Molecular Engineering of Ultrathin Polymeric Films

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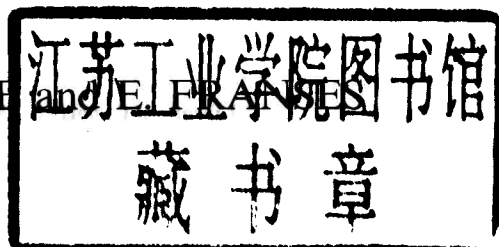
MOLECULAR ENGINEERING OF ULTRATHIN POLYMERIC FILMS

Proceedings of a Workshop on the Molecular Engineering of Ultrathin Polymeric Films, Davis, California, USA, February 18–20, 1987

EDITORS: P. STROEVE and E. FRANSES

ELSEVIER APPLIED SCIENCE
LONDON and NEW YORK

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Preface

The National Science Foundation sponsored a workshop on "The Molecular Engineering of Ultrathin Polymeric Films", at the University of California, Davis, February 18–20, 1987. The workshop was organized by Professor Pieter Stroeve from the University of California, Davis and Professor Elias I. Franses of Purdue University. Financial support for the workshop was provided by the Thermodynamics and Transport Phenomena Program of the Chemical and Process Engineering Division of the National Science Foundation.

The purpose of the workshop was to assess the state of the art and research needs in the molecular engineering of ultrathin organic monomeric and polymeric films. Unconventional materials such as polymers combined with optically active, magnetic, catalytic, or other organic materials may find a variety of new applications in microelectronics, electro-optical devices, laser technology, optical storage, magnetics, catalysis, biotechnology, and membrane separations. The construction of thin films of solid macromolecular structures consisting of multilayers of molecules of precise order and composition is now feasible. Fabrication techniques include adsorption, self-assembly, Langmuir–Blodgett deposition, spin coating and poling, and epitaxial polymerization. Depending on the molecules used and the fabrication techniques employed, unusual physical properties can be imparted to the macromolecular structure. In many applications organic materials for ultrathin films may have superior characteristics compared with inorganic materials. For example, organic materials have a higher damage threshold to laser irradiation than inorganic materials. Organic solids reveal optical effects many times stronger than those in inorganic solids. Organic materials in the form of polymers offer superior mechanical properties and improved stability compared with low molecular weight materials. The virtually limitless variety of organic molecules will allow for the design of molecules for specific properties and applications.

Twenty four leading scientists and engineers in ultrathin organic film research presented their assessment of the state of the art and research needs in their areas of expertise. These areas included Langmuir monolayers, interfacial properties of thin films, chemistry of polymer molecules, Langmuir–Blodgett films, the characterization of structure and order in monolayers and multilayers, biological structures, biosensors, fabrication techniques, electronically conducting polymers, physical

properties, asymmetric membranes, non-linear optics, and integrated optical structures and devices. Eight of the speakers were from outside the United States, which attests to the international character of ultrathin organic and polymeric film research and of the Workshop. In addition to the speakers, forty researchers (including nine graduate students) attended the workshop.

The majority of the papers presented are included in this volume of *Thin Solid Films*. The presented papers have been carefully revised and edited by Professors Stroeve, Franses and Zemel to avoid excessive overlap and to ensure high quality. The papers include state-of-the-art reviews, some original results, and expert assessments of current trends and future research needs. A summary of the state of the art and research needs as identified by the authors and in discussions in the meeting is given in the last paper of this volume. Although some focus was directed toward Langmuir–Blodgett films, there was considerable breadth in the various fabrication techniques discussed, which includes those listed earlier. Langmuir–Blodgett film research has of course been of considerable interest. *Thin Solid Films* has published the First and Second International Conferences on Langmuir–Blodgett Films. The third conference will take place in Göttingen, West Germany, during July, 1987. However, the more general area of molecular monolayers and ultrathin films of organic materials is of intensifying interest with a recent Gordon Research Conference on Organic Thin Films at Santa Barbara, CA, in 1986, and a Department of Energy Panel Report on the subject in November, 1986. *Thin Solid Films* has taken a leadership role in publishing research in ultrathin films of organic materials. The organizers wish to thank the National Science Foundation and the Program Director Dr. Robert Wellek for the financial support, the speakers for their contributions, all the participants for creating very lively discussions, and the staff of the Faculty club and the Department of Chemical Engineering at the University of California, Davis for their work in organizing the Workshop and helping it run smoothly.

