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3 **New bulk liquid membrane oscillator composed of two coupled oscillators**  
6 **with diffusion mediated physical coupling**

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15 A new type of bulk liquid membrane system, which represents the first example of a  
16 bulk liquid membrane oscillator characterised by the presence of two coupled oscillators, is  
17 described. When the benzyldimethyltetradecylammonium chloride surfactant undergoes an  
18 oscillatory mass transfer through a nitromethane liquid membrane, a new liquid layer (phase  
19 X) appears between the membrane and the acceptor phase. Kinetic analysis provides evidence  
20 that the whole system is composed of two coupled oscillators with diffusion-mediated  
21 physical coupling. The first component oscillator (based on nitromethane) of lower frequency  
22 delivers the driving material to the second one (phase X-based oscillator) leading to additional  
23 higher frequency oscillations. A new molecular mechanism is proposed for interpreting the  
24 experimental observations. The results might enhance understanding of intercellular  
25 communication in biology, where periodic signalling is more efficient than any other type of  
26 signalling mode.

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29 **Keywords:** phase separation, chemical kinetics, numerical simulations, coupled oscillations

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## Introduction

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34 Non-linear oscillations accompanying mass transfer through liquid–liquid interfaces  
35 may play an important role in the engineering of micro-heterogeneous systems such as  
36 colloids and emulsions and in [the](#) processes taking place in biomembranes (Larter, 1990;  
37 Kovalchuk & Wollhardt, 2006). Liquid membrane systems are useful models for studying  
38 these highly complex systems thanks to their simplicity and versatility; they may [also find](#)  
39 [applications](#) in areas such as phase transfer catalysis, taste sensors, and in biological actions  
40 (Rastogi & Srivastawa, 2001).

41 The oscillatory character of the mass transfer across the liquid–liquid interfaces  
42 present in liquid membrane systems is shown by the periodic variation of some  
43 physicochemical property; [this is known as](#) a liquid membrane oscillator (see below).

44 Bulk liquid membrane oscillators are composed of two aqueous phases separated by  
45 an immiscible organic phase (membrane, m). One of the aqueous phases contains a surfactant,  
46 benzyldimethyltetradecylammonium chloride (BDMTACl), in [the](#) donor phase, d, while the  
47 other (acceptor phase, a) may or may not contain some kind of solute (e.g. sucrose). The  
48 organic phase contains appropriate substances (picric acid, HPi) for facilitating the transfer of  
49 [the](#) surfactant from the donor to the acceptor phase. The electric potential difference between  
50 the donor and acceptor phases [exhibits](#) oscillations when the mass transfer occurs in an  
51 oscillatory way (Szpakowska et al. 2002).

52 In order to contribute to elucidation of [the](#) molecular mechanism responsible for the  
53 observed oscillations, the physico-chemical properties of bulk liquid membrane oscillators  
54 with anionic (Szpakowska et al., 2008) and cationic (Szpakowska et al., 2002, 2003, 2006a,  
55 2009) mass transfer surfactants and different membrane materials (Szpakowska et al., 2006a,  
56 2006b, 2008, 2009) [were investigated in detail](#). The influence of taste substances  
57 (Szpakowska et al., 2005, 2006a) was also examined and analysed in depth by [the](#) Gabor  
58 transformation (Płocharska-Jankowska et al., 2005, 2006).

59 The [theoretical](#) interpretation of the mechanism of these oscillations is based on two  
60 different approaches. [In](#) the hydrodynamic approach, it is the hydrodynamic instability of the  
61 liquid–liquid interfaces arising from the Marangoni effect which is responsible for the  
62 oscillations (Kovalchuk & Vollhardt, 2006). The corresponding mathematical analysis  
63 involves the solution of a set of non-linear, non-steady state Navier–Stokes equations and the  
64 surfactant diffusion equation. Notwithstanding the mathematical complexities, this approach  
65 leads to [highly](#) geometry-dependent results (Kovalchuk & Vollhardt, 2007). Hydrodynamic



66 arguments were [also](#) used in the case of biphasic systems to explain the observed periodic  
67 Marangoni instability (Lavabre et al., 2005; Ikezoe et al., 2004).

68 On the other hand, the chemical kinetic approach [completely](#) neglects the  
69 hydrodynamic aspects. It uses the laws of chemical kinetics based on autocatalytic reactions  
70 or cooperative adsorption of the transferring surfactant molecules at the liquid–liquid  
71 interfaces (Kovalchuk & Vollhardt, 2006; Yoshikawa et al., 1988; Yoshikawa & Matsubara,  
72 1983; Toko et al., 1985; Pimienta et al., 2001). Some of the published models present  
73 inconsistencies. The working kinetic equations are not always in [accord](#) with the laws of  
74 chemical kinetics or they are based on unrealistic assumptions (Szpakowska et al., 2006b;  
75 Yoshikawa et al., 1988; Yoshikawa & Matsubara, 1983; Toko et al., 1985; Pimienta et al.,  
76 2001). This situation [led to the proposal of](#) a new sufficiently general and physicochemically  
77 acceptable mechanism for analysis by [the](#) chemical kinetics method of the bulk liquid  
78 membrane oscillations [observed](#) (Szpakowska et al., 2009).

79 In a previous publication (Szpakowska et al., 2009), the physicochemical properties of  
80 a nitrobenzene bulk liquid membrane oscillator containing BDMTACl surfactant in [an](#)  
81 aqueous donor phase [were](#) presented and a molecular mechanism [was](#) proposed using [the](#)  
82 chemical kinetic approach. It was shown that the actual oscillations of the electric potential  
83 difference between the two aqueous phases appeared at the liquid membrane–aqueous  
84 acceptor phase interface (m/a). They originated from the sudden autocatalytic adsorption and  
85 desorption of surfactant molecules at the m/a interface. [The](#) Marangoni effect [also](#) amplified  
86 the observed phenomenon (Kovalchuk & Vollhardt, 2006). These results [clearly showed](#) that  
87 the m/a interface [played](#) a decisive role in the [appearance](#) of oscillations. [Accordingly](#), it  
88 [appeared to be](#) important to investigate how the properties of the liquid membrane [could](#)  
89 influence the characteristics of the oscillations. In particular, it was [assumed](#) that the quality  
90 of interface layer separating the membrane from the aqueous acceptor phase might have [a](#)  
91 decisive influence on the observed oscillations. This could be verified by setting up a liquid  
92 membrane oscillator containing a more water-soluble membrane material.

93 Nitromethane (NM) [was seen to be](#) a good candidate for this purpose. Its dielectric  
94 constant (35.87) is comparable [with](#) that of nitrobenzene (NB) (34.82) at  $T = 298.15$  K  
95 (Reichardt, 1979) but its viscosity is much smaller (0.627 mPa·s for NM and 1.823 mPa·s for  
96 NB) (Weast et al., 1984). On the other hand, NM is much more soluble in water than NB: at  $T$   
97 = 298.15 K, the dissolved organic solvent in water has a mole fraction of  $35.33 \times 10^{-3}$  for NM  
98 and  $0.30 \times 10^{-3}$  for NB (Marcus, 1977). [Also, water](#) dissolves better in NM than in NB:  
99 0.0675 and 0.0162 in mole fractions, respectively (Marcus, 1977).



100 Unexpectedly, this NM-based bulk liquid membrane oscillator [exhibited](#) a completely  
101 new feature not observed in previous studies. During the transport process, a new liquid layer  
102 (phase X) appeared between the membrane and the acceptor phase. [This](#) kind of phase  
103 separation was [previously](#) observed in [the](#) case of a liquid membrane oscillator with anionic  
104 surfactant (Suzuki & Kawakubo, 1992). The authors interpreted the interfacial oscillations  
105 from the hydrodynamic [perspective](#).

106 [The](#) appearance of the new X phase in [the](#) NM bulk liquid membrane oscillator  
107 containing hexadecyltrimethylammonium bromide (Szpakowska et al., 2006b) [was also](#)  
108 [observed previously](#). However, the proposed mechanism could not [satisfactorily](#) account for  
109 the actual interconnection between the behaviour of the liquid membrane and the new phase.

