CROATICA CHEMICA ACTA CCACAA **59** (2) 397—406 (1986)

YU ISSN 0011-1643
CCA-1651 UDC 543.542
Original Scientific Paper

A Technique for Simultaneous Measurements of Dynamic Surface Tension and Surface Potential of Films at the Water/Air Interface

Djurdjica Dragčević, Momir Milunović, and Velimir Pravdić*

Laboratory of Electrochemistry and Surface Phenomena, »Rudjer Bošković« Institute, Zagreb, Croatia, Yugoslavia

Received February 25, 1985

An apparatus is described for simultaneous measurement of the surface tension and surface potential of films at the liquid/air interface in dynamic, steady states. Films are spread in a Langmuir type trough and perturbed by linear cyclic sweeping at predetermined rates and compression ratios in a wide range. Information is obtained on elasticity, electrification, direction and extent of energy transfer, and on the relaxation behavior.

INTRODUCTION

Surface films of insoluble, or slightly soluble, surfactants at the water/air interface have long attracted attention of researchers for a number of reasons. Such films are the essence of detergency,[1] they enable flotation of particles, ions, molecules, and bacteria.[2-4] Films are ever-present at the surface of natural waters, lakes, rivers, and the oceans,[5-6] where they affect evaporation and exchange of gases and particulate matter.[7-9] The interest in such films is maintained also by physiologists studying respiratory processes[10,11] in mammals, where the lung alveoli mediate in the exchange of oxygen and carbon dioxide through surfactant films of mucous and lipo-protein membranes.

There have been controversies with respect to the dynamic behavior of such films.[12,13] Essentially, all such films at the natural water/gas interface are in a perturbed state,[14] and their description in a rigorous thermodynamic treatment is difficult. There have been attempts to use the steady state approximation.[15,16] However, hysteresis phenomena, observed in such films, were sometimes dismissed as artifacts.[12,13,17] Therefore, a technique was developed, based on the principle of the Langmuir trough with a Wilhelmy-plate sensor for surface tension measurements in dynamic conditions. Operating in the same trough with the surface tension sensor is a contactless surface potential electrode. The apparatus thus enables simultaneous measurements of the surface tension and the surface potential response of a film perturbed at some predetermined rate and compression/expansion ratio. Similar devices have been described and offered commercially,[18] but at a considerable expense and less flexibility and simplicity of use than the present one.

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* Extracted in part from the Ph. D. Thesis of Dj. D., University of Zagreb, 1983.

APPARATUS AND METHODOLOGY OF MEASUREMENT

Description of the apparatus

The mechanical part of the apparatus for simultaneous measurements of the surface tension and surface potential in dynamic conditions has been constructed and produced in the laboratories of the authors. The electronic instrumentation used is commercially available, and will be described only to illustrate the requirements relating to the sensitivity, precision, and rate of response.

Figure 1 illustrates the apparatus schematically. Essentially, it consists of two PTFE troughs of which one (1) is large and contains the liquid sample upon which the film is spread. In the present case it has been designed in dimensions which allow neglect of wall effects (length : width : depth = 28 : 13.5 : 2 cm). The smaller through (2) (dimensions 4 : 13.5 : 2 cm) serves as the reference compartment for surface potential measurements, and contains the clean liquid surface to which the changes in potential are referred. The surface potential is measured as the difference between two identical gold-plated electrodes (3), both of them referred to common electrical ground by large area reversible electrodes (4) immersed into the liquid. If measurements are made in chloride containing solutions the Ag/AgCl electrodes serve the purpose well. Other anion, or cation reversible electrodes should be used in special conditions in order to prevent uncontrolled fluctuations of the potential reference point. The surface potential electrodes are positioned as close to the surface of the liquid as electrical considerations allow. The air gap between the electrodes and the surface of the liquid is made conductive by placing radioactive ionization probes above it (5). In the present case two identical ^{241}Am alpha-sources, each of 2.5×10^{10} Bq, were used. Measurements at elevated temperatures require the electrodes to be heated in order to prevent vapour condensation on the surface. A coil heater was found to interfere less with the experiment than a warm dry-air blower. Both electrodes and radiation sources can be positioned vertically, by a microswitch activated device and a wormscrew manipulator (6), to predetermined positions. This is an essential requirement in repeated experiments necessitating exchange of liquid samples. The potential difference is measured with an electrometer (7). The electrometer must have an input impedance of at least 10^{13} Ohms and a response time of the order of 1 ms. A Keithley Model 604 with a 6041 differential shunt has been used here (Keithley Instruments Cleveland,

