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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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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 35.33×10^{-3} for NM
98 and 0.30×10^{-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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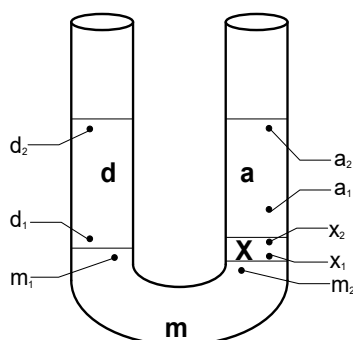
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Experimental

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.



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 cm^3 to 5.0 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 cm^3 of $1.5 \times 10^{-3}\text{ M}$ solution of HPi in NM;
 156 d – 4.0 cm^3 of $5 \times 10^{-3}\text{ M}$ solution of BDMTACl in ethanol–water mixture (1.5 M);
 157 a – 4.0 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 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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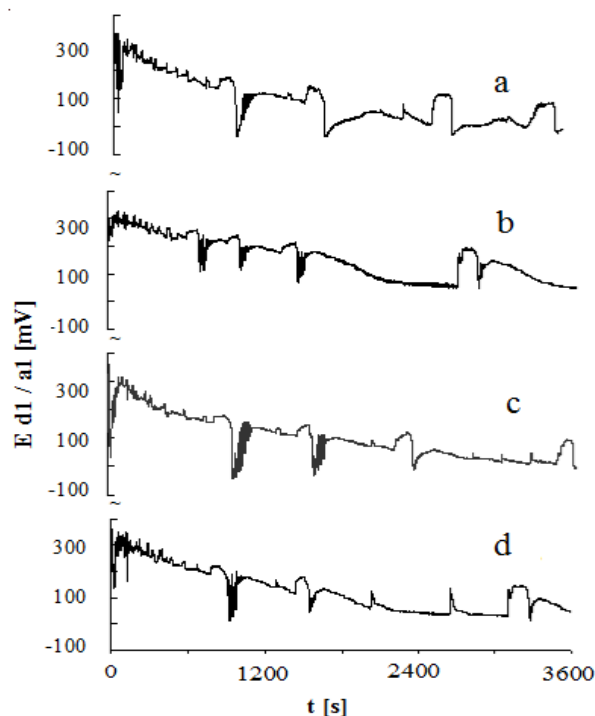
172 Since the behaviour of liquid membrane oscillators is [highly](#) sensitive to the
173 experimental parameters (electrode positions, temperature of measurements, membrane
174 volume, initial concentrations of surfactant and HPI), these parameters had to be optimised.

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 θ /°C: 18.0 ± 0.1 (a), 22.0 ± 0.1 (b), 25.0 ± 0.1 (c), and 28.0 ± 0.1 (d).

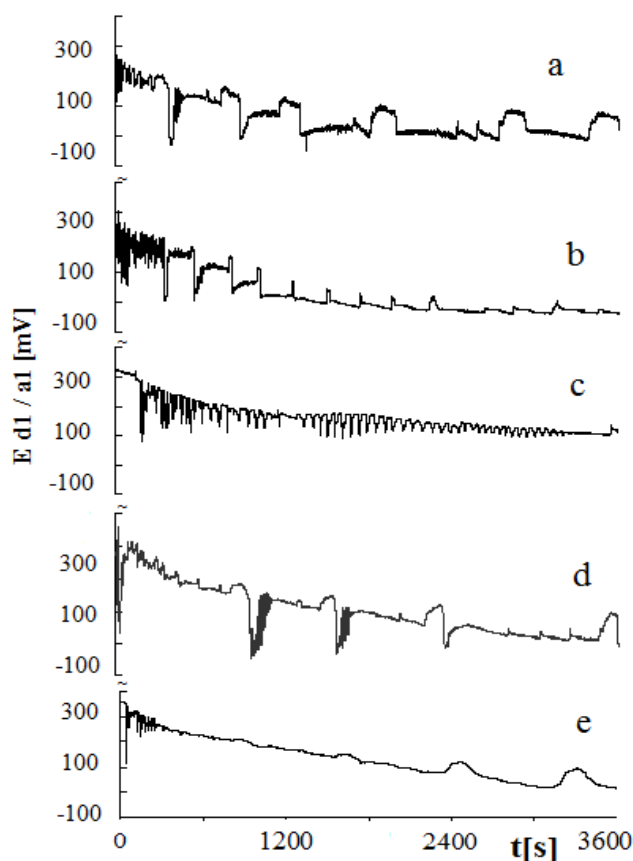
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190 Fig. 3 [shows](#) the influence of electrode distances from the d/m interface and from the
 191 a/m interface on the oscillation pattern. The characteristic peaks are observed for the case
 192 when the electrodes were positioned at 2 cm from the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