110 [An attempt was made](#) to apply a mechanism proposed by Pimienta et al. (2001) to  
111 explain the oscillations of a dichloromethane-based bulk liquid membrane oscillator.  
112 According to these authors, the adsorption sites play a central role in the molecular events  
113 taking place at the water-membrane interfaces. This approach was appropriate [for](#) a strongly  
114 hydrophobic membrane but it did not [afford](#) satisfactory results when a much less  
115 hydrophobic membrane [such as nitromethane](#) is used since this latter is characterised by [a](#) less  
116 [well-defined](#) interface structure. [Hence](#), a new mechanism [is presented here, being](#) a logical  
117 extension of [the](#) mechanism for [the](#) NB bulk liquid membrane oscillator [previously](#)  
118 [considered](#) (Szpakowska et al., 2009).

119 Furthermore, the oscillation patterns [previously published](#) did not [exhibit a](#) satisfactory  
120 regularity. It was hoped that, by changing the transferring surfactant molecule, more regular  
121 oscillation patterns might be obtained. [Accordingly](#), it might be more appropriate for  
122 applications in taste recognition.

123 In the present paper, this new NM-based bulk liquid membrane oscillator containing  
124 BDMTACl is investigated and analysed using the chemical kinetic approach.

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## Experimental

129 [The](#) purification of chemicals, [the](#) experimental set-up and procedure were as  
130 published previously (Szpakowska et al., 2003). [NM, like](#) NB, has [a](#) greater density than  
131 water, [hence](#) the NM liquid membrane occupied the bottom of a U-shaped glass tube and the  
132 two branches contained the aqueous donor (d) and aqueous acceptor (a) phases (Fig. 1). At the  
133 beginning of [the](#) experiment, the electrodes were positioned at different distances from the



134 d/m and a/m interfaces. The following electrode distances were investigated: 1 cm – 1 cm, 1  
 135 cm – 2 cm, 2 cm – 1 cm, 2 cm – 2 cm, 3 cm – 3 cm, where the first number is the electrode  
 136 distance from the d/m interface.

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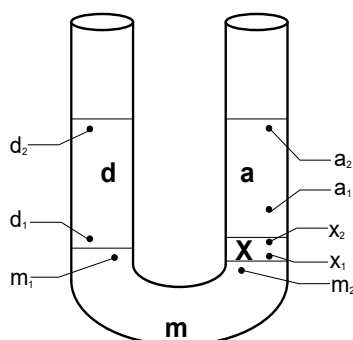
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145 **Fig. 1.** Schematic view of experimental apparatus showing reference points used for  
 146 measuring electric potential differences between the points *i* and *j*,  $E_{ij}$  (Eq. (1)), *d* –  
 147 aqueous donor phase, *m* – membrane, *a* – aqueous acceptor phase.

148

149 The ambient temperature under which the experiments were performed varied between  
 150  $(18 \pm 0.1)^\circ\text{C}$  and  $(28 \pm 0.1)^\circ\text{C}$ . The surfactant concentration in the donor phase was changed  
 151 from 2 mM to 10 mM, while the picric acid (HPi) concentration in the membrane phase was  
 152 examined from 0 mM to 3 mM. The effect of membrane volume (from  $6.0\text{ cm}^3$  to  $5.0\text{ cm}^3$ ) on  
 153 the oscillation pattern was also examined.

154 The actual optimised composition of the three phases was as follows:

155 *m* –  $5.0\text{ cm}^3$  of  $1.5 \times 10^{-3}\text{ M}$  solution of HPi in NM;

156 *d* –  $4.0\text{ cm}^3$  of  $5 \times 10^{-3}\text{ M}$  solution of BDMTACl in ethanol–water mixture (1.5 M);

157 *a* –  $4.0\text{ cm}^3$  of 0.1 M solution of sucrose in water.

158 In the case of the NM oscillator, the microelectrodes used for measuring the electric  
 159 potential differences in the organic membrane phase (Eq. (2)) had to be modified in relation to  
 160 the microelectrode applied in the NB oscillator. In particular, the internal solution of the  
 161 electrode was composed of an an 0.02 M solution of tetrabutylammonium chloride in  
 162 nitromethane.

163 The oscillation curves were repeated at least four times for each case. The curves  
 164 obtained were similar (difference in amplitude and frequency of peaks within 15 %). They  
 165 were sensitive to the initial conditions, e.g. temperature, the manner of preparation of the  
 166 interfaces.

167 The numerical integration of the differential equations was [effected](#) using the program  
 168 Matlab R 12, ODE 45 with steps 0.01.

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## Results and discussion

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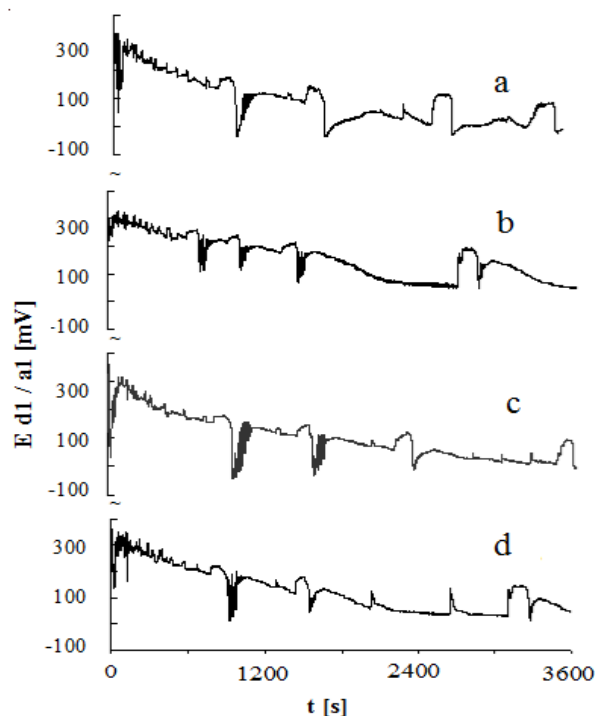
172 Since the behaviour of liquid membrane oscillators is [highly](#) sensitive to the  
 173 experimental parameters (electrode positions, temperature of measurements, membrane  
 174 volume, initial concentrations of surfactant and HPI), these parameters had to be optimised.

175 Fig. 2 shows the influence of temperature on the oscillation pattern [observed](#). This  
 176 figure [actually](#) shows the time-dependence of the electric potential difference between the two  
 177 aqueous phases, d and a, as measured at electrode positions  $d_1$  and  $a_1$  (see Fig. 1).

178 [The](#) oscillations are [shown to be](#) characterised by large low-frequency peaks flanked  
 179 by lateral higher-frequency oscillations. The most satisfactory pattern was obtained at  $\theta = (25$   
 180  $\pm 0.1)$  °C (Fig. 2c). It should be noted that this curve [was](#) [previously](#) used in molecular  
 181 recognition studies (Szpakowska et al., 2005; Płocharska-Jankowska et al., 2005).

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186 **Fig. 2.** Oscillation patterns of liquid membrane oscillator with NM at different temperatures  
 187  $\theta$ /°C:  $18.0 \pm 0.1$  (a),  $22.0 \pm 0.1$  (b),  $25.0 \pm 0.1$  (c), and  $28.0 \pm 0.1$  (d).

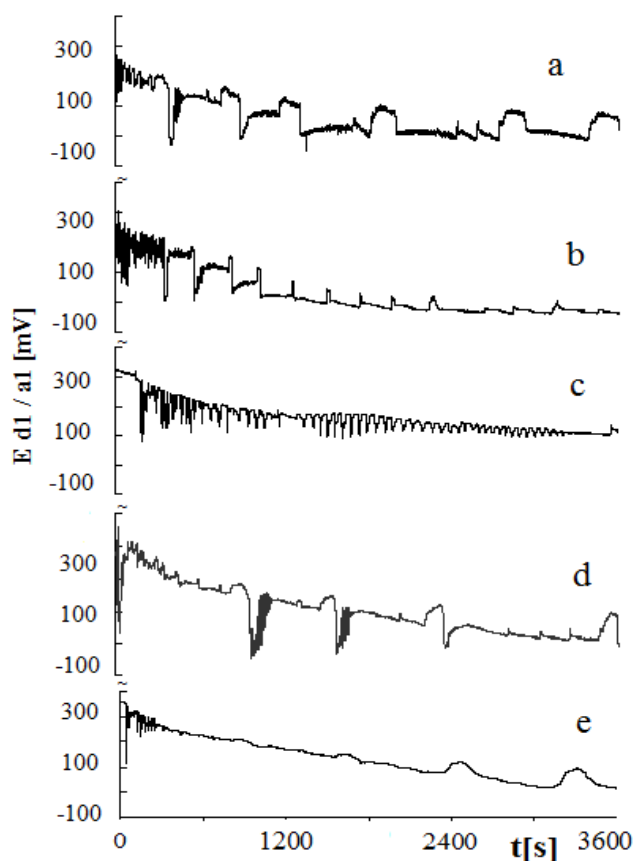
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190 Fig. 3 [shows](#) the influence of electrode distances from the d/m interface and from the  
191 a/m interface on the oscillation pattern. The characteristic peaks are observed for the case  
192 when the electrodes were positioned at 2 cm from the interfaces in both [the](#) donor and  
193 acceptor phases (Fig. 3d).

