

# RELAXATION PHENOMENA AT THE AIR-WATER INTERFACE WITH SURFACTANTS

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Work is focused on experimental determination of dynamic mechanical properties (i.e. compressibility and relaxation parameters) of the air-water interface during compression in the presence of DPPC monolayer. The surface dynamics was studied with the Langmuir-Wilhelmy balance in several temperatures. The influence of another surfactant (CTAB) present in the aqueous subphase on the surface with DPPC was also investigated. Discussion of the results is based on the concepts of surface rheology and physical chemistry of the interface.

**Key words:** surface rheology, compressibility, relaxation, DPPC, CTAB.

## 1. Introduction

Rheological and dynamic properties of the gas-liquid interface are different than the ones of contacting fluids, Van den Tempel (1977), and they strongly influence the conditions of interfacial transfer processes, Sosnowski et al. (2000). Mechanical surface effects play substantial role in physiological functionality of the pulmonary surfactant present in the liquid lining of the lower respiratory tract, Goerke (1992), Podgórski and Gradoń (1993). DPPC (1,2- $\alpha$ -dipalmitoyl-L-phosphatidylcholine) is the main component of this surfactant, while the specific proteins and some other surface-active compounds are the necessary supplements. Surface tension of the lung liquids is distinctively changed during variations of the gas-liquid interface in the lungs (oscillations of alveoli during breathing). This unique variability of the surface tension is associated with changes of the mechanical state of the interface.

The aim of this work is to evaluate experimentally several properties of the air-water interface (i.e. compressibility and relaxation parameters) which is deformed in the presence of surfactants. DPPC was used as a single-phospholipid model of the pulmonary surfactant, while the mixture of DPPC and CTAB (hexadecyltrimethylammonium bromide) was selected for studying interactions of the phospholipid with additional surface-active components in the system.

## 2. Methods

All experiments were done using the thermostated Langmuir-Wilhelmy film balance (KSV, Finland), schematically shown in Fig. 1. The air-liquid interface was compressed symmetrically by two barriers moving in opposite directions with the predefined speed. Surface pressure ( $\pi$ ) changes induced by surface compression were sensed by the measuring system with Wilhelmy plate and collected by the computer program. More detailed information on the experimental system can be found elsewhere, Pawelec (2002). DPPC and CTAB (Sigma Aldrich) were used without additional purification. Small amount (10  $\mu$ l) of the chloroform solution of DPPC (1 mg/ml) was introduced at the surface of distilled water to produce the phospholipid monolayer after

solvent evaporation. Such surface was compressed with the constant speed of barriers ( $u$ ). The experiments discussed in this work were done for  $u = 35$  mm/min for the system kept at temperatures: 20, 25 and 35 °C. The influence of other surfactants on surface properties of DPPC was studied using  $10^{-4}$  M CTAB solution as a liquid subphase instead of pure water. These studies were limited to single temperature (25°C).

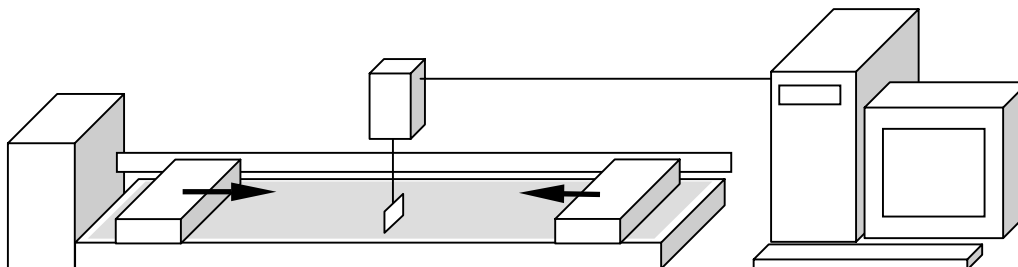


Fig.1. Schematic of Langmuir-Willhelmy film balance (KSV, Finland).

### 3. Results

Figure 2 presents changes of surface pressure value (defined as:  $\pi = \sigma_{\text{water}} - \sigma$ ) during compression of a water surface with adsorbed DPPC monolayer. These results were obtained at 20, 25 and 35 °C.

Figure 3 illustrates the surface compressibility computed as, Gaines (1966):

$$\kappa = - \frac{1}{A} \frac{dA}{d\pi} \Big|_{T=\text{const}} \quad (1)$$

which is plotted as a function of the surface pressure.

