



**INVESTIGATION OF NITROBENZENE LIQUID MEMBRANE  
OSCILLATOR CONTAINING  
BENZYLDIMETHYLTETRADECYLAMMONIUM CHLORIDE**

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**ABSTRACT**

The oscillatory behaviour of a nitrobenzene liquid membrane oscillator containing benzyldimethyltetradecylammonium chloride was investigated in order to recognize the oscillation mechanism. The influence of temperature and electrode distances from the interfaces as well as the donor, membrane and acceptor phase composition on the changes of electric potential difference between aqueous phases was examined. The effect of the surfactant structure on the oscillation characteristics was discussed.

It was shown that the appearance of oscillations requires the simultaneous presence of surfactant, picric acid and ethanol in the system. The mechanism of oscillations in this system should be similar as the one in an oscillator containing hexadecyltrimethylammonium bromide where oscillations of electric potential difference between the two aqueous phases are produced by sudden adsorption and desorption of the surfactant and the ionic pair: a surfactant-picric anion at the a/m interface. The diffusion fluxes of all these species in the vicinity of a/m interface also play an important role. They might couple, which leads to the nonlinear behaviour of the system.

The oscillation curves obtained for the liquid membrane oscillator with benzyldimethyltetradecylammonium chloride and different taste substances were analyzed by the construction of the corresponding attractors in two-dimensional space using the time delay method. Each system has its own attractor differing in shape and surface. Therefore, these properties might be used for identifying an unknown taste substance present in the acceptor phase.

Keywords: Liquid membrane, Membrane oscillators, Cationic surfactant, Electric potential difference, Taste substances

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## INTRODUCTION

The high complexity of non-linear phenomena in biological systems requires a designation of artificial systems as models for investigation of processes appearing in biomembranes [1,2]. As a matter of fact, the transport of ions through the liquid membrane accompanied by the membrane potential oscillations is closely related to the electrical excitability in living cells. Such a system is called liquid membrane oscillator (LMO).

It is composed of two aqueous phases separated by an immiscible organic phase. The first of these aqueous phases, called the donor phase (d) contains an ionic surfactant with alcohol. It plays the role of a source for any transport processes across the liquid membrane phase (m) containing some additional substances. The other of the aqueous phases, called the acceptor phase (a) may be pure water only or it may contain some substances responsible for taste.

Liquid membrane oscillators show a great variety of oscillating patterns which are very sensitive to the experimental conditions [3-7,10-13]. It was proved that oscillations show chaotic behaviour [14-16]. This property did not exclude the possible applications of LMO [10]. It was already suggested that such a system, containing a cationic surfactant (hexadecyltrimethylammonium bromide, HTMABr) [11] or an anionic surfactant (sodium oleate) [4,11], might be applied for quantifying molecules responsible for taste.

The mechanism of oscillations and physico-chemical properties of the liquid membrane oscillator containing HTMABr were investigated by many authors [3,5,6,8,9,14,15,18]. On the contrary, only few works were devoted to LMO with other cationic surfactants [10,16].

In this paper the influence of various factors, such as electrode distance, temperature, the donor, membrane and acceptor phase composition on oscillatory behavior of LMO with benzyldimethyltetradecylammonium chloride (BDMTACl) is presented. The liquid membrane contains picric acid (HPi) dissolved in nitrobenzene. The effect of the surfactant structure on the oscillation characteristics will be discussed since a molecule of BDMTACl contains the benzyl group and a chain shorter than HTMABr.

## EXPERIMENTAL

All the reagents used were commercial products of analytical grade purity (>99%). Picric acid was recrystallized from the ethanol – water mixture (1:2 v/v). Twice-distilled water was used in all the experiments.

