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Surface potential studies of monolayers of surfactant donor and acceptor molecules

F. Rustichelli, S. Dante and P. Mariani
Institute of Physical Science, University of Ancona, Via Ranieri 65, 60131 Ancona (Italy)

I. V. Myagkov and V. I. Troitsky
Zelenograd Research Institute of Physical Problems, 103460 Moscow (Russia)

Abstract

The surface potential technique was used for investigation of donor, acceptor and mixed monolayers, containing molecules suitable for deposition of conducting LB films. It is shown that the donor and acceptor monolayers are neutral at the air–water interface. Big positive values of surface potential in the case of donor molecules are explained by peculiarities of dipole depolarization near the surface of the water and by charge transfer salt formation with water-soluble impurities. The dipole moment arising due to charge transfer between donor and acceptor molecules in mixed monolayers is parallel to the layer plane. Other details of charge transfer complexes or salt formation in the mixed monolayers are discussed.

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1. Introduction

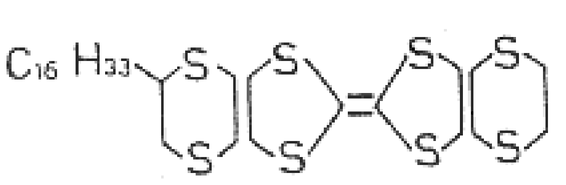
Langmuir–Blodgett (LB) films attract a lot of attention from researchers because molecular-scale structures can be created using them as a basis [1, 2]. Discovery of conductance in LB films [3–6] seems to give additional possibilities for their practical application. Moreover, the field effect discovered in conducting LB films provides the opportunity for device operation [7]. Another promising possibility is the deposition of polar structures with the alternation of donor and acceptor monolayers possessing pyroelectric properties. For the preparation of conducting LB films, charge transfer complexes and salts based on surfactant donor and acceptor molecules are widely used as well. Such films can be used for the development of devices for molecular electronics. However, the improvement of quality of film deposition, the increase of conductivity values, and search for new perspective materials are necessary for real applications. For this purpose careful investigations of the monolayers used for LB film preparation are required.

The surface potential technique is a simple but powerful tool for studying monolayers at the air–water interface [8, 9] and multilayers deposited onto a substrate [10]. Surface potential data in connection with information obtained from surface pressure–area isotherms offer the possibility of determining the charge of a monolayer and its dependence on the composition and on the pH value of the water subphase, and the projection of the dipole moment of a hydrophilic group along the normal to the layer plane, as well as giving information on the molecule orientation, the viscosity of the monolayer and the quality of spreading. Some monolayers of charge transfer complexes were studied previously [9], but LB films deposited using such monolayers were not conductive.

In this work monolayers of donor and acceptor molecules used for deposition of conducting LB films are studied at the air–water interface by the surface potential technique.

2. Experimental details

The chemical formulae of the utilized compounds are the following:



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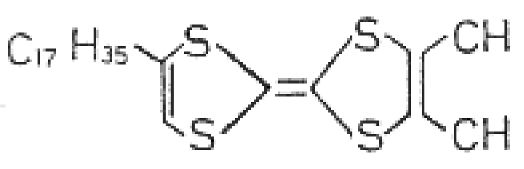
(C16-BEDT-TTF)



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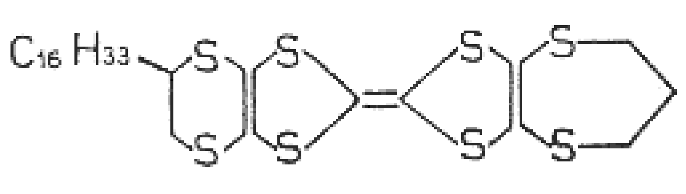
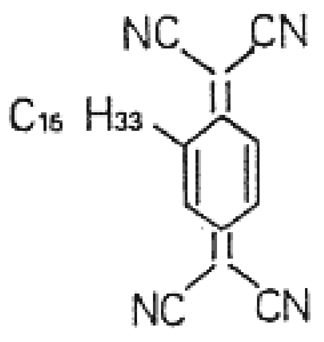
(C17-DMTTF)

