Translated from *Uspekhi Khimii*, 52 1263-1299 (1983) U.D.C. 539.233

Physical Properties and Applications of Langmuir Monomolecular and Multimolecular Structures

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The physicochemical and physical properties of monomolecular and multimolecular structures obtained by the Langmuir-Blodgett method are surveyed. Attention is concentrated on the examination of the microscopic picture of the phenomena underlying the applications of these structures in optoelectronics and micro-electronics.
The bibliography includes 122 references.

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I. INTRODUCTION

This review deals with the problem of the creation of complex molecular assemblies by the consecutive transfer of one monomolecular layer of organic molecules after another from the surface of water onto solid supports. A three-dimensional multimolecular structure is thus obtained, whose properties can be specified by the experimenter at will at least along one direction (perpendicular to the plane of the layers). It is striking that with the exception of one translated article[1] which has also become appreciably obsolete, there are apparently no reviews on this subject in the Russian language. Nevertheless, during the last two decades approximately 1000 communications, including several tens of reviews (see, for example, Refs.2–12), a special issue of the journal Thin Solid Films (1980, **68**, No.1) and a monograph[13]† have been published on this question. Molecular or supermolecular construction[9], molecular engineering[11], molecular and biomimetric electronics[8], and the creation of synthetic "organisates"[6]—these apparently constitute what is still an incomplete list of names given to this new branch of research in the field of the physics and chemistry of organic matter. We shall call this branch of science "molecular architectural design" which we believe fully reflects its essential features.

The history of such investigations began with an early study by Franklin[4,14], who carried out numerical estimates of the area of an oil film spreading on the surface of water and observed the suppression of waves in a small lake induced by the film. The results of first systematic studies on the surface tension of water contaminated by organic substances were obtained by Pockels[15]. Subsequently Rayleigh himself carried out a series of studies on the contaminated surface of water and arrived at the following fundamental conclusion[16]: "evidently the observed phenomena are outside the framework of the Laplace theory in which the medium is assumed to be continuous and their explanation requires a molecular approach".

Credit for the determination of the monomolecular nature of the layers at the liquid–gas interface is due to Langmuir. He was the first to establish the possibility of the transfer of monolayers from the surface of water onto solid supports[17]. Subsequently Blodgett perfected this technique and developed a method for the preparation of multilayer structures[18,19]. At the present time the term "Langmuir films" or "Langmuir–Blodgett films" is generally accepted and refers to monomolecular and multimolecular layers transferred from the surface of water onto a solid support.

The idea of molecular architecture, i.e. the creation of complex molecular assemblies with a predetermined architecture in order to obtain specific electrical and optical characteristics, is apparently due to Kuhn. Extensive studies on the optical[2,3] and photoelectric[5–7] properties of the Langmuir multistructures incorporating dye and phosphor molecules were carried out under his supervision in Göttingen in the 1960's–1970's. During very recent years, active studies designed to create molecular assemblies have been prosecuted by the Xerox Company (Canada)[9,12], at a number of English universities[10,11], and also in Japan[8]. There exist also Soviet publications on this topic (see, for example, Refs.20–23).

Nowadays molecular architectural design has aroused the interest of investigators in most varied branches of science. From the standpoint of physics, it gives rise to the possibility of investigating the properties of two-dimensional solid and liquid-crystal structures and microscopic interactions of molecules at rigorously controlled distances from one another and with a rigorously controlled mutual orientation. From the standpoint of chemistry, the possibility of studying the anisotropy of the reactivity of molecules and also of carrying out chemical reactions with molecules fixed in a specially selected matrix are of interest.

For biology, monomolecular and multimolecular structures are primarily systems which model cell membranes. For engineers working in the field of electronics, molecular architecture opens the way to the creation of fundamentally new instruments with spatial resolution at the molecular level by analogy with biological structures[7,8]. The Langmuir method (and also its variant using the adsorption of molecules from solution) is at present one of the most promising ways of creating molecular assemblies and it undoubtedly has a great future.

