Thermochimica Acta, 103 (1986) 129—135
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PREVENTING LEAKAGES IN THE LANGMUIR-WILHELMY METHOD

P. GIELES, P. AERNOUDTS, C. MASSEN

Department of Physics, Eindhoven University of Technology, Eindhoven,
The Netherlands

ABSTRACT

Determination of surface properties of monolayers in the Langmuir-Wilhelmy method is often hampered by leakage. Several possibilities for prevention and correction are presented and discussed. A two barrier system and application of a second surfactant and force transducer yields good reduction of leakage effects.

INTRODUCTION

The measurement of surface pressure versus specific area (π - A) loops contributes considerably to the understanding and determination of surface properties of monolayers. These measurements are mostly carried out in the so called Langmuir-Wilhelmy method.

In this method a rectangular teflon trough is used (see Fig.1), filled with a liquid subphase so that the meniscus appears above the trough rim. A surfactant film is brought onto the surface, equally spreading while the solvent evaporates. A Wilhelmy dipping plate, suspended from an electrobalance, is used to measure surface forces; these forces are interpreted as surface tension (τ) or surface pressure π ($\pi = \tau_o - \tau$, τ_o being the surface tension of the clean surface). π - A curves are then obtained by compressing and expanding the surfactant film, which is done with a moving barrier.

This technique is known to have some complications. A non-zero and varying contact angle between monolayer and Wilhelmy plate (1) and leakage effects along the barrier are well known complications. Although attention has been paid to leakage artefacts (2), the problem is not solved yet. In order to obtain information about leakage some investigators use a second force transducer and Wilhelmy plate placed behind the moving barrier (3). A non zero surface pressure behind the barrier then indicates leakage.

The aim of the present paper is firstly to show that this way of detecting leakage may lead to great inaccuracies and secondly to show how such inaccuracies can be reduced by using special precautions.

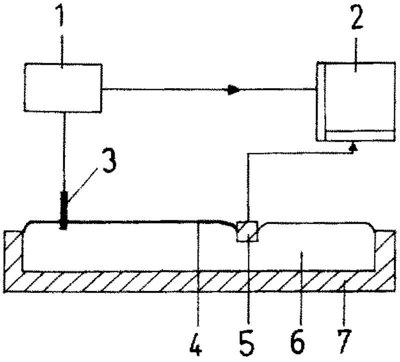

Fig.1. Experimental set up of the Langmuir-Wilhelmy Method:
1 = electrobalance;
2 = xy-recorder;
3 = Wilhelmy plate;
4 = monolayer;
5 = movable barrier;
6 = subphase;
7 = trough.

THEORY

We shall start by showing how corrections for leakage can be carried out taking into account the measured values of the surface pressure behind the moving barrier (right hand side). We will illustrate this with a numerical example and make use of a simplified form of a π - A curve on compression:

$$\pi = \frac{a_1}{A - a_2} \tag{1}$$

in which a_1 and a_2 are parameters. The choice of Eq. (1) is based on the shape of a π - A curve for a DPPC monolayer (*) (3). A numerical least squares fitting procedure, applied between $A = 50.10^{-20}$ and $A = 100.10^{-10}$ m^2 resulted in $a_1 = 132.10^{-23}$ Nm and $a_2 = 45.10^{-20} m^2$.
The original curve as well as the result of the fitting procedure are presented in Fig.2.

We consider a trough in which a barrier divides the surface in a LHS part (area S_l) and a RHS part (area S_r). The surface pressures measured in each part are π_l and π_r respectively. When starting N surfactant molecules are applied to the LHS part.

(*) DPPC: dipalmitoylphosphatidylcholine, the main constituent of lungsurfactant

During the experiment the barrier is moved. If no leakage occurs the measurement of π_ℓ yields the correct π - A curve. However, if leakage does occur the molecules will cover the LHS part (N_ℓ molecules) as well as the RHS part ($N_r = N - N_\ell = x{*}N$ molecules, x being the leakage fraction).

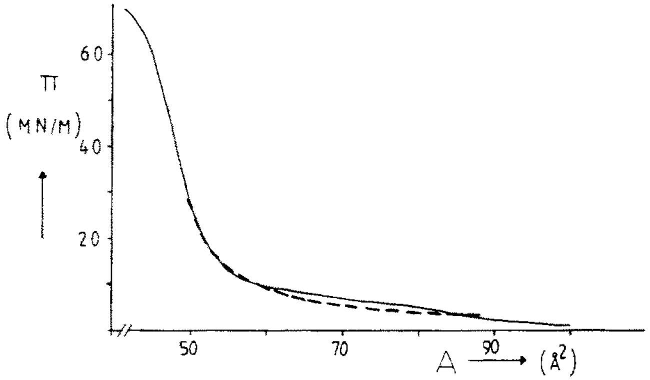

Fig.2. π-A curve of a DPPC monolayer at 20 C (compression); ——— measured curve, ---- result of curve fitting Eq.(1).