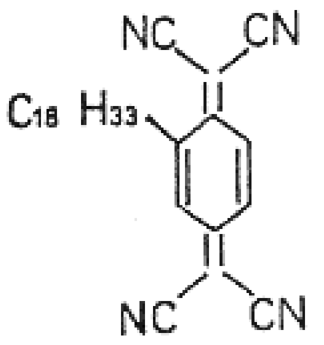


hexadecylethylenedithiopropylenedithiotetrathiafulvalene
(C16-EDT-PDT-TTF)

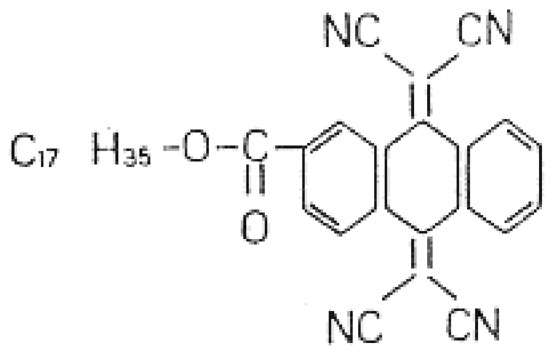
0040-6090/94/$7.00
SSDI 0040-6090(93)04179-V



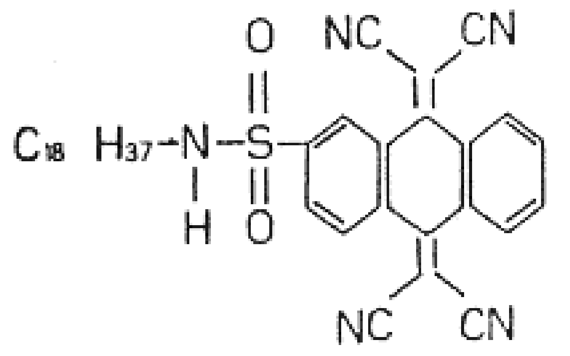
hexadecyltetracyanoquinodimethane (C16-TCNQ)



octadecyltetracyanoquinodimethane (C18-TCNQ)



heptadecyloxycarbonyltetracyanoantraquinodimethane (C17-OC-TCNAQ)



octadecylaminosulphonyltetracyanoanthraquinodimethane (C18-AS-TCNAQ)

Mixed donor–acceptor monolayers with compositions of C17-DMTTF:C16-TCNQ = 1.3:1, C16-BEDT-TTF: C16-TCNQ = 1.3:1, C16-BEDT-TTF:C17-OC-TCNQ = 10:1 and C16-BEDT-TTF: C18-AS-TCNAQ = 10:1 were investigated as well.

The solutions of the compounds in a mixture (2:1) of hexane and chloroform were prepared in concentrations of 0.33 mg ml^{-1}. The measurements were carried out at the MDT 4000 LB trough with a surface potential unit. Pure distilled water and solutions containing 10^{-3} M KCl or 10^{-4} M $FeCl_3$ were used as subphases. The compression speed was equal approximately to 0.3 nm^2 min^{-1} per molecule.

Surface potential measurements were carried out by the Kelvin technique using a resonance amplifier and synchronous detector in a measuring circuit, which ensure a sensitivity of 2.5 mV at an area of the vibrating electrode of 1 cm^2 and at a distance between the electrode and the water surface of 0.5–1 mm. The amplitude of electrode vibrations was equal to approximately 0.1 mm at a frequency of 400 Hz. A reference HgCl–Hg electrode was used in the input circuit.

3. Results and discussion

Results of the measurements are presented in Tables 1–3. Examples of surface pressure–area isotherms and surface potential curves are shown in Fig. 1.

