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MONO- AND MULTILAYERS FROM HEPTADECYLCARBOXY-TETRATHIOFULVALEN MODIFIED BY THE SURFACE-INACTIVE ELECTRON ACCEPTORS

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The monolayers and Langmuir-Blodgett (LB) films on the base of heptadecylcarboxy-tetrathiofulvalen ($C_{17}H_{35}$-TTF-COOH) and its binary mixtures with an electron acceptor from row: tetracyanquinodimethane, chloranil or bromanil were studied. Monomolecular layers on the water surface were investigated using measurements of compression isotherms and curves of the surface potential jump. LB films were studied using the small-angle X-ray scattering method, the optical absorption spectroscopy, the atomic-force microscopy and the electrical measurements with direct and alternating current. It was found that donor and acceptor components in mono- and multilayers is distributed in microheterogeneous way. Characteristic size of the microcrystallites of $C_{17}H_{35}$-TTF-COOH is about 100 nm. An effect of reversible skeletonization with solving and possible inverse insertion of an acceptor component into an LB film volume was discovered. After this process, the bimolecular period of the LB film structure (about 66.2 Å) saves its value. For the first time an anomalously high dielectric permeability $\varepsilon = 18$ was observed in LB films from donor-acceptor mixtures.

Keywords: Monomolecular layers; LB films; tetrathiofulvalen; chloranil; bromanil; tetracyanquinodimethane

INTRODUCTION

The prospects of Langmuir-Blodgett (LB) films application in molecular electronics depends on possibility of the formation of conducting LB films. The present work deals with a building of LB films possessing relatively high planar conductivity. Similar systems were studied earlier, for instance, in the articles [1 – 4]. As a rule, strong electron donors and acceptors were used synthesized by addition of one or two aliphatic radicals to well known molecules of tetrathiofulvalen or tetracyanquinodimethane types. Usually LB films were built either from mixed monolayers with varied donor to acceptor molecular ratio or from alternative monolayers of donor and acceptor molecules.

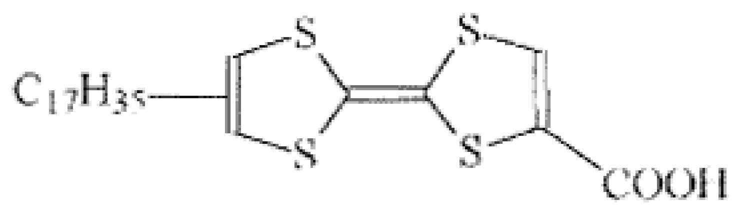
However, it was noted that aliphatic substitutes prevent a close packing of aromatic fragments of a donor and an acceptor [5]. Therefore, an overlapping of the external molecular orbitals of donor or acceptor fragments responsible for the conductivity was not ensured. That is why an idea to use donor-acceptor mixtures for the building LB films, in which one of the components have no aliphatic substitute, is quite natural.

In the present work, for building of conducting multilayers, a surface-active donor heptadecylcarboxytetrathiofulvalen ($C_{17}H_{35}$-TTF-COOH) was used in binary mixtures with an acceptor from a series of tetracyanquinodimethane, chloranil or bromanil. These acceptors are not surface active, *i.e.*, they do not change the surface tension of water noticeably (less than by 1 mN/m) even at a high surface concentration (up to 5 Å^2/molecule).

EXPERIMENTAL DETAILS

Chemical formulas of the compounds used are shown below:

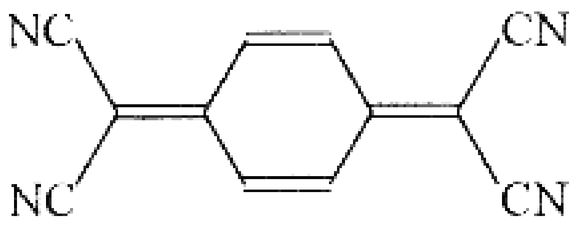
Donor (D):



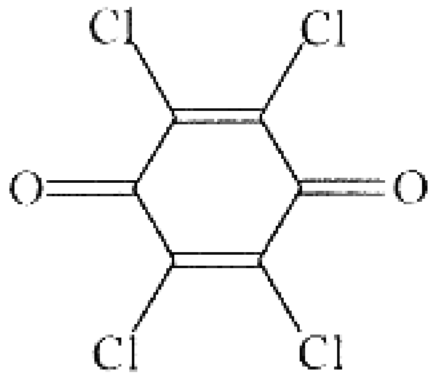
($C_{17}H_{35}$-TTF-COOH)

molecular weight 484,

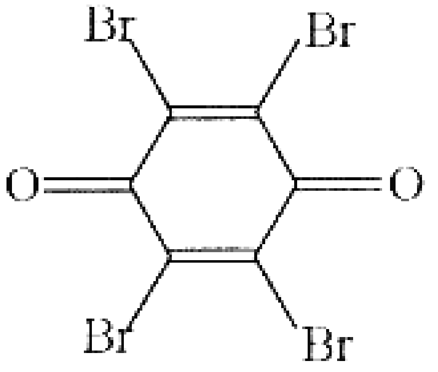
Acceptors (A):



(TCNQ), m.w. 204,



(Chl), m.w. 244,



(Brl), m.w. 323,6.

The molecular weights are given for a rough comparative evaluation of sizes and volumes of the molecules. Chromotographic data shows that compound $C_{17}H_{35}$-TTF-COOH consists of two isomers. Initial solutions of the compounds were prepared using the following solvents: the mixture of benzene - methanol - heptane (volume proportion 1 : 1 : 4) for $C_{17}H_{35}$-TTF-COOH, the mixture of acetonitrile - benzene - methanol (1 : 1 : 1) for TCNQ, benzene for Chl and Brl. Concentration of the compounds was equal to 1 mg/ml for all experiments. Only freshly prepared solutions (aged < 5 hours) were used for monolayer preparation on the water surface.

A study of monolayers on the water surface and LB film preparation were made using an NT MDT-LB5 trough. The monolayers were compressed from both sides by means of two barriers. The trough had an area 45×11 cm^2. The surface pressure was measured using a Wilhelmy plate made of filtering paper. The LB films were formed at surface pressure of 35 ± 0.1 mN/m. The monolayer compression was made in two stages. The barrier motion rate at the initial stage (< 2 mN/m) was 40 mm/min, at the second stage (> 2 mN/m) at 20 mm/min. The speed of the substrate was 2 mm/min during dipping and withdrawing strokes with the waiting time in the up position of 1 min. Distilled water was used as a subphase. The temperature of the water subphase and of the ambient air was 18–20°C.

X-ray diffraction measurements were performed with a small angle diffractometer AMUR-k using Ni-filtered CuK$_{\alpha 1}$ radiation ($\lambda = 0.154$ nm). The X-ray camera was equipped with a Kratky collimation system and a position sensitive linear detector with resolution of 67 μm. The sample-to-detector distance was 700 mm. Diffractograms were recorded with exposure time of 10 min. The surface of LB films was studied by means of the atomic-force microscope Solver P47 (NT MDT, Russia). A scan was made in the tapping mode at the resonance frequency of a silicon cantilever (471.7 kHz). The scan rate was 20 μm/sec, with a step of 7.5 nm.

The transverse electric conductivity $\sigma_{\perp}$ of LB films consisted of 11–41 monolayers was measured on the capacitor structures: a metal (Al) - LB film - a metal (Al) with 1 mm^2 electrode area. A.c. measurements were made by means of an automatic bridge HP 4270A (test voltage 0.2 and 1.0 V, frequency 1 and 10 kHz) within the temperature range 20–90°C. Metal electrodes were deposited through a mask by vacuum evaporation. In addition, the electrical capacity and dielectric loss tangent were measured.

