

# Effect of Organic Tin Compounds on Electric Properties of Model Membranes

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The objective of the present work was to investigate the effect of selected organic tin compounds and potassium chloride (used as a reference substance) on the trans-membrane electric voltage and electric resistance of model membranes, the latter being nitrocellulose filters impregnated with butylene ester of lauric acid. The increasing KCl concentration (in the measurement chambers) caused a rapid rise of the negative trans-membrane voltage, whose value stabilized afterwards. In the case of  $(C_3H_7)_3SnCl$  an abrupt maximum of the negative voltage was observed followed by a monotonic drop to zero. In the case of highest concentrations of this compound the voltages, after having reached zero, changed their polarization to the opposite. Within the range of small concentrations two slight voltage maxima were observed. Non-ionic tin compounds like  $(CH_3)_4Sn$  and  $(C_2H_5)_4Sn$  had an insignificant influence on the electric properties of the studied membranes.

**Key words:** Lauric Acid, Nitrocellulose Filters, Tin Compounds

## Introduction

The view on toxic properties of heavy metals and their compounds is generally accepted. These metals become deposited in large quantities in the surrounding environment in the form of products of industrial technological processes or plant protection chemicals. They are then transferred from the environment (as food and various kinds of liquids) inside living organisms, causing changes in metabolic processes and poisonings. On the level of the cell these compounds inhibit, among others, oxidative phosphorylation and accelerate hemolysis of erythrocytes (Falcioni *et al.*, 1996; Gray *et al.*, 1987; Kleszczyńska *et al.*, 1997; Krug, 1992; Käfer and Krug, 1994; Hamasaki *et al.*, 1995).

An interaction between any substance and cell occurs by means of the membrane which separates the inside of the latter from the external surrounding. Research concerning compounds of heavy metals has shown that the structure and physical properties of both cell membranes and their lipid models change in the presence of these compounds. In particular, organic compounds of heavy metals, including those in an ionized form, display a considerable activity as regards the interaction with the membranes (Gabrielska *et al.*, 1997; Ra-

decka *et al.*, 1999; Przestalski *et al.*, 2000; Fogt and Przestalski, 2001; Kleszczyńska *et al.*, 1999). Methods which prove especially effective to investigate interactions of ionized compounds with membranes are the electric ones, in which the membrane is treated as a receiver of electric current or the source of the latter (Podolak *et al.*, 2005, 1992). The ionized compounds manifest (by these methods) effects of the interactions in the form of relatively big changes in the electric parameters of the examined membranes.

The aim of the present work was to investigate the influence of selected organic compounds of tin (representing heavy metals) and that of inorganic potassium chloride (as a model-like comparative substance) on the electric parameters of liquid model membranes made of filters impregnated with butylene ester of lauric acid. The present work is a continuation and extension of the research carried out earlier (Podolak *et al.*, 2005).

## Materials and Methods

Nitrocellulose filters, manufactured by SYN-POR company (Czech Republic), of 150  $\mu m$  thickness and with the diameter of pores reaching 0.4  $\mu m$  were used in this research. They were im-

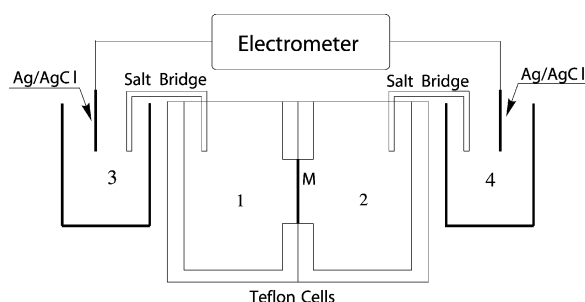


Fig. 1. Measuring system: 1, measurement chamber; 2, reference chamber; 3, 4, indirect chambers; M, membrane; Ag/AgCl, Ag/AgCl electrodes.

pregnated with butylene ester of lauric acid ( $C_{16}H_{32}O_2$ ). A membrane separated two teflon cylindrical chambers of 10 ml volume each [measurement chamber (1) and reference chamber (2)] filled with  $10^{-2}$  M aqueous KCl solution (Fig. 1). The filter of 1 cm in diameter (the diameter of the hole in the chambers) was treated with 0.02 ml ester of lauric acid.