TABLE 1. Results of the study of one-component monolayers on the surface of distilled water

	Area per molecule (nm^2)	Surface potential (mV)	Stability[a]
C16-BEDT-TTF	0.27	1400	Stable
C16-EDT-PDT-TTF	0.33	1300	Stable
C17-DMTTF	0.25	920	Non-stable
C16-TCNQ	0.20	−145	Non-stable
C18-TCNQ	0.18	−10	Non-stable
C17-OC-TCNAQ	0.37	210	Stable
C18-AS-TCNAQ	0.37	250	Stable

[a] The monolayer is considered to be stable (suitable for deposition) if the value of the area per molecule after relaxation diminishes by less than 2% during 1 min at a surface pressure 30% below the collapse value.

TABLE 2. Properties of mixed monolayers spread on the surface of distilled water

	Area per molecule (nm^2)	Collapse pressure (mN m^{-1})	Surface potential (mV)
C16-BEDT-TTF: C16-TCNQ = 1.3:1	0.38	40	390
C16-BEDT-TTF: C17-OC-TCNAQ = 10:1	0.35	35	1400
C16-BEDT-TTF: C18-AS-TCNAQ = 10:1	0.34	38	1470
C17-DMTTF: C16-TCNQ = 1.3:1	0.40	40	650

TABLE 3. Areas per molecule and surface potential values for C16-BEDT-TTF and C16-TCNQ monolayers spread on different water subphases

	Area per molecule (nm^2)		Surface potential (mV)	
	C16-BEDT-TTF	C16-TCNQ	C16-BEDT-TTF	C16-TCNQ
10^{-7} M KCl	0.27	–	1410	–
10^{-3} M KCl	0.30	0.24	1490	−205
10^{-4} M $FeCl_3$	0.28	–	1575	–

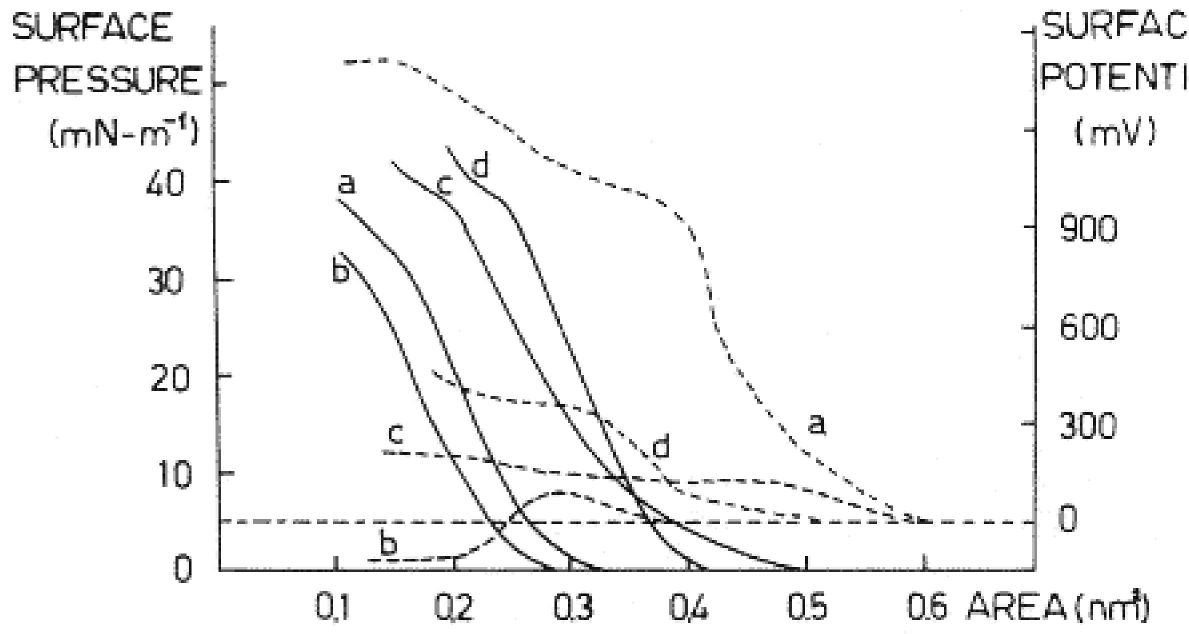


Fig. 1. Surface pressure–area isotherms (——) and potential curves (- - -) of C16-BEDT-TTF (curves a), C16-TCNAQ (curves b), C17-OC-TCNAQ (curves c) and C16-BEDT-TTF mixed with C16-TCNQ in the ratio of 1.3 to 1 (curves d) on distilled water.

