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INCLUDING CATALYSIS\*

## REPORTING EXPERIMENTAL PRESSURE- AREA DATA WITH FILM BALANCES

(Recommendations 1984)

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## Reporting experimental pressure-area data with film balances (Recommendations 1984)

Abstract - The present guide provides the principles for reporting pressure-area data obtained with film balances for spread films. It contains six sections, a check-list covering the basic features discussed in the guide and a list of symbols. In setting up the present guide, the main concern of Commission I.6 was to specify criteria for the reliability and reproducibility of reported results. Except for one modification, the nomenclature used is that recommended in (Ref.1). Although the guide deals only with the presentation of pressure-area data of spread films, it applies or may be extended to other properties of spread films. Section I deals with the films and film balances in general. Two film properties : the total area and surface pressure are defined and several experimental conditions which may affect the results are mentioned. The concept of the monolayer state for spread films and criteria for reliability of the data are introduced and discussed in Section II. Recommendations for the description of experimental conditions, of the apparatus and of the procedures involved are dealt with in Sections III and IV. In Section V, the presentation of the (numerical) values of the data and their units is considered. Several applications of the film balance are briefly discussed in Section VI. The check-list covers the basic features discussed in the present guide.

### INTRODUCTION

The aim of the present guide is to provide principles for reporting pressure-area data obtained with film balances. It is divided as follows.

Section I contains :

- a) a general description of films at fluid-fluid interfaces ;
- b) a general description of the film balance and the definitions of two measurable film properties : the total area  $A$  and the surface pressure  $\pi^S$  ;
- c) a list of experimental conditions which may affect the results.

In Section II we discuss  $a_i$  the average area per molecular unit in spread layers (see Note a) and the film thickness. We also deal with the origins of various errors in the values of  $a_i$  and of the surface pressure  $\pi^S$ . Ways of assessing reliable values of  $a_i$  and  $\pi^S$  are provided in this section. The macromolecular films are dealt with in a distinct subsection. Sections III and IV contain recommendations for the description of the experimental conditions, of the apparatus and of the procedures involved in the study.

Section V deals with the presentation of the (numerical) values of  $a_i$  and  $\pi^S$  and with the corresponding units. It includes a description of the various  $\pi^S$  vs  $a_i$  diagrams and of the relevant nomenclature.

In Section VI several applications of the film balance are briefly discussed (see Note b). A check-list covering the basic features discussed in the present guide and a list of symbols concludes it.

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Note a. In the present context  $a_i$  is used instead of  $a_{i,s}$  [see (Ref.1)].

Note b. The principles enunciated here would also apply to presentation of data obtained from studies of films by techniques other than those treated in the document e.g. surface viscosity and potential measurements, ellipsometry, radiotracer studies.

## SECTION I. GENERAL CONSIDERATIONS

Films at fluid-fluid interfaces

In the context of the present report, films are defined as thin layers of any interfacially active substance accumulated at interfaces. The mode of accumulation of a substance depends on the solubility of the substance in the adjacent fluid phases : films may form either spontaneously by *adsorption* from one or both of the adjacent bulk solutions or by *deposition* or *spreading* directly onto the interface.

Film balances have been designed for the study of area and pressure of spread films. For them, the total number  $n_i^S$  of deposited molecules  $i$  and the film area  $A$  are primary data (for  $A$ , see Fig. 1 and Section below). They are generally not suitable for measuring the pressure of adsorbed films.

The *average area per molecule* in the film is  $a_i = (A/n_i^S)$ . The *surface concentration* or the film density is  $\Gamma_i = (n_i^S/A)$ .

Film balance

The film balance (Fig. 1) is a device which provides simultaneously two types of data :

- the *total film area*  $A$ , which can be varied ; this area is enclosed by non-wettable materials (B, trough,  $f$ , thread, ribbon in Fig. 1) which prevent escape of the film ;
- the *net force*  $F$  exerted on the mobile non-wettable float which separates the film from a clean surface (Fig. 1). The float  $f$  is attached to the trough by flexible floating non-wettable threads or ribbons which permit freedom of motion of the float while preventing leakage.