The planar conductivity $\sigma_{\parallel}$ was measured on LB films deposited onto sapphire substrates with interdigitated chromium electrodes prepared by photolithography using electromer PAR-136. The width of the electrodes and the gap between them were 50 μm. The total length of the gap between the electrodes was 50 cm. Geometry of the electrodes allowed the measurements of resistance of the structure during the LB film deposition process. However, in most of experiments the measurements of $\sigma_{\parallel}$ were made in the uppest position of a substrate.

RESULTS AND DISCUSSION

The compression isotherms and the curves of the electrical potential jump for monomolecular layers of TTF and its binary mixtures with Chl and Brl are presented in Figures 1 and 2. All monolayers were stable up to the collapse surface pressure. However, for mixtures D + A, a value of the collapse pressure exceeded that of pure D by approximately 10 mN/m and reached 43–45 mN/m.

Compression isotherms and the surface potential curves for TTF + TCNQ (1 : 1) monolayers are similar to those for TTF + Brl and TTF + Chl. The surface potential curve of the TTF + TCNQ mixture is located slightly below and has a jump of + 550 mV at the collapse pressure. As a result of a partial dissolution of TCNQ in the water subphase the experimental data are not well reproducible and not presented here.

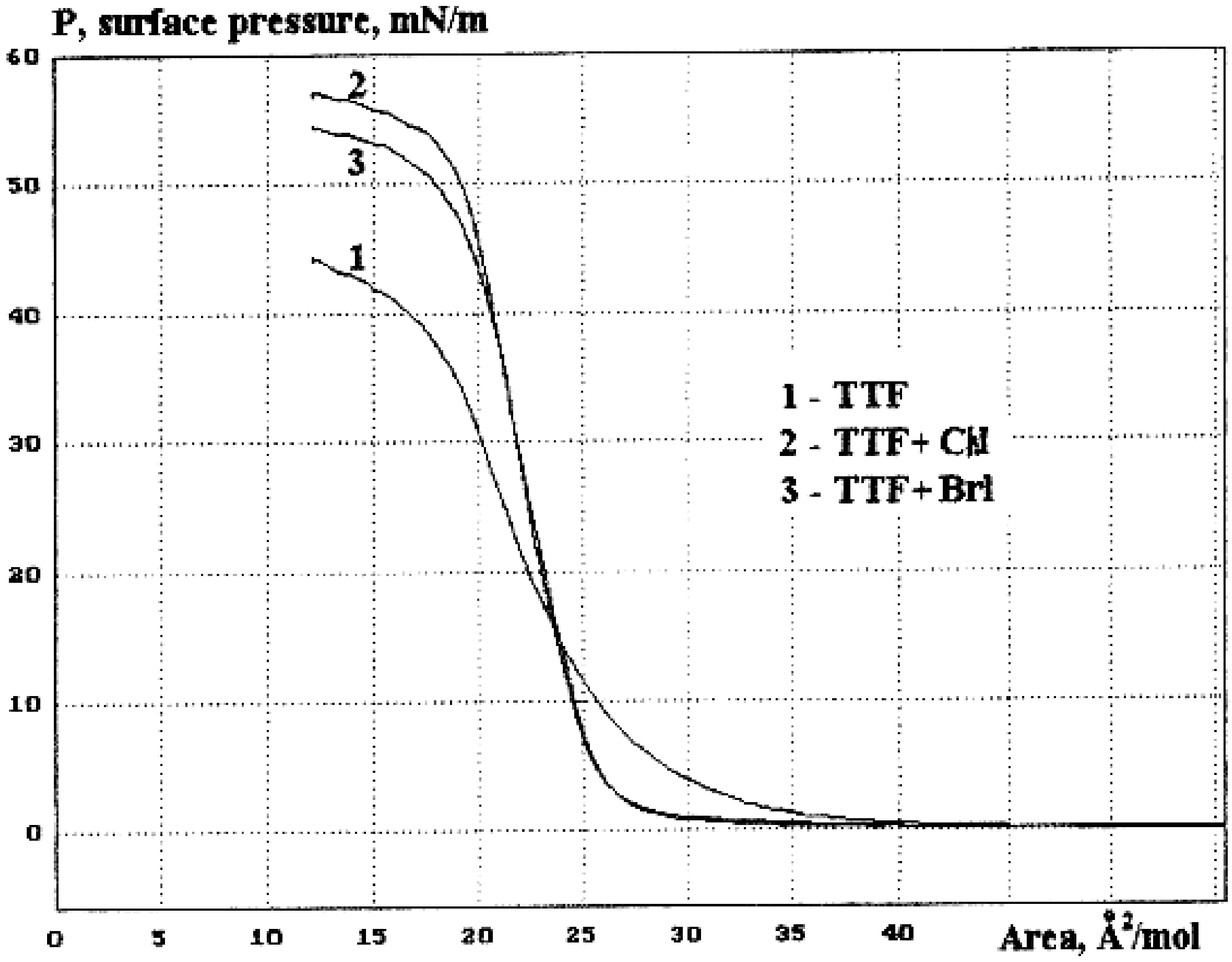


FIGURE 1 Compression isotherms of monomolecular layers on distilled water (*X*-axis scale: area per molecule of TTF). 1. heptadecylcarboxytetrathiofulvalen (TTF); 2. a binary mixture of TTF with chloranil (molar ratio 1 : 1); 3. a binary mixture of TTF with bromanil (1 : 1).