In the present review, attention is concentrated on the properties of monomolecular and multimolecular layers deposited on solid supports. We shall therefore scarcely discuss the behaviour of monolayers on the surface of water and the general problems of the application of surfactants.

† See also Thin Solid Films, 1983, **99**, Nos.1–3, 1.

These problems have been examined in detail in a monograph[24]. Nor shall we be concerned with the properties of artificial lipid double layers to which an extensive literature has been devoted[25,26]. We have endeavoured to devote much space to the discussion of new ideas having a direct bearing on molecular architectural design avoiding the quotation of numerous specialist investigations. Instead the reviews already mentioned will be widely used[2-12].

Certain compounds used in molecular architectural design.

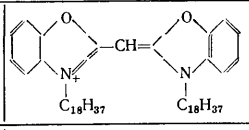
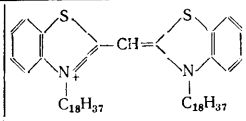
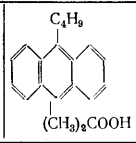
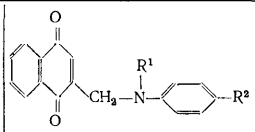
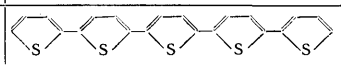
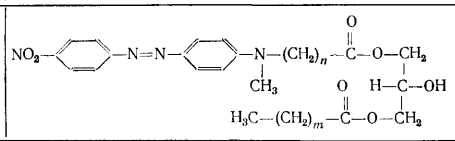
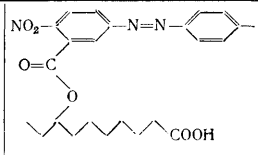
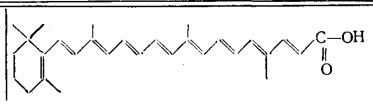
No.	Chemical formula	Name	Refs.	Remarks
(I)	$CH_3(CH_2)_nCOOH$	aliphatic acid	[1]	classical objects for the preparation of Langmuir films
(II)	$CH_3(CH_2)_{16}COO\backslash$ $CH_3(CH_2)_{16}COO/ Ba^{2+}$	barium stearate	[1]	ditto
(III)	$C_{17}H_{35}COOCH_3$	methyl stearate	[28]	stable Langmuir films
(IV)	$CH_3(CH_2)_{14}COO-CH_2$ $CH_3(CH_2)_{14}COO-CH_2$ $(CH_3)_2N-(CH_2)_2(PO_3)-O$	dipalmitoylphosphatidylcholine (artificial lecithin)	[29, 30]	model compound for artificial two-layer membranes
(V)	$(CH_3)(CH_2)_n-C\equiv C-C\equiv C-(CH_2)_nCOOH$	diacetylene derivatives	[10, 11]	compounds polymerising on irradiation with ultraviolet light
(VI)		3,3'-dioctadecyloxacyanine	[2, 6, 33]	(1) energy donor; (2) dichroism on the cleavage plane of crystalline gypsum
(VII)		3,3'-dioctadecylthiacyanine	[6]	energy acceptor, electron donor
(VIII)		10-anthryl-9-butylpropionic acid	[34]	electrophosphor
(IX)	 $R^1 = H,\ R^2 = OC_{18}H_{37};\ R^1 = C_{14}H_{29},\ R^2 = H$	autocomplexes based on 1,4-naphthoquinone	[35]	donor-acceptor properties, intramolecular charge transfer
(X)		quinquethienyl	[85]	dichroism
(XI)		3-*o*-acyl-1-*o*-ω-(*N*-methyl-4'-nitrophenylazophenylamino)acylglycerol	[5, 32]	conformational transitions
(XII)		12-(4'-dimethylamino-4-nitroazo-3-benzoyl)stearic acid	[31, 32]	"molecular conductor"
(XIII)		trans-β-apo-8'-carotenoic acid	[56]	ditto

Table Cont'd...