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198 **Fig. 3.** Dependence of oscillation pattern of NM liquid membrane oscillator on initial  
199 electrode distances from d/m and a/m interfaces: 1 cm – 1 cm (a), 1 cm – 2 cm (b), 2  
200 cm – 1 cm (c), 2 cm – 2 cm (d), 3 cm – 3 cm (e).

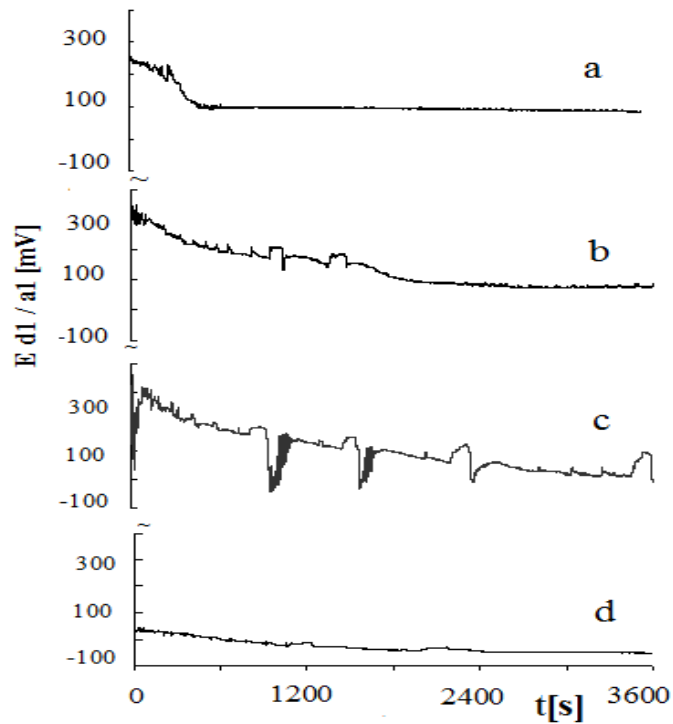
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203 Fig. 4 [indicates](#) that too low and too high an initial concentration of surfactant in the  
204 donor phase [does](#) not produce oscillations. The most satisfactory oscillation pattern was found  
205 for the initial surfactant concentration of 5.0 mM (Fig. 4c).

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211 **Fig. 4.** Influence of initial surfactant concentration in donor phase on oscillation patterns of  
 212 liquid membrane oscillator with NM: 2 mM (a), 3 mM (b), 5 mM (c), 10 mM (d); ( $\theta =$   
 213  $(25.0 \pm 0.1)$  °C).

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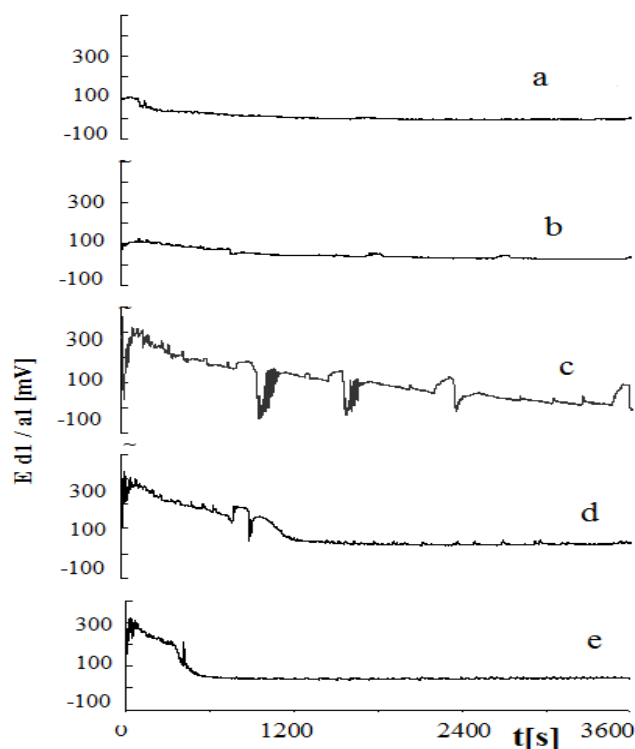
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216 The initial HPI concentration in the membrane phase also influences the  $E_{d/a} = f(t)$   
 217 dependence (Fig. 5). The oscillation pattern is only observed at 1.5 mM initial HPI  
 218 concentration in the membrane phase.

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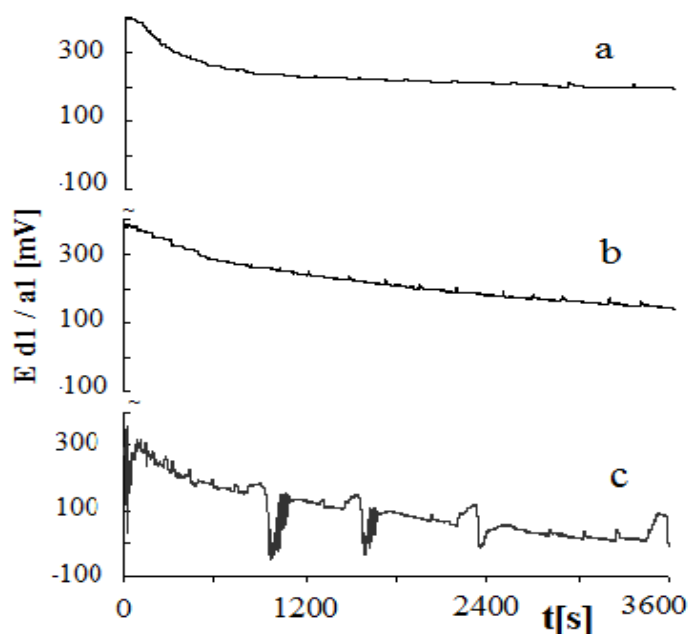
224 **Fig. 5.** Influence of initial HPi concentration in NM membrane phase on oscillation patterns:  
 225 0 mM (a), 0.75 mM (b), 1.5 mM (c), 2 mM (d), 3 mM (e); ( $\theta = (25.0 \pm 0.1) ^\circ\text{C}$ ).

226

227 The membrane volume [also](#) has [an](#) effect on the oscillation (Fig. 6). The  $5.0 \text{ cm}^3$   
 228 [volume appears](#) to be optimal for [observing the](#) oscillations, [hence](#) was chosen for further  
 229 experiments (Fig. 6c). Greater volumes increase the diffusion path between the donor and  
 230 acceptor phases leading to oscillations, the beginning of which is delayed by several hours. At  
 231 [a](#) membrane volume of  $5.5 \text{ cm}^3$ , this delay is [around](#) 2 h, while for [a](#) volume of  $6.0 \text{ cm}^3$  the  
 232 delay [extends up](#) to 5 h. Experiments with [a](#) membrane volume lower than  $5.0 \text{ cm}^3$  could not  
 233 be [performed](#) due to mutual leaking of [the](#) aqueous donor and acceptor phases.

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240 **Fig. 6.** Oscillation patterns of liquid membrane oscillator with NM at different liquid  
 241 membrane volume: 6.0 mL (a), 5.5 mL (b), 5.0 mL (c); ( $\theta = (25 \pm 0.1) ^\circ\text{C}$ ).

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The optimized values of the experimental parameters are [detailed under Experimental](#);  
 these were used in all the experiments. [Although](#) the experimental conditions were similar to  
 those of the NB oscillator (Szpakowska et al., 2009), the behaviour of the oscillator under  
 study [proved to be](#) completely different from previous observations. A spectacular new  
 phenomenon [appeared](#) at about  $t = 300$  s after the beginning of the experiment: a new separate  
 layer [denoted as](#) phase X [developed](#) between the liquid membrane and the aqueous acceptor  
 phase (Fig. 1).