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PIETER STROEVE
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Davis, CA
April 1987

EXPERIMENTAL CRITERIA FOR MONOLAYER STUDIES IN RELATION TO THE FORMATION OF LANGMUIR–BLODGETT MULTILAYERS*

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Langmuir–Blodgett (LB) multilayers are formed by the dynamic transfer of molecules to a solid support from a preformed monolayer, usually at the air–water interface. Control of this process depends in part on knowing the properties of the air–water monolayer. These properties are discussed in terms of the variables defining equilibrium reference states and of the several rate processes which govern the transport and transfer of the monolayer substance to the solid support. The need for agreed reference states and new rheological studies to support further advances in LB technology is evident.

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1. INTRODUCTION

The present interest in Langmuir–Blodgett (LB) systems has several sources, notably their use as analog structures for biophysical studies and their potential for the fabrication of a variety of electrical, optical and data storage devices. For the most part the LB structures are produced by some variant of a "dipping" technique in which a solid or gelatinous pick-up material is passed cyclically through an air–water interface at which a monolayer of lipid, protein or other suitable substances singly or in mixtures has been formed. In all but qualitative studies, which are altogether too common in the literature, critical examination of the physical chemistry of the monolayer of origin is of paramount importance. The factors involved are firstly those that define equilibrium: overall composition, number of phases, tension (surface pressure), temperature and, for mixed monolayers, the state of the mixture (*e.g.* whether the components are actually mixed in mutual solution or form micelles, separate gross phases etc.). Study of equilibrium states provides the necessary reference points for checking calibrations, techniques and chemical purity. Without such reference points, in surface science as in three dimensions, experimental comparisons between investigators are insecure. Secondly, description of the relaxation processes in monolayers undergoing displacements from equilibrium is required as relevant to the transfer to a moving support. These relaxation processes will describe the time variations in pressure and density over the whole monolayer

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* Paper presented at a Workshop on the Molecular Engineering of Ultrathin Polymeric Films, Davis, CA, U.S.A., February 18–20, 1987.

during compression, expansion and transfer. Additional dynamic descriptors will apply to the transferred monolayers and multilayers, but little appears to be known of these processes. Perhaps the most difficult of the dynamic sequences to describe are those at the actual transfer line, especially where the contact angle undergoes sharp changes when the movement of the support is reversed.

2. EQUILIBRIUM REFERENCE STATES IN MONOLAYERS

The basic representation of monolayer behaviour is the pressure–area isotherm at a given temperature. In numerous studies the measured isotherms do not represent equilibrium states because of solution or evaporation of the monolayer substance, variations in concentration of retained spreading solvent or other impurities, and processes such as slow and irreproducible changes of phase. For some substances, equilibrium isotherms (not dependent on monolayer history and the specifics of technique and time) will be impractical to achieve under the conditions of interest, but for others reproducible equilibrium parameters should be accessible. Thermodynamic reference states have the same importance in surface science as for three-dimensional systems. It is all the more remarkable therefore that 60 or so years after the basic work in the period from Langmuir to Adam, there are no generally agreed values for thermodynamic fixed points for monolayers. Recent proposals have been made for three sets of fixed points. These are the surface pressures for equilibrium spreading[1], for the transitions from so-called liquid-expanded to liquid-condensed phases[2,3] and for the liquid–vapour phase transitions[2,4] in monolayers of fatty acids at designated temperatures. It is to be hoped that these proposals and the experiments on which they are based will be thoroughly criticized and that agreed thermodynamic standards will emerge. It is plainly unacceptable for the future of the subject that researchers continue to disagree on essentially unambiguous quantities such as phase transition pressures. In the future, experimentalists should be able to check their techniques of manometry, purity, spreading, compression etc. by reference to these standards.