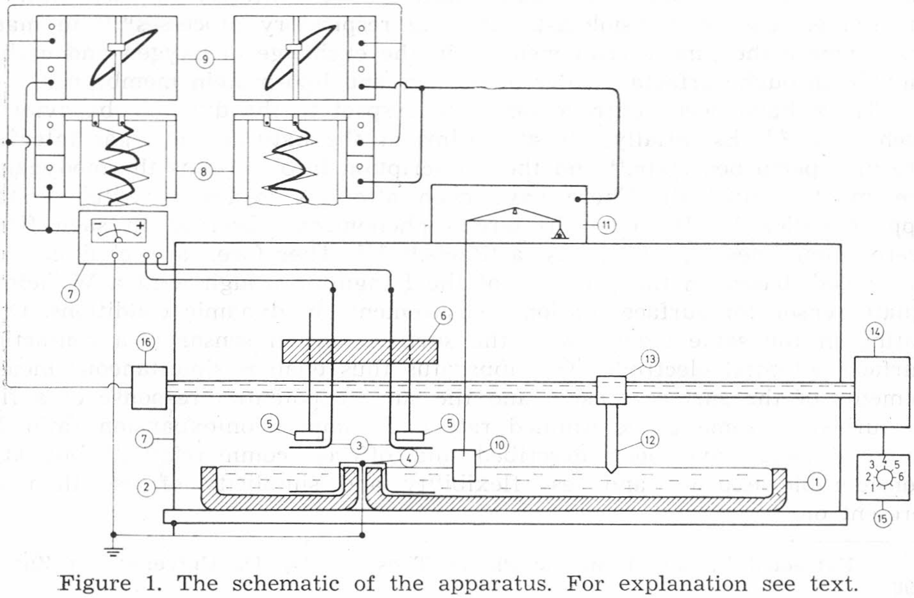

Figure 1. The schematic of the apparatus. For explanation see text.

Ohio, USA). The recording devices of proper precision, shown here, are chart recorders of both x-time (8) and x—y capabilities (9).

The surface tension is measured by the Wilhelmy plate method using a Pt foil sensor (10) attached to an electrobalance (11). A Cahn RG microbalance (Ventron Corp. Palo Alto, Ca., USA) has served well for this purpose. Its output is fed into the recorders. The surface of the liquid is swept by a PTFE sweeper (12), a rigidly held plate immersed approximately 0.1 cm into the liquid, maintaing a tight contact with the longitudinal PTFE walls of the through. In this way the surface is compressed and expanded without overflow or loss of the surface film forming material. The plate is attached to a spindle (13), driven by an D. C. motor (14) controlled by a precise speed controller (15) and direction reversal switch. This combination exerts a triangular perturbation on the surface at a predetermined sweep rate and compression ratio. The mechanical position of the sweeper is translated into an electric signal through a simple potentiometer drive, and fed into the recording devices: it provides the area parameter of the surface film (16). The whole apparatus is enclosed in a metal box (17). It serves both as the Faraday cage for the high impedance electrical measurements and allows the humidity and temperature control needed in experiments on temperature dependent parameters.

Sample preparation and procedures

Chemicals. In the test experiments, described in the next section of the paper, the high degree of cleanliness, usual in surface film studies was maintained. The trough requires cleaning with pure ethanol or trichloromethane, followed by an aqueous nitric acid treatment and careful washing with pure water. The water used was quadruply distilled, the last two stages from an all-silica glass still. Its essential criterion of purity and absence of surface film forming material was the static surface tension,[1,13] and the absence of any detectable hysteresis effects. The limit of sensitivity was typically ± 20 μN/m. A water sample showing no changes of this magnitude, at a compression ratio of 1.46 : 1, was considered satisfactory. The inorganic salt (NaCl) used to prepare solutions was of analytical purity grade. If needed, it was purified by heating and/or recrystallization until the solutions passed the above dynamic tension test.