We shall take a measurement before and after compression each consisting of simultaneous reading of the data of π_ℓ and π_r, S_ℓ and S_r. Let the measurement before compression satisfy:

$N_{\ell 1} = N = 2.10^{(16)}$ $\qquad N_{r1} = 0$

$S_{\ell 1} = 4.10.^{(-2)}\ m^2$ $\qquad S_{r1} = 10.^{(-2)}\ m^2$

$\pi_{\ell 1} = .85.10^{(-3)}\ N/m$ $\qquad \pi_{r1} = 0\ N/m$

and let the measurement after compression be given by

$N_{\ell 2} = N.(1 - x)$ $\qquad N_{r2} = x.N$

$S_{\ell 2} = 10.^{(-2)}\ m^2$ $\qquad S_{r2} = 4.10^{(-2)}\ m^2$

$$\pi_{\ell 2} = \frac{(1-x).a_1}{S\ _2/N - (1-x).a_2}\ N/m \qquad \pi_{r2} = \frac{x.a_1}{S_{r2}/N - x.a_2}\ N/m$$

We can now calculate the influence of the leakage fraction x on $\pi_{\ell 2}$ and π_{r2}. The results are presented in Fig.3a and curve 1 of Fig.3b respectively. If we take the inaccuracy of the π measurement to be .5 mN/m we see in Fig.3b curve 1 that the measured value of π_{r2} does not exceed this value, not even for values of x as big as 40%, so that corrections make no sense. This is due to the fact that the surface in the RHS compartment contains at the beginning of an experiment only a small amount of surfactant. Moreover, the RHS surface area is expanding while compressing the monolayer and therefore the pressure values π_r are points on the flat part of the π - A curve. So small inaccuracies of the π_r values will cause great inaccuracies in the values of Nr. The value of the extra measurement behind the barrier can be improved considerably by using a second barrier. By moving this barrier we can control the value of S_r. The influence on the π_{r2} value of reduction of S_{r2} is - for the same numerical example as used above - shown in Fig.3b. curves 2-5. We see that appropriate compression of S_{r2} makes the π_{r2} value exceed the inaccuracy of the measurement.

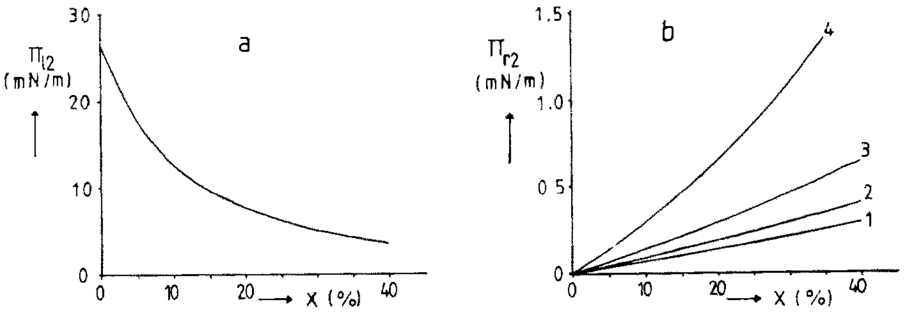

Fig.3. Influence of leakage fraction x on a) $\pi_{\ell 2}$, and b) π_{r2}; parameter in b) is S_{r2}: 1 : 4.10^{-2} m^2; 2 : 3.10^{-2} m^2; 3 : 2.10^{-2} m^2; 4 : 10^{-2} m^2.

FEEDBACK METHOD

Another solution to reduce or even eliminate the influence of leakage is based on the fact that it is caused by a surface pressure difference over the barrier. This surface pressure difference can be eliminated with a set up in which the position of the second barrier is controlled by a feedback and servo-system, in such a way that the surface pressure difference remains zero (see Fig.1). This is achieved by using a surfactant between the two barriers. As second surfactant DPPC is preferred because of its very low surface tension under compression (near zero) which serves the feedback method.

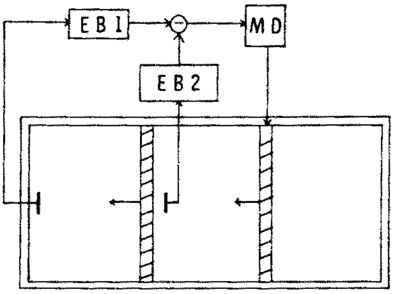

Fig.4 Set up of the two barrier system with feedback.

