Ars Separatoria Acta 2 (2003) 64-70

ARS SEPARATORIA ACTA

www.ars_separatoria.chem.uni.torun.pl

SPECTROPHOTOMETRIC INVESTIGATIONS OF NITROBENZENE LIQUID MEMBRANE OSCILLATOR WITH HEXADECYLTRIMETHYLAMMONIUM BROMIDE

Maria SZPAKOWSKA* and Izabela CZAPLICKA

Commodity Science Laboratory, Faculty of Economics and Management, Gdańsk University of Technology, 80-952 Gdańsk, Narutowicz str 11, Poland
e-mail: Maria.Szpakowska@zie.pg.gda.pl

ABSTRACT

The oscillations of electrochemical potential difference between aqueous phases of a liquid membrane oscillator containing cationic surfactant are presented. By UV-VIS spectroscopy, the concentrations of liquid membrane components (nitrobenzene and picric acid) in the both aqueous phases were established during the oscillation process. It was shown that nitrobenzene molecules are transferred to the aqueous phases from the beginning of that dynamic process. Picric acid molecules are not observed in the donor phase, meanwhile, from the beginning of the process they are transported to the acceptor phase. It can be concluded that the transport of the liquid membrane components to the aqueous phases is not responsible for the observed oscillations of electrochemical potential difference.

Keywords: Oscillations; Liquid membrane oscillator; Liquid membrane; Cationic surfactant; Nitrobenzene absorption spectra, Picric acid spectra

INTRODUCTION

In recent years, quite a lot of studies have been devoted to oscillators based on liquid membranes in order to model the oscillatory behaviour of biological membranes and for the development of new taste sensors [1-3]. The liquid membrane oscillator consists of two aqueous phases (the donor phase containing hexadecyltrimethylammonioum bromide, HTMAB, with ethanol and the acceptor phase containing sucrose) separated by the liquid membrane phase (picric acid in nitrobenzene). In this system, the transport

* Corresponding author

of certain molecules from the donor and the membrane phases to the acceptor phase is realized in an oscillatory way [3]. This is accompanied by the oscillations of electrochemical potential difference between the aqueous phases, $\Delta E_{d/a}$, after certain induction time. The mechanism of this process is still not well established [1,3,4]. It is even not known, which molecules present in the system are transferred from one to the other phase of the oscillator. In the first step membrane component transfer to the appropriate aqueous phases during oscillation process was examined. For this purpose, the time-dependent amount of picric acid (HPi) and nitrobenzene (NB) in certain layers of the donor and acceptor aqueous phases was established using UV-VIS spectroscopy. The examination of the transport of liquid membrane components to the aqueous phases may contribute to the recognition of the oscillation process mechanism. For this purpose, the amount of picric acid (HPi) and nitrobenzene (NB) present in certain layers of the donor and acceptor aqueous phases was investigated using UV-VIS spectroscopy.

MATERIALS AND METHODS

All reagents were analytical grade purity (>99%) commercial products. HPi was crystallized from ethanol – water mixture (1:2); meanwhile, nitrobenzene was distilled before use.

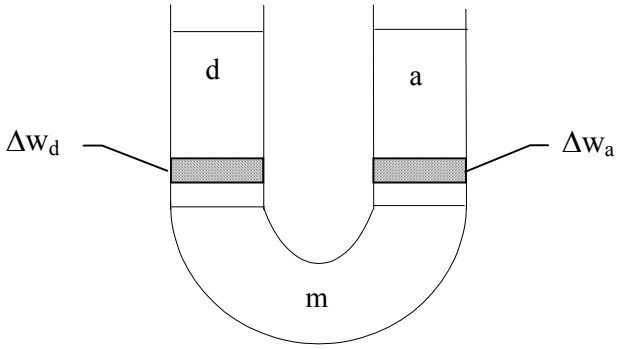

Fig. 1. Experimental setup: liquid membrane oscillator; m: liquid membrane; d: donor phase; a: acceptor phase; Δw_d, Δw_a donor and acceptor layers, respectively.