For calibration purposes only a single component chemical was used. The soluble surface active, film forming agent, sodium dodecylsulfate, SDS, (BDH Laboratories, London) was a specially pure chemical (99.0%). It was recrystallized twice from ethanol, and the product was tested by gas chromatography. Oleic acid (*cis*-9,10-octadecenoic acid) and stearic acid (*n*-octadecanoic) were high purity samples (Kemika, Zagreb) and were used as 3.0×10^{-3} mol/dm^3 solution in 96% v/v ethanol.

Sample preparation. Measured quantities of solution were poured into both troughs. Considering the precisely machined troughs, such a procedure assured a precise levelling of the liquid surfaces. The surface film forming agent was spread by adding measured quantities to the liquid surface in the larger trough, assuring its spread over the entire surface. Experience has shown that films reached an equilibrium state after standing unperturbed for a couple of hours. Sweeping the surface of such stabilized films yielded reproducible surface tension — area and surface potential — area curves after only 5 to 10 sweeps.

RESULTS

Three main categories of information can be obtained in studies of surface films on liquid surfaces using the technique and methodology described here. They are:

1. The typology of films with respect to their elasticity and electrification;
2. the extent and direction of energy transfer in dynamic cycling; and
3. the relaxation behavior.

1. *The typology of surface films.* Figure 2 shows the x-y recording of the surface tension (left) or of the surface potential (right) *vs.* the film area of oleic acid films spread in the trough.

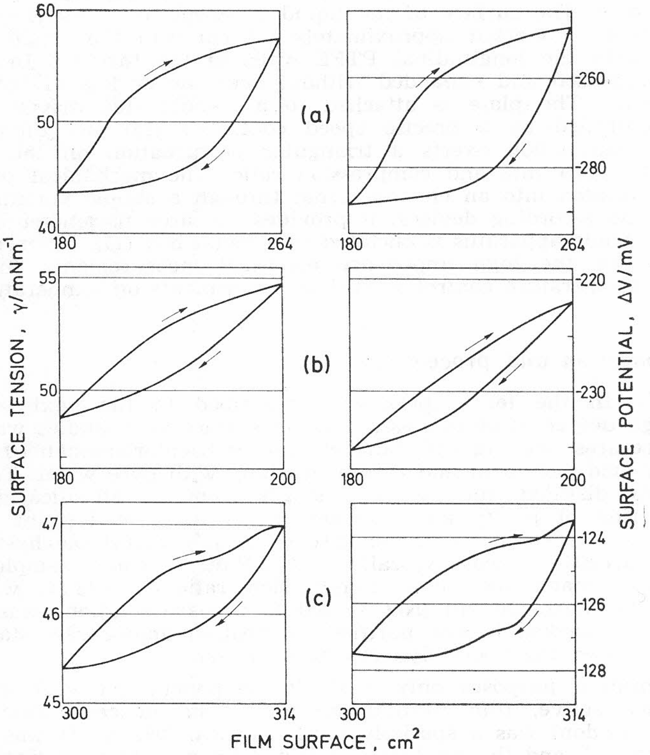

Figure 2. Oleic acid films spread on the 10^{-5} mol/dm^3 NaCl. Surface tension — area curves (left) and surface potential — area curves (right), for three compression ratios. (a): 46%; concn. of oleic acid was between 0.13 (commpressed state) and 0.18 nm^2/molecule (expanded state). (b): 10.5%; concn.: 0.17—0.18 nm^2/molecule. (c): 5.0%; concn.: 0.18—0.19 nm^2/molecule.