At the bottom of a thermostated ( $298.1 \pm 0.1$  °C) U-shaped glass tube (Fig. 1) liquid membrane solution was introduced. The aqueous phases were put simultaneously into the two branches of the glass tube. The composition of the three phases was as following:

-aqueous donor phase, d: 4 ml of BDMTACl ( $5 \times 10^{-3}$  M) in the ethanol (1.5 M) – water mixture;

-liquid membrane, m: 5 ml of picric acid (HPi,  $1.5 \times 10^{-3}$  M) in nitrobenzene;  
 -aqueous acceptor phase, a: 4 ml of various added substances in water [sucrose, (0.1 M), sodium chloride (0.1 M), acetic acid (0.1 M), caffeine (0.05 M)].

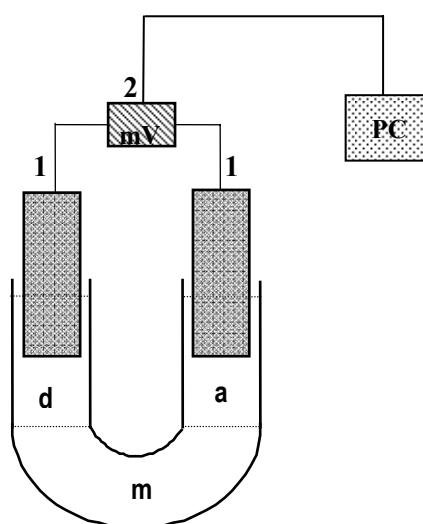


Fig. 1. Scheme of liquid membrane oscillator, d - aqueous donor phase, m - liquid membrane, a - aqueous acceptor phase, 1 - Ag/AgCl/Cl<sup>-</sup> electrodes, 2 - millivoltmeter controlled by PC.

The electric potential difference between the two aqueous phases,  $\Delta E_{d/a}$ , was measured by means of two Ag/AgCl/Cl<sup>-</sup> reference electrodes using an  $\sim 10$  M $\Omega$  input resistance voltmeter controlled by PC (sampling speed  $5$  s<sup>-1</sup>). The electrode distances were 1 cm, 2 cm or 3 cm from the acceptor phase/membrane (a/m) and donor phase/membrane (d/m) interfaces, respectively. Each experiment was repeated at least four times. The obtained oscillation characteristics for each case were similar, but never exactly the same, i.e. they were sensitive to initial conditions. Therefore, all the parameters except one were kept constant and equal in appropriate experiments.

The curves were analyzed by the contraction of attractors in two-dimensional phase-space using time delay method [17]. The dependence of  $\Delta E_{d/a}(t + d')$  ( $d'$  - certain time delay value) in function of  $\Delta E_{d/a}(t)$  based on time series was calculated for each case. By varying the time delay value,  $d'$ , attractors of different size were obtained. To compare the different systems, the attractors which occupied the largest surface in the phase-space portraits were chosen.

### RESULTS AND DISCUSSION

The influence of the electrode position from the aqueous phase/membrane interfaces on the oscillation curves of electric potential difference between the aqueous phases of the BDMTACl oscillator is presented in Fig. 2. The  $\Delta E_{d/a}$  values (1 cm, 2 cm, and 3 cm distances from d/m and a/m interfaces, respectively) were measured with thick Ag/AgCl/Cl<sup>-</sup> electrodes.