Spreading of the monolayers of C16-BEDT-TTF, C17-DMTTF, C16-TCNQ and C18-TCNQ at the air–water interface is not satisfactory because the values of the area per molecule are less than those obtained in other experiments described below as well as those predicted by electron diffraction data [11, 12]. Moreover, monolayers of the last three compounds are not stable so that additional defects arise under compression. Really, according to these data, a film with mean thickness 45%–90% more than that of one monolayer (depending on the compound) is formed. However, such a layer can be considered for many experiments as a monolayer with included bulk aggregates. Indeed, the minimum thickness of bulk defects arising during spreading is equal to three monolayers and they can occupy 22%–45% of the maximum monolayer area, but this value is 2–3 times less in reality because more thick bulk aggregates arise as well. For C16-BEDT-TTF films, this estimation can be obtained, for example, from transmission electron microscopy data presented in ref. 12. Under such conditions, surface potential measurements, in particular, give information in practice about the monolayer area since bulk aggregates consist of bilayers arranged parallel to the water surface, which do not provide a significant signal because of the opposite directions of the dipole moment normal components of the molecules in neighbouring monolayers.

Among the three donors listed above, C16-BEDT-TTF seems to be the most promising for deposition of highly conductive films.

The best conductivity of approximately $2\ \Omega^{-1}\ \mathrm{cm}^{-1}$ is obtained when using water subphase with 10^{-4} M concentration of $FeCl_3$ [13]. Small additions of C17-OC-TCNAQ or C18-AS-TCNAQ acceptors into C16-BEDT-TTF monolayers do not change the conductive properties of the deposited films but improve considerably the quality of spreading because the value of the area per molecule increases. In this case a uniform monolayer is formed due to strong interaction of acceptor molecules with the donor matrix on the one hand and with water through formation of hydrogen bonds on the other hand. Spreading of C16-EDT-PDT-TTF monolayers is satisfactory. This donor shows the same properties at the air–water interface of C16-BEDT-TTF, but conductivity of the LB films appears to be approximately 5 times less.

A way to suppress formation of bulk aggregates in the monolayers is the use of mixtures of donor and acceptor molecules in approximately equal ratios as was previously demonstrated for mixtures of C16-TCNQ with C17-DMTTF or C16-BEDT-TTF. (The films with the best morphology are deposited when their ratio is equal to 1.3.) The areas per molecule increase in this case also.

All donor monolayers show high positive surface potential. In the case of C16-BEDT-TTF on distilled water this value is equal to 1400 mV. The introduction of KCl in water in a considerable concentration (10^{-3} M) does not change the surface potential within the accuracy of the experiment, thus showing that the monolayer is practically neutral. However, the LB films are conductive without doping. This fact can be explained by formation of charge transfer salt with some dissolved impurity in an uncontrolled way. If the solution of $FeCl_3$ is used as subphase, formation of salt with impurities is suppressed with high probability because the value of the surface potential changes, and the conductivity of the deposited film becomes high and reproducible. New charge transfer salt is formed. Introduction of KCl in water shows that the monolayer is neutral as well.

In any case, a considerable value of surface potential should be produced by the dipole structure of the molecule under such conditions. However, separate C16-BEDT-TTF molecules cannot possess big dipole moments because the donor fragment is practically symmetrical and the dipole moment of the hydrocarbon chain is equal to approximately 0.4 D only. Two factors can change the dipole moment of a molecule at the air–water interface. These are the charge transfer salt formation mentioned above and the different degrees of depolarization of the C–S bonds with a big dipole moment near the water surface and far from the latter. According to the approach developed by Myagkov [14] dipoles in contact with water are in a medium with a dielectric constant equal to approximately 10–11 while those near the hydrophobic matrix are in a medium with a dielectric constant of 2–4. If the main axis of the donor fragment is tilted with respect to the normal to the layer plane, a big projection of dipole moment along the normal appears, due to the different degrees of depolarization. The influence of this factor is confirmed by the rather large surface potential of the C17-DMTTF monolayer because LB films produced from this compound when pure water is used as subphase are not conducting and no charge transfer salt is formed.