The oscillation experiment was carried out in a thermostated U-shaped glass tube (Fig. 1) (T=25±0.1^{0}C) of 12-mm inner diameter At the bottom, the liquid membrane was introduced. In the two branches of the glass tube, the aqueous phases were put simultaneously above the membrane layers. The composition of the three phases was as follows:

- liquid membrane (m): picric acid (HPi, 1.5×10^{-3} M) in nitrobenzene – 5 cm^3;

- aqueous donor phase (d): HTMAB (5×10^{-3} M) in ethanol (1.5 M) - water mixture – 4 cm^3;
- aqueous acceptor phase (a): sucrose in water (0.1 M) – 4 cm^3;

The electrochemical potential difference between the two aqueous phases, $E_{d/a}$, was measured by means of two Ag/AgCl/Cl^- electrodes using a MΩ input resistance voltmeter controlled by PC (sampling frequency 4 s^{-1}). Electrodes were situated 1 cm from the aqueous phase – membrane interfaces.

The UV-VIS absorption spectra of: a) nitrobenzene and HPi in water (initial donor and acceptor composition solutions); b) donor and acceptor phase solutions of Δw_d and Δw_a layers (1cm^3), taken during the oscillation process were measured on a Cary 5E UV-VIS-NIR spectrophotometer at room temperature (23±0.5^{0}C). The Δw_d and Δw_a layers were situated 1 cm^3 above the liquid membrane/aqueous phase interfaces, respectively (Fig. 1).

RESULT AND DISCUSSION

$\Delta E_{d/a}$ oscillations in time for the liquid membrane oscillator are presented in Fig.2.

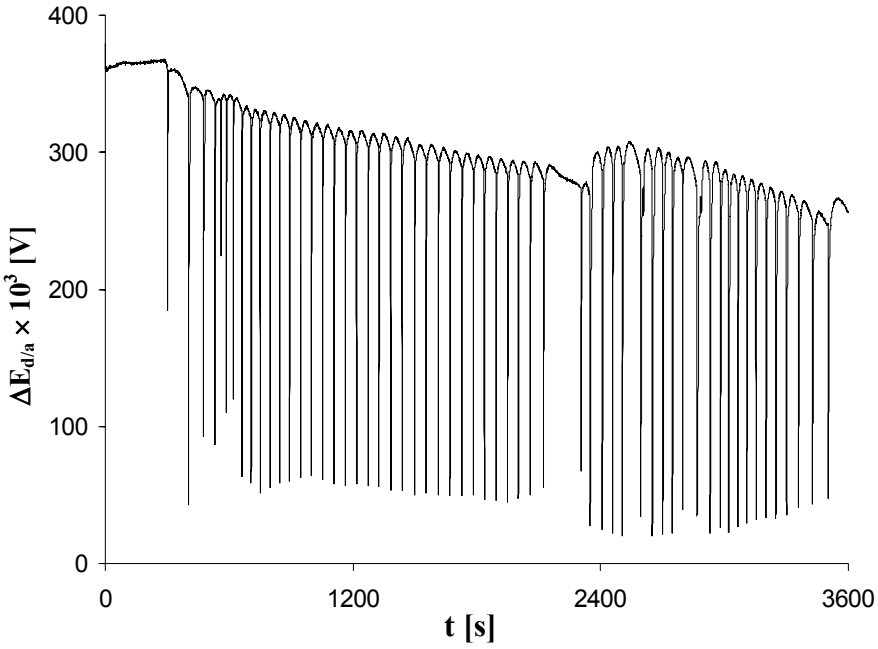

Fig.2. Oscillation of electrochemical potential difference between aqueous phases of the oscillator; composition of three phases:
d-HTMAB (5×10^{-3} M) in water + ethanol (1.5 M) mixture, m – HPi (1.5×10^{-3} M) in nitrobenzene, a- aqueous solution of sucrose (0.1 M).

The initial $\Delta E_{d/a}$ value is about 335 mV. Oscillations of $\Delta E_{d/a}$ start after the induction period of 300s and they are observed till the end of the experiment. The overall oscillation pattern has two regions of different amplitudes separated by a part without oscillation. These observations are similar to those published in literature [3] for a similar system. To understand which processes are responsible for these oscillations, the UV-VIS spectroscopy was used for determining the concentration of membrane components transported to the aqueous phases time-dependent.

Nitrobenzene spectra

It was found previously that the spectra of nitrobenzene in hexane consists of three bands at λ_{max}=252 nm (ε_{max}=10000), λ_{max}=280 nm (ε_{max}=1000), λ_{max}=330 nm (ε_{max}=125) [5]. The latter is due to n-π^* transitions. In water only two bands responsible for (π-π^*) transitions at λ_{max}=196 nm and λ_{max}=268.5 nm are observed. To estimate nitrobenzene concentration in the aqueous donor and acceptor phases during the oscillation process, the molar absorption coefficients (ε_{max} values) of nitrobenzene in appropriate solutions were found. Their values calculated as a slope of A=f(c) with a correlation coefficient > 0.999 are as follows:

- initial donor phase composition (HTMAB 5×10^{-3} M, in water + ethanol, 1.5 M, mixture), ε_{max}=6800 [cm^2/mol];
- initial acceptor phase (sucrose, 0.1 M), ε_{max}=10200 [cm^2/mol];
- pure water, ε_{max}=10600 [cm^2/mol].