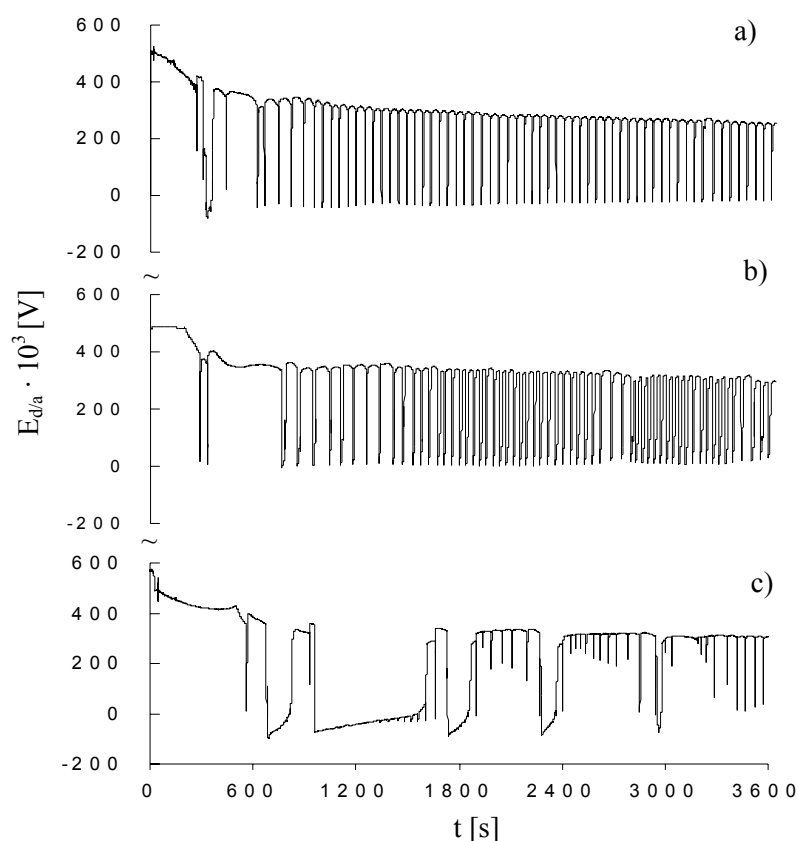


Fig. 2. Oscillation curves of  $\Delta E_{d/a}$  of nitrobenzene oscillator with BDMTACl measured by electrodes situated at a) 1 cm, b) 2 cm and c) 3 cm from the d/m and a/m interfaces, d: BDMTACl ( $5 \times 10^{-3}$  M) + ethanol (1.5 M), a: sucrose (0.1 M), m: 5 ml of HPi ( $1.5 \times 10^{-3}$  M) in nitrobenzene,  $T=298.1 \pm 0.1$  K.

In each case, oscillations appear after a certain induction period. The closer electrodes are situated to interfaces, the shorter induction period is noted. When oscillation begins only few irregular peaks appeared (Fig. 2a,b). Then, after certain regions without oscillations ( $\sim 400$  s in case of 2 cm electrode distance from the interfaces, Fig. 2b), rather regular oscillations of high amplitude (300-350 mV) are observed.

The oscillation pattern is completely different in the case of longer electrode distance from the interfaces (3 cm, Fig. 2c). Peaks of different amplitude (from 20 mV to 400 mV) appear irregularly. These results show that oscillation characteristics are sensitive to changes in electrode distance from the interfaces. A similar conclusion was drawn for LMO with HTMABr [14].

However, the comparison of the oscillation curves obtained for the oscillator with BDMTACl (Fig. 2a) and with HTMABr (Fig. 2a in [14]) under the same experimental conditions shows that the beginning of these curves (till ~ 600 s) is different in both cases. The initial oscillation pattern in the latter system is more regular.

The effect of temperature on the oscillation curves of  $\Delta E_{d2/a2}$  is shown in Fig. 3.