The float should not deform the meniscus so that contact angle hysteresis and tilting of the float are avoided. This can be achieved with very thin floats.

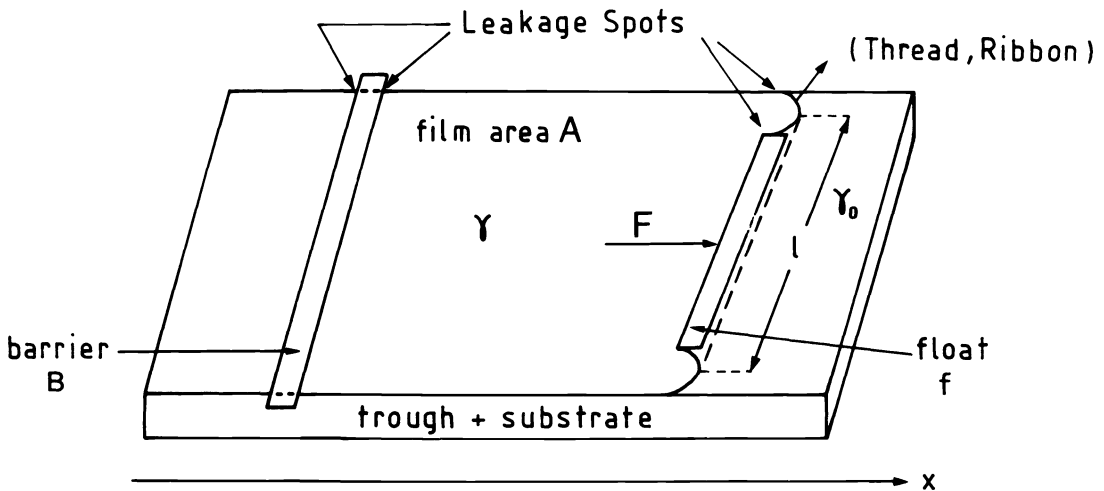


Fig. 1. Schematic diagram of a film balance.

Let  $\gamma$  be the interfacial tension in the film compartment and  $\gamma_0$  that of the clean interface. For a rectangular film, when the mobile barrier of length  $l$  has been displaced parallel to itself, isothermally and reversibly, by an infinitesimal distance  $\delta x$ , the net work of displacement is  $F\delta x$ . During this process the area increases by an amount  $\delta A = l\delta x$ . The net

work of displacement is  $(\gamma_0 - \gamma)l\delta x$ . The condition of mechanical equilibrium for the mobile barrier leads to the following equation :

$$\Delta\gamma = \gamma_0 - \gamma = \frac{F}{l} . \quad (1)$$

When the interface is clean,  $\gamma_0$  is the interfacial tension of the two non-miscible fluids. In that case the difference  $\Delta\gamma$  is called the film surface pressure :

$$\Delta\gamma = \gamma_0 - \gamma = \pi^S . \quad (2)$$

If the barrier separates two film-covered surfaces, the value of  $\Delta\gamma$  corresponds to the difference between two surface pressures.

#### Sources of errors

The factors and conditions listed below may lead to inaccuracies in the values of  $n_i^S$ ,  $A$ ,  $F$  and  $\gamma_0$  :

- presence of surface active contaminants in the trough, the studied components, the bulk fluids and the spreading solvent ; film contamination by the spreading solvent ;
- incomplete spreading or non-uniform distribution of the spread molecules over the interface ;
- incomplete mechanical relaxation of the films either *under* dynamic conditions (expansion or compression), or *subsequent* to a change in the film area (static metastable state) ;
- inaccurate measurement of the temperature at the interface.

Contamination and incomplete spreading or non-uniform film distribution *on a molecular scale* can lead to ill-defined values of  $a_i$  and  $\pi^S$ , useless for further interpretation.

Values of  $\pi^S$  obtained for films that are not in mechanical and thermal equilibrium with their surroundings are useless for interpretation in terms of equilibrium thermodynamics.

## SECTION II. PROPERTIES OF STABLE, WELL-SPREAD, UNIFORM AND NON-CONTAMINATED FILMS

This section deals with well-spread films and elaborates criteria to ascertain that the spread films are uniform and non-contaminated.