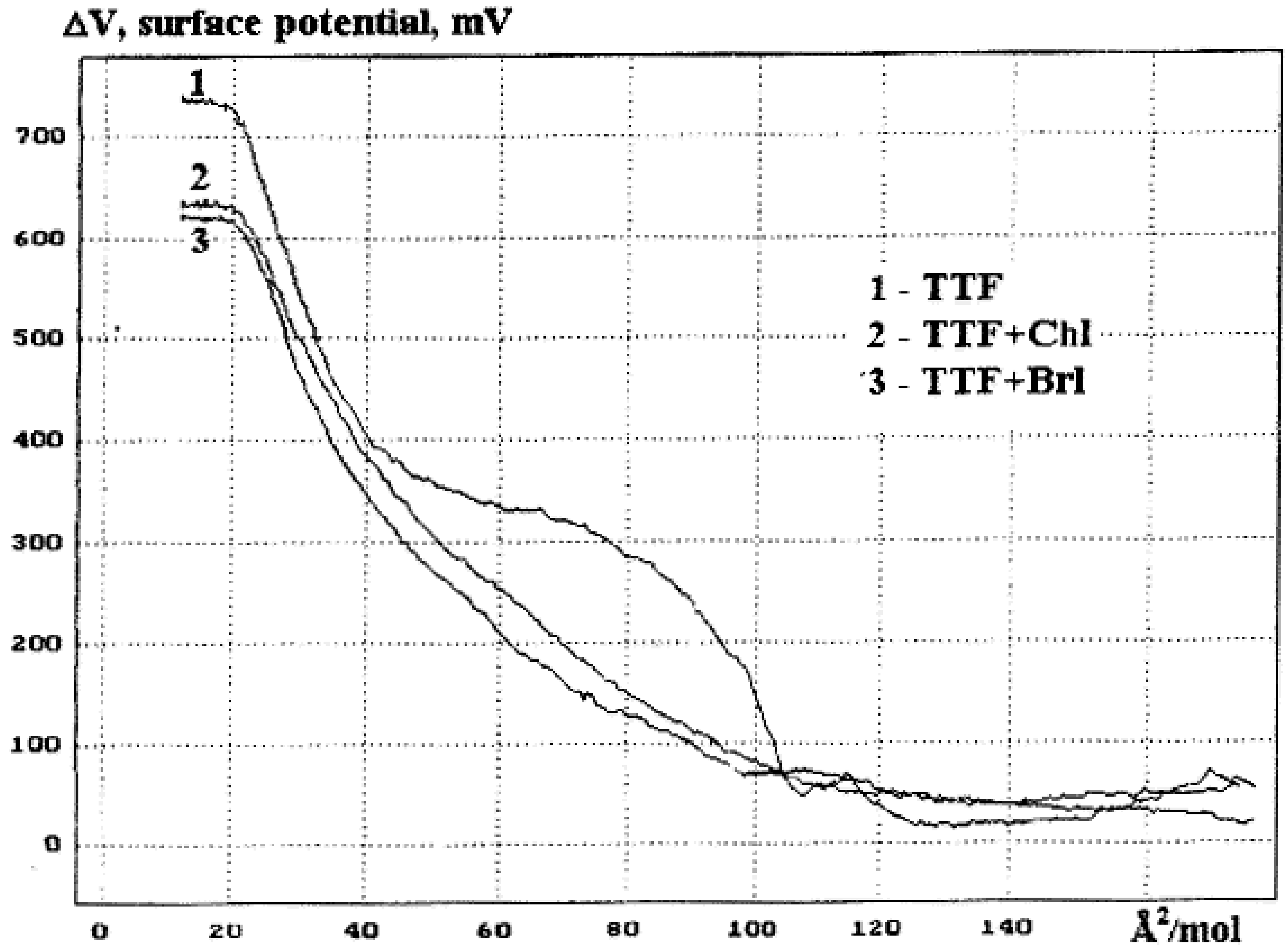


FIGURE 2 Surface potential as a function of area per molecule of TTF upon compression of a layer (see legend to Fig. 1).

Since the acceptor molecules do not show surface activity, all isotherms and potential curves are presented as functions of the area per a TTF molecule. It is seen in Figure 1 that, although the latter changes slightly, the compressibility of the mixed monolayers decreases by factor 2 in comparison with that of pure TTF. These data point to a significant influence of acceptor molecules on rheologic properties of TTF monolayers.

Variation of the surface potential jump ΔV (compare curve 1 with curves 2 and 3 in Fig. 2) also reveals an interaction between the D and A molecules in a monolayer on the water surface. At the collapse point, ΔV reduces by 100 mV for mixtures TTF + Chl or TTF + BrI and by 200 ± 30 mV for mixture TTF + TCNQ. Furthermore, a monotonous decrease of ΔV is observed at large area per molecule, when the surface pressure is about 1 mN/m or lower. Such behaviour of curves 2 and 3 in Figure 2 points to a homogeneous distribution of the compounds in the form of small weakly interacting islands with their size much smaller than the diameter (1 cm) of the vibrating electrode [6]. For pure TTF, the curves of the surface potential at areas larger than 40 Å^2/mol are not well reproduced, that points to a distribution of the material in the form of large islands. The compression isotherm for binary mixture A + D is not an additive function of the compression isotherms for A and D components. This points to either homogeneous or micro-heterogeneous mixing A and D components on the water surface (for heterogeneous distribution the isotherms are additive [6]).

Multilayers were produced by the Langmuir-Blodgett method. The transfer process was quite regular. For TTF and for TTF + A, the transfer coefficient was constant 0.94 ± 0.04 on both down and up strokes except the first dipping stroke. A mutual dependence of a substrate position and the coordinate of a barrier in the process of forming LB films from mixture TTF + BrI (1 : 1) is shown in Figure 3. On the first dipping stroke (left side) a monolayer is not deposited onto a saphire substrate with chrome electrodes. A certain apparent decrease in the transfer coefficient on substrate withdrawing and a decrease of monolayer area during the waiting time in the up position may be explained by a long relaxation time of the surface pressure in the monolayer. A quasi-solid phase state of the monolayer limits a rate of transfer. For substrates wider than 15 mm and its motion faster than 3 mm/min, the transfer coefficient decreases by 10–30%. This points to insufficient rate of monolayer arrival to the meniscus area.

For X-ray reflectometric measurements the LB films were prepared on silicon substrates. Before forming LB films, a surface of silicon

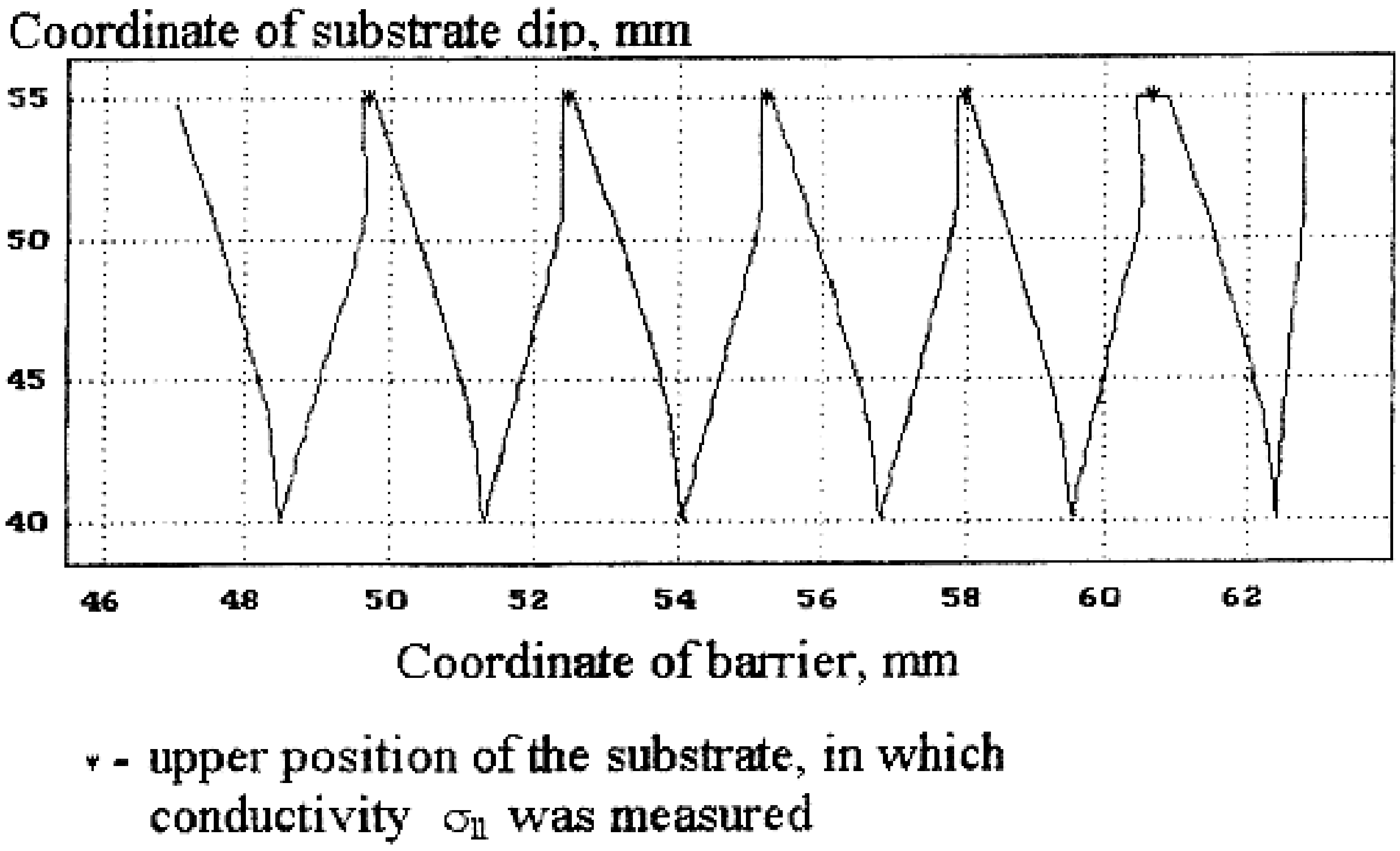


FIGURE 3 Dependence of the barrier co-ordinate in the process of the LB film formation (horizontal axis) on position of a saphire substrate (vertical axis).

substrates was made hydrophobic by treatment in a 10% water solution of the hydrofluoric acid. An example of small-angle X-ray scattering curves is shown in Figure 4 for samples of pure donor (curve 1) and mixtures D + Brl with molar ratios 4 : 1 (curve 2) and 1 : 1 (curve 3) with the same number of monolayers in a LB film equal to 20. The Bragg peaks in curves 1 and 2 are explained by bimolecular periodicity of LB films structure 66.2 ± 0.5 Å. From molecular models, a length of a TTF molecule is 33.5 Å.