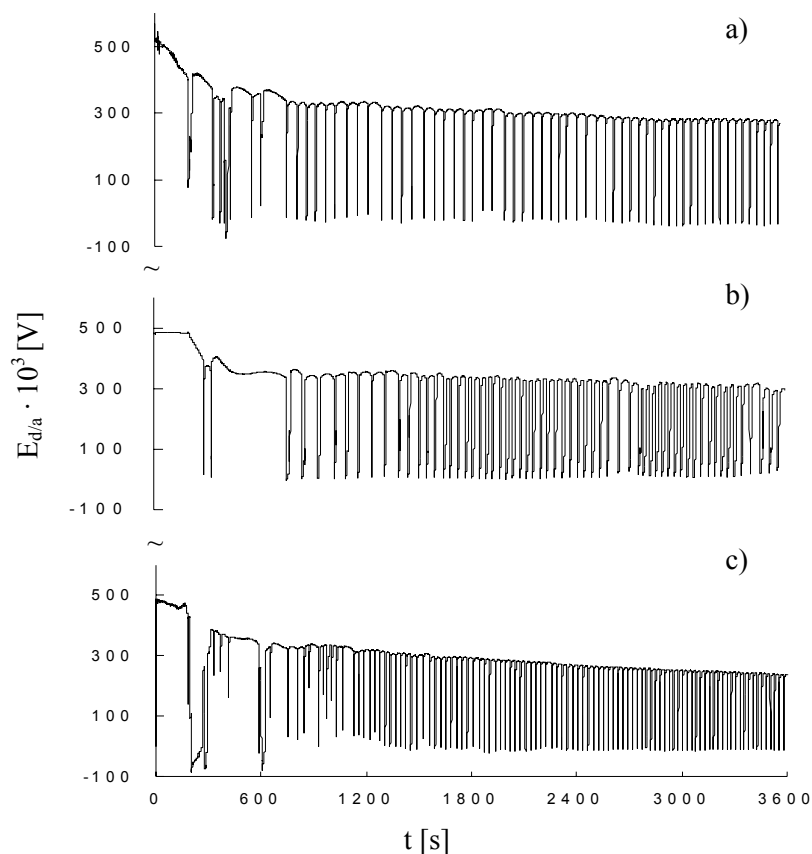


Fig. 3. Influence of temperature on  $\Delta E_{d/a}$ , a) 291.1 K, b) 298.1 K, c) 301.1 K; 2 cm electrode distance from the interfaces, d: BDMTACl ( $5 \times 10^{-3}$  M) + ethanol (1.5 M), a: sucrose (0.1 M), m: 5 ml of HPi ( $1.5 \times 10^{-3}$  M) in nitrobenzene.

At lower temperature (291.1 K, Fig. 3a) after certain induction period (~250 mV) chaotic oscillations which became more regular after ~800 s of

process time were noted. Increasing temperature influences mainly the initial oscillation pattern (till 800 s).

In order to investigate the influence of other parameters on oscillation curves, the temperature of 298.1 K and 2 cm distance of electrodes from the interfaces were applied in each experiment.

The  $\Delta E_{d2/a2}$  (2cm electrode distance from the d/m and a/m interfaces) is composed of: 1) the diffusion potential difference in the donor phase,  $\Delta E_{d2/d1}$ , 2) the potential difference across d/m,  $\Delta E_{d1/m2}$ , 3) the diffusion potential difference in the liquid membrane,  $\Delta E_{m2/m1}$ , 4) the potential difference across the a/m interface,  $\Delta E_{m1/a1}$ , 5) the diffusion potential difference in the acceptor aqueous phase,  $\Delta E_{a1/a2}$ .

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

It was already established that the diffusion potentials  $\Delta E_{d2/d1}$ ,  $\Delta E_{m2/m1}$ ,  $\Delta E_{a1/a2}$  are similar in comparison to the membrane potentials [3,13] and they may be safely neglected. In this case, Eq. (1) gives:

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

It means that the overall electric potential difference between the aqueous phases,  $\Delta E_{d2/a2}$ , is composed of two membrane potentials between the appropriate interfaces.

It was already shown that oscillations in liquid membrane systems with HTMABr take place at the a/m interface. The appearance of the oscillations requires a simultaneous presence of a cationic surfactant, picric acid and ethanol [14].

The question was if the presence of these components in nitrobenzene LMO with BDMTACl is also necessary for  $\Delta E_{d/a}$  oscillations to appear. Therefore, changes of  $\Delta E_{d/a}$  for systems without a cationic surfactant (Fig. 4a), without ethanol in the donor phase (Fig. 4b) and without HPi in the membrane (Fig. 4c) were measured.