#### Average areas per molecule

Small molecules. The primary experimental quantities needed to calculate  $a_i$  are  $A$  and  $n_i^S$ . In some cases radiolabelled substances have been used to estimate  $n_i^S$ .

The values of  $A$ , which include the contributions originating in the loops and the displacement of the float, are known with an accuracy which depends in part on the ratio of substrate area to perimeter and on the wettability of the trough, barrier and float materials : the relative contribution of the meniscus area to  $A$  increases when  $A$  decreases and should be taken into account.

The accuracy of  $n_i^S$  is mainly determined by the accuracies of the volume and concentration of solution spread.

Reproducibility may be poorer or drifting values may be obtained when losses occur through leakage from the film compartment or through dissolution into the adjacent bulk phases.

Leakage can take place between the trough and the barrier or the float (see Fig. 1). For films at the air-water interface leakage can be detected by the movement of talcum powder sprinkled on the surface at the suspected leakage spot. To avoid the dissolution of films

into water, concentrated solutions of inorganic electrolytes are sometimes used as the substrate. Then the effect of the electrolytes on film properties should be considered. At oil-water interfaces it is difficult to distinguish loss of film material by leakage from that by dissolution. When dissolution occurs, reproducibility of the rate  $(d\pi/dt)_A$  or  $(dA/dt)_{\pi}$  may be considered a reliable test for absence of leakage.

If leakage and rate of dissolution are very small, the relative loss  $(\Delta n_i^S/n_i^S)$  may be negligible. This criterion is often satisfied by the spread "insoluble" films defined in (Ref. 1), p.584.

When no loss of film molecules occurs, the following test may help to establish whether or not the film is well-spread and in stable equilibrium.

A well-spread film, at equilibrium on a given area  $A$ , has the same surface pressure when formed by any of the three following techniques :

- the film is spread from a solution of known concentration on a large initial area which is subsequently compressed to  $A$  ;
- the film is spread from a solution of known concentration on the given  $A$  ;
- the film is spread on the area  $A$  from a solid of known mass.

Such a film does not display hysteresis upon successive compression and expansion cycles. However, metastable monolayers may exist which do not satisfy the first three requirements for equilibrium, yet do not display hysteresis on limited compression and expansion.

The second technique above is useful when one studies the penetration of a radio-labelled, substrate-soluble constituent, into spread insoluble films.

The third technique is best. It can be used only with rapidly spreading virtually insoluble substances, when available, because it provides pure films not contaminated by the spreading solvents. Volatile non-polar solvents are the least contaminating for films spread on aqueous substrates. They may not always be appropriate solvents, so that polar solvents have to be used. A test for film contamination is available (see section below).

In a well-spread pure film of small spherical molecules,  $a_i$  cannot be smaller than the molecular cross section in the crystalline state.

In general, spread films consist of asymmetric or symmetric elongated molecules. In their crystals, several distinct molecular cross sections may be defined depending on the crystalline face considered. Usually, a spread film formed by elongated asymmetric molecules with their long axes normal to the interface is considered monomolecular as long as  $a_i$  is larger than the *smallest* molecular cross section in the crystalline state which serves as a reference value. If substrate molecules penetrate the film and separate its molecules, the minimum values  $a_m(i)$ , which is the area per molecule in a complete monolayer of substance  $i$  (Ref. 1), is larger than this reference value. If data exist for these reference values they should be quoted for comparison.

Macromolecules. Spread films of macromolecules are handled in the same way as spread films of small molecules. In several respects, spread films of macromolecules behave differently from those of low molecular mass substances. Therefore the principles and criteria discussed in section *Small molecules* apply only to a limited extent to polymeric materials. Experience with macromolecular films is still not very extensive so that no definite recommendations can be given. The following properties of macromolecules and the ensuing effects on the behaviour of spread films deserve attention.

- Synthetic polymers are usually polydisperse, i.e. the films contain molecules of different masses.
- The conformation at the interface of molecules of unequal size may be different.
- Some natural polymers are homodisperse but may retain part of their three-dimensional conformation upon spreading.