Three different compression ratios of 46, 11 and 5% are shown. The obtained hysteresis curves indicate the reality of the hysteresis phenomena. The phenomenon is observed by both measuring techniques, by the Wilhelmy sensor (mechanical contact with the liquid), and by the electrodes (no mechanical contact with the liquid). Figure 2 also shows that the shape and direction of the hysteresis curves are the same, or in the same fashion, for both parameters. For all the other measurements the compression ratio of 46% was chosen. This ratio yields characteristic curve shapes containing information on film elasticity.

Figure 3 shows the results obtained for three different films: (a) for an elastic film of oleic acid, (b) a rigid film of stearic acid, both spread on a 10^{-5} mol/dm^3 NaCl solution, and (c) a soluble surfactant SDS dissolved in the same solution.

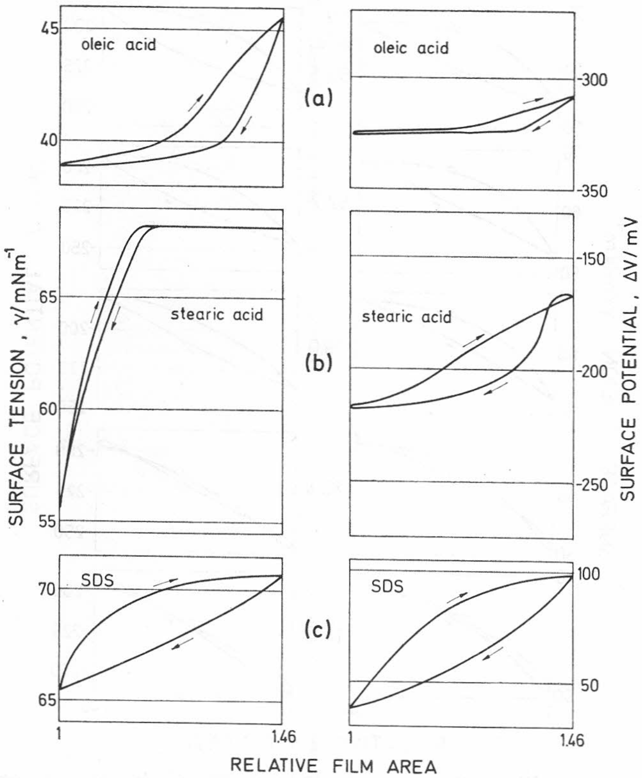

Figure 3. Surface tension (left) and surface potential (right) vs. area curves for three types of film forming agents spread on 10^{-5} mol/dm^3 NaCl: (a): oleic acid, concn. 0.10—0.15 nm^2/molecule; (b): stearic acid, concn. 0.07—0.10 nm^2/molecule; (c): sodium dodecylsulfate concn. 6.0×10^{-5} mol/dm^3.

2. *The extent and direction of energy transfer in dynamic cycling.* Figure 4 illustrates the influence of the perturbation (surface sweep) rates on the shape of the hysteresis curves. The results obtained for the model of the oleic acid film are shown at the compression ratio of 46% and at sweep rates from 65.5 to 14.6 Hz^{-1} (seconds per cycle). The most important phenomenon observed is the reversal of the sense of the hysteresis curves, from clockwise to anticlockwise as the rate of perturbation increases. This is the case for both surface tension and surface potential. It should be remembered that, in analogy with the Carnot cycle engine, this amounts to a change in the direction of heat transfer. A clockwise hysteresis curve indicates that mechanical energy (*e. g.* the work done on the film at the sea surface by wind) is converted into heat and delivered to the liquid sublayer. The anticlockwise curve indicates a film that absorbs energy during the expansion half-cycle. The results shown in this figure indicate that energy transfer is related to both mechanical and electrical parts of the total interfacial energy.