As it can be seen from Fig. 4a, the  $\Delta E_{d/a}$  values are close to 0, when a surfactant is not present in the system. Two cases are possible (Eqn (2)):

1) both interfaces (d/m and a/m) are empty with no molecules adsorbed ( $\Delta E_{d2/m2} = \Delta E_{a2/m1} = 0$ ) or

2) both interfaces are equally occupied by some molecules. Since no surfactant in the system is present, it seems that interfaces are "free" and membrane potentials of the both interfaces are close to 0.

If only the surfactant is present in the aqueous donor phase (no ethanol), the value of  $\Delta E_{d/a}$  is very high (~500 mV) (Fig. 4b). This means that the d/m interface is fully occupied by the surfactant molecules in contrary to the a/m interface:  $\Delta E_{d2/m2} = \sim 500$  mV,  $\Delta E_{a2/m1} = \sim 0$  (Eqn (2)). The decline in the

$\Delta E_{d/a}$  curve with time suggests that, by slow diffusion through the membrane, some surfactant molecules reach the a/m interface and occupy it.

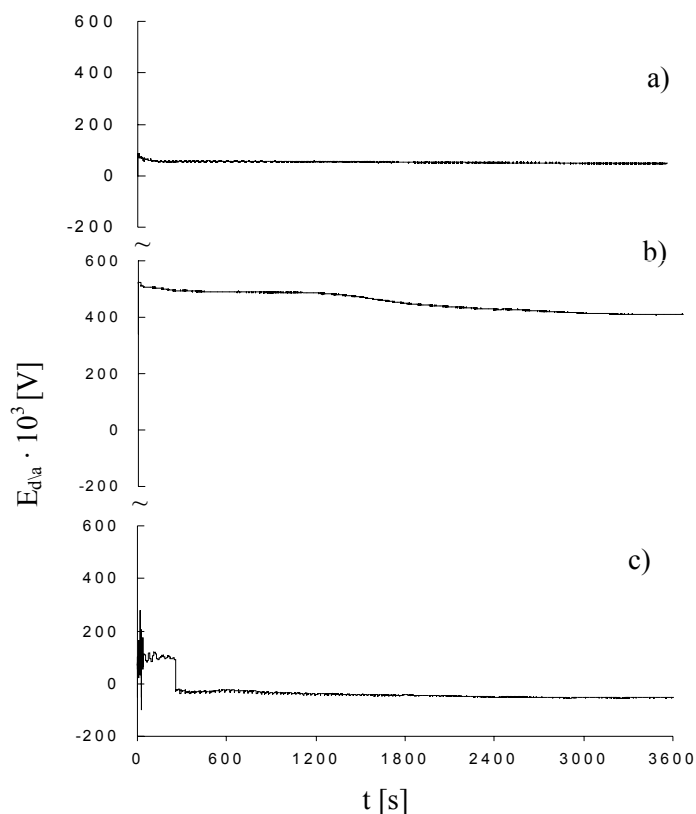


Fig. 4.  $\Delta E_{d/a}$  changes of LMO without: a) surfactant, BDMTACl in the donor phase, b) ethyl alcohol in the donor phase, c) HPi in the membrane,  $T=298.1$  K (further experimental conditions as in Fig. 3).

A comparison of this curve (Fig. 4b) to the one obtained when alcohol is present in the donor phase (Fig. 2b) shows the important role played by alcohol in the diffusion of the surfactant by the liquid membrane. The alcohol molecules which are transported to the membrane facilitate the diffusion process of the surfactant allowing it to reach quickly the a/m interface (after  $\sim 200$  s, Fig. 2b).

It was also shown that the molecules of HPi are necessary for  $\Delta E_{d/a}$  oscillations (Fig. 4c) to appear.

All the results obtained show that, analogously to LMO with HTMABr [13,14], the appearance of oscillations requires the simultaneous presence of the surfactant, HPi and ethanol.

