DYNAMIC SURFACE TENSION MEASUREMENTS ON SURFACE ACTIVE MATERIALS

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ABSTRACT

   Surface tension measurements by the Wilhelmy plate method are being done at our laboratory using an automatic balance. Surface-active material (surfactant) is spread as a monolayer on an air-water interface and a Pt plate, suspended from a micro-balance, is brought vertically into contact with the interface. The water is contained in a trough, two opposite sides of which can move independently, one producing a large variation in surface area and the other generating a longitudinal wave in the monolayer. This set-up is a new, asymmetric variant of the Benjamins-De Feyter method. Results of measurements on visco-elastic interfacial properties of model compounds of lung surfactant are reported.

INTRODUCTION

   Surface tension of liquids can be determined by means of force measurement. In the well known Wilhelmy plate method a Pt plate (ref. 1) is suspended from a balance and is brought in contact, but only just, with a liquid-gas interface (see Fig. 1). The resulting vertical force is measured and is generally of the order of 10^{-3} N, corresponding to 0.1 gram. Surface tension is an important parameter in the description of the physical properties of surface-active materials, e.g. lung surfactant (LS) (ref. 2). In the present contribution, dynamic surface-tension measurements will be reported, since the response of surface tension to variations of other system parameters is often more important than its equilibrium value (ref. 3).

THEORY

   The relation between the variation ($d\sigma$) of the surface tension (σ) as a function of variation (dA) of the surface area (A) reads

$$d\sigma = \varepsilon_d d\ln A \tag{1}$$

where ε_d is the surface dilational elasticity. This equation is valid when shear forces in the plane of the monolayer are absent.

In the case of a pure liquid interface $\varepsilon_d = 0$, whereas in the presence of a monolayer of a surface active agent (surfactant) $\varepsilon_d \neq 0$. In order to measure ε_d, slight harmonic variations of A (dA/A 0.01) are introduced. For ε_d we now write

$$\varepsilon_d = |\varepsilon_d| \exp(j\phi_d) \qquad (2)$$

where $|\varepsilon_d|$ is the modulus of the surface dilational elasticity and ϕ_d is the loss angle. Here we present experiments with a new, asymmetric variant of the Benjamins-de Feyter (B-F) method (ref. 4, 5). this method enables the value of $|\varepsilon_d|$ to be determined from the amplitudes of the harmonic variations of A and of σ, ΔA and $\Delta \sigma$, respectively,

$$|\varepsilon_d| = A \frac{\Delta \sigma}{\Delta A} \qquad (3)$$

which is valid when satisfying the condition that kL≪1 (ref. 5-a), with k the real wave number of the longitudinal wave, and L the length of the monolayer in the direction in which the wave travels. The loss angle ϕ_d is found from the difference in phase between σ and A. The variant of the B-F method introduced here provides a quick way to determine $|\varepsilon_d|$ in relation to σ.

MATERIALS AND APPARATUS

One experiment is made on a monolayer of dipalmitoylphosphatidylcholine (DPPC), the main component of LS. In LS, DPPC is mixed with other lipids. In particular, the unsaturated phospholipids are known to alter the surface properties of DPPC drastically (ref. 6). As an introductory experiment, $|\varepsilon_d|$ and ϕ_d have been determined for a DPPC-dioleoylphosphatidylglycerol (DOPG) 7:3 **mixture**, where DOPG serves as a model compound for unsaturated phospholipids in LS. (DPPC and DOPG supplied by the Sigma Chemical Company. Inorganic salts and organic solvents by Merck, p.a. grade. As subphase a complex, physiological-relevant buffer solution from triple distilled water.) Fig. 1 shows the principles of the experimental set-up. It consists of a Teflon Langmuir trough (Lt) provided with a standard moving barrier (mb) (ref. 1) and a harmonically oscillating barrier (ob). The displacement of the ob is measured by means of a Sangamo-Schlumberger DF/2.5/G displacement transducer with a sensitivity of 764 mV/mm (10 V dc power supply). An electrolytically roughened platinum Wilhelmy plate (Wp) with a perimeter of 4.0 cm is suspended from a Cahn RH automatic electrobalance (eb) which measures the force generated by the surface tension. A monolayer (m) at the air-liquid interface (a-1) is contained within a closed elastic ribbon perpendicular to and partly immersed in the interface, forming a rectangle (er) with width b = 125 mm and variable length L.
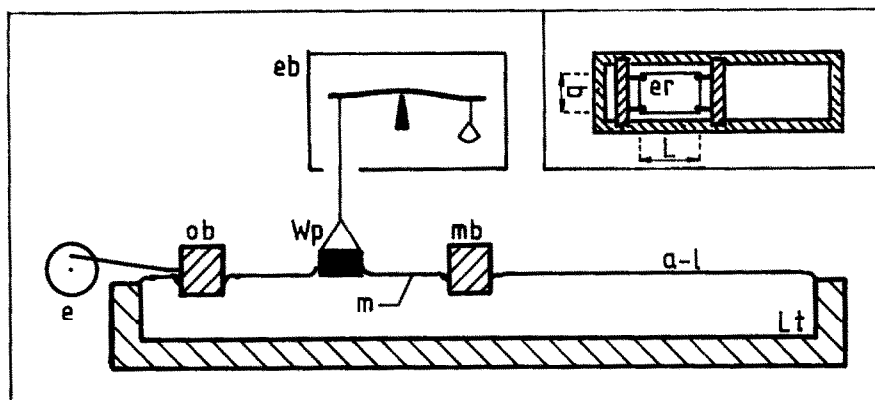
Fig. 1. Principle of the aparatus of the asymmetric method. The insert shows a top view. e: excenter. For meaning of other abbrevations, see text below.