The ε_{max} values are lower when nitrobenzene is in solutions containing surfactant and ethanol in comparison to water or water containing sucrose. This suggests a different type of interactions of nitrobenzene with environment containing surfactant.

Picric acid spectra

The HPi spectrum measured in water in the presence of sucrose shows an asymmetric band in the range of λ=290-500 nm with its maximum at λ=355 nm. On the other hand, when the spectrum is measured under initial conditions of the donor aqueous phase containing a cationic surfactant, the absorption maximum is shifted to λ=351 nm, and a new band appears at λ=422nm.

In order to estimate HPi concentration in aqueous donor and acceptor phases during transport process, the ε_{max} values were established at the initial donor phase composition (ε_{max}=11900), the initial acceptor phase composition (ε_{max}=13200) and in pure water (ε_{max}=13200) from the relationship A=f(c). The correlation coefficients were > 0.990.

The ε_{max} values are lower in the presence of surfactant than in the presence of other solutions as it was already found for nitrobenzene.

Spectrophotometric investigations of aqueous phases during oscillations process

UV-VIS absorption spectra of samples taken from Δw_d and Δw_a layers (Fig. 1) were measured in time. For the both aqueous phases (Fig. 3, a and b) only one band λ_{max}=268 nm typical for nitrobenzene solvent is observed. The nitrobenzene concentrations in the both phases were calculated for various time intervals (Table 1).

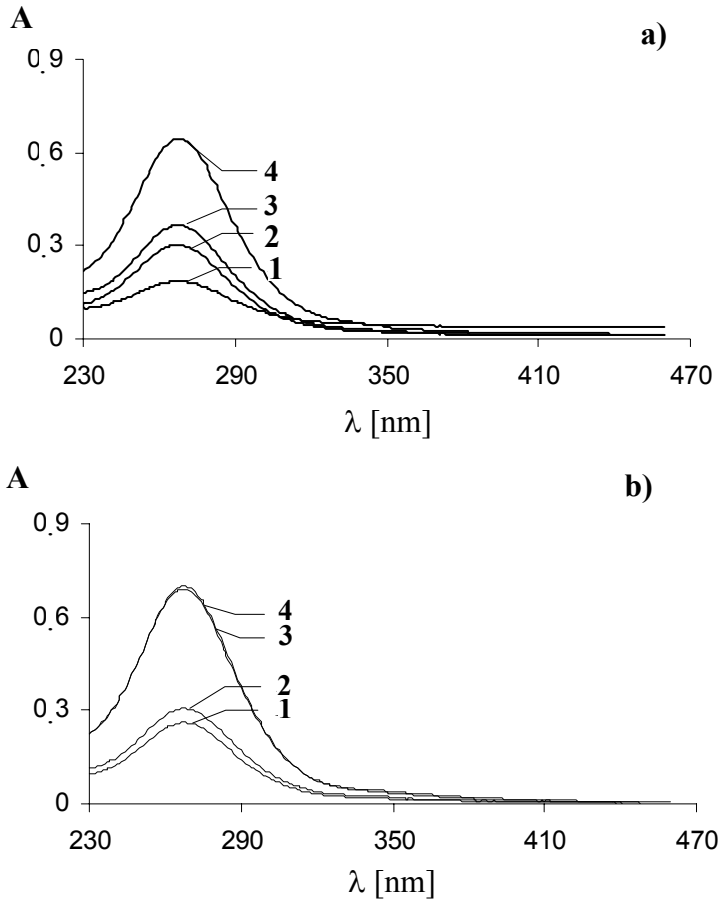

Fig.3. Absorption spectra of a) Δw_d, b) Δw_a layers of membrane oscillation aqueous phases with time: 1 – 180 s; 2 – 900 s; 3 – 1800 s; 4 – 3600 s; (experimental conditions in: Material and methods).