- Molecular relaxation processes in macromolecular films are often very slow so that non-equilibrium states are easily frozen in.

- Hysteresis, or in general the observation that film properties depend on spreading history, is more common with macromolecular than with low molecular mass films. Because of these considerations in reporting spread film data of macromolecules, it is important to give full details including the molecular mass distribution, the nature of the spreading solvent and the effect of film preparation and history on the results. For spread macromolecular films a quantity  $a_i$  can be mathematically computed. It is usually expressed per monomeric unit. Its physical meaning is simple only in a few favourable cases.

#### Surface pressure in well-spread mechanically relaxed monolayers

The force  $F$  and effective length  $L$  of the float (as shown in Fig. 1) lead to the film surface pressure  $\pi^S$  according to (2). Strictly speaking, the measured  $\Delta\gamma$  value in (1) or (2) equals the difference between the interfacial tension on each side and contiguous to the float. When the area  $A$  is varied by a stepwise movement of the barrier, the surface pressure relaxation may be monitored for each step as a function of time and the thermodynamic stable equilibrium value of  $\pi^S$  may be obtained. It is the same at the float and at the barrier and corresponds to static or mechanical equilibrium conditions of the film and the substrate.

In contrast, under dynamic conditions  $A$  is varied continuously. A surface pressure difference  $\Delta\pi^S$  may occur, between barrier and float, coupled to substrate movement. Then a state of non-equilibrium may occur such that the pressure measured by the float does not represent the film surface pressure everywhere. In automatic film balances, the continuous film compression or expansion process may induce such non-equilibrium conditions of the film. Then, for a given value of  $a_i$  different values of  $\pi^S$  may be measured on compressing and on expanding respectively the film area (hysteresis). The difference  $\Delta\pi^S$  decreases when the speed of the barrier decreases. Phase transition may also be involved in such effects.

#### Compression and expansion isotherms

The function relating the surface pressure  $\pi^S$  to the molecular area  $a_i$  for films formed by any of the three spreading techniques mentioned under *Average areas per molecule* above, at a given temperature are named compression or expansion isotherms when  $A$  is decreased or increased respectively.

For well-spread, uncontaminated films, continually in stable equilibrium, the isotherms are independent of the techniques of film formation and of both the concentrations and the spread volumes of spreading solutions. For such films compression and expansion are reversible processes.

Figs. 2a & 2b represent typical compression and expansion isotherms for various films. The isotherms may display plateaus and/or kinks (transitions).

For one-component spread films the plateaus correspond to first order transitions either between two coexisting films or between a film and a coexisting condensed bulk phase.

The sections between the transitions shown in the Figs. 2a and 2b, correspond to the vapour V, liquid L and solid S state of the film in analogy with the bulk phases. This nomenclature is not in use for the isotherms of macromolecular films.

Films and transitions. The S monolayers are characterized by a seemingly linear variation of  $\pi^S$  with  $a_i$  in contrast to the monolayers L or V. The transition  $V \rightleftharpoons L$  is characterized by  $a_i^V$ ,  $a_i^L$ ,  $\pi^{LV}$  which are the partial areas in the coexisting films and the equilibrium

transition surface pressure, respectively. For the  $V \neq S$  transition the corresponding parameters are  $a_i^V$ ,  $a_i^S$ ,  $\pi^{SV}$ . Extrapolation of the linear part of the isotherm  $\pi^S(a_i)$  for an S film to  $\pi^S = 0$  provides the molecular area  $a_{i0}^S$  of the component  $i$  in a corresponding solid, close-packed monolayer. Evidently  $a_{i0}^S > a_{m(i)}$ . It is stressed that the analogous extrapolation for L films is not accurate.