Of the three phase transitions mentioned above, equilibrium spreading is perhaps of most interest to LB practitioners since the monolayer density is usually high during transfer (although the possibility of substantial density fluctuations at the liquid-expanded–liquid-condensed transition may be important in some practical cases). In addition to the obvious benefit of checks on technique, measurement of the equilibrium spreading pressure is valuable for the reason that some monolayers may prove to be intrinsically metastable. It has been shown that monolayers spread from a solvent can give reproducible isotherms at surface pressures well above their equilibrium spreading pressures[5]. Transfer to multilayers from these monolayers is thus somewhat akin to nucleation from supercooled or supersaturated states in three dimensions.

It seems worth remarking that monolayer measurements involve control of temperature. It is surprising that some published papers do not even refer to the temperature. In this regard, even when the temperature is stated it will not usually be the temperature at the monolayer for the simple reason that control over the relative humidity is rarely made. Water cools by evaporation, which is itself modified by the

monolayer. All these matters are simple, but apparently too tedious for many investigators. Until editors of significant journals decline papers in which these variables are not controlled, the flow of incomplete poor papers will continue. It is a cheering thought that industrial pressures will eventually oblige adoption of the appropriate standards once LB devices become objects for production.

3. CHEMICAL COMPOSITION

An obvious thing we need to know about a monolayer is what molecules it contains, leading on at once to the inevitable debate about impurities, which hard-line surface chemists always seem to enjoy. For LB systems, however, the issue of purity takes on a new significance, which can be illustrated by reference to solid state electronics. The progress of solid state practice and theory depended greatly on studying and eliminating a variety of impurities and controlling the addition of dopants at exceedingly low concentration levels. The technology for obtaining reproducible base substances was developed from necessity and is both complex and expensive. If LB systems are to become widely useful in similar contexts, it is idle to imagine that purity and controlled doping will not be of major significance. It is all the more regrettable that the bulk of the data now being generated is on systems where impurities are quite definitely present at significant levels and that the available techniques for assessing and controlling these impurities are being widely ignored. What is presently required is both the use of these known methods (see, for example, refs. 2 and 6–9) and research into better and (preferably) more user-friendly techniques for observing impurities.

Papers in this field frequently omit impurity-related measurements. The surface tension of the water used is usually not mentioned, and hardly anyone works at a sensitivity better than 0.1 mN m^{-1}, thus making simple tests of pressure changes on compression or expansion of a "clean" surface altogether too crude. Even when good water has probably been prepared, it is often promptly spoiled by dissolving commercial "pure" salts which are usually surface-chemically unacceptable. Solvent retention from spreading is not often discussed, let alone checked. In fact, control of the purity of monolayer substances and solvents is often relatively straightforward, using repeated careful crystallization, for example[2,3], and Dr. Mingins[10] will speak with special skill at this conference on spreading, solvent retention and other important issues.

Supply of pure water continues to be a problem, particularly if large volumes are required for development studies and industrial processes. Some laboratories interested in electronic applications of LB films have adopted "clean-room" methods borrowed from the solid state industry, including the use of ultrafiltration and ion exchange techniques to purify water. These are inadequate. Ion exchange resins elute a variety of molecules of low and high molecular weight. Bacteria and other life forms readily appear in the filters and lines, requiring intermittent chemical sterilization and subsequent extensive flushing. What is needed is for some entrepreneur to develop a suitably large-scale distillation system—perhaps fed by an ultrafiltration supply. The system should use oxidation to destroy surface-active impurities. If the oxidant is in the boiler, the device should work on a batch basis in

which the first fraction of each batch is rejected to remove steam-volatile residues. If the oxidation is in the vapour phase, *e.g.* by passage of the steam over an incandescent catalyst, the system could be continuous. In either event, condensation in glass or silica vessels will sometimes be undesirable. These substances dissolve in water, typically giving colloidal dispersions, which can be transferred as particles in a dipping process. If gold-plated condensers and storage vessels sound extravagant, they will be cheap by comparison with the waste resulting from poorly executed experiments.