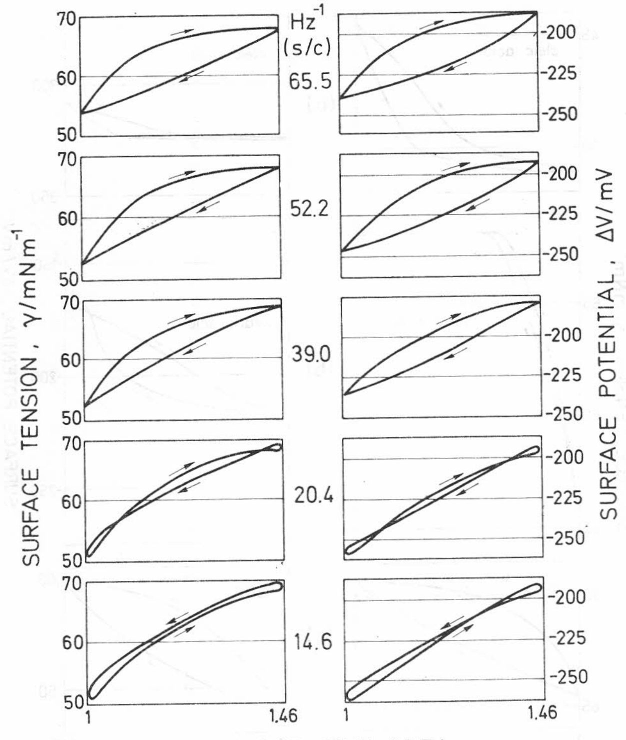

Figure 4. Surface tension (left) and surface potential (right) *vs.* area curves for an oleic acid film (concn. 0.24—0.17 nm^2/molecule), spread on 10^{-5} mol/dm^3 NaCl solution for different sweep rates in Hz^{-1} = s/cycle.

Figure 5 gives the hysteresis (transfer) energy plotted against the sweep rates for various concentrations of the film forming substances. The hysteresis energy, calculated from surface tension, is easily understood in mJ per m^2 of the film surface. Calculation of the electrical energy would require assumptions on the total charge involved and the dielectric constant of the impacted layer. This idea will be pursued in a later paper. An indication is only given that the mechanisms operative are different for the total interfacial energy, and for its electrical part, as exemplified by curves 1 and 2. Curve 1 was obtained for a concentration below monolayer coverage in the compressed state. Curve 2 is for a film that approaches the monolayer state under compression, and curve 3 results from a film which is compressed from below monolayer concentration to above. Values of 0.22 nm^2 per molecule for the equilibrium monolayer were assumed for this purpose. It should be emphasized once again that these films are in a steady state, and not at equilibrium. However, it is the steady state that more likely prevails under sea surface conditions.

3. *The relaxation behavior of surface films.* The apparatus allows measurements of relaxation times during film rearrangement under compression

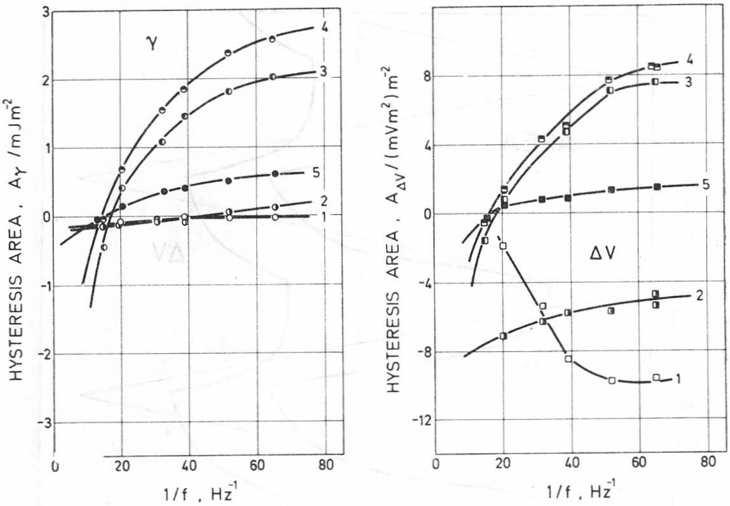

Figure 5. Hysteresis area *vs.* sweep rates, Hz^{-1}, for surface tension (left) and surface potential (right), for five oleic acid films spread on 10^{-5} mol/dm^3 NaCl solution. Concns. in nm^2/molecule at max. expansion and compression: (1): 0.73—0.50; (2): 0.37—0.25; (3): 0.24—0.17; (4): 0.18—0.13; (5): 0.15—0.10.

and expansion. The relaxation behavior can be measured if the perturbation function (area of film) is plotted parallel with the response function (surface tension or surface potential) against time. The results of such an experiment are shown in Figure 6.