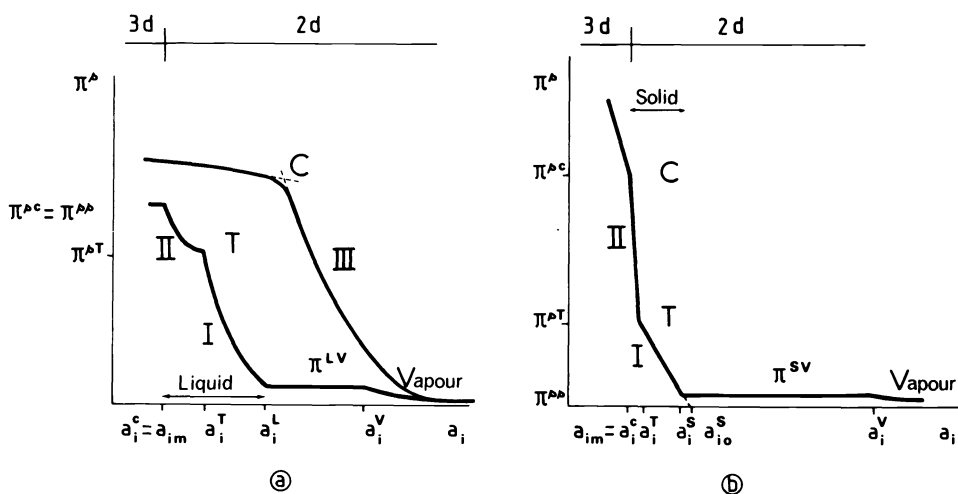


Fig. 2. Pressure-area isotherms for spread films of small molecules.  $\pi^{LV}$ ,  $\pi^{SV}$  1st order transitions ; I, II, III film states ; T = 2nd order transitions ; C collapse. See also list of symbols.

The condensed S or L films may display polymorphism. The various forms are characterized by distinct compressibilities (Fig. 2a I & II, Fig. 2b I & II). Highly or moderately compressible L films are respectively named *expanded* or *condensed*.

The presence or absence (see Fig. 2a), and the location of plateaus or kinks in the isotherms obtained with films depend on both the chemical nature and the structural characteristics of the film material as well as on various experimental conditions (temperature, substrate composition, pH, ionic strength, etc.).

The two plots shown in Fig. 2a and the one in Fig. 2b are typical of films of small molecules under various experimental conditions.

When the values of  $\pi^{LV}$  and  $\pi^{SV}$  are smaller than  $1 \text{ mN m}^{-1}$  microbalances sensitive to within several  $\mu\text{N m}^{-1}$  are used. They provide the isotherms of the monolayers in the vapour state V and the values  $\pi^{LV}$  and  $\pi^{SV}$ .

In general, even these microbalances do not reveal any condensation phenomena in the spread films of macromolecules at low surface pressure.

Uniformity of molecular distribution in films. Often, the uniformity of the molecular distribution in films is taken for granted. However, if uniformity is not ensured, the interpretation of the isotherms and film polymorphism in terms of purely molecular properties becomes obscure, particularly for solid films of small molecules and for macromolecular films.

Both for films comprised of small molecules or macromolecules, complementary studies have sometimes revealed a non-uniform distribution of the molecules at both macroscopic and microscopic levels. Surface potential studies have shown the presence of macroscopic

islands in the range of molecular areas corresponding to the plateaus designated by  $\pi^{LV}$  and  $\pi^{SV}$  in Fig. 2a & Fig. 2b, respectively. Electron microscopy of transferred films has revealed a "microporosity" of solid films in the range of surface pressures  $\pi^{SV}$  to  $\pi^{ST}$  (Fig. 2b).

Although the isotherms of macromolecular films may not display kinks or plateaus, surface potential studies have revealed in some cases macroscopic non-uniform distribution of molecules at low surface pressures.

Coexistence of film and bulk phases. The limit of the spread film state is named the collapse point ( $a_i^C, \pi^{SC}$  in Figs. 2a & 2b). This is the transition between the film and the bulk phase. Below  $a_i^C$  the film is unstable. At the point of collapse, folds, fibers, liquid and gel droplets, or solid particles may coexist with the film at the interface. For collapsed films,  $\pi^{SC}$  may (Fig. 2b) or may not (Fig. 2a, curve II) vary with  $a_i$  when  $a_i < a_i^C$ .