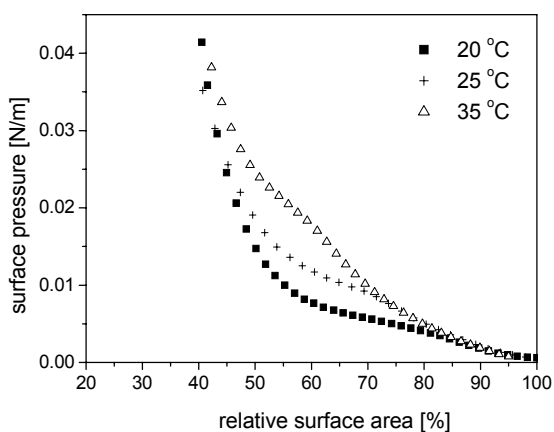


Fig.2. Compression isotherms for DPPC monolayer on water surface at different temperatures,  $u = 35$  mm/min.

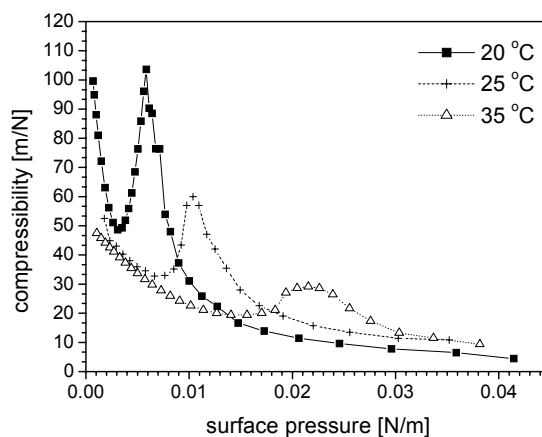


Fig. 3. Compressibility of DPPC monolayer on water surface at different temperatures,  $u = 35$  mm/min.

Three states of molecular organization of the monolayer (called the surface phases) can be distinguished at each temperature: expanded liquid (LE), intermediate (I) and condensed liquid (LC), Gaines (1966). Surface pressure

range, which corresponds to the I-phase, is similar to the one corresponding to the maximum of compressibility. When CTAB is additionally present in the system, both the compression isotherm, Fig.4, and the compressibility function  $\kappa(\pi)$ , Fig.5, are noticeably altered.

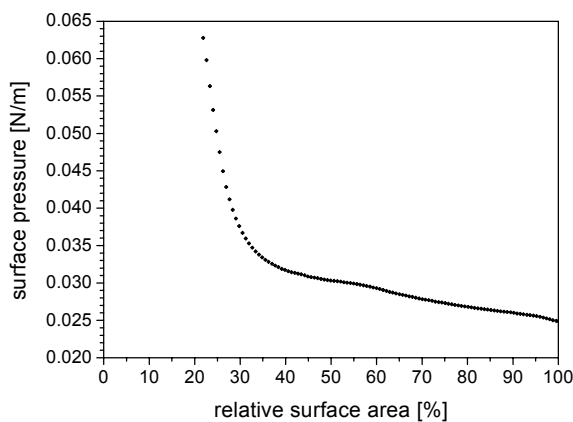


Fig.4. Compression isotherm for DPPC monolayer on water with CTAB ( $10^{-4}$  M),  $T=25$  °C,  $u = 35$  mm/min.

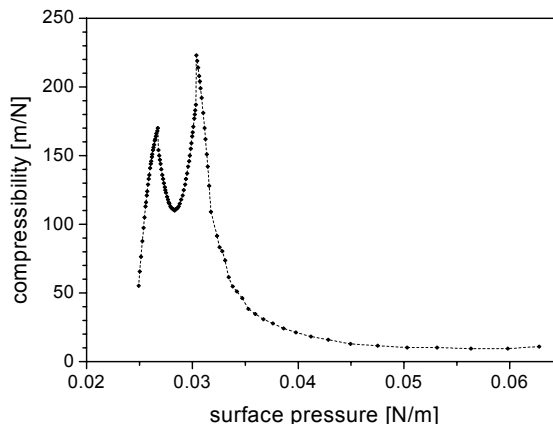


Fig.5 Compressibility of DPPC monolayer on water with CTAB ( $10^{-4}$  M),  $T=25$  °C,  $u = 35$  mm/min.