For a sample of mixture TTF-Brl (4 : 1), the Kiessig oscillations originated from interfaces are well seen. LB film thickness (674 ± 15 Å) was calculated from the oscillation periodicity. This value is close to 662 Å obtained from a number of monolayers in the LB film structure and a bimolecular period, obtained from the location of Bragg's peaks in the curves 1 and 2. Proximity of these values indicates, that Brl molecules in mixture TTF : Brl at molar ratio 4 : 1 stay within the volume of TTF monolayer. It should be noted that Brl of Chl molecules cannot be not dissolved in water or be evaporated at room temperature. With increasing amount of Brl molecules (TTF : Brl = 4 : 1, curve 3), the period slightly decreases, but the total thickness found

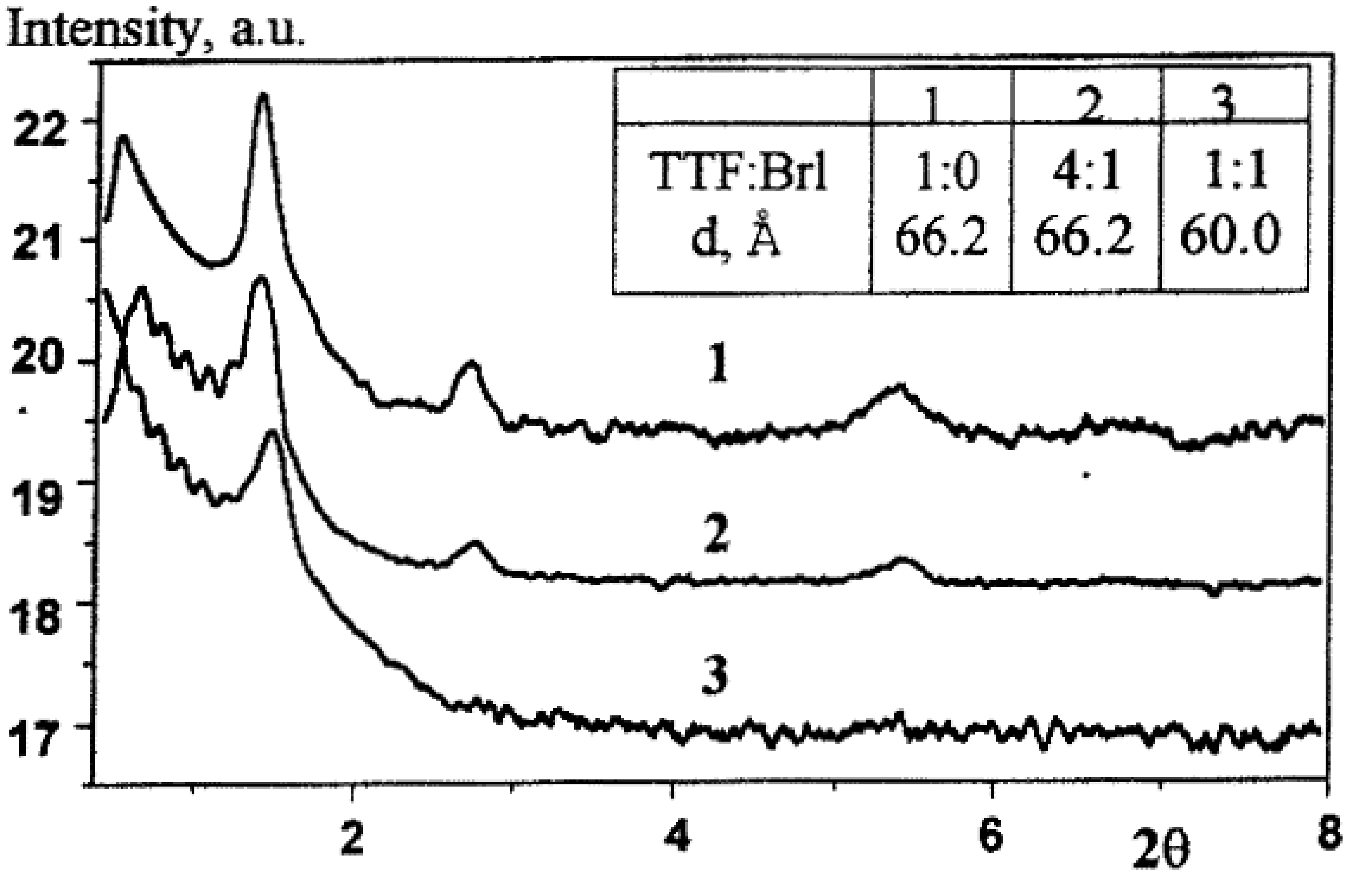


FIGURE 4 X-ray scattering intensity for 20 monolayer LB films of different composition (for convenience, the curves are shifted along the *y*-axis). 1. TTF; 2. mixtures TTF + Brl (molar ratio 4 : 1); 3. mixtures TTF + Brl (1 : 1).

from Kiessig's oscillations increases approximately by 40 Å. A quantitatively similar picture was observed, when other molecules (TCNQ or Chl) were used as acceptors.

A comparison of the small-angle scattering curves 1 and 2 and analysis of data for monolayers on the water surface allows us to make a conclusion about micro-heterogeneous distribution of components A and D in the structure of mono- and multilayers. It is clear, that the period of LB film structure must increase in the case of homogeneous mixing at a fixed area per one TTF molecule or when charge transfer TTF + A complexes form in the monolayers on the water surface. The latter has not been observed.

A schematic picture of the component distribution in a monolayer formed from mixtures A and D on the water surface is shown in Figure 5. The molecules of surface-inactive acceptor are located as associates in a space between crystallites of surface-active TTF. In LB films from a TTF : Brl mixture (molar ratio 4 : 1) voids between TTF crystallites are filled, the monolayer surface becomes smoother and Kiessig's oscillations appear in curve 2, Figure 4. In curve 1 Kiessig's oscillations are absent, that points to some roughness of the air - LB film interface in the case of pure TTF films. The micro-heterogeneous