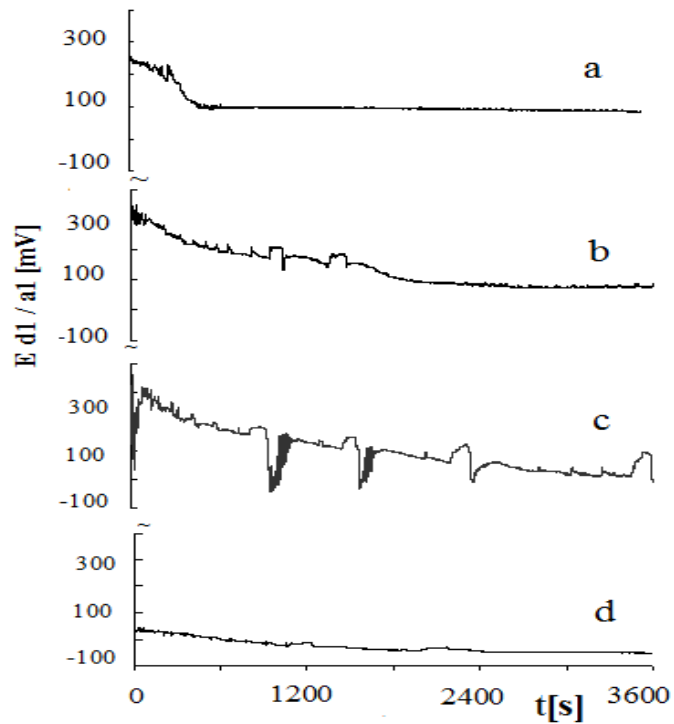
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203 Fig. 4 [indicates](#) that too low and too high an initial concentration of surfactant in the
 204 donor phase [does](#) not produce oscillations. The most satisfactory oscillation pattern was found
 205 for the initial surfactant concentration 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 ± 0.1) °C).

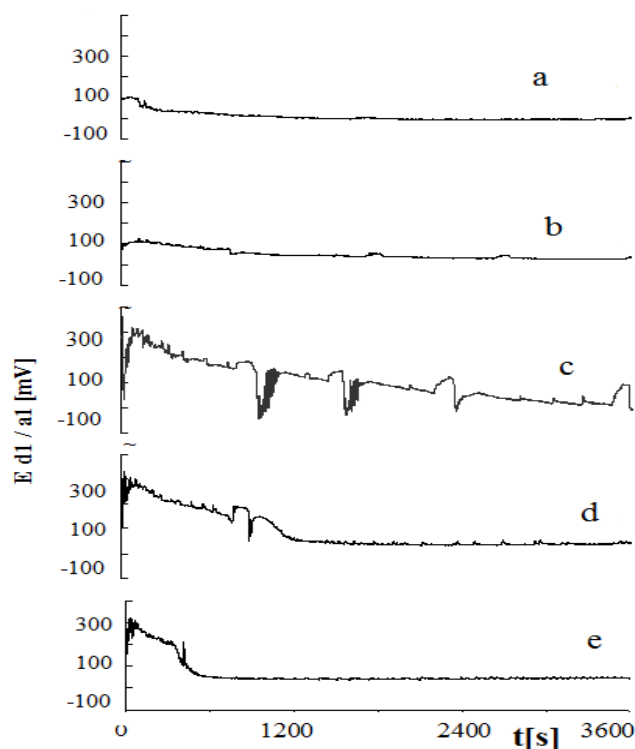
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216 The initial HPI concentration in the membrane phase also influences the $E_{d/a} = f(t)$
 217 dependence (Fig. 5). The oscillation pattern is only observed at 1.5 mM initial HPI
 218 concentration in the membrane phase.