A small addition of C17-OC-TCNAQ and C18-AS-TCNAQ acceptors into a C16-BEDT-TTF matrix does not change the surface potential in practice. Thus the influence of these additions on monolayer structure or on charge transfer formation is negligible. The only function of these acceptors is the stabilization of the monolayer. The surface potential curve of the monolayer of C16-TCNQ mixed with C17-DMTTF in the ratio of 1 to 1.3 looks like a simple superposition of the curves for one-component monolayers. For this reason the structure of molecular stacks in one-component and mixed monolayers must be approximately the same, as is confirmed in other works [8], and the dipole moment arising due to charge transfer is approximately parallel to the layer plane. However, it appears that this moment possesses a small projection on the normal to the layer plane. Indeed, for a monocomponent monolayer, the surface potential can be expressed as

$$\Delta V = N\mu_n/\varepsilon_0 \tag{1}$$

where N is the surface concentration of the molecules, μ_n is the normal projection of the dipole moment of the molecule, and ε_0 is the vacuum permittivity. In the absence of any changes providing the appearance of an additional normal component of the dipole moment, the contributions of the different components to the total value of the surface potential could be determined. If in a mixed monolayer the ratio N_1/N_2 of the surface concentrations of the different molecules is equal to ν, these contributions are equal to

$$\begin{aligned}\Delta V'_0 &= \Delta V_0/(1 + A_1/(\nu A_0))\\ \Delta V'_1 &= \Delta V_1/(1 + \nu A_0/A_1)\end{aligned} \tag{2}$$

where ΔV_0 and ΔV_1 are the surface potential values measured for monocomponent monolayers, and A_0 and A_1 are appropriate areas per molecule. In the case of C17-DMTTF mixture with C16-TCNQ the A_0 and A_1 values measured by the electron diffraction technique [11] are equal to 0.455 nm^2 and 0.389 nm^2 respectively. Calculations with surface potential values from Table 1 and ν of 1.3 give us the sum $\Delta V'_0 + \Delta V'_1$ of 500 mV, which is less by 150 mV than the surface potential of the mixed monolayer.

This difference may be caused by the normal component of the dipole moment arising from charge transfer. In accordance with the models of molecular packing patterns calculated previously for monocomponent monolayers of C17-DMTTF and C16-TCNQ in the paper cited above, the distances between closely packed stacks of the donor and acceptor molecules are equal to 0.713 nm and 0.818 nm respectively. The centre of the TTF fragment of the C17-DMTTF molecule is located approximately 0.07 nm lower than that of the TCNQ fragment of the C16-TCNQ molecule. With the additional suggestion that such stacks of donor and acceptor molecules are packed in the mixed monolayer with the same closeness, the distance between alternating donor and acceptor rows can be taken to be equal to 0.765 nm, *i.e.* the average value between 0.713 and 0.818 nm. For the model of charge transfer practically parallel to the layer plane it is reasonable to suppose also that the distributions of electron density through TCNQ and TTF fragments are approximately symmetrical with respect to their centres. Then we suggest the model shown in Fig. 2, where the difference of 0.07 nm between h_1 and h_2 determines the appearance of a normal component of the dipole moment.