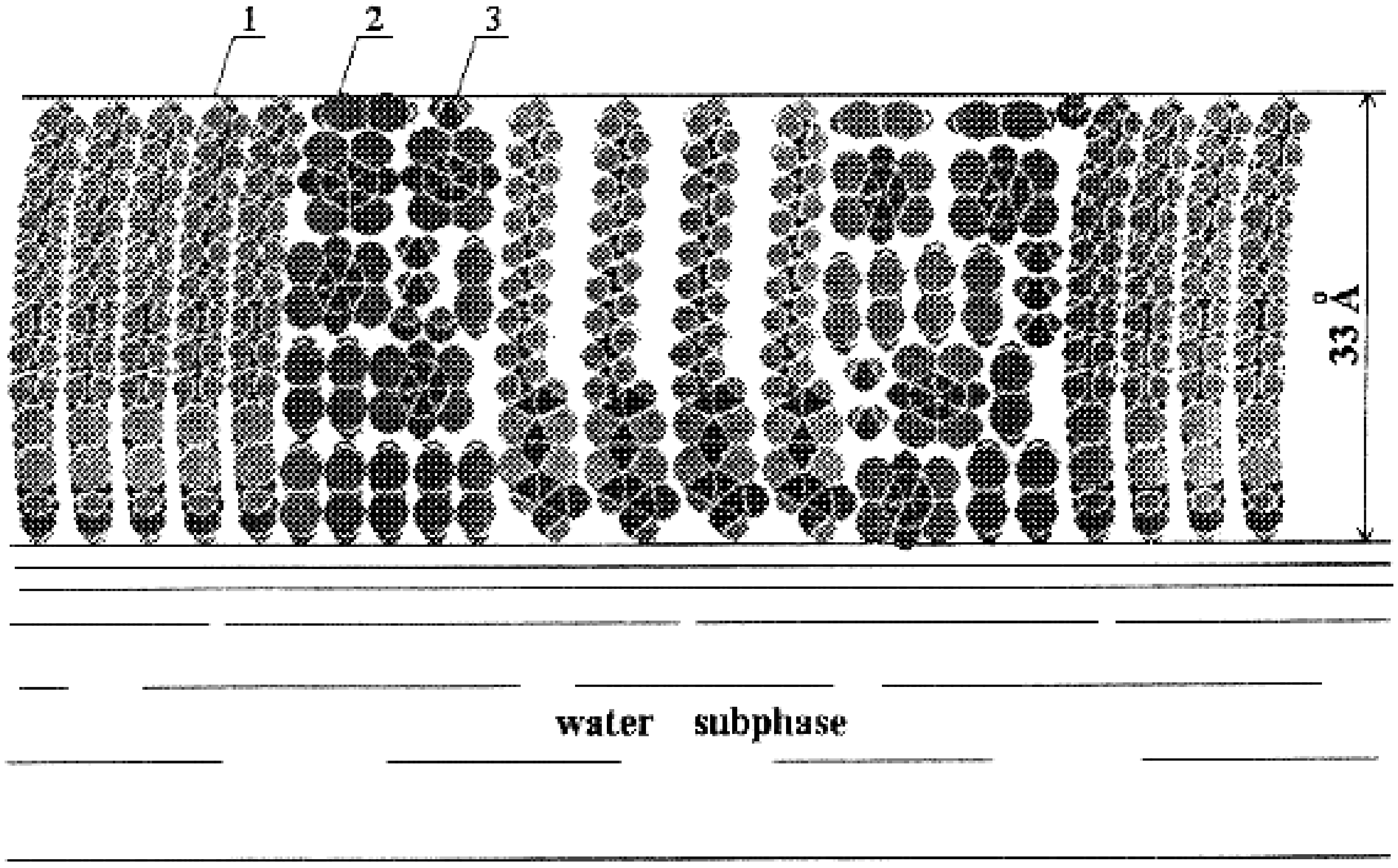


FIGURE 5 Schematic picture of micro-heterogeneous distribution of components in a mixture (4 : 1) of TTF (1) with bromanil (2) in a monomolecular layer on the water surface; (3) water molecules within the layer.

picture of the acceptor distribution is indirectly confirmed by optical measurements. Broad absorption bands characteristic of the charge transfer complexes are not observed in spectra of mixed LB films.

All these data indicate that, in the system under study, on the water - air interface the energy of the donor-acceptor interaction is less, than the (cohesion) energy of the intermolecular tangential interaction in micro-crystallites of TTF derivatives. For comparison [7, 8], even weaker donor-acceptor quinohydrone pairs (surface-active donor or acceptor accordingly with surface-inactive acceptor or donor) form stable charge transfer complexes in monolayers on the water surface. However, in such complexes, at least one hydrogen bond is available within each D + A pair.

During a study of electrical properties of mixed TTF + TCNQ LB films, an interesting phenomenon has been observed. As small-angle X-ray scattering data show, in certain solvents, *e.g.*, in water - methanol mixtures, the TCNQ component may be completely removed from an LB film for 30 min without any change in the layer structure. Herewith, the optical thickness of LB films can decrease by 10% or even more. Moreover, the inverse process of TCNQ insertion is possible at soak of the same samples or new LB films from pure TTF in saturated TCNQ solutions. For a few hours, the optical thickness of LB films increases by 10 – 15% with conservation of layer structure period. Selective removing of Brl and Chl molecules from LB films occurs also on heating of the films up to 70°C for a few minutes.

The relief and morphology of the surface were also studied by the atomic force microscopy. Typical pictures of samples surface are shown in Figures 6a and 7a. They correspond to X-ray curves 1 and 2 in Figure 5. Areas of 2.5 × 2.5 μm size were selected for analysis with resolution 7.5 nm (256 × 256 elements). Characteristic sizes of crystallites were equal to 100 nm in both cases. However, in the LB films prepared from mixture TTF + Brl (4 : 1) the areas between TTF crystallites are occupied by the second component (Brl) and have viscoelastic properties different from those of TTF. Histograms showing inhomogeneity of the film surface are shown in Figures 6b and 7b with respect to a reference plane. For a sample of pure TTF, the distribution curve is narrower than the corresponding curve for a TTF + Brl sample.

Electrical properties of our LB films are consistent with a general microheterogeneous picture of the component distribution shown