Tab. 1. Nitrobenzene concentrations and $\Delta c/\Delta t$ values in Δw_d and Δw_a layers during transport process

t [s]	phase d		phase a	
	$c_{NB}^{*1)} \times 10^3$ [M]	$\Delta c/\Delta t \times 10^6$ [mol/dm^{3}s]	$c_{NB}^{*1)} \times 10^3$ [M]	$\Delta c/\Delta t \times 10^6$ [mol/dm^{3}s]
180	2.0±0.2	11.1	2.1±0.2	11.7
900	3.4±0.2	1.9	3.5±1.1	1.9
1800	4.9±0.5	1.7	5.5±0.6	2.2
3600	6.5±0.6	0.9	5.6±0.6	<0.1

[1)] ε_{max} = 10200 [cm^2/mol] from Lambert-Beer relationship

The results demonstrate that nitrobenzene molecules are transferred from the liquid membrane to aqueous phases immediately after the beginning of the dynamic process. This means that the transport of organic solvent to the aqueous phases is not occurring in an oscillatory way since the oscillation of electrochemical potential difference is observed only after 300s (Fig. 2). The concentration of nitrobenzene in the Δw_d layer of the donor phase increases with time, meanwhile, it reaches a steady value after 1800s in the Δw_a layer of the acceptor phase. These observations result from the effect of the material balance between the number of molecules penetrating Δw_d and Δw_a layers and the number of molecules diffusing to the upper part of the aqueous phases (Fig.1).

$$N_{w_d} = N_{P_d} - N_{D_d} \tag{1}$$

$N_{w_d} = (\Delta c/\Delta t)_{w_d} \cdot \Delta w_d \cdot s \cdot \Delta t$ - number of NB moles in Δw_d layer;

$N_{P_d} = (\Delta c/\Delta t)_{P_d} \cdot \Delta w_d \cdot s \cdot \Delta t$ - number of NB moles penetrating to Δw_d layer;

$N_{D_d} = (\Delta c/\Delta t)_{D_d} \cdot \Delta w_d \cdot s \cdot \Delta t$ - number of NB moles diffusing to upper part of donor phase;

s - surface of Δw_d layer.

It can be shown that the speed of appearing of nitrobenzene molecules in Δw_d is the result of two processes, the permeation of NB molecules to Δw_d and diffusion to the upper part of donor the phase:

$$(\Delta c/\Delta t)_{w_d} = (\Delta c/\Delta t)_{P_d} - (\Delta c/\Delta t)_{D_d} \tag{2}$$

The same considerations can be done for Δw_a layer of the acceptor phase.

$(\Delta c/\Delta t)_{w_d}$ and $(\Delta c/\Delta t)_{w_a}$ values are the greatest for the first time interval (180s) oscillations process (Tab.1). After that the values $(\Delta c/\Delta t)_{w_d}$ diminish whereas for the acceptor phase, $(\Delta c/\Delta t)_{w_a}$ values are close to zero in the last part of the experiment. It means that the rate of the both processes: penetration to Δw_a and diffusion to the upper part of the acceptor phase are the same.

It should be noted that the absorption band in the range of the 300-460 nm characteristic for picric acid was not observed in solution taken from the donor phase. On the contrary, a small amount of HPi in the acceptor phase was found after 180s when no oscillation was observed. At the end of experiment the concentration of HPi in this phase is equal to 1.91×10^{-5} M.

CONCLUSION

All the results show that the transport of nitrobenzene and HPi molecules from the liquid membrane to the aqueous phases can not be responsible for the observed oscillations. It seems that the transport of surfactant molecules from the donor to the acceptor phase should be responsible for the oscillatory behaviour of the system. Unfortunately, the spectrophotometric method cannot be used for HTMAB concentration estimation in the acceptor phase because of lack of an appropriate absorption band. Other techniques must be used to find support for the above suggestion.

REFERENCES

[1] K. Yoshikawa, M. Shoji, S. Nakata, S. Maeda, H. Kawakami, *Langmuir*, 1988, *4,* 759-762.
[2] M. Szpakowska, I. Czaplicka, J. Szwacki, O.B. Nagy, *Chem. Pap.,* 2002, *56,* 20-24.
[3] K. Arai, F. Kusu, K. Takamura, *Chem. Lett.*, 1990, 1517-1520.
[4] M. Szpakowska, I. Czaplicka, E. Płocharska-Jankowska, O. B.Nagy, *J. Interf. Sci.,* 2003, *261,* 451-455.
[5] W. Zielinski, A. Rajca, *Metody spektroskopowe i ich zastosowania do identyfikacji związków organicznych*, WNT, Warszawa 1995, p. 380.