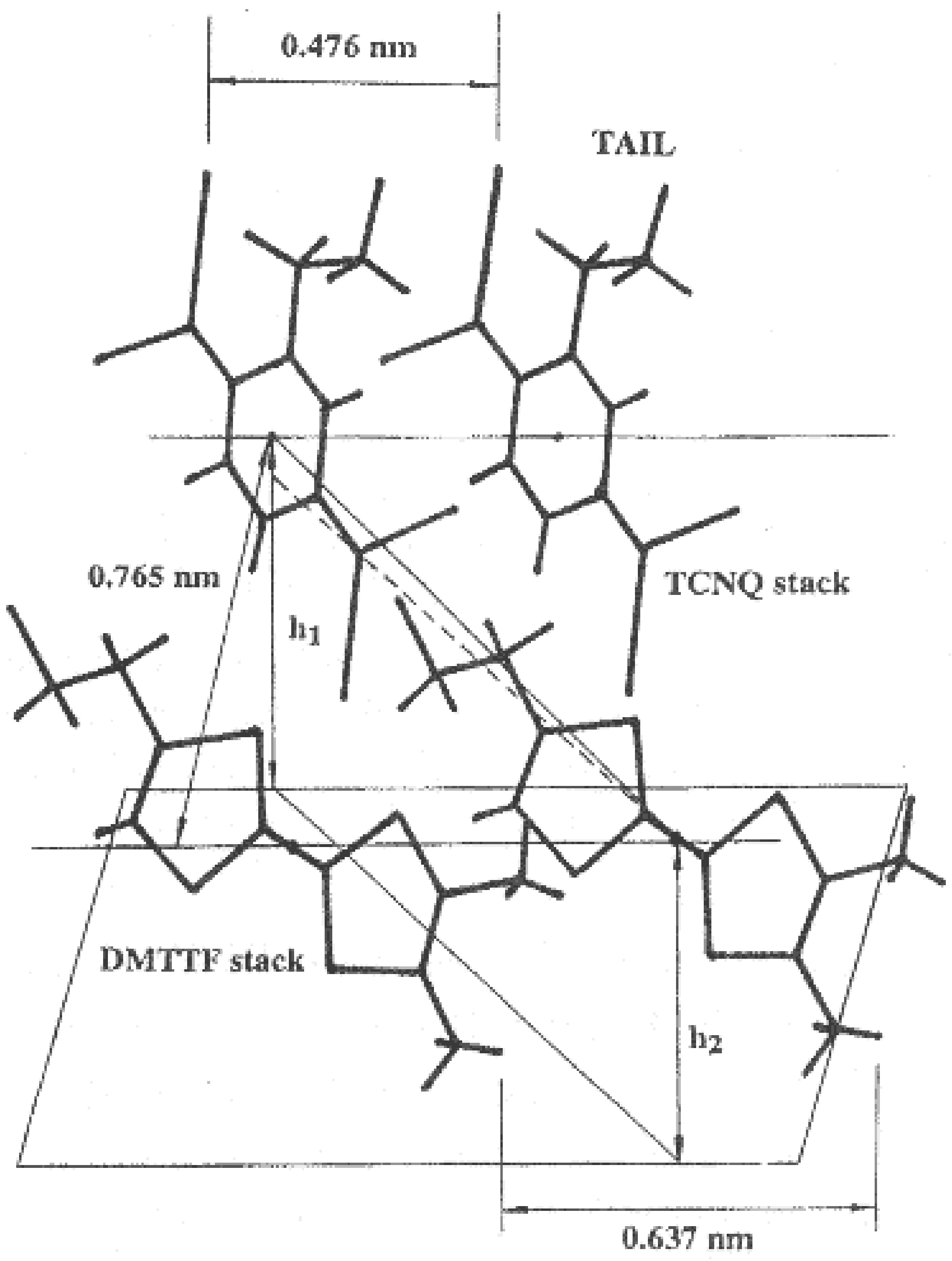


Fig. 2. Model of packing of C16-TCNQ and C17-DMTTF molecules in mixed monolayers.

The value of μ_n calculated with eqn. (1) and the total value of the dipole moment μ are equal to 0.4 D and 4.3 D respectively. In this case N was calculated proceeding from the formal molecular unit consisting of one acceptor and 1.3 donor molecules because the surplus of 30% of donor molecules used to improve the quality of deposition can be considered formally as neutral. For the proposed model the charge transfer value δ is equal to 0.11. Unfortunately, in spite of the accuracy of μ_n determination of about 10%, the errors in μ and δ determination can be considerably worse because μ and δ changes depend strongly on variations of the electron density distribution through the TTF and TCNQ groups. Evaluation of μ and δ values for several models shows that a reasonable error in their determination can be taken to be equal to approximately 40%–50%.