In that case the isotherm is shifted towards higher values of the surface pressure because  $10^{-4}$  M CTAB solution used as the subphase is characterized by the equilibrium surface pressure of 0.025 N/m. DPPC monolayer on the surface of this subphase exhibits broader range of the surface area ( $A$ ) associated to I-phase. Maximum of compressibility, which corresponds to this phase, is still evident (Fig.5). Additional peak of  $\kappa$  observed for a lower surface pressure can be explained by the properties of a CTAB-rich monolayer, Pawelec and Sosnowski (2003).

In the next step of our study, compression of the monolayer was done until the surface pressure reached the certain value  $\pi_0$ , determined from the previous measurements close to the end of I-phase ( $\pi_0$  depends on  $T$ ). After the compression had been stopped, the relaxation of the surface pressure,  $\pi(t)$ , was measured. Examples of dynamic relationships  $\pi(t)$  are shown in Fig. 6 (DPPC) and Fig. 7 (DPPC+CTAB).

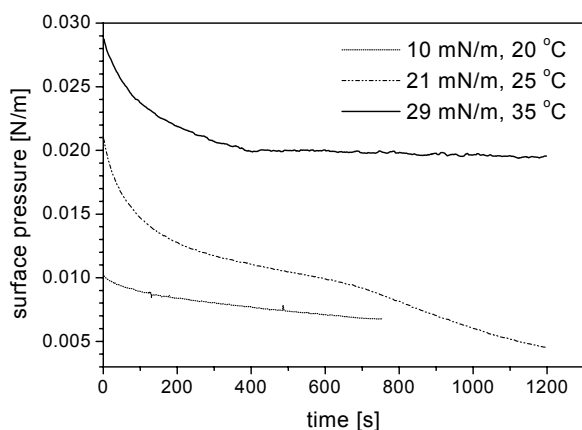


Fig.6. DPPC relaxation curves on water at various temperature and initial surface pressure  $\pi_0$ .

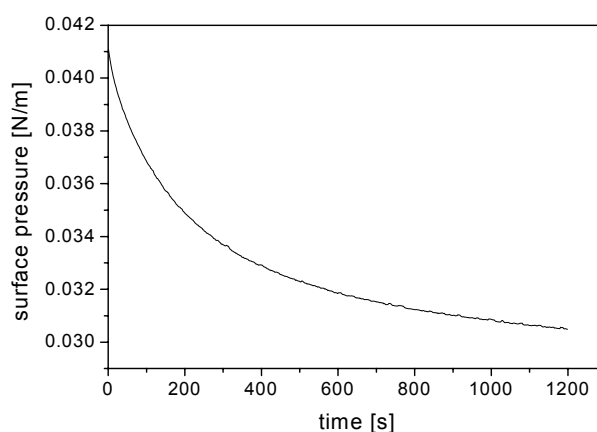


Fig.7. DPPC relaxation curve on  $10^{-4}$  M CTAB,  $T = 25$  °C.  $\pi_0 = 41$  mN/m.

During the relaxation, molecules in the DPPC monolayer may reorganize what is represented by different stages of the measured relationship, each corresponding to the separate surface phase. The relaxation curve was analyzed using Maxwell model of the visco-elastic surface, Sosnowski (2003), which predicts that the surface pressure decay, after deformation is stopped, takes the form:

$$\pi(t) = \pi_{eq} + (\pi_0 - \pi_{eq}) \cdot \exp\left(-\frac{t}{\tau}\right) \quad (2).$$

The occurrence of phase transitions in the relaxing DPPC monolayer requires fitting the separate equation for each surface phase. Only one phase transition is observed for surface pressure relaxation if CTAB is present in the system.

Relationships between the relaxation time ( $\tau$ ) and the surface pressure ( $\pi_0$ ), for which the compression was stopped, are shown in Fig. 8 (DPPC) and Fig. 9 (DPPC+CTAB).

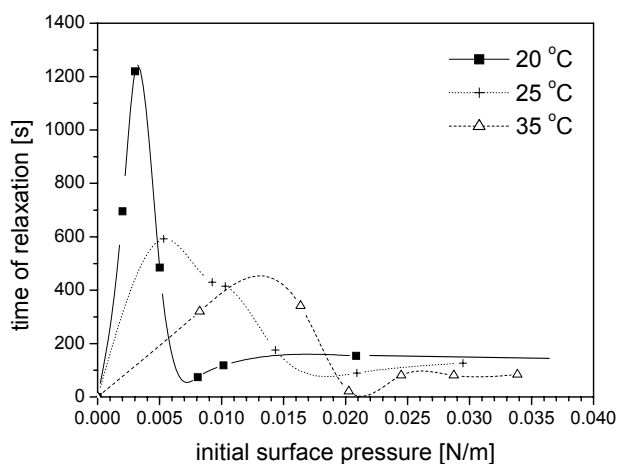


Fig.8. Time of relaxation vs. initial surface pressure  $\pi_0$  for DPPC on water at different temperatures,  $u = 35$  mm/min.