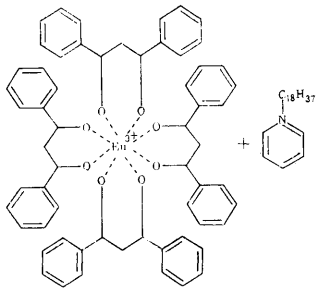
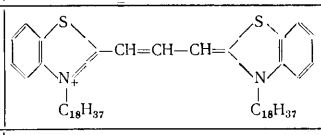
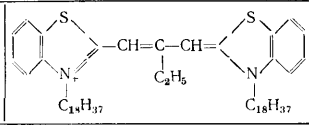
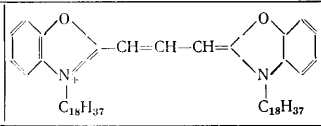
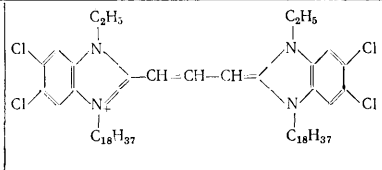
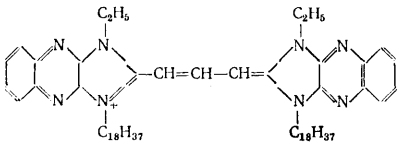
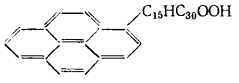
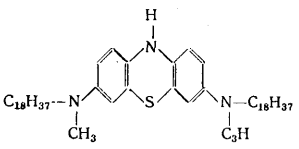
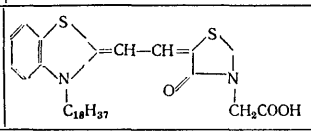
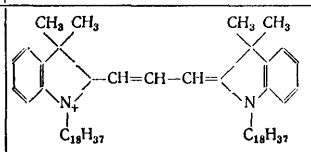
No.	Chemical formula	Name	Refs.	Remarks
(XIV)		mixture of *N*-octadecylpyridine with the dibenzoyloctane complex of europium	[3]	luminescence
(XV)	$C_{18}H_{37}O$—⟨⟩—N=N—⟨⟩—R R = SO_2NH_2, COOH, CN и др.	*p*-substituted derivatives of octadecyloxyazobenzene	[23]	"spontaneous" polarisation
(XVI)		[bis(3-stearylbenzoxazole(2)] trimethinecyanine	[6, 31]	energy acceptor
(XVII)		9-ethyl-3,3'-dioctadecylthiacarbocyanine	[33]	dichroism on the cleavage plane of a crystal
(XVIII)		[bis(3-stearylbenzoxazole(2)] trimethinecyanine	[1]	energy acceptor
(XIX)	$C_{18}H_{37}O$—⟨⟩—OH	*m*-octadecyloxyphenol	[80]	pyroeffect
(XX)	$C_{18}H_{37}$—N⁺⟨⟩—⟨⟩—N⁺—$C_{18}H_{37}$	distearylbipyridylium salt (viologen)	[6]	electron acceptor
(XXI)		5,5',6,6'-tetrachloro-3,3'diethyl-*N*,*N*'-dioctadecylbenzimidocarbocyanine	[2]	electron donor
(XXII)		3,3'-diethyl-*N*,*N*'-dioctadecylbenzopyrazinoimidocarbocyanine	[6]	electron acceptor
(XXIII)		ω-1-pyrenylpalmitic acid	[5]	electron acceptor
(XXIV)		leuco-form of Stearylene Blue	[5]	electron donor

Table Cont'd...

No.	Chemical formula	Name	Refs.	Remarks
(XXV)		5-[1'-(3''-octadecyl-2''-benzothiazolinylidene)ethylidene-2'-rhodanine] 3-acetic acid	[87]	photoconduction sensitiser
(XXVI)		*N,N'*-dioctadecylindocarbocyanine	[54]	electron donor

II. PHYSICOCHEMICAL ASPECTS AND TECHNIQUE OF THE PREPARATION OF MONOLAYERS AND MULTILAYERS

1. Amphiphilic Compounds

In order to obtain Langmuir films from any one substance, it is in the first place necessary that it should form stable monomolecular layers on the surface of water. This condition is as a rule satisfied by molecules with a polar hydrophilic "head" and a long lipophilic (i.e. soluble in fats or hydrophobic) hydrocarbon "tail". Such molecules are called biphilic or amphiphilic.