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Phase X [was found to be an](#) NM/water mixture, [with](#) its volume increasing [over](#) time.  
 The intensive surface movements (Marangoni instability) observed visually at the m/a  
 interface [decreased](#) considerably after  $t = 120$  s and [disappeared](#) completely after  $t = 600$  s.  
 No surface movements were observed at the d/m interface. This [confirmed](#) that the  
 oscillations [in the electric](#) potential difference between the two aqueous phases [appeared](#) at  
 the m/a interface.

256

257

The physicochemical aspects of the liquid membrane oscillators were analysed in  
 detail in a previous publication (Szpakowska et al., 2009). [The overall electric potential](#)

258 difference between the d and a aqueous phases,  $E_{d/a}$ , [was shown to be](#) the sum of different  
 259 contributions. [In](#) considering the scheme in Fig. 1, it [may](#) be written [as](#):

260

$$261 \quad E_{d/a} = E_{d2/a2} = E_{d2/d1} + E_{d1/m1} + E_{m1/m2} + E_{m2/X1} + E_{X1/X2} + E_{X2/a1} + E_{a1/a2} \quad (1)$$

262

263 where:  $E_{d2/d1}$ ,  $E_{a1/a2}$ ,  $E_{m1/m2}$  and  $E_{X1/X2}$  are diffusion potentials in donor, acceptor, membrane  
 264 and X phases, respectively.  $E_{d1/m1}$ ,  $E_{m2/X1}$  and  $E_{X2/a1}$  are the potential differences across the  
 265 donor phase/membrane, membrane/X phase and X phase/acceptor phase interfaces.

266

267 The diffusion potential differences in the two aqueous phases,  $E_{d2/d1}$  and  $E_{a1/a2}$ , are  
 268 ignored since their values are negligibly small (Szpakowska et al., 2003).

269 In principle, the different components in Eq. (1) can be measured experimentally by  
 270 means of microelectrodes. However, this was impossible for the components involving phase  
 271 X on account of the small volume of the latter. [Accordingly](#), the last three components [were](#)  
 272 [combined, affording](#) Eq. (2):

273

$$274 \quad E_{d/a} = E_{d1/m1} + E_{m1/m2} - E_{a1/m2} \quad (2)$$

275

276 [where](#)  $E_{m2/a1} = E_{m2/X1} + E_{X1/X2} + E_{X2/a1}$ .

277

278 The results are collected in Table 1.

279

280 **Table 1.** Comparison of experimental and calculated (Eq. (2)) electric potential differences  
 281 between the donor and acceptor phases,  $E_{d/a}$ , in function of time

282

Time, $t$	Potential difference/mV				
	s	$E_{d1/m1}$	$E_{a1/m2}$	$E_{m1/m2}$	$E_{d/a}$ (calc)
600	115	-130	25	270	265
1800	110	-100	5	215	230
2400	110	-60	0	170	180
3000	110	-50	0	160	165

283

284 It can be seen that  $E_{d1/m1}$  essentially remains constant throughout the experiment. This  
 285 indicates that the d/m interface is saturated with surfactant molecules. The diffusion potential  
 286 in the membrane,  $E_{m1/m2}$ , only makes a small contribution. It is noteworthy that the calculated  
 287 values of the overall electric potential difference,  $E_{d/a}$  (calc), are in fairly good agreement with  
 288 the directly measured values,  $E_{d/a}$  (exp). This confirms the validity of Eq. (2) throughout the  
 289 experiment.

290 According to theory (Suzuki & Kawakubo, 1992; Sternling & Scriven, 1959; Brian,  
 291 1971), the Marangoni effect observed in the initial stage of the experiments depends on the  
 292 relative magnitudes of the kinematic viscosities ( $\eta_i$ ) of the two phases in contact and of the  
 293 solute diffusion coefficients ( $D_i$ ) in the two phases, as well as on the direction of the solute  
 294 transfer gradient and the sign of change in interfacial tension with solute concentration. When  
 295 a surfactant is transferred from phase A to phase B, and if  $\eta_A/\eta_B > 1$  and  $D_A/D_B < 1$ , a large  
 296 Marangoni effect can be expected. With A = nitrobenzene and B = water, these conditions  
 297 were fulfilled at the m/a interface and a significant Marangoni effect was observed  
 298 (Szpakowska et al., 2009). On the other hand, if  $\eta_A/\eta_B < 1$  and  $D_A/D_B > 1$ , the interface  
 299 remains stable and the Marangoni effect is absent. This pertained for the d/m interface with  
 300 NB membrane.

301 In the present case, the kinematic viscosity of NM is smaller ( $0.554 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ )  
 302 (Weast et al., 1984) than that of water (w) ( $0.891 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ) (Weast et al., 1984), i.e.  
 303  $\eta_{NM}/\eta_w < 1$ . With  $D_i \sim \eta_i^{-1}$ , there is  $D_{NM}/D_w > 1$  and no Marangoni effect, which originates  
 304 from the solute transfer gradient, could be detected at the m/a interface.

305 The significant Marangoni effect observed experimentally at the m/a interface  
 306 conflicts with this theoretical prediction based on solute transfer gradients (Sternling &  
 307 Scriven, 1959). However, a more precise theory based on linear stability analysis predicts that  
 308 an interface is always unstable under the conditions of surfactant transfer if the adsorption  
 309 kinetics is diffusion-controlled (Hennenberg et al. 1979).

310 Another explanation may be presented for the effects observed in the present case. It is  
 311 well known that the interpenetration of two liquids (e.g. water and nitromethane) under non-  
 312 equilibrium conditions may provoke a dynamic interfacial tension gradient which can lead to  
 313 large Marangoni effects (Ostrovsky & Ostrovsky, 1983). The increased mutual solubility of  
 314 NM and water induces a much greater interface instability than in the case of NB. The  
 315 Marangoni effect disappears after  $t = 600$  s (see above) when the interpenetration of the two  
 316 phases stops at the equilibrium state determined by the mutual solubility.



317 The oscillatory behaviour of the overall electric potential difference between the  
 318 aqueous donor and acceptor phases,  $E_{d/a}$ , at the actual optimized initial composition of the  
 319 three phases is represented in Fig. 2c (and also in Figs 3d, 4c, 5c and 6c).

320 It can be seen that the oscillation pattern observed is quite different from that of the  
 321 NB oscillator. This latter had regular, high-frequency oscillations with apparently constant  
 322 amplitudes throughout the experimental run. On the other hand, the NM oscillator may be  
 323 characterised by the presence of much larger peaks of smaller amplitudes. These peaks appear  
 324 after a long induction period and after the vanishing of high-frequency irregular transient  
 325 oscillations.

326 An important new feature of the NM oscillator is that the large peaks are accompanied  
 327 on their right by much higher frequency oscillations. This contrasts with the rather long  
 328 periods observed for the large peaks.

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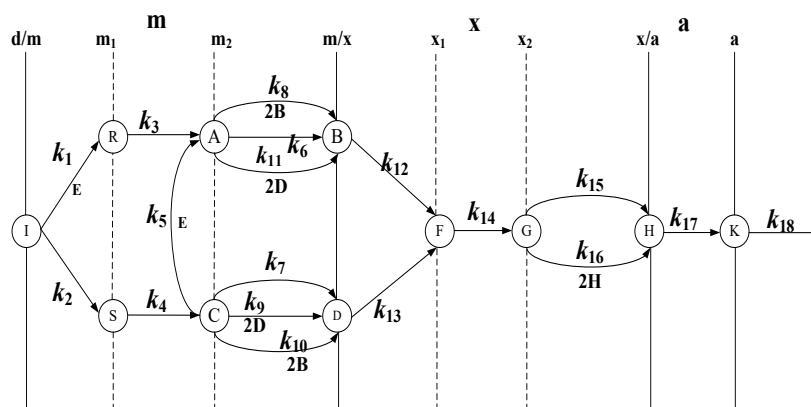
### 330 *Kinetics and mechanism*

331

332 In order to obtain greater insight into the molecular events taking place in the  
 333 oscillator at hand, the same chemical approach is applied as for the NB oscillator using the  
 334 laws of chemical kinetics (Szpakowska et al., 2009). In this approach, a given molecule is  
 335 considered as a different species if situated in different environments. It is further admitted  
 336 that the transformation of one species into another is governed by the laws of deterministic  
 337 chemical kinetics.