Figure 7 shows the phase angles *vs.* reciprocal frequency for four concentrations of oleic acid films spread on NaCl solution, read-out from surface tension and from surface potential. The observation of both positive and negative phase angles offers a broad field for speculation and experimental design in order to understand the mechanisms involved. Interpretation of these phenomena will be given in a subsequent paper.[21]

The phase angle of the response can be recalculated into the relaxation time using the expression:[15,19]

$$\tau = 1/e\ (\tan \varphi/2\,\pi f)$$

in analogy with mechanical or electrical relaxation phenomena. For surface tension the phase angle is negative (response preceds the perturbation) at concentrations below mono-molecular layer. It gradually becomes positive as concentration in increased to above monolayer coverage. Depending on concentration and the rate of perturbation, the relaxation times for surface tension range from 20 to 0.04 s, as calculated from the data in Figure 7 and for samples taken from the field.[15] The surface potential relaxation time distribution is more complex, apparently because the surface potential probe looks into the contribution of molecules below the first surface layer.[13] A detailed study will be reported elsewhere.[21]

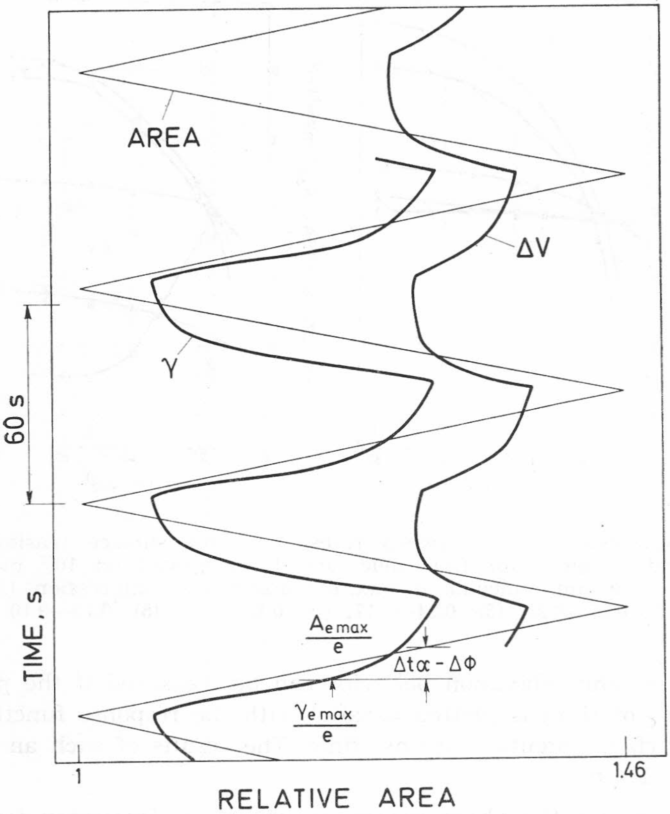

Figure 6. Simultaneous plotting of the perturbation (area) the surface tension (γ) and the surface potential (ΔV) response curves. The phase angle is measured as the time delay between the point of $1/e$ maximum area in expansion ($A_{e,\,\max}/e$), and the $1/e$ maximum surface tension in expansion ($\gamma_{e,\,\max}/e$), or the $1/e$ maximum surface potential difference ($\Delta V_{e,\,\mathrm{mas}}/e$).