On the other hand, when macroscopic droplets or solid particles of the film forming substance are deposited upon the interface, a coexistent spread film is obtained at a final equilibrium spreading pressure  $\pi^{SS}$  independent of the apparent molecular area. If  $\pi^{SC} = \pi^{SS}$  spreading and collapse are reversible processes. Then the film is in a state which satisfies the criterion of equilibrium stability and the reported results have thermodynamic significance (see also Section *Small molecules* above).

Generally, L and V films satisfy the criterion of stability, viz. the surface pressure of their collapsed films is independent of the molecular area when  $a_i < a_i^C$  (Fig. 2a) and  $\pi^S < \pi^{SS}$  for  $a_i > a_i^C$ .

For some films spread from a solution and then compressed  $\pi^{SC} > \pi^S > \pi^{SS}$ . They are metastable, collapse irreversibly and will not respread. Solid films of low molecular weight substances and soluble or insoluble (in the substrate) spread macromolecules may form such metastable films. For solid films of small, elongated, asymmetric molecules on first compression  $a_i^C = a_m(i)$  defined in Section *Small molecules* above. A value of  $a_m(i)$  cannot be defined in all the cases of macromolecular films (see Section *Macromolecules* above). This value of  $a_m(i)$  depends on the molecular conformation in the spread film. The general conclusion of this section is that, once the film contamination and the accuracy of the results have been assessed, information on the state of equilibrium of the spread films may be obtained from studies of reproducibility of total area  $A$  at given pressures of films spread using different techniques, reproducibility of surface pressure  $\pi^S$  of a film on expansion and compression, equality of the spreading pressure and collapse pressure or  $\pi^{SS} = \pi^{SC}$ .

Equilibrium films need not be uniform at a molecular level. Coexisting gaseous and liquid films are clear examples of film non-uniformity. In such cases, the film balance combined with surface potential studies can provide qualitative information on the macroscopic heterogeneity. Similar heterogeneities may be present close to the kinks shown in the Figs. 2a & 2b. Then direct observation techniques, such as electron microscopy, may provide additional information of film uniformity. Interpretation of average molecular areas in structural terms requires generally that the film be both in equilibrium and uniform.

### SECTION III. MATERIALS AND TEMPERATURE

The description of the film material should include chemical composition, distribution of molecular mass, molecular conformation, degree of hydration, melting or softening



point. Preparation and purification methods must be described. The purity and purification methods of the spreading solvents and of the liquid substrate as well as their composition should be given. The pH might be reported if the liquid substrate is water. Traces of surface active contaminants in the spreading solvents may considerably modify  $\gamma$  (but not  $\gamma_0$ ) and  $\pi^S$ . For acidic surfactants, traces of  $\text{Ca}^{2+}$  act as severe contaminants ; for basic surfactants the same applies to  $\text{CO}_2$ .

A spreading film compresses any surface active impurity that may inadvertently be present in the substrate. This may cause significant errors in the results. If prior to spreading rapid compression of the "clean" surface does not lead to any measurable surface pressure this fact could be taken as a criterion of substrate purity. The mobility of talcum powder, upon blowing air, throughout the surface is another criterion.

The temperature of the film depends on the temperature(s) of the adjacent phases and of any heat or material transfer between them. In the case of an aqueous substrate and an air phase of low humidity, water evaporation may produce a local (lower) temperature, different from that of the bulk phases. On the other hand, if the air is supersaturated with vapour, condensation would lead to an interfacial temperature higher than that of the bulk phases. In the case of two incompletely miscible liquids the evolution towards mutual saturation may again produce a different local interfacial temperature. Therefore, precautions must be taken to ensure thermal equilibrium in the system.

Contamination of the film by the spreading solvent may occur. A dependence of the results  $\pi^S(a_i)$  on the initial spreading area and on the spreading solution volume and concentration is then observed.

For polymeric substances the nature of the spreading solvent determines the molecular conformation inside the spreading solution and may affect the spread film isotherm. Complete knowledge of the composition of the mixed spreading solvent is important. When macromolecules or small molecules soluble in the substrate are spread, dissolution of film material into the adjacent phases must be prevented during the spreading period.