338 The ion pair mechanism previously proposed is adopted and modified to take into  
 339 account the presence of the new phase X. The various mechanistic steps are represented in  
 340 Fig. 7.

341



350

351

352 **Fig. 7.** Mechanistic scheme of NM-based oscillator.

353

354

355 The interface d/m is saturated with surfactant I which desorbs to vicinity  $m_1$  of the  
356 interface in the NM membrane in [the](#) form of ion pairs with counter ions  $\text{Cl}^-$  (S) and  $\text{Pi}^-$  (R),  
357 where E denotes HPi and  $k_1$  and  $k_2$  are appropriate rate constants.

358 The tendency of the surfactant to penetrate into the membrane from the donor phase is  
359 indicated by the large value of its partition constant:  $K_m/K_d = 45 \pm 1$  at  $(25 \pm 0.1)^\circ\text{C}$ .

360 The ion pairs R and S diffuse [through](#) the membrane to vicinity  $m_2$  of the m/X  
361 interface (rate constants  $k_3$  and  $k_4$ ). Ion pairs C may react with HPi to form the other type of  
362 ion pairs A ( $k_5$ ).

363 The ion pairs at  $m_2$ , A, and C, [suddenly](#) adsorb into the m/X interface in non-catalysed  
364 (rate constants  $k_6$  and  $k_7$ ) and catalysed steps (rate constants  $k_8$  and  $k_9$ ). [Clearly](#), cross-catalytic  
365 steps may also occur (rate constants  $k_{10}$  and  $k_{11}$ ). Due to these adsorption steps, interface m/X  
366 becomes positively charged and the [electric](#) potential difference,  $E_{d/a}$ , [suddenly decreases](#) to a  
367 smaller value.

368 In subsequent steps, ion pairs B and D are desorbed to vicinity  $X_1$  of the m/X interface  
369 in phase X (rate constants  $k_{12}$  and  $k_{13}$ ). It is [assumed](#) that, in phase  $X_2$ , both ion pairs are  
370 completely dissociated due to the high dielectric constant of water present. [Hence](#), both ion  
371 pairs give the same cationic species F.

372 The desorbed surfactant diffuses across phase X to vicinity  $X_2$  of the X/a interface,  
373 giving G ( $k_{14}$ ). Desorption ( $k_{12}$  and  $k_{13}$ ) eliminates the positive charge from interface m/X and  
374  $E_{d/a}$  [regains](#) a value which is close to its original value.

375 Once more, the surfactant ion is suddenly adsorbed to the X/a interface in [non-](#)  
376 catalysed ( $k_{15}$ ) and catalysed steps giving H ( $k_{16}$ ). As a result, these adsorption steps decrease  
377 the value of  $E_{d/a}$ .

378 Finally, the surfactant is [suddenly](#) desorbed to vicinity  $a_1$  of the X/a interface ( $k_{17}$ ),  
379 followed by the diffusion of the desorbed surfactant K from  $a_1$  into the bulk of the acceptor  
380 phase,  $a_2$  ( $k_{18}$ ). The desorption step [again](#) provokes the increase [in](#)  $E_{d/a}$  value.

381 Repetition of the adsorption–desorption steps leads to oscillation of the [electric](#)  
382 potential difference  $E_{d/a}$ . [The oscillations observed are](#) seen [as](#) due to the mass transfer of  
383 surfactant from the aqueous donor to the aqueous acceptor phase in an oscillatory way  
384 (Szpakowska et al., 2009). [Spectrophotometric measurements revealed](#) that, for the initial



385 surfactant concentration of  $I_0 = 5.0 \times 10^{-3}$  M in the donor phase, the values of  $5.0 \times 10^{-6}$  M  
 386 were found after  $t = 3600$  s in the acceptor phase. At the same time, the counter ion  
 387 concentration dropped to  $[Cl^-] = 4.1 \times 10^{-4}$  M in the acceptor phase. The difference is due to  
 388 the different partitioning of the surfactant and its counter ion in the membrane and in phase X.

389 The presence of surfactant in the acceptor phase was also confirmed by NMR  
 390 measurements. HPi is also transferred to the acceptor phase. Its concentration was  $6.0 \times 10^{-5}$   
 391 M after  $t = 3600$  s, as revealed by UV spectroscopy. Again, the NMR results confirmed the  
 392 presence of HPi in the acceptor phase. On the other hand, no HPi was detected in the donor  
 393 phase.

394 The time evolution of the molecular events participating in the oscillation process can  
 395 be described by the corresponding chemical kinetics equations (for simplicity, the charges are  
 396 not represented in these equations). Only the forward reaction steps are considered (far from  
 397 equilibrium situation) and the hydrodynamic effects are not taken into account explicitly.

398 The proposed mechanistic scheme (Fig. 7) shows that its first part (steps  $k_1 - k_{14}$ ) is  
 399 identical with the scheme applied to the nitrobenzene-based oscillator previously published  
 400 (Szpakowska et al., 2009). The second part is due to the presence of phase X.

401 The following rate equations can be established for the proposed mechanism:

402

$$403 \quad \frac{dR}{dt} = k_1IE - k_3R \quad (3)$$

$$404 \quad \frac{dS}{dt} = k_2I - k_4S \quad (4)$$

$$405 \quad \frac{dA}{dt} = k_3R + k_5EC - k_6A - k_8AB^2 - k_{11}AD^2 \quad (5)$$

$$406 \quad \frac{dB}{dt} = k_6A + k_8AB^2 + k_{11}AD^2 - k_{12}B \quad (6)$$

$$407 \quad \frac{dC}{dt} = k_4S - k_5EC - k_7C - k_9CD^2 - k_{10}CB^2 \quad (7)$$

$$408 \quad \frac{dD}{dt} = k_7C + k_9CD^2 + k_{10}CB^2 - k_{13}D \quad (8)$$

$$409 \quad \frac{dF}{dt} = k_{12}B + k_{13}D - k_{14}F \quad (9)$$

$$410 \quad \frac{dG}{dt} = k_{14}F - k_{15}G - k_{16}GH^2 \quad (10)$$

$$411 \quad \frac{dH}{dt} = k_{15}G + k_{16}GH^2 - k_{17}H \quad (11)$$

$$412 \quad \frac{dK}{dt} = k_{17}H - k_{18}K \quad (12)$$

413

414 Eqs. (3)–(12) represent a system of autonomous first-order coupled non-linear  
 415 differential equations in as much as time does not appear explicitly (however, see below). The  
 416 solution of this system was obtained by numerical integration using the Matlab program.

417 The actual values of the different rate constants  $k_i$  were chosen according to the  
 418 physical chemistry of the system (Szpakowska et al., 2009). By analogy,  $k_3$  and  $k_4$  represent



419 normal diffusion steps. Hence, their values might be around  $10^{-5}$  as suggested by data in the  
 420 literature (Cussler, 1995). As in a previous publication (Szpakowska et al., 2009), these values  
 421 were taken only as indications for diffusion steps  $k_3$  and  $k_4$ . They were used as the starting  
 422 point for further numerical experimentation but other values might also have been used. There  
 423 is also  $k_3 < k_4$  due to the size difference of the diffusing species. On the other hand, the  
 424 diffusion step in phase X is characterised by the rate constant  $k_{14}$  which represents super-  
 425 diffusion (i.e. diffusion promoted by the Marangoni effect), hence its value must be much  
 426 higher than that of  $k_3$  and  $k_4$ . A further contribution to the higher value of  $k_{14}$  derives from the  
 427 fact that the new phase X is much thinner than the liquid membrane.