One last topic will conclude these comments on equilibrium states, namely the situation in mixed monolayers—mixed by deliberate inclusion of two or more supposedly pure compounds in a monolayer on a pure aqueous substrate. Of course, the commonly present adventitious additives are subject to the same rules as deliberate additives, and can readily interfere with the behaviour and corresponding interpretation of supposedly pure mixed systems. LB practitioners, among others, have studied mixed monolayers, and some artistic and imaginative drawings in published papers imply that the molecules are actually well mixed. It is only necessary to refer to the work of Tajima and Gershfeld[11] on cholesterol-phospholipid "mixtures" to realize that mixing in monolayers cannot be taken for granted. Even at an oil–water interface, separation of two homologous phospholipids differing by only two carbon atoms per chain has been demonstrated[12]. The methods to check for mixing include surface potential fluctuation (for gross separation), careful pressure–composition–surface-density experiments and application of the Phase Rule and, in some useful instances, direct optical observation. Direct observation by fluorescence microscopy has recently shown most interesting substructure[13] in monolayers at the micron level. In some instances it has been claimed that these structures represent the actual aggregation in the region of monolayer phase transitions. This is almost certainly incorrect since it has been demonstrated that in pure monolayers, such as those of pentadecanoic acid or phospholipids, the phase transitions are simply first order, implying macroscopic regions of dense and dilute phases. This is confirmed by gross surface potential fluctuations[2,3,14]. The recently demonstrated microscopic structures are the result either of the presence of impurities in the water or monolayer substance and/or of the addition of the fluorescent probe molecule, in each case with the attendant increase in variance required by the Phase Rule. Personal enquiry has revealed that the probes themselves are in some instances not single components. The structures observed optically suggest that two-dimensional emulsions and micelles are being formed, and further study will probably lead on to defining the linear adsorption at the edges of these two-dimensional structures. Whether from impurities or from deliberate addition of extra components, the discovery of micron-level monolayer substructures (particularly at phase transitions) is an imporant new opening in surface chemistry—perhaps one should say linear chemistry. The relevance to LB multilayers is obvious.

4. DYNAMIC AND RELAXATION PROCESSES

The time-dependent behaviour of monolayers arising from the presence of

pressure and density gradients is part of the subject of surface rheology. Good studies on monolayer rheology are rare, and reference should be made particularly to the work of Lucassen[15] to understand the issues and opportunities. The situation can be illustrated by looking at a typical experiment in which a solid plate is raised and lowered through a monolayer spread on a rectangular trough, such that the monolayer is transferred whilst a sensor–feedback system maintains a constant reading at the sensor by controlling the overall area available to the monolayer. This is called a "constant pressure" transfer, but it is doubtful whether transfer is ever achieved at a genuine constant pressure, particularly for close-packed monolayers. The actual situation is one of complicated concentration and pressure gradients. The reasons relate to the several surface viscosities which define the flow of the monolayer molecules under the force gradients in a non-equilibrium monolayer[16]. Sliding a barrier along a rectangular trough compresses a monolayer unequally in the directions normal or tangential to the barrier, and relaxation to homogeneous conditions involves both the ordinary shear viscosity and the dilatational viscosity. Removal of a monolayer at a small flat plate in a large trough generates complex pressure and composition gradients, and if standing states are ever achieved their parameters will depend on the geometry of the plate and trough, the rates of transfer and the response time of the sensor–compression mechanism. The monolayer parameters at the compressing barrier and dipping plate will be different, and if the sensor is at yet another spot its readings will correspond to a third set of conditions. Furthermore, given that the dilatational viscosity also reflects the transfer of monolayer components to the adjacent bulk phase, partially soluble impurities or added components can be particularly important.

Many of these effects can be illustrated by reference to simple observations during the measurement of a pressure–area isotherm. Many modern surface balances are automated and can be set to read constant surface pressure whilst compressing or expanding the film continuously. Particularly with dense monolayers, the compression and expansion branches give wide pressure discrepancies corresponding to so-called monolayer hysteresis. This "hysteresis" reflects in part the time lags across and within the monolayer between compression at a barrier and arrival of the related force at the sensor. This is readily made obvious by switching to discontinuous stepwise compression, when a slow approach to steady pressure from either direction can usually be observed. If the monolayer is near the spreading pressure, it is common for collapse or crystallization to occur near the barrier. If the surface pressure is being measured by a Wilhelmy plate, it is common to see the plate displaced because of density and pressure gradients resulting from movement of a remote barrier. If the monolayer is close to a phase transition, surface potentials can show very large differences in density in various regions of a monolayer between the moving barrier and a dipping plate.