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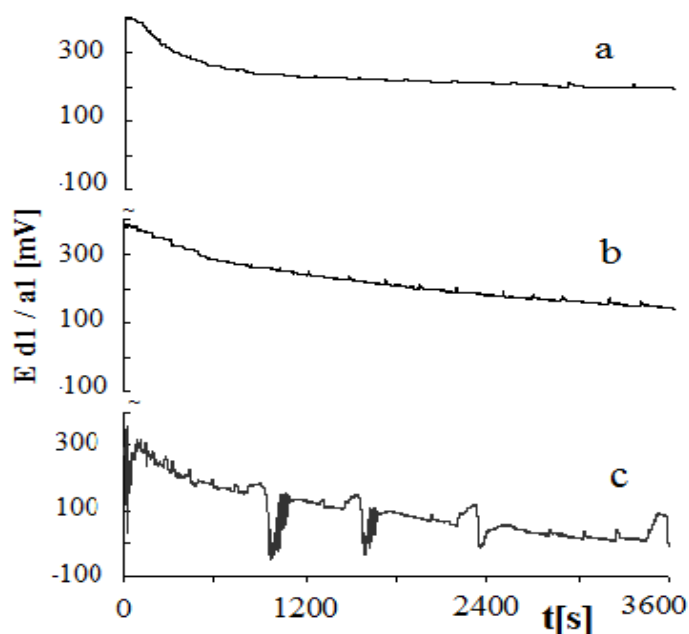
224 **Fig. 5.** Influence of initial HPi concentration in NM membrane phase on oscillation patterns:
 225 0 mM (a), 0.75 mM (b), 1.5 mM (c), 2 mM (d), 3 mM (e); ($\theta = (25.0 \pm 0.1) ^\circ\text{C}$).

226

227 The membrane volume [also](#) has [an](#) effect on the oscillation (Fig. 6). The 5.0 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 cm^3 , this delay is [around](#) 2 h, while for [a](#) volume of 6.0 cm^3 the
 232 delay [extends up](#) to 5 h. Experiments with [a](#) membrane volume lower than 5.0 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 (η_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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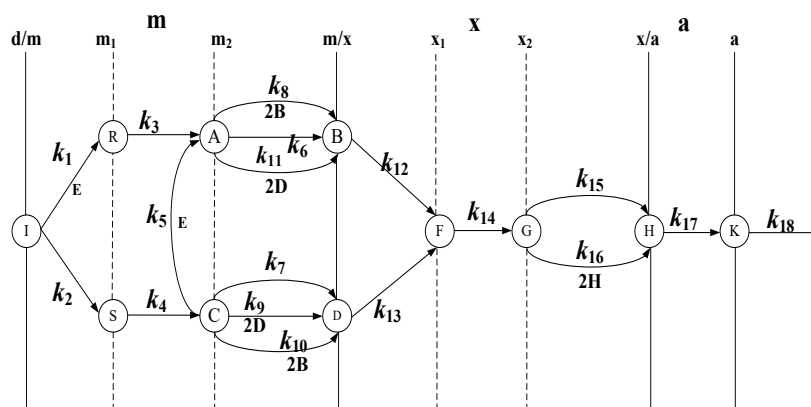
330 *Kinetics and mechanism*

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

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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 Cl^- (S) and 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 5.0×10^{-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 6.0×10^{-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 α and β 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.