Classical examples of amphiphilic compounds are aliphatic acids [see, for example, compound (I) in the Table] or their salts (soaps) [compound (II)]. The polar heads of these molecules are smoothly incorporated in the local water structure (we have in mind the short-range structural order). On the other hand, the hydrophobic hydrocarbon tails are not incorporated in the water structure, since the hydrogen bonds in liquid water would have to undergo a rearrangement to avoid falling within the region occupied by the hydrocarbon tail; such a structural rearrangement decreases the entropy of the system and is therefore unfavourable. Thus the hydrophobic effect does not presuppose the presence of any special repulsion forces between water and hydrocarbon molecules and appears solely due to the mutual attraction of the water molecules leading to the "expulsion" of the hydrocarbon to the outside[27]. As a result, a monolayer of molecules of the amphiphilic substance, whose hydrocarbon tails are "forced out" into the gas phase while the polar heads are in the liquid phase, arises on the surface of water. A small proportion of the molecules are then in the bulk of the liquid, since the solubility of amphiphilic compounds in water is usually 10^{-6}–10^{-10} M depending on the length of the hydrocarbon tail: an increase in the length of the tail by two carbon atoms reduces the solubility approximately by an order of magnitude.

Apart from aliphatic acids and their salts, stable monolayers on the surface of water are formed by ethers[28], the phospholipids used to obtain artificial two-layer membranes[29,30], certain diacetylenes capable of polymerisation[10,11], and also a number of dyes[31–33], aromatic compounds[34], and autocomplexes[35] with a wide variety of structures but virtually always possessing a long hydrocarbon chain (quinquethienyl is an exception[85]). Examples of the corresponding compounds are presented in the Table [see compounds (III)–(XII)].

There exist also a series of biologically active compounds such as cholesterol, chlorophyll, various proteins, etc., which form monomolecular layers capable of being transferred from the surface of water on to solid supports[1]. Many compounds which do not form monolayers themselves are readily incorporated in the structure of Langmuir monolayers of other compounds, in particular aliphatic acids. Examples of dyes of this kind are quoted in a review[2].

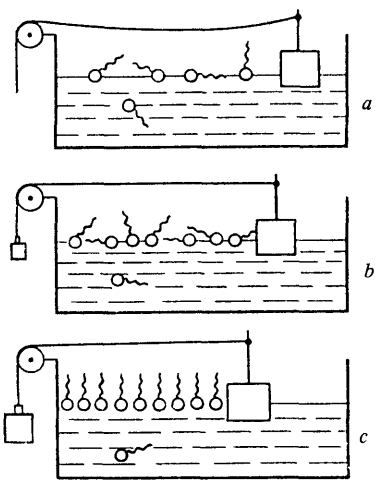


Figure 1. The molecules of an amphiphilic compound on the surface of water: *a*) in the two-dimensional "gaseous" phase; *b*) in the two-dimensional "liquid" phase; *c*) in the two-dimensional "liquid crystal" phase.

2. The Polymorphism of Monolayers

At a low concentration of the amphiphilic compounds on the surface of water the monomolecular layer is not continuous (Fig. 1*a*). Their molecules hardly interact, their tails above the surface of water are oriented at random, and such a phase may be regarded as a two-dimensional gas by analogy with the usual gas phase. If the surface area occupied by the amphiphilic molecules is reduced by means of a floating barrier, they initially approach one another but remain oriented at random (Fig. 1*b*). Such a phase may be called a two-dimensional liquid. With increase of pressure from the

side of the floating barrier, the amphiphilic molecules acquire orientation order but retain the ability to migrate within the plane of the layer. There is then no long-range positional order and the new phase is a two-dimensional liquid crystal (Fig. 1c) equivalent to one (polar) layer of a smectic liquid crystal[36,37]. Further increase of the surface pressure leads to the "puckering" of the monolayer or its collapse. In certain cases after the collapse there is a possibility of two-, three-, or four-layer structures[38].

