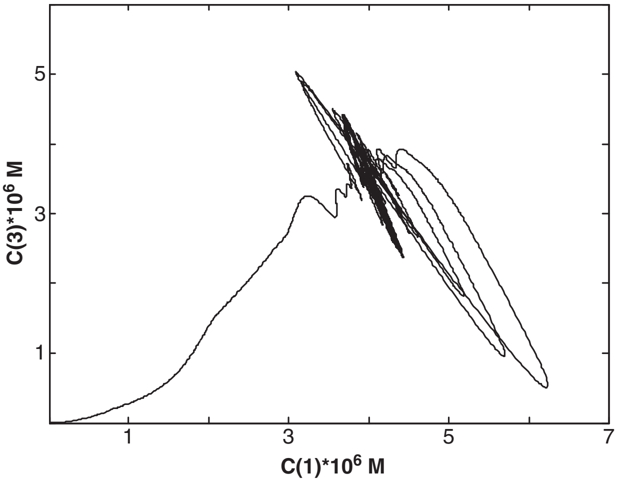

Fig. 8. Phase portrait of the oscillatory system based on the two species $HTMAPi_{ia}$ (C(1)) and $HTMA^+$ I (C(3)).

values of $[HTMAPi_{id}]_0 = 5 \times 10^{-5}$ M and $[HTMABr_{id}] = 10^{-5}$ M. The large excess of $[HPi_m] = 10^{-3}$ M is also considered constant. The initial concentration of the site present in the interface I_o is estimated to 10^{-5} M. The various rate constants used in the calculations are the following: $k_1 = 5 \times 10^{-2}[s^{-1}]$, $k_2 = 10^{-1}$ $[s^{-1}]$, $k_3 = 10^5$ $[M^{-1}$ $s^{-1}]$, $k_4 = 10^5[M^{-1}$ $s^{-1}]$, $k_5 = 10^6$ $[M^{-2}$ $s^{-1}]$, $k_6 = 10[M^{-1}$ $s^{-1}]$, $k_7 = 1[s^{-1}]$.

k_1 is chosen smaller than k_2 since the ion pairs containing the picrate ions diffuse slower than HTMABr due to their greater size. It is assumed that the adsorption processes have the same rate for both ion pairs ($k_3 = k_4$). The rate of the autocatalytic step is considered greater than the corresponding non-catalytic one ($k_5 > k_3$). The desorption process is considered to be slower than the adsorption to the interface ($k_7 < k_3$, k_4, k_5).

The obtained results are represented on Fig. 6. It can be seen that after a rather irregular initial behaviour the species present regular oscillations. The two oscillations show the same fine structure but differ in amplitude and phase. The oscillations for $HTMA^+I$ species have greater amplitude than in case of $HTMAPi_{ia}$. $HTMABr_{ia}$ shows similar oscillatory behaviour to $HTMAPi_{ia}$. I oscillates with the same amplitude as $HTMA^+$ I but with opposite phase.

Experimentally the sum of all these contributions is observed. When adding all four oscillatory curves resulting from the numerical simulations Fig. 7 is obtained. Closer examination shows that only $HTMAPi_{ia}$ and $HTMABr_{ia}$ contribute to the final results since the contribution from I and $HTMA^+I$ neutralize each other.

The dynamical behaviour of the system can be followed by the corresponding two-dimensional phase portrait (Fig. 8). It can be seen that the obtained attractor has chaotic character. After an initial oscillatory region small oscillations appear followed by larger amplitude oscillations. Finally the system settles to a regular oscillatory stage.

All these results obtained by numerical simulations suggest that the proposed mechanism may account for the observed oscillations and also for the chemical compositions of the different phases as presented in Table 2:

a) acidification of aqueous phases during process,
b) excess of bromide ions in comparison to surfactant cations in the acceptor phase,
c) presence of Pi^- ions in the acceptor phase,
d) small amount of $HTMA^+$ cations in acceptor phase since they are transferred to acceptor phase only by adsorption/desorption processes connected with diffusion.

4. Conclusion

The present work shows clearly that the oscillations in liquid membrane systems with HTMABr take place at acceptor phase/membrane interface. The appearance of significant oscillations requires the simultaneous presence of cationic surfactant, picric acid and ethanol in the system. The proposed mechanism suggests that the sudden adsorption and desorption of surfactant molecules at the a/m interface reinforced by the continuous feeding by diffusion is responsible for the observed oscillations of electric potential difference between the two aqueous phases. The time evolution of the various chemical species involved in the mechanism was represented by a set of non-linear differential equations: the mathematical simulations show that the proposed mechanism may account for the observed oscillations. It accounts also for the chemical compositions of different phases.

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