The surface tension of the monolayer is set with the moving barrier. The oscillating barrier is displaced with an amplitude of 0.5 mm which creates a maximum area variation of 1.25 cm^2 and thus generates a longitudinal wave in the monolayer. The elastic ribbon reduces shear between the monolayer and the side walls of the compartment and excludes leakage of monolayer molecules. The apparatus is placed in a glove box to control the temperature, and the humidity of the air. A microcomputer (LSI) monitors the electric signals related to surface tension and the displacement of both barriers. The LSI communicates with a minicomputer (PDP-11/23) for purposes of data handling. The signals are also measured by means of an X-Y recorder (Hewlett Packard).

The feedback system of the electrobalance introduces an apparent loss angle. A correction is determined by means of an independent method and amounts to 7° at the frequency of 0.17 Hz used.

METHOD

Fig. 2A shows a plot of surface pressure ($\pi = \sigma_{water} - \sigma$) as a function of A, which is derived from a DPPC monolayer at 37°C and a relative humidity of over 90%, recorded by means of an X-Y recorder. This plot will be described briefly with respect to experimental procedure. The monolayer molecules are spread from a chloroform-methanol (95:5) solution until π equals 6.2 mNm^{-1}, at a surface area of 213 cm^2, which is then expanded to A_{max} = 313 cm^2. After 10 minutes the measurement is started (curve M). The monolayer is compressed at a rate of 4.7 $cm^2 s^{-1}$ to π_1 = 11 mNm^{-1} at surface area A_1 (P_1). After the end of compression, π relaxes to a lower value. The value of π which is recorded when the decrease of π becomes less than 0.5% in 10 seconds will be referred to as the static surface pressure π_{sl} at area A_1.
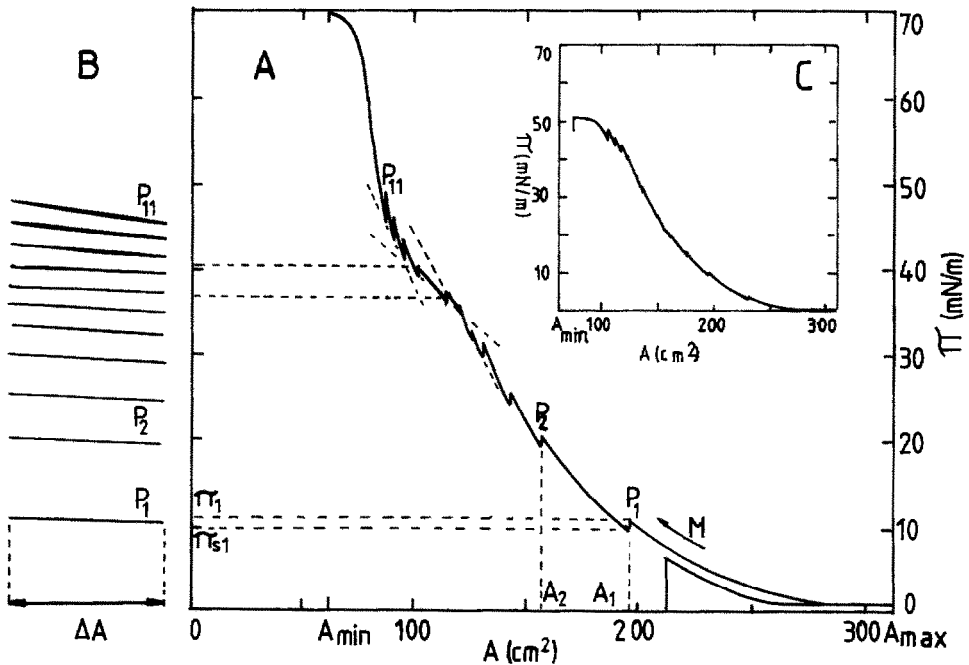
Fig. 2. A: quasi-static plot of surface pressure vs surface area (π-A) of a DPPC monolayer at 37°C. B: π-A plot (DPPC) recorded during cycling of the oscillating barrier (A-signal is 55 times amplified compared to Fig. A). C: (insert) quasi-static π-A plot of a DPPC-DOPG (7:3) mixed monolayer at 37°C. For details, see text.