428 The experiment reveals that the thickness of phase X increases over time. This means  
 429 that diffusion across phase X becomes more and more retarded as the diffusion path increases.  
 430 As a result, the value of  $k_{14}$  must decrease with time. The time-dependence of  $k_{14}$  could be  
 431 expressed by the equation  $k_{14} = \alpha/(1 + \beta t)$ , where  $\alpha$  and  $\beta$  are the appropriately chosen  
 432 constants and  $t$  represents the time. It should be noted that, by introducing an explicitly time-  
 433 dependent rate constant, the system of differential equations becomes non-autonomous. For  
 434 obvious reasons, the catalytic ( $k_8, k_9, k_{16}$ ) and cross-catalytic ( $k_{10}, k_{11}$ ) adsorption rate  
 435 constants must have much greater values than the non-catalysed rate constants ( $k_6, k_7, k_{15}$ ).  
 436 Furthermore, sustained oscillations can be obtained only if the Gray–Scott condition  
 437 (Szpakowska et al., 2009; Gray & Scott, 1990) is fulfilled: the desorption rate constants ( $k_{12},$   
 438  $k_{13}, k_{17}$ ) must be substantially greater than the non-catalysed adsorption rate constants ( $k_6, k_7,$   
 439  $k_{15}$ ) at the m/X and X/a interfaces. More precisely, the following relationships must be  
 440 satisfied:  $k_{12} > 8k_6, k_{13} > 8k_7$  and  $k_{17} > 8k_{15}$ . Clearly, many different  $k_i$  values can satisfy these  
 441 conditions.

442 In the present work, the following set of rate constants was used for model  
 443 calculations:  $k_1 = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_2 = 2 \text{ s}^{-1}$ ;  $k_3 = 9 \times 10^{-6} \text{ s}^{-1}$ ;  $k_4 = 10^{-5} \text{ s}^{-1}$ ;  $k_5 = 1 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_6$   
 444  $= 10^{-4} \text{ s}^{-1}$ ;  $k_7 = 5 \times 10^{-4} \text{ s}^{-1}$ ;  $k_8 = 10^5 \text{ M}^{-2} \text{ s}^{-1}$ ;  $k_9 = 8 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ ;  $k_{10} = 9 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ ;  $k_{11} =$   
 445  $10^{-1} \text{ M}^{-2} \text{ s}^{-1}$ ;  $k_{12} = 1.8 \text{ s}^{-1}$ ;  $k_{13} = 2.7 \text{ s}^{-1}$ ;  $k_{14} = 0.02/(1 + 5 \times 10^{-4}t) \text{ s}^{-1}$ ;  $k_{15} = 3 \times 10^{-3} \text{ s}^{-1}$ ;  $k_{16} =$   
 446  $10^6 \text{ M}^{-2} \text{ s}^{-1}$ ;  $k_{17} = 1.2 \text{ s}^{-1}$ ;  $k_{18} = 0.08 \text{ s}^{-1}$ .

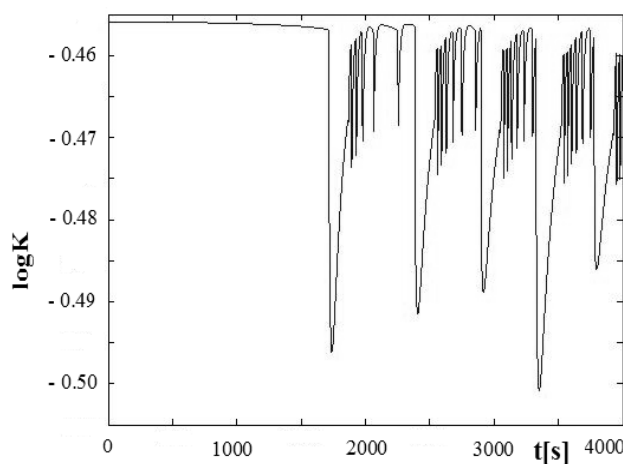
447 With these  $k_i$  values and constant initial concentrations,  $I_0 = 5.0 \times 10^{-3} \text{ M}$  and  $E_0 = 1.5$   
 448  $\times 10^{-3} \text{ M}$  (the initial concentrations of all the other species were zero), numerical integration  
 449 gave the oscillation curve (time series) represented in Fig. 8.

450

451







452

453 **Fig. 8.** Calculated oscillation profile of surfactant concentration,  $K$ , in aqueous acceptor phase  
454 (arbitrary scale).

455

456 It can be seen that the theoretical curve [appropriately reflects](#) the general  
457 characteristics of the experimental oscillation profile (Fig. 2c). Oscillations appear [only](#) after  
458 an induction period. The oscillation peaks are large, have low frequency and on their right  
459 they are accompanied by higher frequency oscillations with narrower peaks of [lower](#)  
460 amplitudes.

461

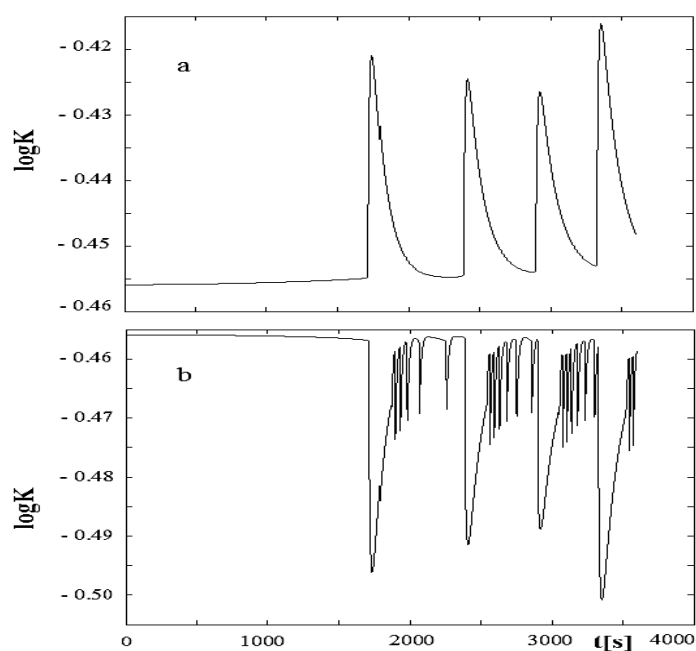
462 The proposed model can [also](#) be used for establishing the origin of the two types of  
463 oscillations present in the oscillation pattern. The presence of the new phase X suggests that  
464 the NM oscillator can be [regarded](#) as composed of two subsystems: the first is an oscillator  
465 having NM as membrane (m-oscillator) while the membrane of the second oscillator is the  
466 new phase X, i.e. a NM–water mixture (X-oscillator). It is quite [probable](#) that these two  
467 oscillators produce different oscillations. It is [anticipated](#) that, if the oscillations of one of  
468 these oscillators [are suppressed](#), the oscillations of the other oscillator can be observed  
469 separately. A given oscillation can be [readily](#) blocked if the Gray–Scott condition (Gray &  
470 Scott, 1990) is not fulfilled. This occurs for an appropriate [selection](#) of the desorption and  
471 [non-catalysed](#) adsorption rate constants at the membrane exit interface (Szpakowska et al.,  
472 2009).

472

473 For example, if the inequality characterising the X-oscillator is reversed, i.e. if  $k_{17} <$   
474  $8k_{15}$ , the corresponding stationary state cannot lose its stability and sustained oscillations are  
475 impossible. This [pertains, for example](#), for the following choice of rate constants:  $k_{15} = 3 \text{ s}^{-1}$   
476 and the previous  $k_{17} = 1.2 \text{ s}^{-1}$ . The values of the other rate constants [remained](#) as for the curve  
477 presented in Fig. 8.

477

478



479

480 **Fig. 9.** Selective suppression of oscillations taking place in phase X;  $k_{17} < 8k_{15}$  (a);  $k_{17} > 8k_{15}$   
 481 (b).

482

483

484 Fig. 9 shows that the narrow small-amplitude higher-frequency peaks disappear from  
 485 the right of the wide lower-frequency peaks. It may be concluded that the suppressed peaks  
 486 originate from the oscillations taking place in the X-oscillator at the X/a interface. On the  
 487 other hand, the remaining wide peaks represent the oscillations in the m-oscillator at the m/X  
 488 interface. This is confirmed by the oscillation curve in Fig. 9a being identical with the  
 489 oscillation pattern of species F.

490 The two component oscillators are coupled so that the first m-oscillator delivers the  
 491 starting amount of surfactant to the second X-oscillator in an oscillatory manner; hence  
 492 chemical-coupling in series (Epstein & Pojman, 1998). These oscillations of the first  
 493 oscillator are modulated subsequently by the oscillations occurring in the second oscillator.  
 494 Consequently, the experimental oscillation profile exhibits contributions from both parts of  
 495 the investigated oscillator: one cycle of the m-oscillator is followed by several cycles of the  
 496 X-oscillator. This complex oscillation pattern could be the result of a bursting mechanism or  
 497 some kind of intermittency (Epstein & Pojman, 1998) observed for certain single oscillators.  
 498 However, these possibilities can be excluded in the light of the above analysis.