Admixtures of the examined compounds were introduced into the measurement chamber (1). They were either: potassium chloride, KCl, or organic tin compounds: tetramethyltin  $[(CH_3)_4Sn]$ , tetraethyltin  $[(C_2H_5)_4Sn]$  and tri-*n*-propyltin chloride  $[(C_3H_7)_3SnCl]$ . The organic tin compounds investigated in this work are highly hydrophobic substances, insoluble (or weakly soluble) in water environment. They were dissolved in methanol in order to obtain base solutions of concentrations chosen in such a way that treating each of them with 0.025 ml of should yield the desired value of concentration of the admixture in the measurement chamber. The base solution for KCl was a 3 M aqueous solution. The concentrations of the KCl admixtures were changed in the measurement chamber during the time of taking measurements, ranging from 3 mM to 310 mM, whereas the concentrations of the organic compounds were constant for each measurement at: 15  $\mu$ M; 30  $\mu$ M; 60  $\mu$ M; 90  $\mu$ M; 120  $\mu$ M; 300  $\mu$ M; 3000  $\mu$ M and 20000  $\mu$ M concentrations for individual measurements.

With the Keithley 6517 constant-current electrometer the trans-membrane voltage by the admixtures induced was measured. Measurements were taken by the bridge system, shown in Fig. 1 [the method of taking measurements was modeled by Podolak *et al.* (1992)].

## Results and Discussion

Fig. 2 shows the dependence of trans-membrane voltage ( $U$ ) on natural logarithm of the KCl concentration ratio in the measurement chamber ( $c$ ) and reference chamber ( $c_0$ ). The concentration of KCl in the reference chamber was constant and amounted to 10 mM. A rise in the concentration of KCl in the measurement chamber (1), at a constant concentration in the reference chamber (2), caused the formation of a membrane voltage with a negative potential of the solution in this chamber. The value of the voltage increased by jumps along a rise in the concentration and stabilized on an even level.

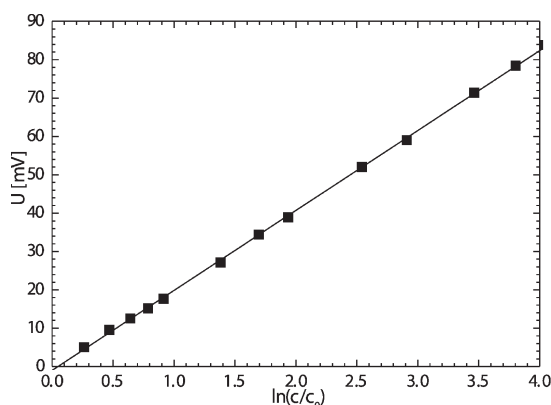


Fig. 2. Dependence of membrane voltage ( $U$ ) on logarithm of the ratio of KCl solutions concentrations in the measurement chamber ( $c$ ) and in the reference chamber ( $c_0$ ) ( $c_0 = 10$  mM constant).

Measurements of the electric resistance of the membrane showed that it practically did not depend on the admixture concentration and equaled about 51  $M\Omega/cm^2$  of the membrane surface (the resistance of the non-impregnated membrane together with the system of electrodes was 2.5  $M\Omega/cm^2$ ).

The diagram of dependence  $U = f(\ln c/c_0)$  has a shape of a straight line, according to the Nernst formula

$$U = \frac{RT}{zF} \ln \frac{fc}{f_0c_0}, \quad (1)$$

where  $R$  is the gas constant,  $T$  the absolute temperature,  $F$  the Faraday constant,  $z$  the valence of potassium ions and  $c$  and  $c_0$  are the concentrations of KCl in the measurement and reference chambers, respectively,  $f$  and  $f_0$  are the ions activity co-

efficients;  $fc = a$  and  $f_0 c_0 = a_0$  are the ions activities.