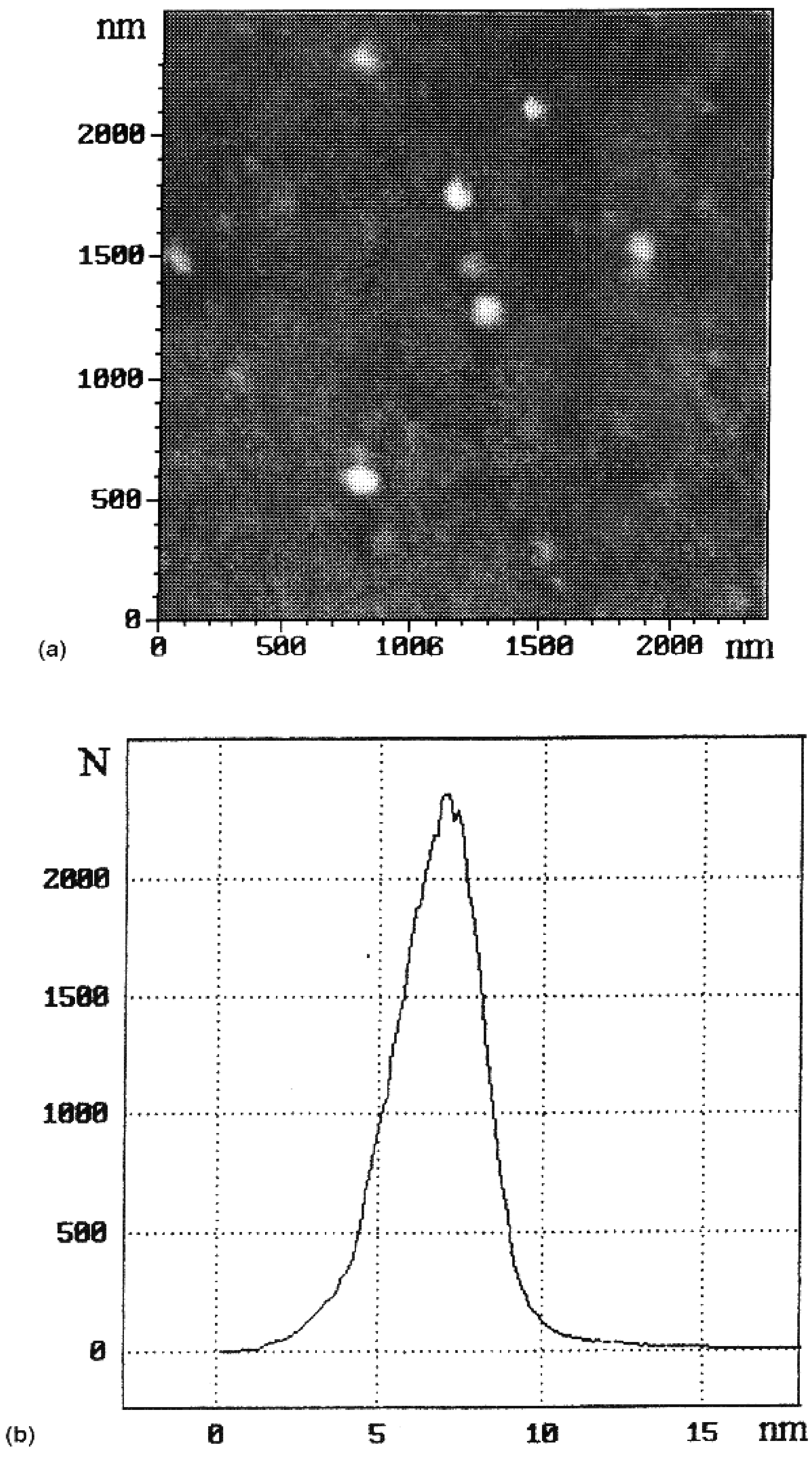


FIGURE 6 a) Surface topography of a 20 monolayer TTF film obtained by an atomic-force microscope; b) Histogram of inhomogeneity distribution for the same surface.

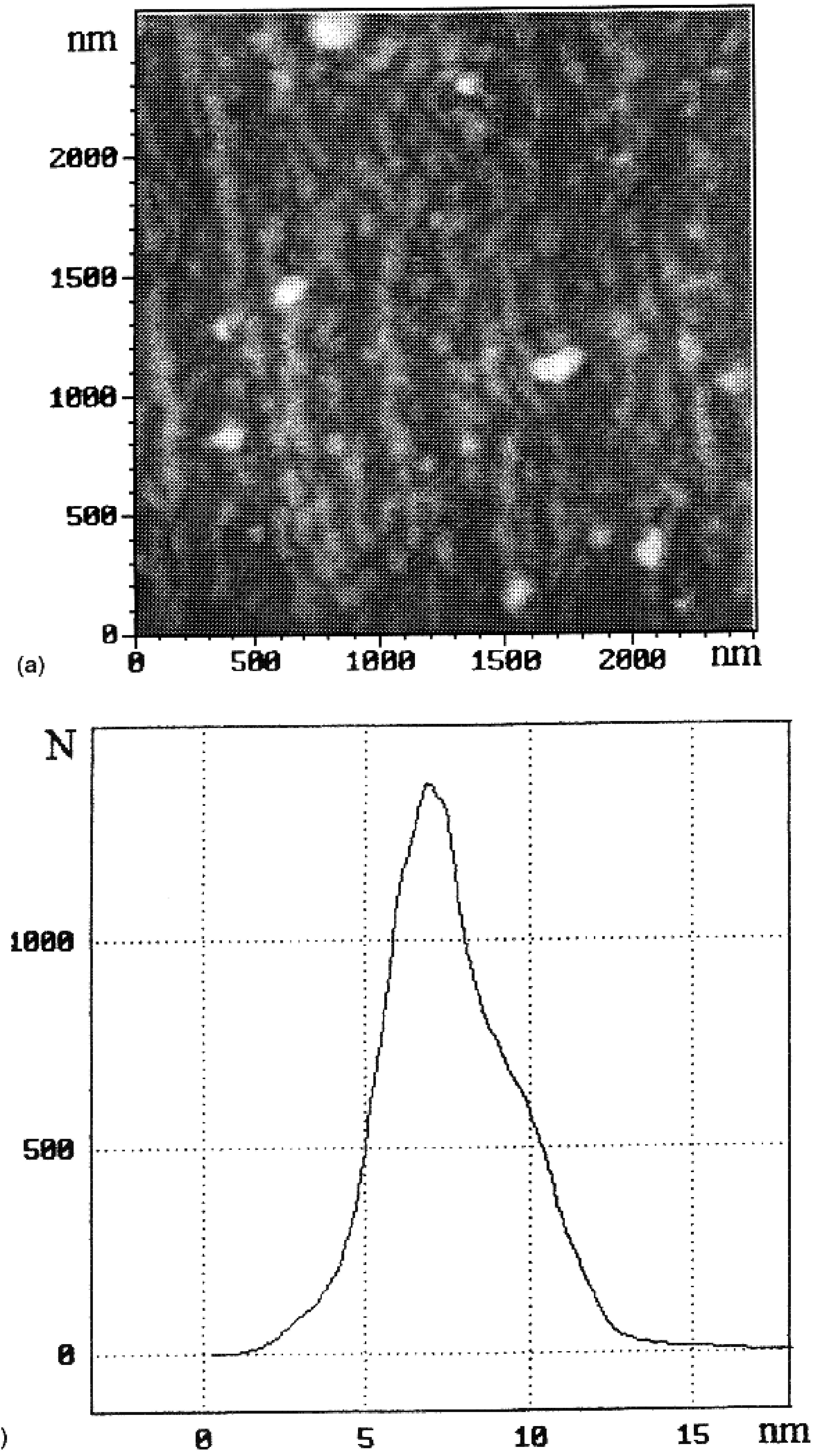


FIGURE 7 a) Surface topography of a 20 monolayer TTF + BrI (4 : 1) film obtained by an atomic-force microscope; b) Histogram of inhomogeneity distribution for the same surface.

schematically in Figure 5. It is well known, that conductivity of charge transfer complexes is considerably higher, than that of the separate components. In our experiments, an increase in conductivity for mixed $D + A$ film has not been observed. For example, a set of curves in Figure 8 shows a change in the longitudal resistance with increasing number of monomolecular layers in the LB film with different ratios of the TTF:Brl components in mixtures. A curve for pure TTF would coincide with curve 4. However, due to significant scatter of data the former is not shown in Figure 8. For the same reason, we do not present data on resistance for one monolayer LB films.

When the ratio of components is 4 : 1, a minimum resistance is reached for a three monolayer LB film. In fact, further increase of number of monolayers N and a change in molar ratio D : A for $N \geq 7$ does not influence the absolute value of sample resistance. This result is a consequence of high anisotropy of the film conductivity, $\sigma_{\parallel} \gg \sigma_{\perp}$. Besides, it shows that the charge transfer complexes do not form in the system under study. Indeed, a limiting resistance is equal for both the pure TTF and mixed $D + A$ samples. The value of the limiting resistance (20 kOhm for a given geometry) corresponds to the three-dimensional conductivity $10^{-2} (\mathrm{Ohm} \cdot \mathrm{cm})^{-1}$. A scatter of data on film resistance at small number of N points to some difference in quality of molecular packing in the film structure. Assumption, that the amount of defects is minimum at the component ratio 4 : 1 is consistent with the X-ray data and results of investigations by atomic-force microscopy.

Very interesting data were obtained on transverse a.c. conductivity $\sigma_{\perp}$ in capacitor structures. Temperature dependencies of capacity and dielectric loss tangent ($\tan \delta$) are shown on Figure 9 at voltage 0.2 V and frequency 1 kHz. At the highest temperature, a thermal decomposition of TTF does not occur. The direction of the temperature scan is indicated by arrows. A sample contains 27 monolayers of 4 : 1 TTF + Brl mixture. With increasing temperature, three peaks are seen in the $\tan \delta$ curves corresponding to drops in the capacitance curve. Such peaks are usually related to phase transitions in a dielectric material [10].