If we recall the large time-dependent hysteresis which often shows up in the compression and expansion branches of a monolayer isotherm, the situations at the dipping plate and at the compressing barrier during most of the transfer correspond roughly to the expansion and compression branches respectively. At the end of a sweep of the dipping plate, the change in shape of the meniscus (corresponding to the switch of contact angles) can give a local compression effect as the motion is

reversed, shifting the situation more toward the compression branch of the isotherm whilst simultaneously "pulsing" the local monolayer fluxes to the plate. Deposition ratios are rarely quoted, and even more rarely studied, as a function of dipping speed, device geometry etc. An overall deposition ratio (even an ideal value of 1.0) can conceal subvariations in the rise and fall phases and at the ends of the strokes.

Neither the experiments nor the theory for these effects are easy, and the experimentalists are particularly rare birds. Clearly the density, composition and pressure at the transfer plate can be quite different from the corresponding variables at the sensor or at the compressing barrier. Until more good work is done, present transfer studies must be regarded as qualitative and essentially uncontrolled. Unfortunately there is little sign that the issue is being addressed seriously for circumstances relevant to LB layers. Hopefully this conference will encourage decent work on this topic—by traditional direct experiments on forces and densities during transfer, and also by the newer scattering methods described by Mann[17]. In all cases, the experiments need to be based on initial equilibrium characterization of the monolayers as described in the previous sections. The next round of advances will be with determined and systematic experimentalists, and surface chemists will be challenged by the critical demands of LB technology.

ACKNOWLEDGMENT

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EXPERIMENTAL CONSIDERATIONS IN INSOLUBLE SPREAD MONOLAYERS*

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When lipid multilayers are prepared by the Langmuir–Blodgett method their quality depends on the deposition process and the condition of an insoluble monolayer spread at the air–water interface. It is shown how trace impurities can drastically alter the properties of this monolayer. Several sources of impurities are identified and methods of reducing their level are reviewed. Attention is focused on water purification and the preparation of surface chemically pure, virtually ion-free water is described. Methods for the elimination of particles and at the same time maintaining this standard do not seem to be established. A major error in surface pressure *vs.* area isotherms arises from monolayer losses on spreading which can be substantial and the checks described for quantitative spreading are advocated. The two main methods of measuring surface pressure are assessed and possible sources of error are explored.

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1. INTRODUCTION

The fabrication of multilayers by the Langmuir–Blodgett method entails the passage of a solid substrate through an insoluble monolayer resident at an air–water interface. In this paper we shall discuss only the status of the monolayer and not the events at the solid substrate surface and their consequences for multilayer structure. The formation of the multilayer and its structure and/or quality are intimately related to the conditions within the monolayer. Both the preparation and the manipulation of a monolayer at a working interface are seemingly straightforward operations, which have been developed over many decades. Attendant on such development within the monolayer field, there have been many messages published regarding the care necessary to obtain consistent, if not *bona fide*, results, so that matters are not so straightforward. To secure partly a firm basis for multilayer studies it would therefore seem that some benefit would accrue from the "monolayer experience". Unfortunately, as an inspection of two collections of papers on

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*Paper presented at a Workshop on the Molecular Engineering of Ultrathin Polymeric Films, Davis, CA, U.S.A., February 18–20, 1987.

multilayers in issues of *Thin Solid Films*[1] all too readily reveals, little attention has been paid to caveats in the alternative work. For example, issues such as thermal equilibrium, monolayer phase behaviour, quantitative spreading, lipid purity and the surface chemical quality of the aqueous phase have generally received short shrift. In what follows we identify these and other problems associated with monolayer preparation and/or monitoring and we hope thereby to encourage a greater awareness of the needs to maintain surface chemical purity and to devise satisfactory protocols for reproducible monolayer preparation and the valid measurement of surface pressure π *vs.* area A isotherms. Various recommendations are made below to help in these regards.

2. EXPERIMENTAL DETAILS

2.1. The preparation of bulk phases

Apart from those possibly added with the monolayer system, impurities that accumulate at the air–water interface must arrive there either through adsorption from the air or aqueous bulk phases or through spreading from contacting solid surfaces. In addition to cleaning up the two bulk phases then, it is necessary to institute rigorous cleaning routines for everything coming into contact with the aqueous phase just prior to and during measurements on the monolayer.