It was also observed that if the distance between the d/m and a/m interfaces increases (higher volume of the liquid membrane than 5ml) oscillations of  $\Delta E_{d/a}$  are not noted during the time of experiment (3600 s). This suggests indirectly that the a/m interface is responsible for  $\Delta E_{d/a}$  oscillations.

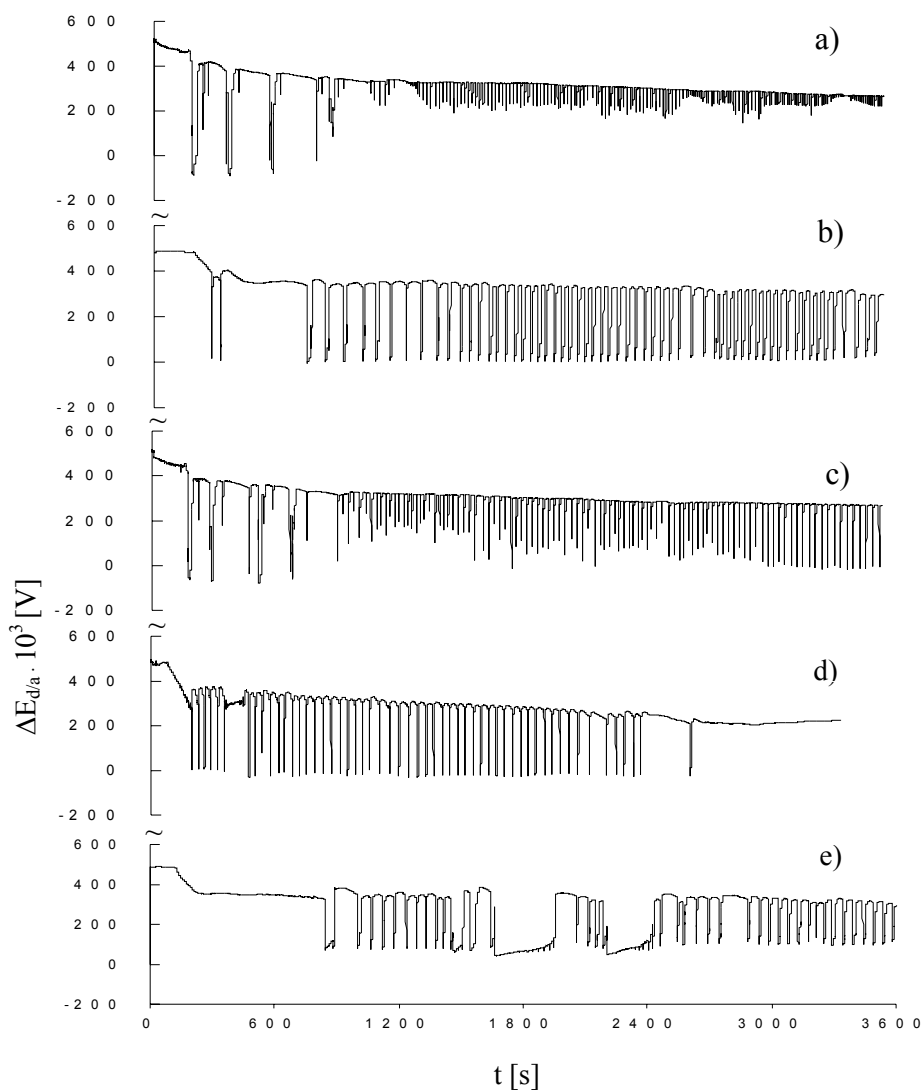


Fig. 5. Influence of substances in the acceptor phase on oscillation curves of LMO with BDMTACl, acceptor phase composition: a) pure water (0.1 M), b) sucrose (0.1 M), c) acetic acid (0.1 M), d) caffeine (0.05 M), e) NaCl;  $T=298.1$  K (further experimental condition as in Fig.3).



