Rheological Properties of the Air-Liquid Interface

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Introduction

Many phenomena in gas-liquid systems, such as: bubble growth, bubble coalescence or foam drainage, depend on mechanical properties of air-liquid interface. By influencing rheological characteristics of the surface, surfactants strongly modify dynamic behavior of such systems, the practical significance of which extends beyond technology (e.g., in the pulmonary surfactant system of the lungs [1]). This communication is focused on experimental evaluation of the dilatational rheological properties of air-water interface in the presence of surfactants with various properties.

Experiments

Two types of surface-active compounds were studied: DPPC (dipalmitoyl phosphatidylcholine) - the main phospholipid found in the pulmonary surfactant - and CTAB (hexadecyltrimethylammonium bromide). DPPC is insoluble in water, while CTAB is a soluble cationic surfactant. The Langmuir-Wilhelmy film balance (KSV, Finland) described in details elsewhere [2], was used to measure changes of surface pressure ($\pi$, [Nm$^{-1}$]), during compression of interfacial area ($A$, [m$^2$]) with various rates (3.75 - 90 cm$^2$/min) and in various temperatures (20-35$^\circ$C). From the dynamic $\pi$-$A$ curves, the compressibility of the interface was evaluated as:

$$\kappa = -\frac{1}{A} \left. \frac{\partial A}{\partial \pi} \right|_T$$

allowing also for determination of so called Gibbs elasticity of the interface: $E_G = 2/\kappa$ [3].

The same experimental device was used to study the surface pressure relaxation after termination of the predefined contraction of the interface. The results obtained in both types of experiments were then compared and discussed in respect to their practical meaning in technical and biological systems.

Results and discussion

The compressibility values for CTAB solutions interface were in the range of 100-6000 mN$^{-1}$ depending on concentration, temperature and the compression rate, Fig.1. For similar conditions of surface deformation, the interface containing DPPC exhibited compressibility in the range of 10-150 mN$^{-1}$. This observation can be explained based on the molecular structure of the interface or by the mass exchange in the interfacial region. For DPPC, which forms a stable insoluble surface film, molecular aggregation during surface contraction is responsible for phase transitions in the monolayer, resulting in the two-phase condensation region (maximum $\kappa$) followed by a condensed surface phase characterized by a low compressibility (i.e. high Gibbs elasticity) at increased values of $\pi$. By contrast, adsorbed CTAB molecules may be excluded from the superficial film during contraction of the interface what results in a high surface compressibility (low $E_G$). In this case, i.e. for soluble surfactant, desorption and mass exchange, rather than molecular aggregation, determine the overall response of the interface to the disturbance.

The results of relaxation experiments confirm the above speculations. The interface which contain DPPC may relax in a few steps indicating structural rearrangements in the film undergoing transition from the condensed to the expanded surface phase. The surface of CTAB solution always relaxes smoothly, what confirms that the mass transfer plays here the substantial role. All relaxation curves may be described with the first order kinetics [4]:
\[ \pi - \pi_{eq} = (\pi_{\text{max}} - \pi_{eq}) \exp\left( -\frac{t}{\tau} \right) \]  

(2).

where \( \tau \) is the characteristic relaxation time (for DPPC - within the given step of the decay), \( \pi_{\text{max}} \) - the maximum surface pressure (at the start of the decay), and \( \pi_{eq} \) - the equilibrium (asymptotic) value. It follows from this approach that both types of interface have visco-elastic properties resulting from either molecular rearrangements (DPPC) or mass exchange (CTAB). The relaxation time indicates the ratio of dissipative-to-elastic components in the surface response to contraction. The experimental fits show that \( \tau \) is short for the condensed (i.e. more solid) phospholipid monolayer and much longer for expanded (i.e. more fluid-like) DPPC film. Interface with CTAB relaxes at the rate between these two extremes, although via the different mechanism.

These results are applicable for dynamic interfaces of practical interest. The pulmonary surfactant being a multi-component structure adsorbed at the air-liquid interface periodically deformed during breathing presents a complicated dynamic system, which probably cannot be described quantitatively in details. However, a macroscopic rheological approach, demonstrating the effective visco-elastic properties, is capable of explaining the origin and role of the surface pressure hysteresis observed in such system [5].

Conclusions

The quantitative results of experimental studies showed differences in surface dynamics between insoluble and soluble surfactants. They allow for further investigations and discussion of the influence of surfactants on mechanical properties and dynamic behavior of the gas-liquid interface, which appeared to be strongly dependent on temperature, surfactant concentration and conditions of surface deformation. The results of such studies may be used in analysis of the role of active interface in the physiology (pulmonary surfactant) and technology (e.g., foaming systems).

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References

Figure 1. Comparison of surface compressibility of CTAB (various concentrations) and DPPC monolayer, 25 °C.