In our case, however, the following picture of structural changes seems to be reasonable. An escape of water molecules from the film volume begins at temperature 40 – 55°C. Evaluation of a dielectric permeability from data on N, electrode geometry and film thickness

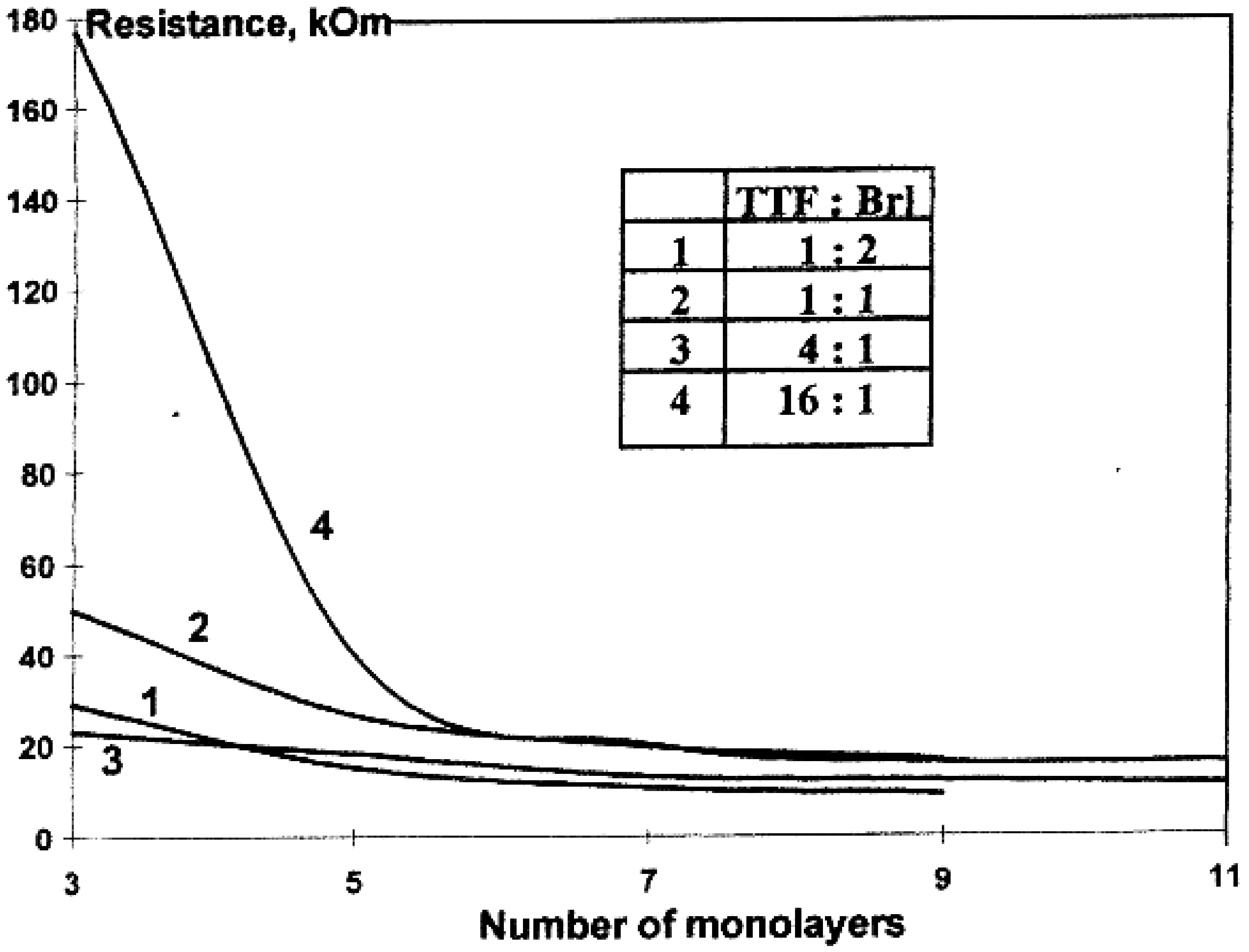


FIGURE 8 Resistance as a function of the number of monomolecular layers for LB films with different D : A molar ratio.

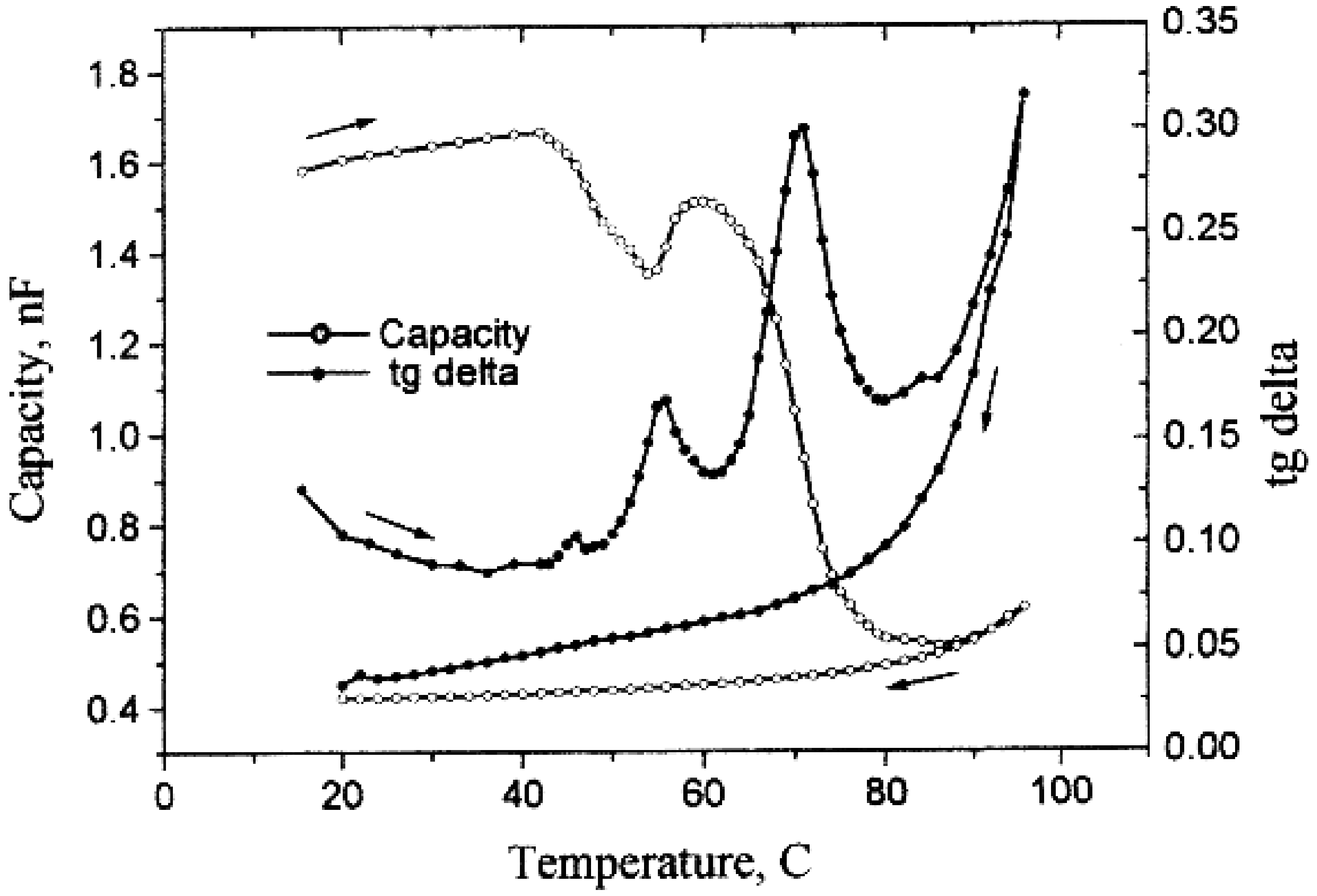


FIGURE 9 Temperature behaviour of capacitance and tan δ (voltage 0.2 V, frequency 1 kHz) for a 27 monolayer mixed TTF + BrI (4 : 1) LB film.

results in unexpectedly high value $\varepsilon = 18.0 \pm 1.2$. Acceptor molecules (Brl, Chl and TCNQ) have a dipole moment equal to zero. Even for molecular crystals of ion-radical salts $\varepsilon < 5$ [11]. Therefore, we believe that the presence of water molecules is responsible for high ε of our films.