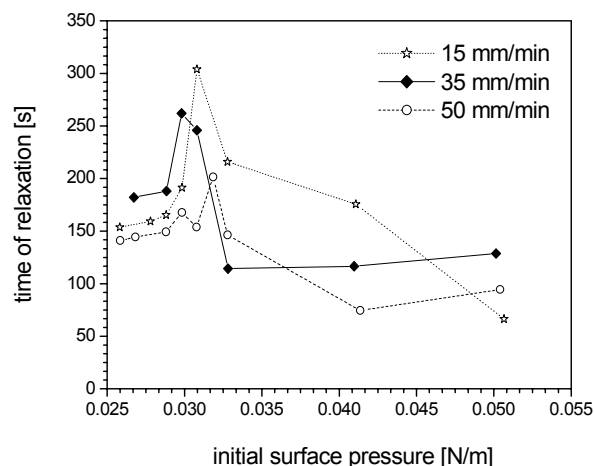


Fig.9. Time of relaxation vs. initial surface pressure  $\pi_0$  for DPPC on  $10^{-4}$  M CTAB;  $T = 25^\circ\text{C}$ .

The characteristic maximum of the relaxation time can be observed for the surface pressure values corresponding to the intermediate surface phase. Such observation can be made for both DPPC on water and DPPC on CTAB solution, however in the latter case values of maximum  $\tau$  are lower.

The equilibrium surface pressure ( $\pi_{eq}$ ) is the second parameter determined using the relaxation equation (Eq.2). Its value is presented as a function of the initial surface pressure  $\pi_0$  in Fig. 10 (DPPC) and Fig. 11 (DPPC+CTAB). For DPPC on water (Fig. 10), the  $\pi_{eq}$  values are grouped along two straight lines – the first for the LE + I phase, and the second for LC-phase. If CTAB is present in the system, all  $\pi_{eq}$  values are located close to the single straight line, what was confirmed also for different compression speeds (Fig. 11).

#### 4. Discussion

The relaxation of surface pressure indicates the visco-elastic properties of the surface film. The time of relaxation,  $\tau$ , determined from the experiments, represents - according to the Maxwell theory of linear visco-elasticity - the ratio of surface dilatational viscosity and elasticity, Sosnowski (2003). Dissipative (i.e. viscous) mechanisms in surface response to deformation explain the occurrence of the surface pressure hysteresis during

successive compression and expansion of the monolayer. Such hysteresis is believed to play a substantial role in physiological functions of the pulmonary surfactant, Podgórski and Gradoń (1993), Notter et al. (1982).

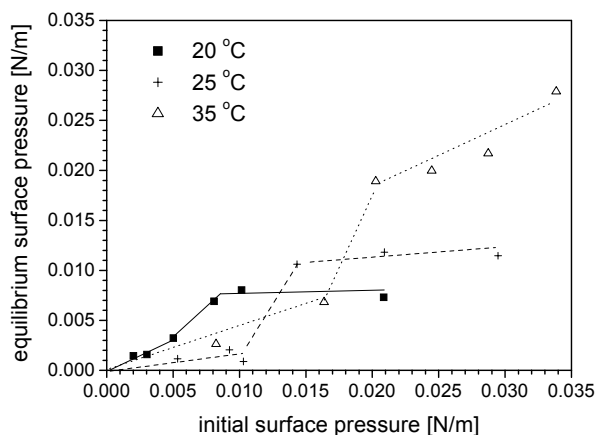


Fig.10. Equilibrium surface pressure  $\pi_{eq}$  as a function of the initial surface pressure for DPPC on water,  $u = 35$  mm/min.