Another situation arises when a C16-TCNQ mixture with C16-BEDT-TTF is used. The surface potential diminishes strongly. This phenomenon may be due to the competition between a water-soluble impurity and C16-TCNQ acceptor to form a charge transfer salt of complex. In the first case the dipole moment is normal and in the second case it is parallel to the layer plane. In principle quantitative data on the dipole moment formed between the impurity and donor molecule can be obtained in such a way, but another study [12] shows that the situation is more complicated. The packing of molecules in mixed monolayers differs from their packing in one-component monolayers. Moreover, two different crystalline structures arise. These facts can also change the surface potential value.

Nevertheless, comparison of the areas per C16-BEDT-TTF molecule for the different types of monolayers presented here and measured under conditions of good spreading, as well as calculated from electron diffraction [12] and scanning tunneling microscopy [15] data including those for monocomponent films shows that the value of the area is equal to 0.37 nm^2 with an accuracy of 7%. Electron diffraction for the monocomponent film gives the value of 0.396 nm^2. Thus, under these conditions of close packing of the molecules, at least the tilt angle of the axes of BEDT-TTF groups cannot vary strongly for the different monolayers studied. Moreover, the absence of exact data on the electron density distribution over the donor and acceptor groups introduces considerable mistakes and the error in the calculations is determined on the whole by this fact.

For this reason, we proceed from the model of the C16-BEDT-TTF molecule packing pattern presented in ref. 15. (Fig. 3), in which the single important parameter for the present calculations is the tilt angle of the BEDT-TTF fragment. All the suggestions made above for the monolayers of C16-TCNQ mixed with C17-DMTTF seem to be reasonable for those of C16-TCNQ mixed with C16-BEDT-TTF as well. However, in this case, according to the models, the centres of the TCNQ and BEDT-TTF groups are located at a distance of 0.6 nm from the lower boundary of the monolayer, and no normal component of the dipole moment appears due to charge transfer.

For this monolayer the value of $\Delta V'_0 + \Delta V'_1$ is equal to 390 mV and ΔV_1 for the monocomponent C16-TCNQ monolayer equals -145 mV. Then the theoretical values ΔV_0 of surface potential for a monocomponent C16-BEDT-TTF monolayer without any charge transfer is equal to 795 mV according to eqns. (2). At the same time

$$\Delta V_0 + \Delta V_2 = 1400 \text{ mV}$$
$$\Delta V_0 + \Delta V_3 = 1575 \text{ mV} \qquad (3)$$