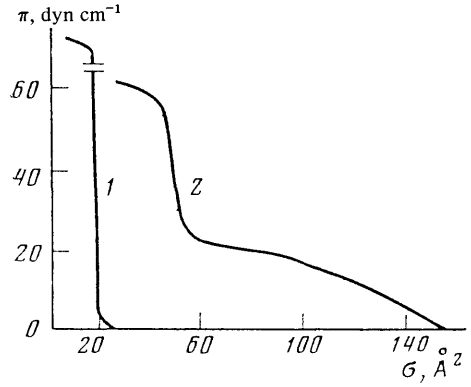


Figure 2. The π–σ isotherms for arachidic acid (curve *1*) and the dye (VII) (curve *2*).[2]

The sequence of phase transitions or the polymorphism of the monolayer can be investigated by following the relation between the surface pressure and the area occupied by the monolayer. Here there is an analogy with the equation of state for a normal three-dimensional substance and one usually measures π–σ isotherms, where π is the surface pressure in dynes per unit length of the floating barrier and σ is the area per molecule. Examples of such isotherms are presented in Fig. 2 for arachidic acid [compound (I) in Table, $n = 18$] and a dye (VII) which has two hydrocarbon chains attached to the side of the chromophore. It is clearly seen from Fig. 2 that from the very beginning the arachidic acid molecules occupy an area approximately equal to the cross-sectional area of the hydrocarbon chain (approximately 20 Å²), i.e. they virtually "stand" vertically on the surface of water. The transition from the "gas" phase to the "liquid crystal" phase takes place almost instantaneously, by-passing the "liquid" phase. For the dye (VII), the situation is different: before the hydrocarbon tails stand at right angles to the surface (to which $\sigma = 50$ Å² corresponds), there is a gradual growth of the surface pressure reflecting the interaction of the molecules which have not yet been oriented ("liquid" phase). In fact the isotherm for the dye (VII) shows two phase transitions, one at $\sigma = 150$ Å², which is approximately equal to the area of the molecule with the hydrocarbon chains lying on the surface of water, and the other at $\sigma = 50$ Å², which corresponds to the cross-sectional area of two vertically oriented chains. Furthermore, curve *2* (Fig. 2) reveals the collapse of the monolayer at $\sigma = 30$ Å².

A more complex example of polymorphism is presented in Fig. 3. According to Heeseman[32], a rearrangement of the conformation of the molecule of the azo-dye (XI) with increase of surface pressure may be observed. The molecular geometries are illustrated schematically in Fig. 3 in the corresponding part of the isotherm.

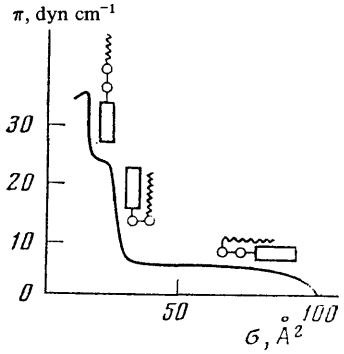


Figure 3. The polymorphism of a surface-active azo-dye (XIII) monolayer. Rectangle—azo-fragment; circles—ester groups; wavy lines—hydrocarbon chains[32].

At a specified temperature it is possible to achieve the required phase state of the monolayer by specifying a particular surface pressure. This can be done automatically by establishing an electrical connection between the motor moving the barrier and the surface pressure measuring device. The latter usually consists of a Wilhelmy balance, which measures the surface tension (the surface pressure is the difference between the surface pressures of the clean water surface and the surface covered by a monolayer of the surfactant).