DISCUSSION AND CONCLUSIONS

The description of the apparatus and the methodology of measurement points to its merits in studies of surface films in steady state and at low rates of perturbation. Such steady-states are comparatively easily established and are reproducible. Parallel recording of surface tension and of surface potential is a proof that hysteresis phenomena are real film properties and not experimental artifacts. They result in energy storage and release in the structure of the film. Quantitative calculation of this energy storage for field samples allows significant conclusions to be drawn on the influence of such films on the heating and cooling of the surface of the sea, lakes and other aqueous surfaces. The described techniques also offer a contribution to the knowledge of interfacial parameters controlling the properties of ejected microdroplets and their associated selective transport of halide and metal ions, of bacteria and viruses.[3,4,20] The new version of the apparatus with

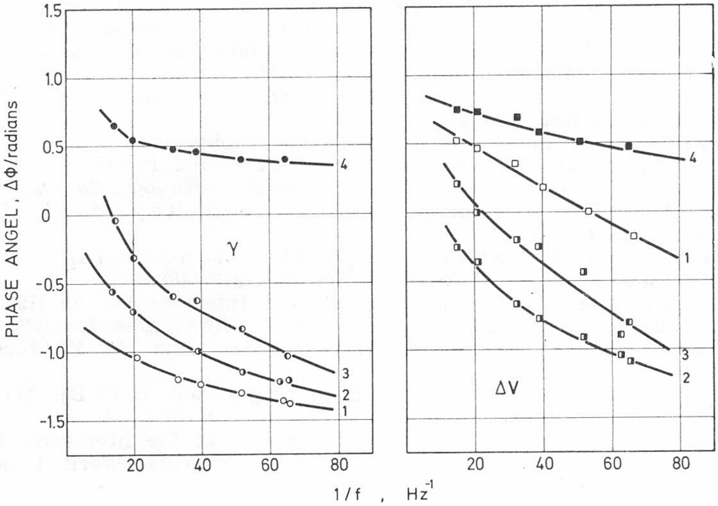

Figure 7. Phase angle in radians *vs.* the perturbation rate (reciprocal frequency), Hz^{-1}, read out from surface tension (left), and surface potential (right) curves, for four concentrations of oleic acid films spread on 10^{-5} mol/dm^3 NaCl. Concns. in nm^2/molecule in the max. expansion: (1): 0.37; (2): 0.24; (3): 0.18; (4): 0.15.

its linear sweep velocities and precision movement control represents a substantial improvement in comparison with the ones previously used[15,19] by the present authors, or those commercially available.[22]

Acknowledgement. — This work was supported by the Authority for Scientific Research of the SR of Croatia. The equipment used was obtained through a grant from the USEPA within the frame of the agreement on scientific cooperation between the USA and SFR of Yugoslavia.

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SAŽETAK

Tehnika za simultano mjerenje dinamičke napetosti površine i površinskog potencijala filmova na granici faza voda/zrak

Djurdjica Dragčević, Momir Milunović i Velimir Pravdić

Opisana je aparatura za simultano mjerenje površinske napetosti i površinskog potencijala filmova na granici faza tekućina/zrak u dinamičkom, stacionarnom stanju. Filmovi su priređeni u Langmuirovoj kadi i izloženi linearnim cikličkim perturbacijama pri različitim brzinama i omjerima kompresije u širokom području. Dobivene su informacije o elastičnosti, o predznaku i veličini površinskog potencijala, o smjeru i stupnju prijenosa energije i o relaksacijskom panašanju filma.

Pokazano je da je veličina petlje histereze površinske napetosti prema stupnju kompresije ovisna o vrsti tvari, njezinoj koncentraciji i brzini perturbacije, i da se mijenja od pozitivne (smjer prijenosa energije od filma prema podlozi) na negativnu uz povećanje brzine kompresije/ekspanzije filma i koncentracije materijala koji tvori film.

Izračunavanje iznosa prijenosa energije po jednom kompresijsko-ekspanzijskom ciklusu filma za površinsku napetost iznosi od +2,8 do —1,0 mJ/m^2. Izračunavanje električnog dijela ukupne energije filma po ciklusu zahtijeva pretpostavke o dielektričkoj konstanti u molekulskim dimenzijama pa je nije moguće direktno izračunati. Pokazano je, da je fenomen histereze napetosti površine i površinskog potencijala realan, jer je prvi mjeren direktnim kontaktom s filmom i podlogom, a drugi beskontaktnom probom.