All the obtained experimental results suggest that the mechanism of  $\Delta E_{d/a}$  oscillations in LMO with BDMTACl should be similar to the one in LMO with HTMABr [14,18] where the oscillations of electric potential difference between the two aqueous phases are produced by sudden adsorption and desorption of the surfactant and the ionic pair surfactant-Pi at the a/m interface. The diffusion fluxes of all these species in the vicinity of the a/m interface also play an important role. They might couple which leads to a nonlinear behaviour of the system.

The acceptor phase composition (addition of various taste substances) also influence the oscillation pattern (Fig. 5a-e).

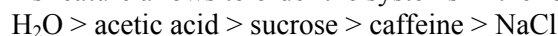
If no additional substances are present in the aqueous acceptor phase (Fig. 5a) the oscillation pattern is chaotic in nature. After short induction time several high amplitude (~500 mV) peaks followed by low amplitude peaks (20 mV-100 mV) till the end of the experiment are observed.

The presence of sucrose in the acceptor phase (Fig. 5b) produces regular oscillations after ~760 s. The amplitudes of the peaks remain reasonably constants (330-350 mV) till the end of experiment. Addition of acetic acid to the system (Fig. 5c) strongly influences the amplitude of the peaks which is changing with time. The frequency of oscillations is higher than in the system with sucrose (Fig. 5b).

In the case of the system with caffeine in the acceptor phase (Fig. 5d), the average amplitude of peaks observed is as high as for the system with sucrose (Fig. 5b) but oscillations stop at ~ 2800 s. Addition of sodium chloride to the acceptor phase provokes a few changes in the oscillation pattern (Fig. 5e). The induction period is much longer than in the previous cases and the frequency of peaks is modified. Furthermore, windows without oscillations appear during the intervals 1600-1900 s and 2100-2500 s.

To compare the systems investigated the oscillation curves were analyzed by constructing two-dimensional attractors using the time delay method [17]. They are presented in Fig. 6.

The attractors differ slightly in shape but more significantly in the surface they occupy. This feature allows to order the systems in the following way:



The surface of the attractor for system with the most ionic substance (NaCl) in the acceptor phase is the smallest in comparison to the other one.

Since each system with a substance of appropriate taste in the acceptor phase has its own attractor, this methods might be used for identifying an unknown substance present in this phase (so called "fingerprint"). The attractor of the system with an unknown substance might be compared with the set of data obtained for different systems. This could lead to the recognition of this substance.