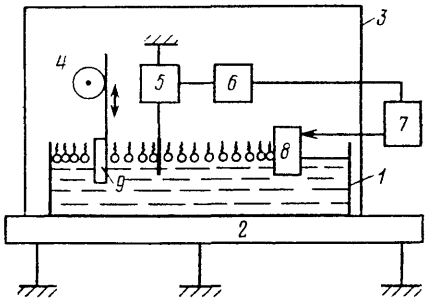


Figure 4. Device for the deposition of Langmuir–Blodgett films: 1) bath; 2) stand on shock absorbers; 3) protecting jacket (transparent); 4) mechanism for the raising and lowering of supports *9*; 5) Wilhelmy electric balance; 6) motor control circuit; 7) motor controlling the mobile barrier *8*.

3. The Langmuir–Blodgett Method

In order to obtain a monolayer, the surfactant is dissolved in a volatile solvent (for example, in chloroform) and is deposited dropwise on the surface of specially purified doubly

distilled water. The solution spreads on the surface and the solvent volatilises. The residual surfactant is compressed by the floating barrier until a continuous film is obtained. The instant of the attainment of the liquid crystal phase state of the monolayer can be detected by means of the Wilhelmy balance; after that one monolayer after another is transferred in succession onto the solid support. This requires the application of a mechanical device, which slowly (at a rate of several mm per minute) lowers or raises the solid support through the surface of the monolayer[17,18]. As the monolayers are deposited consecutively onto the support, the amount of substance on the surface of water naturally diminishes and the floating barrier must be moved automatically to keep the surface pressure constant. The general schematic illustration of the corresponding apparatus is shown in Fig. 4.

Depending on the direction of motion of the support through the monolayer, it is possible to obtain Langmuir films with different orientations. Usually three types of layers are distinguished: two polar layers of types *X* and *Z* and one symmetrical non-polar layer of type *Y* (Fig. 5). In order to deposit the first monolayer of type *X* or *Z*, the support must be hydrophobic or hydrophilic respectively. It is noteworthy that multilayers of type *X* or *Z* cannot always be obtained by the experimenter at will. In many instances, for example, when attempts are made to obtain layers of the *X* type with aliphatic acids, *Y* layers are obtained. This means that the molecules can "capsize" during the deposition of the monolayer. The mechanism of the capsizing process is at present unknown although numerous studies are being devoted to it[1,39]. In general the technique of preparation of Langmuir films still requires much skill from the experimenter, because the quality of the films is influenced by an unduly large number of factors, among which the most important are (a) the purity of water and general cleanliness of the apparatus, (b) the pH of the buffer (i.e. aqueous) solution, (c) the temperature, (d) the preparation of the support, (e) the rate of deposition and variation of the surface pressure, and (f) the absence of mechanical vibrations in the system.

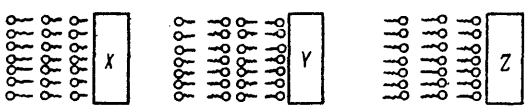


Figure 5. Types of multilayers obtained in accordance with the direction of motion of the plate through the surface of water.

X-Ray diffraction and electron diffraction studies have shown that the Langmuir films frequently have a solid crystal structure[1,40]. This means that, in the course of the deposition of the film, the substance as a rule crystallises although it may be in a vitreous state. However, the orientational order in a liquid crystal phase, including the polar order, persists in the solid crystal phase (with the exception of the case of the capsizing of molecules already mentioned). Thus one obtains ultimately solid multilayer layers with a predetermined composition, thickness, and orientation. This constitutes the uniqueness and value of the Langmuir–Blodgett technique.

In recent years the Langmuir method has been appreciably improved. For example, successful attempts have been made to obtain multilayers of different molecules. Double[41] and also multisector[42] baths, permitting the automatic transfer of supports from one solution to another and conversely, have been developed for this purpose. This increases sharply the productivity of the apparatus and in addition permits the avoidance of the contamination of the specimens.