2.1.1. Air

A dust-free environment is a prime requirement for monolayer and multilayer studies and this is readily achieved by air filtration through micropore filters into a laboratory maintaining a positive pressure, sealing dusty and/or scaling surfaces and instituting a rigorous cleaning routine within the laboratory. A bed of active charcoal on line in the filtration system may be necessary in some environments to remove solvent vapours etc. The use of open solvent systems, the handling of surface-active powders and the siting of equipment such as oil pumps, which produce oil aerosols, should not be done within the laboratory. Isolated laminar flow cabinets are an effective alternative at much lower costs. Temperature and humidity control within the whole laboratory helps with control of the environment local to the monolayer or multilayer.

2.1.2. Water

The description pure water has many connotations which devolve on the end use of the water. For our purposes pure denotes water where the levels of particles, ions or surface-active materials do not significantly affect the surface properties of our monolayer or multilayer systems. Unfortunately the requirement is generally for very low levels indeed and many recipes for purification fail to reach the stringent standards required. It really goes without saying that the preparation of pure water should be undertaken in a clean environment and that the storage and transport to the site of measurement should not effect any deterioration in the quality.

The traditional method of purification has been distillation usually with one oxidative stage, typically using alkaline permanganate. On occasion this can be inadequate as shown by Fig. 1. Here curve 2 shows the π–A isotherm for stearic acid spread on surface chemically pure water at pH 2 and this contrasts markedly with the grossly expanded isotherm of curve 1 for the same molecule under the same

conditions of temperature and pH but with water of inferior quality. This is despite the fact the latter water was distilled three times, once from alkaline permanganate. The usual practice of taking a middle cut from a batch distillation in this instance served to concentrate this particular component so that repeated distillation made matters worse. Depending on the water supply, a steam-volatile component (or components) can thus be present which alkali permanganate fails to degrade. This is not a unique occurrence. We have found similar behaviour in another laboratory with a completely different water supply. Removal of the component(s) in both instances was effected by passing water distilled from copper through a mixed bed ion exchange resin prior to the distillation from alkaline permanganate. Breakdown products from the resins affect markedly the surface properties of water[2,3], but fortunately they are susceptible to alkaline permanganate and provided distillation takes place up an efficient column a high quality distillate can be obtained in Pyrex vessels. For more critical work on monolayers another distillation from Pyrex on the day of use is advocated. Provided carbon dioxide is excluded, water of high resistivity is received from either distillation with trace amounts of the common cations as judged by atomic absorption spectroscopy[4] (typically 40 ppb Na, 13 ppb Ca, 35 ppb Mn, and 30 ppb Cu) save for silicon (about 1 ppm). The latter arises from silica particles in the water of the order of 500 Å in diameter (as judged by light scattering) which derive from dissolution of Pyrex glass particularly under the action of steam. The presence of such particles may pose problems for the use of such water in multilayer studies. The use of stainless steel or tin, say, would eliminate this problem and ostensibly introduces no further trace ions. The water from the Pyrex system provides no stability to bubbles when shaken, has a high surface tension (73.0 ± 0.1 mN m^{-1} at 20 ± 0.1 °C) and shows no detectable aging over 20 min (sensitivity better than 0.02 mN m^{-1}) after which time a tenfold compression of the surface generates no detectable change in surface pressure. A sample of permanganate-distilled water left overnight in a clean-air laboratory aged 0.15 mN m^{-1}, and
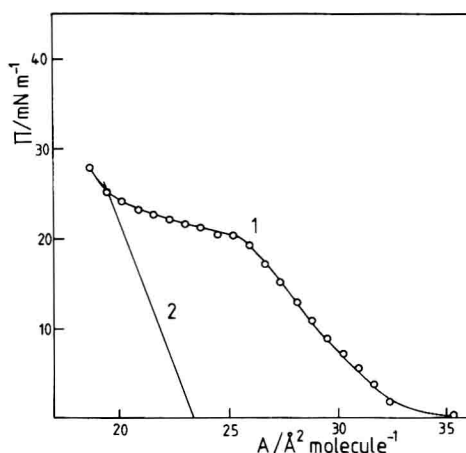

Fig. 1. Surface pressure $vs.$ area per molecule for stearic acid at pH 2: curve 1, expanded isotherm on water containing trace contaminants; curve 2, condensed isotherm obtained on surface chemically pure water.