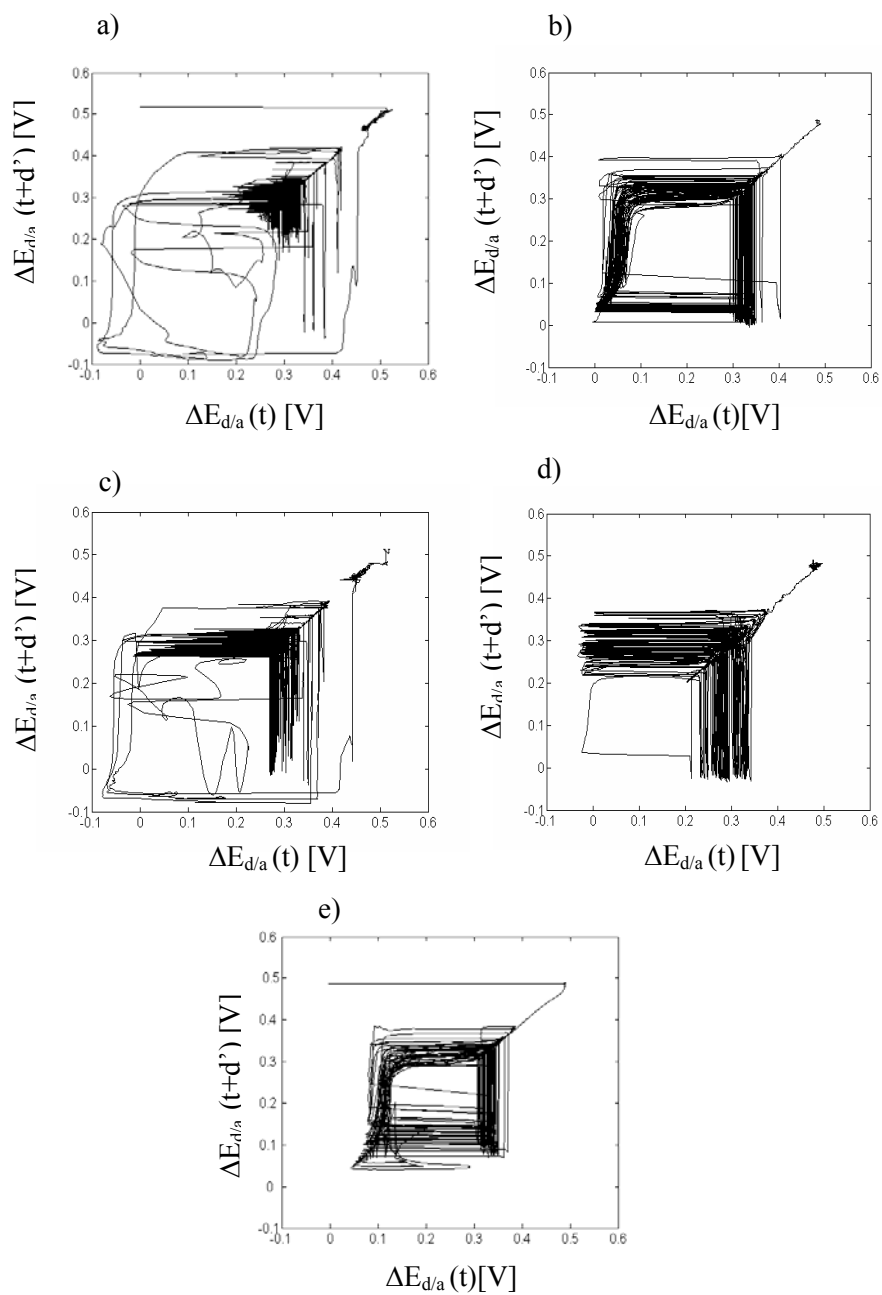


Fig. 6. Attractors for LMO with BDMTACl: a) pure water (0.1 M), b) sucrose (0.1 M), c) acetic acid (0.1 M), d) caffeine (0.05 M), e) NaCl.

## CONCLUSIONS

The oscillation curves presented in this work for nitrobenzene oscillator with BDMTACl and with HTMABr in the same experimental conditions have similar patterns. However, they are more chaotic at the beginning of the process time.

They are sensitive to the electrode distance from the interface and temperature of the experiment. The appearance of oscillations requires a simultaneous presence of a surfactant, HPi and ethanol in the system.

The present work suggests that the mechanism of  $\Delta E_{d/a}$  oscillations in LMO with BDMTACl should be similar as in LMO with HTMABr where oscillations of electric potential difference between the two aqueous phases are produced by sudden adsorption and desorption of a surfactant and ionic pair surfactant-Pi at the a/m interface. The diffusion fluxes of all these species in the vicinity of the a/m interface also play an important role. They might couple leading to the nonlinear behaviour of the system.

The influence of taste substances belonging to different taste classes (sweetness, sourness, bitterness, saltiness) on oscillation characteristics was examined. The oscillation curves were analyzed by a construction of corresponding attractors in two-dimensional space using the time delay method. The shape differs slightly but more significantly in the surface occupied by the attractor. Since each system with substance of appropriate taste in the acceptor phase has its own attractor, this method might be used for identifying unknown substance present in this phase (so called "fingerprint").

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