The Nernst formula can be changed to a more practical form, where in the logarithm expressions the activities will be replaced by concentrations. This transformation results in the introduction of a constant ( $r$ ) selected in such a manner that

$$U = \frac{RT}{zF} \ln \frac{fc}{f_0 c_0} = \frac{RT}{zF} \ln \frac{a}{a_0} = \frac{RT}{zF} r \ln \frac{c}{c_0}, \quad (2)$$

$$\text{hence} \quad \frac{fc}{f_0 c_0} = \frac{a}{a_0} = \left( \frac{c}{c_0} \right)^r \quad (3)$$

$$\text{and} \quad \frac{f}{f_0} = \left( \frac{c}{c_0} \right)^{r-1}. \quad (4)$$

Equation (2) can be written in the following form:

$$U = \frac{RT}{\frac{z}{r}F} \ln \frac{c}{c_0} + U_0 \quad (5)$$

where  $\frac{z}{r} = z_{\text{ef}}$  is the effective valence of ions,

$$\text{hence} \quad r = \frac{z}{z_{\text{ef}}}. \quad (6)$$

Equation (6) determines the constant  $r$ . This constant is the valence factor; it is a coefficient of proportionality between the theoretical valence ( $z$ ) and its effective valence ( $z_{\text{ef}}$ ).

Factor  $r$  is very closely related to the inclination of the straight line which represents the dependence  $U = f(\ln c/c_0)$ . Factor  $r$  can, among others, constitute a measure of effectiveness of electrical influences between the solution and the membrane that is immersed in it. In the case of KCl solution (Fig. 2) the valence factor is equal to 0.8.

The negative sign of the electrical potential in the measurement chamber is induced, as it may be supposed, by the non-compensated negative charge of the filter. From Podolak (1971) it follows that the density of the surface charge of this filter amounts to about  $2 \cdot 10^{-7} \text{ C/cm}^2$ . The negatively charged membrane can attract positive  $\text{K}^+$  ions, leaving in the solution negative  $\text{Cl}^-$  ions, which determine the sign of the electric potential of the solution in the measurement chamber.

Fig. 3 presents the dependence of membrane voltage on time following the introduction of