4. Other Methods of Preparation of Multilayer Structures

Stable monomolecular layers on solid supports can also be obtained by the adsorption of surface-active molecules from the liquid phase[43]. For example, solid films of aliphatic acids or their perfluoro-derivatives are easily adsorbed on glass covered with aluminium or nickel and immersed in a solution of these acids in hexadecane[5]. Monolayers of trichloro-n-octadecylsilane can also be obtained by adsorption. Successive repetition of this procedure can give rise to a multimolecular layer. This method is technically simpler than the Langmuir method but it imposes more stringent requirements on the structure of the corresponding molecules. Monomolecular layers of aliphatic acids on solid supports can be obtained in principle also by the thermal sputtering method[4].

The introduction of surface-active dyes into the solution already containing aliphatic acid molecules can yield mixed monolayers in which the dye molecules are incorporated in the matrix of aliphatic acids. With the aid of another solvent, it is possible "to wash out" the dye molecules selectively from the monolayer leaving behind the so-called skeletised monolayer. Skeletised monolayers possess a "memory" of their initial structure, which can be restored by the readsorption of the same dye or another one with a suitable molecular geometry.

Monolayers and multilayers prepared by the Langmuir technique can be transferred from one solid support to another by the contact method illustrated schematically in Fig. 6[6,7]. For example, a flexible poly(vinyl alcohol) film can be conveniently used as the second support[2]. It is of interest that the information recorded on one support (in the form of, for example, a certain distribution of dimers and monomers) can be "copied" onto another plate[7].

III. ELECTRICAL PROPERTIES OF LANGMUIR FILMS

1. Dielectric Characteristics

Fairly numerous studies have been made for the dielectric properties of multimolecular layers in view of their wide scale employment as calibrated dielectric plates in transistors based on metal–dielectric semiconductor structures[11]. Stringent requirements must be met by the dielectric plates as regards the reproducibility of their capacitance, stability, and resistance to electrical breakdown.

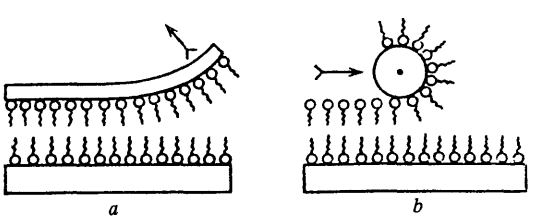


Figure 6. Illustration of the principle of the separation (*a*) and contact deposition (*b*) of a monolayer[7].

The dielectric properties of Langmuir films are usually investigated in sandwich structures with a lower aluminium electrode. The aluminium is deposited by vacuum sputtering onto a glass support, the multimolecular layers are introduced in succession, and then the upper metallic electrode is deposited by vacuum sputtering. The lower electrode can also consist of a sputtered tin film[44] or transparent semiconducting layers of tin dioxide[23], as well as other semiconducting materials[11]. The application of other metals (other than tin and aluminium) frequently leads to non-reproducible results. The Langmuir films exhibit poor adhesion to noble metals.

Carefully prepared (defect-free) sandwich structures usually withstand the application of electric fields up to 5×10^6 V cm^{-1}, which is characteristic of the best of the known dielectrics[45,46]. The reciprocal of the capacitance C^{-1} of the sandwich structures varies linearly with the overall thickness of the multilayer regardless of whether the number of monolayers (Fig.7*a*) or the thickness of each monolayer (Fig.7*b*) are varied.

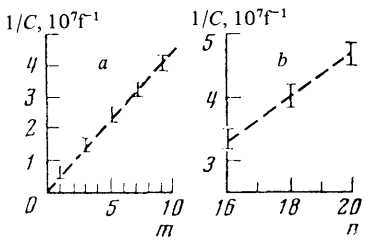


Figure 7. *a*) Dependence of the capacitance of a multilayer palmitic acid structure (number of carbon atoms $n = 16$) on the number of monolayers[8]; *b*) dependence of the capacitance of a seven-layer structure on the length of the aliphatic acid molecule with $n = 16-20$ (frequency 10^{-2} Hz; 300 K)[8].