Most probably, the water is situated in the vicinity of molecular associates of acceptors, as shown in Figure 5. For comparison, the LB films of pure TTF have $\varepsilon = 2.6 \pm 0.3$ without any peaks. An intensive sublimation of acceptor component accompanied by lost of water begins upon further heating. Indeed, in similar samples deposited on a silicon substrate, a 10% reduction of the optical thickness was observed on heating. This may be accounted for by the skeletonization of LB films described above for the case of mixed TTF + TCNQ films kept in the methanol-water solutions. The capacitance and tan δ curves obtained on cooling point to irreversibility of composition changes in the LB film volume. On assumption of constant film thickness, the dielectric permeability of the film changes with temperature by factor 4 or more. The corresponding variation of electric conductivity on heating the same sample is shown in Figure 10. As expected, it has a similar character as the tan δ curve. At room temperature, $\sigma_{\perp} \approx 10^{-9}$

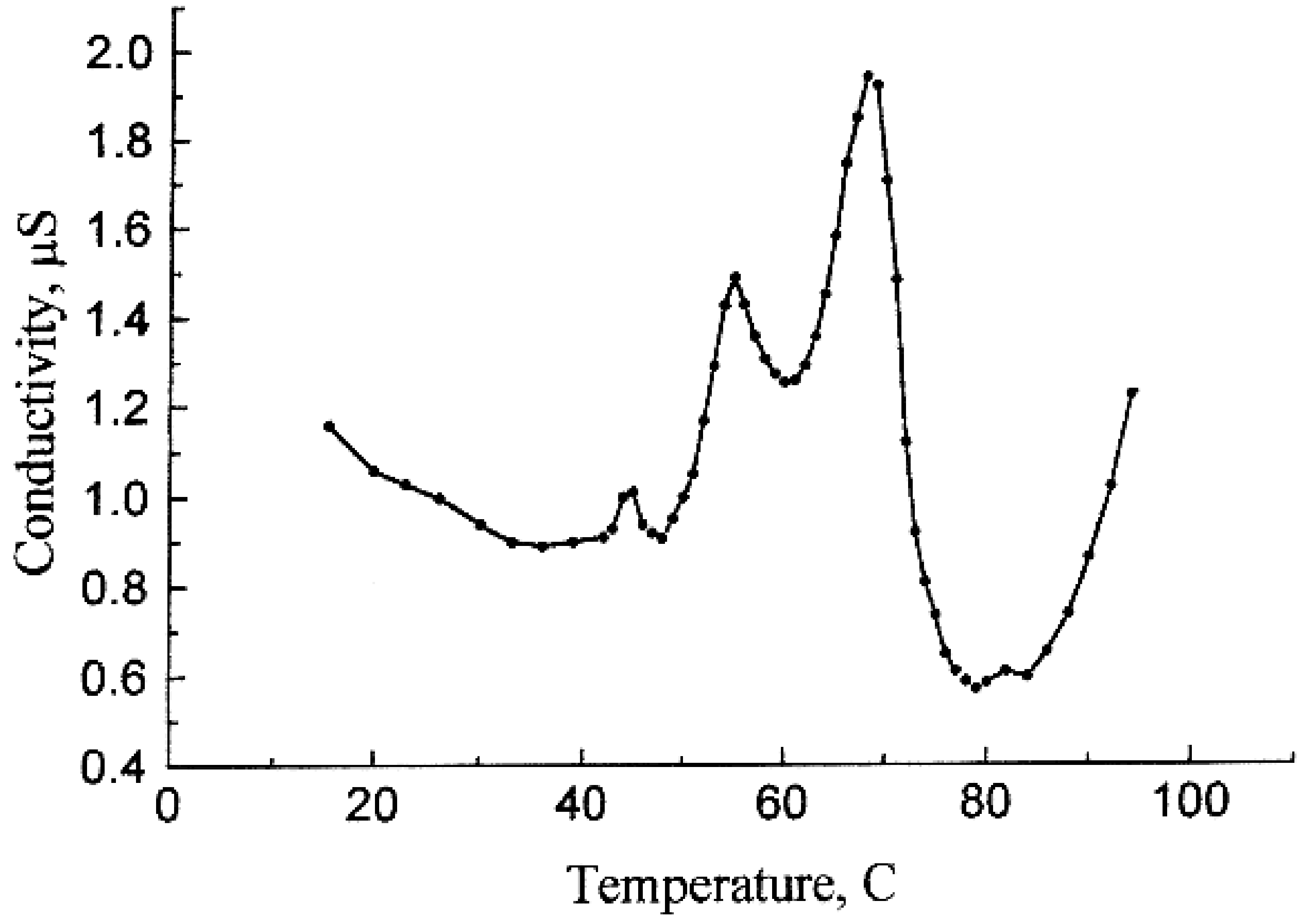


FIGURE 10 Variation of conductivity with increasing temperature of the same sample as in Figure 9.

(Ohm · cm)$^{-1}$ for both a.c. and d.c. measurements. Exposition of both pure TTF and mixed films to iodine vapours result in a decrease of their longitudinal conductivity by several orders of magnitude.

CONCLUSION

Monomolecular layers of $C_{17}H_{35}$-TTF-COOH on the water surface consist of solid micro-crystallites with a characteristic size equal to 100 nm. There are voids between the micro-crystallites even in the collapse point. In mixed monolayers of a donor with surface-inactive acceptors (chloranil, bromanil or tetracyanquinodimethane) with molar ratio exceeding 4 : 1, these voids are filled without a break of the monolayer structure and a change in efficient area per donor molecule. Therefore, the components in mixed mono- and multilayers are distributed in micro-heterogeneous way. Charge transfer process were not detected in optical and electrical measurements.

In mixed LB films, there was observed an effect of the reversible skeletonization, *i.e.*, a selective removal of the acceptor component under an action of a solvent that dissolves a donor but does not dissolve an acceptor. The bimolecular layer period of the LB film structure is kept constant with accuracy of a part of an angstrem. On the other hand, in saturated solutions of acceptors, donor LB films are capable to accumulate in their volume a considerable amount ($>10\%$) of acceptor molecules without destroying the initial structure. The acceptor components can also be removed by sample heating up to 70°C.

Longitudinal and transverse conductivity were found to be of the order of 10^{-2}(Ohm · cm)$^{-1}$ and 10^{-9}(Ohm · cm)$^{-1}$, respectively. Besides, anomalously high dielectric permeability $\varepsilon = 18$ was observed in mixed LB films. Probably, this is related to a capture of water molecules in the acceptor micro-associates. This water can be removed together with the acceptor component on heating. This phenomenon may have interesting technological applications.

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