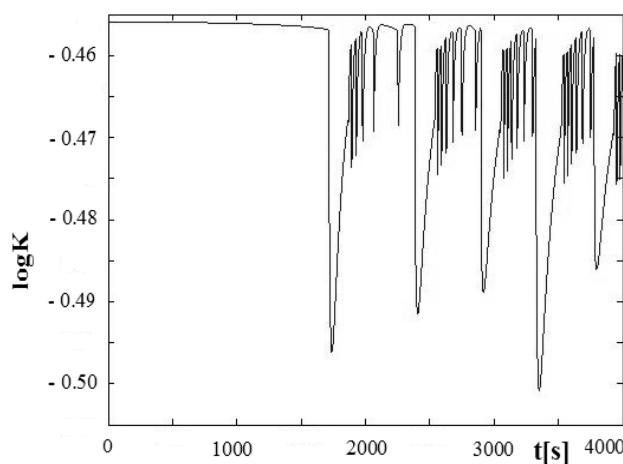
442 In the present work, the following set of rate constants was used for model
 443 calculations: $k_1 = 2.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$; $k_2 = 2 \text{ s}^{-1}$; $k_3 = 9 \times 10^{-6} \text{ s}^{-1}$; $k_4 = 10^{-5} \text{ s}^{-1}$; $k_5 = 1 \text{ M}^{-1} \text{ s}^{-1}$; k_6
 444 $= 10^{-4} \text{ s}^{-1}$; $k_7 = 5 \times 10^{-4} \text{ s}^{-1}$; $k_8 = 10^5 \text{ M}^{-2} \text{ s}^{-1}$; $k_9 = 8 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$; $k_{10} = 9 \times 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$; $k_{11} =$
 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

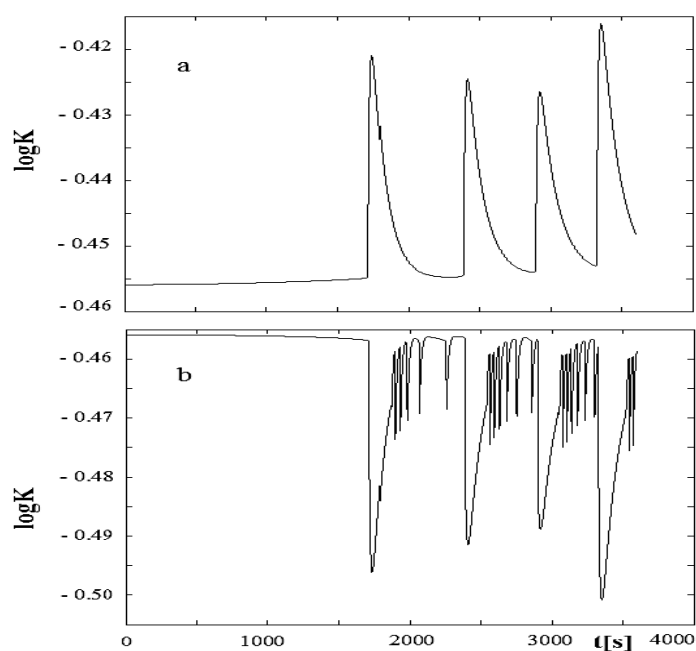
462 The proposed model can [also](#) be used for establishing the origin of the two types of
463 oscillations present in the oscillation pattern. The presence of the new phase X suggests that
464 the NM oscillator can be [regarded](#) as composed of two subsystems: the first is an oscillator
465 having 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 [non](#)-catalysed adsorption rate constants at the membrane exit interface (Szpakowska et al.,
471 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 α for a given value of β), 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 β for a given value of α , 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 β , 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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