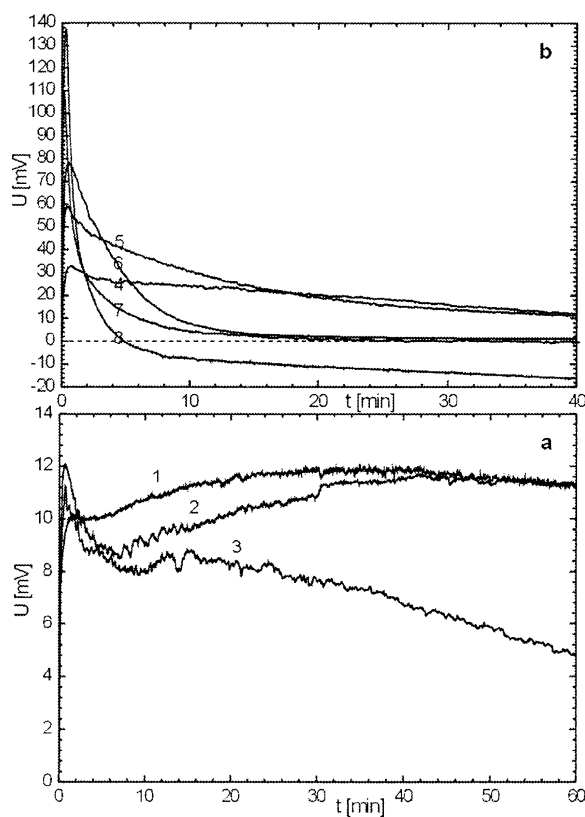


Fig. 3. Dependence of membrane voltage ( $U$ ) on time  $t$  for selected concentrations of admixtures  $(\text{C}_3\text{H}_7)_3\text{SnCl}$  in the measurement chamber. Concentrations of the admixtures were as follows: a) 1,  $15 \mu\text{M}$ ; 2,  $30 \mu\text{M}$ ; 3,  $60 \mu\text{M}$ ; and b) 4,  $90 \mu\text{M}$ ; 5,  $0.12 \text{ mM}$ ; 6,  $0.3 \text{ mM}$ ; 7,  $3 \text{ mM}$ ; 8,  $20 \text{ mM}$ .

admixtures of compound  $(\text{C}_3\text{H}_7)_3\text{SnCl}$  into the measurement chamber. Each of the curves in this figure corresponds to a constant concentration of  $(\text{C}_3\text{H}_7)_3\text{SnCl}$ . Research has proved that at all the concentrations of this admixture the trans-membrane voltage increased at the beginning and then – after reaching the maximum value – fell to zero. In the case of admixtures with highest concentrations (this is especially visible for the  $20 \text{ mM}$  concentration; Fig. 3b, curve 8) the voltage changed the direction after having reached zero. Furthermore, along with the increase in the concentration of the admixture there increased the value of the maximum membrane voltage and the speed at which this voltage lowered to reach zero. In the case of low concentrations (Fig. 3a) there were observed two voltage maxima: the first was shortlived (similar to that at higher concentra-

tions), and the other, much more lower, broadened with time.

In aqueous solution, tri-*n*-propyltin chloride,  $(C_3H_7)_3SnCl$ , dissociates into the organic positive ion  $(C_3H_7)_3Sn^+$  and the negative  $Cl^-$  ion. While contacting the investigated membrane, the positive ions easily penetrate inside it due to electrostatic influences (in a similar way as potassium ions), yet also because of the hydrophobic properties of lauric acid which fills up pores in the membrane. Both of the above-mentioned factors may affect both the value and polarization of trans-membrane voltage in the presence of this compound in the measurement chamber. The lack of stabilization of the voltage at a given concentration of the compound can mean that the positive ions “drag” (with certain delay) the hydrophilic chlorine ions, as a result of which the negative potential of the solution in the measurement chamber as well as membrane voltage decrease. The two voltage maxima observed at small concentrations of the admixture can mean that the above-discussed process is divided into stages (voltage impulses). On a certain portion of positive ions entering the membrane (followed by chlorine ions to neutralize the charge of the former), there follows the second stage – the second portion of positive ions penetrate into the membrane followed by another portion of negative ions. In the case of high concentrations there is observed only one voltage maximum of far greater value. This high value can cause some further lower maxima to pass unnoticed. The changing of the sign of the trans-membrane voltage in the case of the highest concentration of  $(C_3H_7)_3SnCl$  in the measurement chamber (Fig. 3b, curve 8) can mean that in this case the  $Cl^-$  concentration in the membrane (those following the positive ions) is so high that, as a result of the difference in concentrations (between the inside of the membrane and the reference chamber), they begin to diffuse into the reference chamber, altering the sign of the potential of the chamber from the positive into the opposite one. This process can be commented on, in short, as follows: at high concentrations of  $(C_3H_7)_3SnCl$ , the organic tin ions penetrate into the inside of the membrane to form in it ionic channels which enable the hydrophilic chlorine ions to diffuse onto the other side of the membrane.