499 The chemical-coupling between the m- and X-oscillators is only formal since no actual  
 500 chemical reactions take place in the system. The coupling between the two component

501 oscillators is physical, being based on the diffusion of species F from the m/X interface area  
502 (m-oscillator) to the X/a interface area. This can be shown by examining the role played by  
503 the diffusion rate constant,  $k_{14}$ , in the oscillation mechanism. When  $k_{14}$  increases es (increasing  
504 constant  $\alpha$  for a given value of  $\beta$ ), the oscillations due to the m-oscillator (large peaks) remain  
505 almost unchanged: the amplitudes show little variation while the number of peaks and the  
506 periods are the same. However, the number of small narrow peaks (X-oscillator) and their  
507 amplitudes decrease considerably.

508 When  $k_{14}$  is decreased by increasing constant  $\beta$  for a given value of  $\alpha$ , the  
509 characteristics of the large peaks again remain unchanged. On the other hand, the number of  
510 narrow peaks and their amplitudes increases s and the oscillation in the X-oscillator begins later  
511 and later. When the narrow peaks reach the same amplitude as the large peaks, these latter  
512 become completely hidden and their presence is more and more difficult to detect. At a  
513 sufficiently high value of the constant  $\beta$ , no traces of the large peaks are visible and the  
514 oscillation pattern of the oscillator undergoes a transition to pure X-oscillations.

515 These results can be interpreted as follows: when  $k_{14}$  is high, the diffusion connecting  
516 the m- and X-oscillators is fast and the coupling is strong. The amount of F appearing near  
517 interface m/X in an oscillatory fashion is quickly delivered to vicinity  $x_2$  of interface X/a.  
518 Oscillations at this interface start for each cycle of the appearance of the surfactant (species F)  
519 and both m- and X-oscillations appear in the oscillation pattern. On the other hand, the low  $k_{14}$   
520 value means slower diffusion. As a consequence, more F accumulates near interface m/X and  
521 it has time to lose its oscillatory character before it is delivered slowly to the vicinity of the  
522 X/a interface. This means that, when  $k_{14}$  has a low value, the coupling between the m- and X-  
523 oscillators is weak and ultimately only the X-oscillations can be observed. It should be noted  
524 that the same result can be obtained by blocking the m-oscillator by choosing appropriate  
525 adsorption and desorption rate constants (see above). These results show that a strong  
526 physical coupling occurs in the NM liquid membrane oscillator.

527 For completeness, the chemical coupling present in the m-oscillator should also be  
528 mentioned. The coupling occurs between the oscillations of the two types of ion pairs, A and  
529 C, due to the presence of cross-catalytic steps ( $k_{10}$  and  $k_{11}$ ). The strength of this chemical  
530 coupling is controlled by the corresponding rate constants,  $k_{10}$  and  $k_{11}$ , as shown in a previous  
531 publication (Szpakowska et al., 2009). In the present case also,  $k_{11}$  has a greater influence than  
532  $k_{10}$  on the oscillation pattern. The systematic variation in both  $k_{10}$  and  $k_{11}$  shows that the actual  
533 experimental oscillation profile corresponds to weak chemical coupling.



534 This detailed analysis [reveals](#) that the kinetic approach [previously](#) proposed  
535 (Szpakowska et al., 2009) can [also](#) be used successfully in the case of more complex coupled  
536 oscillators.

537 The NM-based oscillator containing BDMTACl investigated in this work represents  
538 the second example of a liquid membrane oscillator showing phase separation and analysed  
539 by the chemical kinetics approach. In the first example, hexadecyltrimethylammonium  
540 bromide (HTMABr) was used as the transferring molecule. The oscillation patterns were  
541 different and less regular than in the present case. This [indicates](#) the high sensitivity of liquid  
542 membrane oscillators to their actual composition. This property can be [successfully](#) exploited  
543 [in](#) taste recognition. The mathematical description of the first case [also](#) involved the  
544 interphase structure but it did not lead to [a wholly](#) satisfactory description of the observed  
545 oscillation. In the present work, the mathematical description avoids [considering the](#)  
546 interphase structure and [relies](#) exclusively on chemical kinetics. This approach [affords a](#)  
547 [highly](#) satisfactory interpretation of the observed oscillations. Furthermore, it provides  
548 evidence for [the](#) coupling of the two component oscillators. [It transpired that](#) the new phase X  
549 which appeared between the liquid membrane and the aqueous acceptor phase [was](#) the site of  
550 a second oscillator. The strong coupling of this latter to the basic oscillator of the system is  
551 responsible for the complex oscillatory behaviour. The importance of phase separation [is](#)  
552 clearly [indicated, hence](#) its presence should be [carefully](#) investigated in each case [prior to](#) any  
553 interpretation of [the](#) experimental results [being attempted](#).

554

555

556

## Conclusions

557

558 The present work [clearly](#) demonstrates that, when the characteristics of the liquid-  
559 liquid interfaces present in a liquid membrane oscillator are modified, [somewhat un](#)[predicted](#)  
560 results can be obtained.

561 More specifically, when a more “water-soluble” solvent, nitromethane, is used as [a](#)  
562 membrane in the liquid membrane oscillator, [a wholly](#) new oscillatory behaviour is observed.  
563 First of all, the [rapid](#) interpenetration of the two liquids in contact, water and nitromethane,  
564 produces a powerful Marangoni effect. Unexpectedly, a new phase X is formed between the  
565 membrane and the aqueous acceptor phase. The oscillator profile corresponds to a new type of  
566 oscillation system. Unusually large and small amplitude peaks are accompanied by several  
567 narrower peaks of higher frequency. It was shown that these [high](#)-frequency peaks are due to



568 oscillations taking place in phase X at the X/a interface (X-oscillator). On the other hand, the  
569 large peaks represent oscillations taking place at the m/X interface (m-oscillator). Their  
570 unusual width probably stems from the fact that the interface layer separating two liquids  
571 having partial mutual solubility is considerably larger than in the case of only slightly soluble  
572 liquids [such as](#) water and nitrobenzene.

573 The NM-based oscillator investigated in the present work is actually composed of two  
574 component oscillators which are coupled in series by physical coupling. The final state of the  
575 transferring surfactant F in the m-oscillator is the starting material for the X-oscillator. The  
576 degree of coupling is controlled by diffusion of [the](#) surfactant from the vicinity of the m/X  
577 interface to the proximity of [the](#) X/a interface. The proposed mechanistic scheme implies a  
578 formal chemical coupling also between the two kinds of ion pairs present in the m-oscillator  
579 (cross-catalytic steps).

580 By applying the laws of chemical kinetics to the proposed mechanistic steps, [the](#) time-  
581 evolution of the concentrations of all the species present could be obtained by numerical  
582 integration of the kinetic equations. The results [accord relatively](#) well [with](#) the general  
583 features of [the](#) experimental oscillation profile. Analysis shows that the physical coupling is  
584 rather strong while the chemical coupling is relatively weak. In agreement with previous  
585 results (Szpakowska et al., 2009), the present study [also](#) shows that the chemical kinetic  
586 approach is quite versatile and can be [successfully](#) used for unravelling mechanistic details  
587 even in the case of coupled liquid membrane oscillators. [Accordingly,](#) the [results](#) obtained  
588 [here](#) might contribute to a better understanding of intercellular communication in biology  
589 where the periodic signalling is more efficient than any other type of signalling mode  
590 (Goldbeter, 1996).

591 Finally, it should be stressed that the present work provides evidence for the coupling  
592 in a spontaneously created coupled oscillator [as opposed](#) to artificially constructed oscillatory  
593 systems (Tatsuno et al., 2012).

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## References

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598 Brian, P. L. T. (1971). Effect of Gibbs adsorption on Marangoni instability. *AIChE Journal*,  
599 17, 765–772. DOI: 10.1002/aic.690170403.