Then the oscillating barrier is started with a frequency of $f = \omega/2 = 0.17$ Hz. After two cycles, the microcomputer starts sampling (40 per cycle) the force on the electrobalance and the displacement of the oscillating barrier. In addition, π-A plots are made by means of the X-Y recorder during two cycles. (Fig. 2B). After the oscillating barrier has been stopped, the monolayer is compressed further to π_2 by reduction of the surface area to A_2. The described procedure is followed at 11 different values of A. The surface area was ultimately reduced to a minimum value $A_{min} = 1/5 A_{max} = 63.5$ cm^2.

The mixed DPPC-DOPG monolayer is spread at 213 cm^2 to a surface pressure of 5.6 mNm^{-1}. The procedure at each point P_i is identical with the sequence of measurements on the DPPC monolayer. The insert in Fig. 2 (C) shows the quasi-static π-A plot.

RESULTS

The most striking difference between the two quasi-static π-A plots is that the DPPC monolayer collapses at 70 mNm^{-1} and the mixed monolayer at 52 mNm^{-1}.

We consider the points which represent the values of π_{si} as a function of A (Fig. 2.A and C) to be close approximations of static π-A plots. If, in the case of the DPPC monolayer, a curve is drawn to connect these points, 2 points of inflection would show at π values of 37 and 40 mNm^{-1}, which values are found by means of the dotted 'tangents'. These points of inflection indicate the onset and termination, respectively, of the transition from the liquid-expanded to the liquid-condensed state (LE-LC transition) of the monolayer. The mixed monolayer does not show an LE-LC transition.
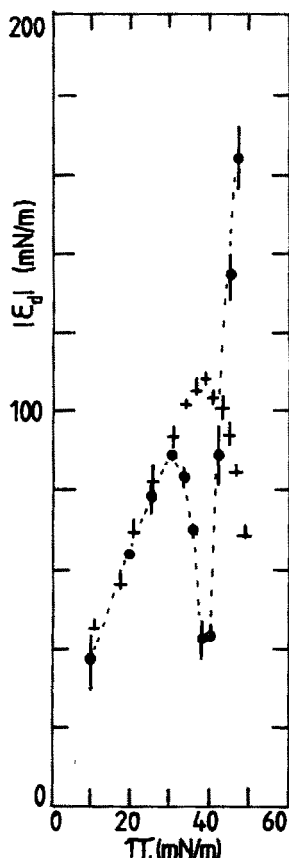
The values of $|\varepsilon_d|$, calculated according to eq. (3), are plotted against π_{si} in Fig. 3. This figure shows that $|\varepsilon_d|$ values of both monolayers are similar and increase almost linearly with π up to about 90 mNm^{-1} at 30 mNm^{-1}. Then the $|\varepsilon_d|$ of the DPPC monolayer decreases at values where the LE-LC transition occurs. At higher values of π, the strong increase in $|\varepsilon_d|$ with π in the case of DPPC, to a mean value of 164 mNm^{-1} at 47 mNm^{-1}, obviously reflects the liquid-condensed nature of this monolayer beyond the LE-LC transition. The $|\varepsilon_d|$ values of the mixed monolayer do not show any sign of the LE-LC transition. They reach a maximum of about 110 mNm^{-1} when the $|\varepsilon_d|$ of DPPC are low because of the LE-LC transition. Furthermore, they decrease at surface pressures where $|\varepsilon_d|$ of DPPC just attains its maximum values.

The measured values of ϕ_d are slightly above zero (between 1 and 10°, mean value 4°) and are independent of π, since the deviations from the mean values are of the same order of magnitude.

Fig. 3. Plot of $|\varepsilon_d|$ vs σ. $\bullet$: DPPC monolayer; $+$: mixed DPPC-DOPG (7:3) monolayer. Temp. 37°C, rel. humidity over 90%.

DISCUSSION

The values of $|\varepsilon_d|$ and ϕ_d as calculated with equation (3) are true values if $kL \ll 1$ (ref. 5-a), as quoted in the Section on Theory. Values of this product are found to range from 0.8 at low values of π to 0.2 at high values of π. If the condition $kL \ll 1$ is interpreted as '$kL \sim 0.1$', then this condition is not satisfied. At the frequency used, the corrections of the values of $|\varepsilon_d|$ (ref. 7) vary from +5% when $|\varepsilon_d| = 38$ mNm^{-1} (at $\pi = 10$ mNm^{-1}) to almost 0% when $|\varepsilon_d| = 164$ mNm^{-1} (at $\pi = 47$ mNm^{-1}). The experimental error in $|\varepsilon_d|$ is of the order of a few percent.

The values of $|\varepsilon_d|$, obtained by the asymmetric method presented here, are of the same order of magnitude as reported previously (ref. 5). The occurrence of the LE-LC phase transition, normally found with a DPPC monolayer below $41^{\circ}C$, and which correlates with monolayer collapse at a very high π value of 70 mNm^{-1} (π_c), is more emphatically reflected in the plot of $|\varepsilon_d|$ vs π. The absence of the LE-LC transition in the case of the mixed monolayer, correlating with a lower π_c value, yields a quite different pattern of the $|\varepsilon_d| - \pi$ plot. In the authors opinion, the asymmetric variant of the Benjamins-de Feyter method provides a sensitive way to detect phase transitions of monolayers.

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