Fig. 4 presents the dependence of the maximum value of membrane voltage  $\Delta U_{max}$  on natural logarithm of the ratio of concentration  $c$  of admix-

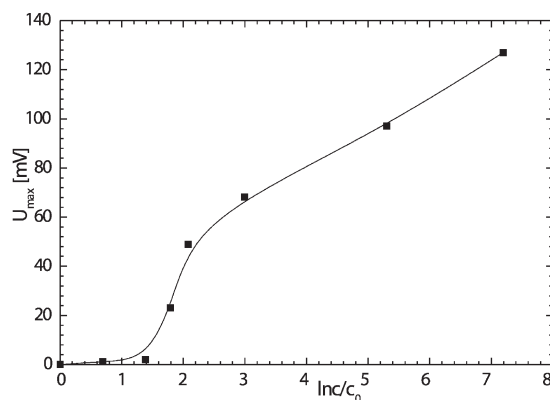


Fig. 4. Dependence of the maximum value of voltage ( $\Delta U_{max}$ ) on natural logarithm of the ratio of concentration ( $c$ ) of admixtures  $(C_3H_7)_3SnCl$  in the measurement chamber to the lowest concentration of admixture ( $c_0$ ). The concentrations of admixtures in the measurement chamber were as follows:  $15 \mu M$ ;  $30 \mu M$ ;  $60 \mu M$ ;  $90 \mu M$ ;  $120 \mu M$ ;  $300 \mu M$ ;  $3000 \mu M$ ;  $20000 \mu M$ .

tures of compound  $(C_3H_7)_3SnCl$  to the lowest concentration of admixture  $c_0$  in the measurement chamber. The dependence consists of three straight sections of differing inclinations. Within the range of the lowest concentrations:  $15 \mu M$ ,  $30 \mu M$ ,  $60 \mu M$ , the inclination of the section is the smallest; within the medium concentrations:  $60 \mu M$ ,  $90 \mu M$ ,  $120 \mu M$ , the inclination is the biggest, while within the highest concentrations:  $120 \mu M$ ,  $300 \mu M$ ,  $3000 \mu M$ ,  $20000 \mu M$  it is medium. The three different inclinations of the sections representing, the dependence  $U = f(\ln c/c_0)$  may suggest that the interaction between  $(C_3H_7)_3SnCl$  and the membrane is a complex process. It differs basically from the interaction between potassium chloride and this membrane. In the case of KCl, the interaction is, as it may be supposed, of superficial character, and the process of formation of trans-membrane voltage is similar to that of charging a condenser. On the other hand, in the case of organic  $(C_3H_7)_3SnCl$ , the interaction is of capacity-like character and the process of formation of trans-membrane voltage resembles the composition of two processes: charging and discharging of a condenser.

Moreover, research into the effect of organic compounds of tin,  $(CH_3)_4Sn$  and  $(C_2H_5)_4Sn$ , that do not contain chlorine, on the electric properties of membranes was also carried out in the work. The presence of  $(CH_3)_4Sn$  in the measurement chamber, despite a relatively high concentration

reaching 3000  $\mu\text{M}$ , did not cause appearance of a membrane voltage exceeding the limit of electrode asymmetry amounting to 2 mV. Compound  $(\text{C}_2\text{H}_5)_4\text{Sn}$ , which contains more  $\text{CH}_2$  groups surrounding the tin atom in comparison with compound  $(\text{CH}_3)_4\text{Sn}$ , displayed only slight activity in producing trans-membrane voltage, which was, however, much lower than in case of  $(\text{C}_3\text{H}_7)_3\text{SnCl}$ . The concentration of 300  $\mu\text{M}$  of this compound in the measurement chamber caused an appearance of voltage, whose value changed over time, reaching two small maxima. The first of them appeared

1 min after the introduction of the admixture and reached about 6 mV, while the other – on reaching the value of 5 mV – stabilized (within the examined time span) on this level.

The relatively weak influence of the two tin compounds  $(\text{CH}_3)_4\text{Sn}$  and  $(\text{C}_2\text{H}_5)_4\text{Sn}$  on the electric properties of the investigated membranes is probably related to the fact that they exist in aqueous solutions in a non-ionized form. Therefore, as it may be assumed, their possible influences are not recorded by means of the electric method applied in the present work.

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