EB = electrobalance

MD = motordrive

EXPERIMENTS AND RESULTS

In order to test the feedback method experiments were carried out on DPPC monolayers at 20 C in a Langmuir trough (50x15x1 cm^3) with two barriers, the first of which was provided with a hole to serve as (artificial) leak. Surface pressure in both compartments was measured with Platinum Wilhelmy plates suspended from a Universal Transducer Cell (UC2, Gould) and from an electrobalance (Cahn RH) in the left and right part respectively. The DPPC monolayer was applied to the surface from a spreading solvent (chloroform). The monolayer in the left part was compressed and expanded between $1.8*10^{(-2)}$ and $0.6*10^{(-2)}$ m^2 with a rate of 0.04 m^2/s.

Fig.5 shows a compression curve while holding the second barrier. Due to leakage π_ℓ cannot increase much; at the same time no effect on π_r is recorded since S_r is expanding.

Stopping the barrier motion causes relaxation of π_ℓ to its equilibrium value which equals π_r. Fig.6 shows compression while the second barrier is moved along (manually) in such a way that $\pi_\ell = \pi_r$. When the second barrier approaches the Wilhelmy plate in the RHS part it is stopped while the first barrier continues compression. As a consequence the monolayer in the RHS part, created by leakage, expands so π_r decreases. When the first barrier is stopped both π_ℓ and π_r relax to equilibrium ($\pi_\ell = \pi_r$). The same phenomena are recorded on expansion. The drastic reduction of leakage influence is reflected in the high surface pressure under compression (73mN/m), which is in accordance with the leakage free measured value.

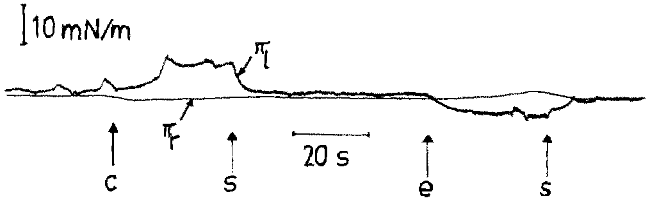

Fig.5. Compressing (c) and expanding (e) a DPPC monolayer in the presence of a leak while holding second barrier (s = stop barrier motion).

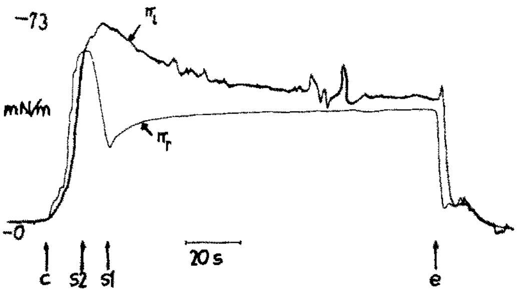

Fig.6. π_ℓ and π_r during compression and expansion while moving both barriers.

DISCUSSION AND CONCLUSION

Whenever the properties of surfactant are evaluated in a Langmuir trough, leakage problems have to be solved. Solutions can be sought in two ways. The first is preventing leakages by special barrier constructions as proposed by Tabak and Notter. However, even in their own opinion, the ribbon type barrier remains 'cumbersome to work with' (2). Furthermore, when dam type barriers are used by other investigators it is often assumed that leakage does not occur and no check is made. The second way is correction by measuring the surface pressure behind the barrier. Although information about leakage artifacts is now gained, no correct π - A curve is actually measured; the effect becomes apparent only after the compression when values of S_r are sufficiently small to allow quantification of the leakage.

The experiments described in this paper indicate a different solution which in fact is a combination of preventing leakage and measuring surface pressure. It is shown that leakage problems can be solved by using a second barrier which compresses the monolayer between the two barriers in such a way that the measured surface pressures satisfy $\pi_\ell = \pi_r$. Fig.6 shows that in this case correct values for π_ℓ are obtained and thus in this way correct π - A curves can be measured.

The main disadvantage of this two barrier method is the difficulty of measuring surface pressure between two moving barriers. On the other hand the results (Fig.3) suggest a solution in which the area behind the first moving barrier is kept small by a second barrier. When a surfactant is applied prevention will be more effective, and will be best when surface pressures are measured to drive the second barrier. Correct measurements, leaving out the second Wilhelmy plate, are, in principle, also possible. If in both RHS and LHS compartments the same surfactant is applied on the liquid substrate with equal surface areas, and if for both parts are equal surface area changes, the resultant surface pressures will be equal and thus the driving force for leakage minimal.

Part of this work was supported by the Netherlands Organization of Pure Research (Z.W.O.).

REFERENCES

1 R.E. Barrow, B.A. Hills, J. Physiol., 295: 217-227, 1979

2 S.A. Tabak, R.H. Notter, Rev. Sci. Instr., 48 (9), 1977

3 A.F.M. Snik, A.J. Kruger, P. Joos, J. Coll. I, Sci., 66 (3), 1978.