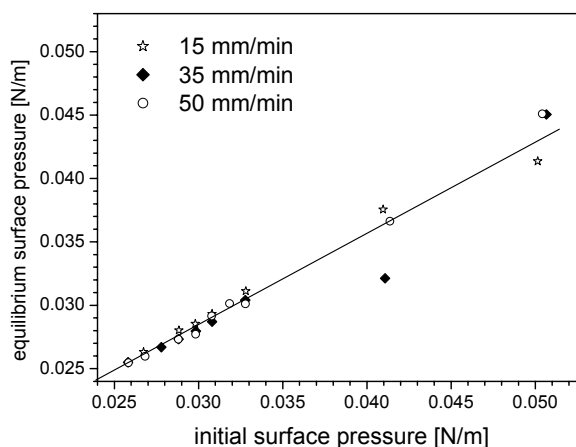


Fig.11. Equilibrium surface pressure  $\pi_{eq}$  as a function of the initial surface pressure for DPPC on  $10^{-4}$  M CTAB,  $T = 25$  °C.

In our measurements the experiments of surface relaxation were preceded by measurements of surface compressibility. It is seen from Fig.2, that the stress in the surface film increases in a nonlinear manner when the surface area is reduced. The reason is that the monolayer forms a dynamic molecular structure, which undergoes structural reorganizations (transitions) during compression as shown by  $\pi(A)$  and  $\kappa(\pi)$  relationships, Figs.2 and 3. Liquid expanded (LE) surface phase can be recognized for  $\pi$  below 0.005, 0.008 and 0.016 N/m in 20, 25 and 35°C, respectively. Similarly, the liquid condensed (LC) phase starts at  $\pi$  close to 0.011, 0.015 and 0.025 N/m at these temperatures. The regions between these values of the surface pressure correspond to the intermediate (I) surface phase, which is characterized by condensed domains and free molecules coexisting in the phospholipid monolayer, Gaines (1966). Both the possibility of partially free movement of the molecules on the surface and their incorporation into domains explain why compression of such film results only in a slight increase of the surface pressure. This effect is confirmed by the maximum of the compressibility ( $\kappa_{max}$ ) observed at  $\pi$  around 0.008, 0.011 and 0.022 (20, 25 and 35°C, respectively), i.e. in the central part of the I-phase at each temperature. The increase of temperature results in reduction of  $\kappa_{max}$  due to the fact that the slope of  $\pi(A)$  curve during I-phase is steeper at higher  $T$ .

The relaxation curves obtained for compressed surface with DPPC (Fig. 8) are qualitatively similar to  $\kappa(\pi)$  relationships. However, relaxation times show the maximum ( $\tau_{max}$ ) for lower values of the initial surface pressures in comparison to  $\pi$  values corresponding to  $\kappa_{max}$ . It means that the decay of surface pressure is slowest for the surface with molecular organization close to the LE-to-I phase transition. Again, the increase of temperature leads to lower values of  $\tau_{max}$ , what can be explained by faster molecular rearrangements at higher temperatures. The equilibrium surface pressure ( $\pi_{eq}$ ), which forms the lower limit of the relaxation curve, depends linearly on the value of the initial surface pressure ( $\pi_0$ ) within the given surface phase (Fig.10). The "jump" of the linear relationship  $\pi_{eq}=f(\pi_0)$  occurs in the range of  $\pi$  values, which correspond to  $\kappa_{max}$  and  $\tau_{max}$ , i.e. to the I-phase.

The mixed film (DPPC+CTAB) exhibits different response to deformation, mainly due to expelling CTAB molecules from the surface during contraction. Therefore the maximum compressibility for such surface is higher (Fig.5) than for the one with pure DPPC monolayer, and the maximum relaxation time is shorter (Fig.9). The equilibrium surface pressure ( $\pi_{eq}$ ) can be correlated with  $\pi_0$  by a single straight line (Fig.11), since no irregularities in the relaxation curve are observed (Fig.7). This observation can be explained by adsorption of

CTAB molecules from the subphase during decay of  $\pi$ . It seems therefore that CTAB in the film and subphase acts as an equalizer of surface pressure variations resulting from deformation of DPPC-rich surface.

## 5. Conclusions

The experimental results allowed determining important mechanical parameters of the gas-liquid interface with surfactants as a function of temperature and surface deformation conditions. These parameters describe the response of the interface to compression (by the value of  $\kappa$ ) and the relaxation of the surface stress (by the values of  $\tau$  and  $\pi_{eq}$ ). It was shown that the interface with adsorbed surfactants specifically reacted to deformation, mainly due to kinetics of structural reorganization of molecules in the monolayer but also due to the mass exchange. Recognition of these effects will be helpful in further analysis of the dynamics of gas-liquid systems with deformable interface in the presence of surface-active compounds. Some of such systems are of great practical significance (e.g., the pulmonary surfactant of the lungs), what makes the motivation for even more intense studies in that field.

## 6. Acknowledgements

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