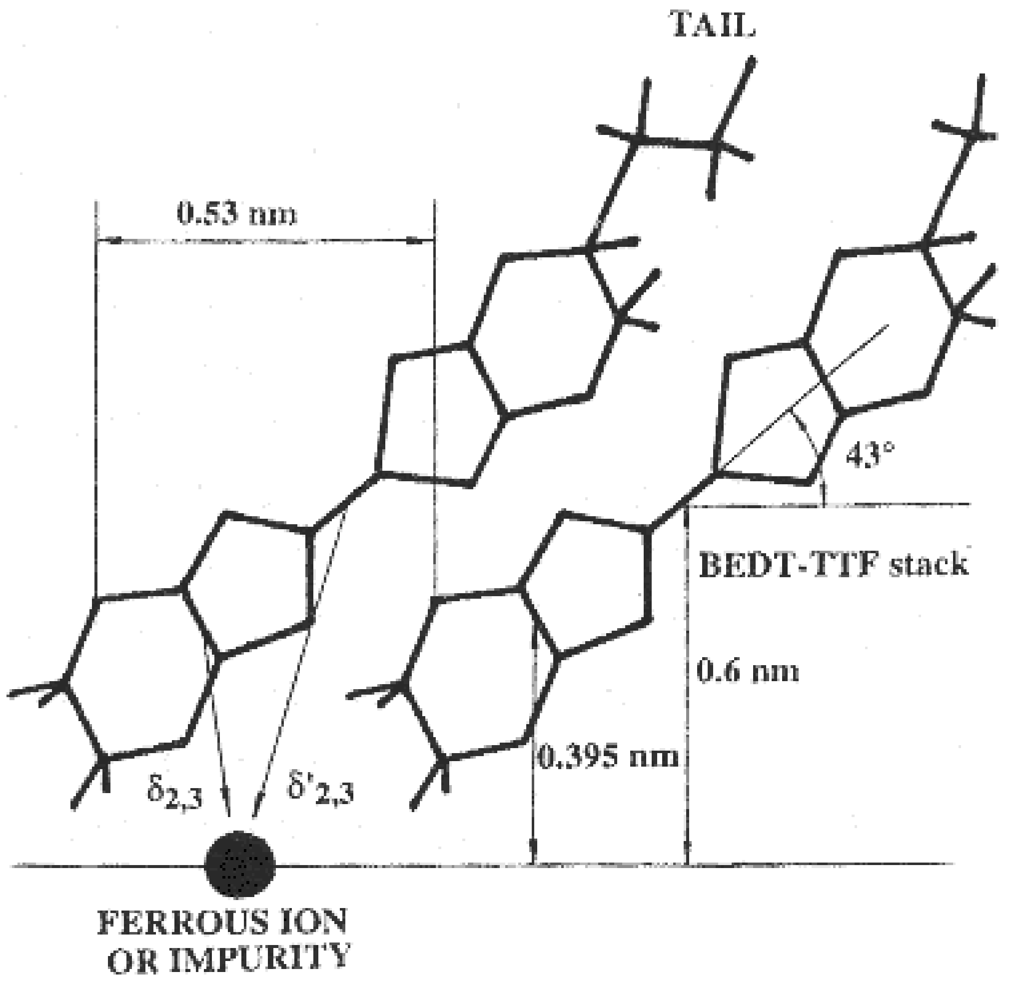


Fig. 3. Packing pattern of BEDT-TTF fragments in monolayers of C16-BEDT-TTF molecules.

where the contributions ΔV_2 and ΔV_3 to the surface potential values are caused by charge transfer to impurity and ferrous ions respectively for C16-BEDT-TTF monolayers spread at the surface of water of FeCl$_3$ solution. The values of ΔV_2 and ΔV_3 found with eqns. (3) give us μ_{n2} of 0.63 D and μ_{n2} of 0.82 D. Nonsymmetrical distributions of electron density over the BEDT-TTF group seems to be the more probable in this case because ferrous ions or impurities are located at the lower boundary of the monolayer. For example, if transfer of electrons takes place preferably from the lower part of the BEDT-TTF group as shown in Fig. 3 the values δ_2 and δ_3 of charge transfer to the impurity and ferrous ion are equal to 0.034 and 0.043 respectively. If a symmetrical distribution of electron density is adopted, the appropriate δ'_2 and δ'_3 values equal 0.022 and 0.028. Thus in this case the error can reach approximately 30%.

In spite of the low accuracy of the charge transfer value determination according to the estimations made, these values for monolayers at the air–water interface are considerably less in general than those for deposited conducting films. For example, electron probe analysis of films of C16-BEDT-TTF mixed with C17-OC-TCNAQ in the ratio of 10 to 1 deposited from 10^{-4} M solution of FeCl$_3$ [13] shows that one ferrous ion is coordinated with C16-BEDT-TTF molecules. These data give a charge transfer value of 0.11–0.2. Such a situation is not surprising because the monolayer at the air–water interface is in a liquid crystal state and considerable improvement of crystalline packing takes place after deposition on the substrate, which can result in increase of the charge transfer value.

4. Conclusions

The surface potential study of donor, acceptor and mixed monolayers which are used for deposition of conducting LB films showed the possibility of obtaining data on the character of charge transfer components involved in the process of interaction. Particular hope is given by these techniques when investigating the interaction between the surfactant molecules spread at the air–water interface and the inorganic compounds dissolved in water to search for new conducting materials. On the one hand, such a method of monolayer formation for conducting LB film deposition is considered to be very promising. On the other hand, the surface potential technique is sensitive to the normal component of the dipole moment, which changes strongly in this case depending on the technological conditions.

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