600 Cussler, E. L. (1995). *Diffusion: Mass transfer in fluid systems*. Cambridge: UK: Cambridge  
601 University Press.



- 602 Epstein, I. R., & Pojman, J. A. (1998). *An introduction to nonlinear chemical dynamics*. New  
603 York, NY, USA: Oxford University Press.
- 604 Goldbeter, A. (1996). *Biochemical oscillations and cellular rhythms*. Cambridge: UK:  
605 Cambridge University Press.
- 606 Gray, P., & Scott, S. K. (1990). *Chemical oscillations and instabilities: Non-linear chemical*  
607 *kinetics*. New York, NY, USA: Oxford University Press.
- 608 Hennenberg, M., Bisch, P. M., Vignes-Adler, M., & Sanfeld, A. (1979). Mass transfer,  
609 Marangoni effect, and instability of interfacial longitudinal waves: I. Diffusional exchanges.  
610 *Journal of Colloid and Interface Science*, *69*, 128–137. DOI: 10.1016/0021-9797(79)90087-  
611 0.
- 612 Ikezoe, Y., Ishizaki, S., Yui, H., Fujinami, M., & Sawada, T. (2004). Direct observation of  
613 chemical oscillation at a water/nitrobenzene interface with a sodium-alkyl-sulfate system.  
614 *Analytical Sciences*, *20*, 435–440. DOI: 10.2116/analsci.20.435.
- 615 Kovalchuk, N. M., & Vollhardt, D. (2006). Marangoni instability and spontaneous non-linear  
616 oscillations produced at liquid interfaces by surfactant transfer. *Advances in Colloid*  
617 *Interface Science*, *120*, 1–31. DOI: 10.1016/j.cis.2006.01.001.
- 618 Kovalchuk, N. M., & Vollhardt, D. (2007). Instability and spontaneous oscillations by  
619 surfactant transfer through a liquid membrane. *Colloids and Surfaces A: Physicochemical*  
620 *Engineers Aspects*, *309*, 231–239. DOI: 10.1016/j.colsurfa.2006.11.040.
- 621 Larter, R. (1990). Oscillations and spatial nonuniformities in membranes. *Chemical Reviews*,  
622 *90*, 355–381. DOI: 10.1021/cr00100a002.
- 623 Lavabre, D., Pradines, V., Micheau, J. C., & Pimienta, V. (2005). Periodic Marangoni  
624 instability in surfactant (CTAB) liquid/liquid mass transfer. *The Journal of Physical*  
625 *Chemistry B*, *109*, 7582–7586. DOI: 10.1021/jp045197m.
- 626 Marcus, Y. (1977). *Introduction to liquid state chemistry*. London, UK: Wiley.
- 627 Ostrovsky, M. V., & Ostrovsky, M. J. (1983). Dynamic interfacial tension in binary systems  
628 and spontaneous pulsation of individual drops by their dissolution. *Journal of Colloid and*  
629 *Interface Science*, *93*, 392–401. DOI: 10.1016/0021-9797(83)90422-8.
- 630 Pimienta, V., Etchenique, R., & Buhse, T., (2001). On the origin of electrochemical  
631 oscillations in the picric acid/CTAB two-phase system. *The Journal of Physical Chemistry*  
632 *A*, *105*, 10037–10044. DOI: 10.1021/jp013350w.
- 633 Płocharska-Jankowska, E., Szpakowska, M., Mátéfi-Tempfli, S., & Nagy, O. B. (2005). On  
634 the possibility of molecular recognition of taste substances studied by Gábor analysis of  
635 oscillations. *Biophysical Chemistry*, *114*, 85–93. DOI: 10.1016/j.bpc.2004.10.004.



- 636 Płocharska-Jankowska, E., Szpakowska, M., Matefi-Tempfli, S. & B. Nagy, O. (2006). A new  
637 approach to the spectra analysis of liquid membrane oscillators by Gabor transformation.  
638 *Journal of Physical Chemistry B*, 110, 289-294. DOI: 10.1021/jp0557870
- 639 Rastogi, R. P., & Srivastava, R. C., (2001). Interface-mediated oscillatory phenomena.  
640 *Advances in Colloid and Interface Science*, 93, 1–75. DOI: 10.1016/s0001-8686(00)00037-  
641 3.
- 642 Reichardt, C. (1979). *Solvent effects in organic chemistry*. Weinheim, Germany: Verlag  
643 Chemie.
- 644 Sternling, C. V., & Scriven, L. E. (1959). Interfacial turbulence: Hydrodynamic instability  
645 and Marangoni effect. *AIChE Journal*, 5, 514–520. DOI: 10.1002/aic.690050421.
- 646 Suzuki, T., & Kawakubo, T. (1992). Convective instability and electric potential oscillation in  
647 a water-oil-water system. *Biophysical Chemistry*, 45, 153–159. DOI: 10.1016/0301-  
648 4622(92)87007-6.
- 649 Szpakowska, M., Czaplicka, I., Szwacki, J., & Nagy, O. B. (2002). Oscillatory phenomena in  
650 systems with bulk liquid membranes. *Chemical Papers*, 56, 20–23.
- 651 Szpakowska, M., Czaplicka, I., Płocharska-Jankowska, E., & Nagy, O. B. (2003).  
652 Contribution to the mechanism of liquid membrane oscillators involving cationic surfactant.  
653 *Journal of Colloid and Interface Science*, 261, 451–455. DOI: 10.1016/s0021-  
654 9797(03)00080-8.
- 655 Szpakowska, M., Płocharska-Jankowska, E., & Nagy, O. B. (2005). On the new possibility of  
656 applying oscillating liquid membrane systems for molecular recognition substances  
657 responsible for taste. *Desalination*, 173, 61–67. DOI: 10.1016/j.desal.2004.06.209.
- 658 Szpakowska, M., Magnuszewska, A., & Płocharska-Jankowska, E. (2006a). Possibility of  
659 discrimination of sour substances by liquid membrane oscillators. *Desalination*, 198, 353–  
660 359. DOI: 10.1016/j.desal.2006.04.003.
- 661 Szpakowska, M., Czaplicka, I., & Nagy, O. B. (2006b). Mechanism of four-phase liquid  
662 membrane oscillator containing hexadecyltrimethylammonium bromide. *The Journal of*  
663 *Physical Chemistry A*, 110, 7286–7292. DOI: 10.1021/jp057349z.
- 664 Szpakowska, M., Magnuszewska, A., & Nagy, O. B. (2008). Mechanism of nitromethane  
665 liquid membrane oscillator containing sodium oleate. *Journal of Colloid and Interface*  
666 *Science*, 325, 494–499. DOI: 10.1016/j.jcis.2008.05.059.
- 667 Szpakowska, M., Płocharska-Jankowska, E., & Nagy, O. B. (2009). Molecular mechanism  
668 and chemical kinetic description of nitrobenzene liquid membrane oscillator containing



- 669 benzyltrimethyltetradecylammonium chloride surfactant. *The Journal of Physical Chemistry*  
670 *B*, *113*, 15503–15512. DOI: 10.1021/jp9066873.
- 671 Tatsuno, Y., Kozuru, T., Yoshida, Y., & Maeda, K. (2012). Propagation and synchronization  
672 of potential oscillations in multiple liquid membrane systems. *Analytical Science*, *28*, 1145–  
673 1151. DOI: 10.2116/analsci.28.1145.
- 674 Toko, K., Yoshikawa, K., Tsukiji, M., Nosaka, M., & Yamafuji, K. (1985). On the oscillatory  
675 phenomenon in an oil/water interface. *Biophysical Chemistry*, *22*, 151–158. DOI:  
676 10.1016/0301-4622(85)80037-5.
- 677 Weast, R. C., Astle, M. J., & Beyer, W. H. (1984). *CRC handbook of chemistry and physics*  
678 (64th ed.). Boca Ration, FL, USA: CRC Press.
- 679 Yoshikawa, K., & Matsubara, Y. (1983). Spontaneous oscillation of pH and [electric](#) potential  
680 in an oil–water system. *Journal of the American Chemical Society*, *105*, 5967–5969. DOI:  
681 10.1021/ja00357a001.
- 682 Yoshikawa, K., Shoji, M., Nakata, S., Maeda, S., & [Kawakami, H.](#) (1988). An excitable  
683 liquid membrane possibly mimicking the sensing mechanism of taste. *Langmuir*, *4*, 759–  
684 762. DOI: 10.1021/la00081a046.