#### SECTION IV. APPARATUS AND PROCEDURES

The description of the apparatus should include :

a) the trough and film frame, if any (material, pretreatment, construction and size). Due to the meniscus, film areas smaller than about  $10 \text{ cm}^2$  involve inaccuracies which may be estimated from surface tension and meniscus shape. A comment on minimizing vibration, a brief description of the enclosure for minimizing contamination through the gas phase, temperature variation and the effects of draught are required.

b) Barrier and float (material, pretreatment and dimensions) including the shape and material of the float, shape and material of the thread and ribbon loops which prevent film leakage. A comment might be included that describes the connection of the thread and ribbon loops to the float and to the trough walls.

c) The equipment and devices for spreading the film and measuring the horizontal force  $F$  (Eq. 1).

d) The film barostat device used for kinetic experiments at constant pressure.

The description of experimental procedures should include :

a) The cleaning of the apparatus and of the substrate surface, technique of depositing the spreading solution, time allowed for solvent evaporation or dissolution in the substrate, film compressing technique and relative rate of film compression.

- b) The method used to test for leakage and for stability or equilibrium of the films.
- c) The operations between film spreading and the starting time of the measurements.
- d) The method of checking film contamination by the spreading solvent.
- Extrapolation methods, if any, to obtain the film spreading pressure at time  $t_0$  of monolayer deposition should be described and justified if possible.

## SECTION V. RESULTS AND ACCURACY

### Insoluble, one-component films

The accuracy of measuring the spread volumes, concentration of the spreading solution, float length, force and surface pressure should be reported.

The plots  $\pi^S$  vs.  $a_i$  should be shown with error bars when a stepwise compressing technique is used. With an automatic compressing technique, a full compression - expansion cycle should be reported. It is recommended that tables of  $a_i$  and  $\pi^S$  values be included in the paper unless numerical analysis is used to fit the experimental points in which case the sensitivity of the fit to the values assigned to the parameters should be assessed. The various values of  $\pi^S$  and  $a_i$  characterizing the film transitions are important parameters and should be reported.

### Units

Areas  $A$  are expressed in sq.meters ( $m^2$ ) and forces in newtons (N). Surface tension and surface pressure are expressed in  $N m^{-1}$  or  $J m^{-2}$ ; molar areas in  $m^2 mol^{-1}$  and molecular areas in  $nm^2 molecule^{-1}$ . The recommended units of molar or molecular surface concentrations are  $mol m^{-2}$  and  $molecule nm^{-2}$  respectively. For polydisperse polymeric substances the units are:  $m^2 (mol \text{ of monomer})^{-1}$  or  $nm^2 monomer^{-1}$ . For substances of ill-defined composition, areas may be expressed as specific areas in  $m^2 mg^{-1}$  and the surface concentration in  $mg m^{-2}$ .

The former unit of surface pressure  $dyn cm^{-1}$  is equivalent to  $mN m^{-1}$ . The former unit of molecular area  $\text{\AA}^2 (molecule)^{-1}$  is 100 times smaller than one  $nm^2 (molecule)^{-1}$ .

## SECTION VI. APPLICATIONS

### Mixed films

Spread mixed films are obtained by spreading a solution of two or more film-forming substances in a volatile solvent. When none of the substances dissolves significantly into the substrate the mixed film may be compressed and dealt with experimentally in the same way as a one-component film. If  $i$  is one component of the mixed film and  $x_i^S$  its mole fraction in the film, the average area per molecule  $a$  of the spread mixture is equal to  $a = \sum_i x_i^S \bar{a}_i$ , where  $\bar{a}_i = (\partial A / \partial n_i^S)_{\pi, S}$  is the partial area per molecule of constituent  $i$  in the mixed film at a given surface pressure and temperature. Even more than for one-component films, it should be emphasized that the uniformity of the distribution of constituents on a molecular scale cannot be assessed unambiguously by trough experiments only.

### Built-up films

Film balances with pressure control devices can be used to transfer insoluble spread films onto solid vertical plates (Langmuir-Blodgett films).

Relevant additional information to be provided includes :

- description of the set-up for building-up the films ;
- nature and size of the solid plate ;
- pretreatment of the solid plate (cleaning and polishing) ;
- speed of vertical movement of the plate ;
- the number of layers deposited ;
- molecular area ratios in the film built-up on the solid and in that spread on the liquid surface ;
- orientation of the polar part of the molecules in the first and in the last deposited layers.

#### Kinetics of processes in films

Chemical reactions such as hydrolysis, isomerization, oxidation and photochemical processes can occur in either soluble or insoluble films. In addition, dissolution occurs in soluble films.

Studies of these processes are often carried out at a controlled film pressure. Some controlling device automatically drives the compressing barrier while  $A$  is recorded as a function of time  $t$ . Since  $\pi^S$  is constant the rate of the process per unit film area is expressed as the relative film area change  $|k| = |\partial \ln A / \partial t|_{\pi^S}$  and varies with the surface pressure, temperature and substrate properties. The accuracy of surface pressure measurement and of its control should be reported.

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#### APPENDIX. CHECK-LIST

The following check-list is recommended to assist authors in the presentation of pressure-area data obtained with film balances. It is suggested that the following items be checked and the relevant experimental conditions and results be described and/or reported :

- a) the trough, barrier, float, flexible ribbon or thread loops ;
- b) surface pressure measuring device ;
- c) surface temperature measuring device ; also other temperature conditions ;
- d) origin, purity (or purification) of the substances forming the film, the spreading solvent, the liquid substrate ;
- e) the composition of the liquid substrate and its pH (for aqueous substrates) ;
- f) cleaning procedures for : the apparatus, the water surface (before spreading) ;
- g) contamination of the clean surface (by the spreading solvent too) ;
- h) film leakage (at barrier and loop ends) ;
- i) film contamination by the spreading solvent ;
- j) film solubility ;
- k) film hysteresis (expansion - compression) ;
- l) equality of film collapse and spreading pressures ;

- m) presentation of the data : accuracy, reproducibility, units ;  
 n) assessment of  $a_i$  values for macromolecules.

## LIST OF SYMBOLS

- S = solid-like film ;  
 L = liquid-like film ;  
 V = vapour-like film ;  
 SV = coexisting solid-like and vapour-like films (plateau in pressure-area plot) ;  
 LV = coexisting liquid-like and vapour-like films (plateau in pressure-area plot) ;  
 T = transition in S or in L films (kink in pressure-area plot) ;  
 C = collapse point ;  
 $n_i^S$  = amount of component i in the interfacial layer (Ref. 1) ;  
 A = area of films in the present context (see also Ref. 1) ;  
 $a_i$  = average area per molecule of substance i in pure films of i ;  
 $\bar{a}$  = average area per molecule in mixed films ;  
 $\bar{a}_i$  = partial area per molecule of substance i in mixed films ;  
 $a_i^S, a_i^L, a_i^V$  = values of  $a_i$  in coexisting SV and LV films ;  
 $a_i^T$  = value of  $a_i$  at the kink point T ;  
 $a_{i0}^S$  = average area per molecule of substance i in S films at  $\pi^S = 0$  (extrapolated value) ;  
 $a_i^C$  = value of  $a_i$  at the collapse point ;  
 $a_m(i)$  = area per molecule in complete monolayer of substance i (Ref. 1) ;  
 $x_i^S$  = mol fraction of i in the film ;  
 $l$  = length of the float (Fig. 1) ;  
 $F$  = force on the float (Fig. 1) ;  
 $\gamma_0$  = interfacial tension of clean interface ;  
 $\gamma$  = interfacial tension of the film-occupied interface ;  
 $\Gamma_i$  = surface (excess) concentration (Ref. 1) ;  
 $\pi^S$  = film or surface pressure (Ref. 1) ;  
 $\pi^{SC}, \pi^{SS}$  = collapse and equilibrium spreading pressures ;  
 $\pi^{ST}, \pi^{SV}, \pi^{LV}$  = equilibrium film pressure for the transitions T, SV and LV ;  
 $t$  = time (in the present context ; see also Ref. 1) ;  
 $k = (1/A)(dA/dt)_{\pi^S}$  = relative rate of a process studied at constant pressure.  
 $N_i^S$  = number of molecules i in the interfacial layer