The absolute dielectric constants of aliphatic acids at low frequencies are $\varepsilon = 2.5-2.9$ at 77–295 K.[43] Dielectric constants close to the above values of ε are expected also for dyes with hydrocarbon tails. For perfluoro-derivatives of aliphatic acids, the dielectric constants are appreciably higher ($\varepsilon = 2.9-3.5$ at $T = 77-295$ K)[43].

As frequency is varied, dispersion of ε is observed, which can be attributed to relaxation processes of different types. At frequencies below 1 Hz the slow movements of the polar COOH groups are apparently responsible for the mechanism of the relaxation of ε for aliphatic acids, while at frequencies in excess of 1 Hz the processes associated with jump movements of electrons from one monolayer to another are responsible for the relaxation[47,48]. The presence of residual water in the multilayer leads to an additional mechanism of dielectric losses[49].

2. Electrical Conductivity

At the present time there are no firmly established ideas about the mechanisms of the flow of electric current through metal–dielectric–metal structures, where the Langmuir film plays the role of the dielectric. At a specified potential at the electrodes, the current depends markedly on the thickness of the multilayer, the material of the electrodes, the temperature, the surrounding atmosphere, and naturally the material of the multilayer itself. In the latter case the presence or absence in the multilayer of molecules with a long chain of conjugated bonds plays a significant role.

The case of extremely thin films, with a thickness equivalent to one or two monolayers (which corresponds to 25–50 Å for aliphatic acids), is apparently simpler. The majority of investigators believe that the dominant mechanism of the conduction of current at temperatures in the range from room temperature downwards is tunnelling of electrons through the monolayer[45,46,50–52]. Fig.8 illustrates instances of the tunnel electron transition from one electrode to another through a potential barrier at a potential applied to the electrodes smaller and greater than the height of the barrier[52]. A characteristic feature of the tunnel mechanism is the absence of a dependence of the current on temperature and the exponential decrease of the current with increase of the thickness of the monolayer; the latter can be varied by passing from the lower homologues of aliphatic acids ($n = 14$) to higher homologues ($n = 20$). The thickness of the monolayer then changes from 21 to 28 Å and the effective conductivity diminishes approximately by 5 orders of magnitude[50]. The tunnel current is influenced significantly also by the presence of an oxide film on the metal surface; allowance for this influence is essential in the calculation of the characteristics of the energy barrier for the tunnelling electrons[46].

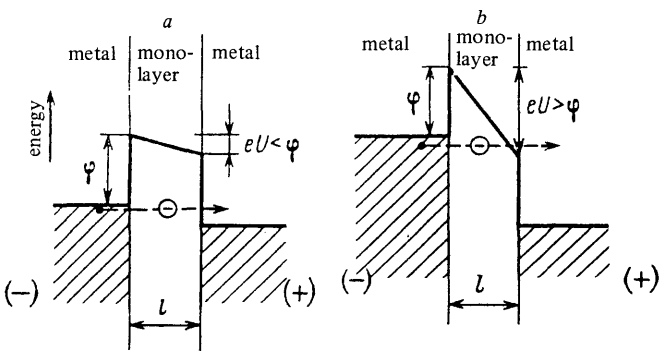


Figure 8. The tunnelling of an electron through a potential barrier at electrode potentials $U < \phi/e$ (*a*) and $U > \phi/e$ (*b*); ϕ = height of barrier; l = thickness of monolayer.

The flow of current through two monolayers in succession is apparently determined also by the tunnel mechanism at least at low temperatures[29]. In the presence of a larger number of monolayers, other processes begin to play an appreciable role. The most probable of these is the jump electron transfer mechanism. Its essential feature is as follows. It is believed that at the boundaries of the monolayers there are large numbers of surface energy states. The electron apparently moves across the multilayer from the negative electrode to the positive electrode not via a single tunnel transition (which would be already extremely unlikely when the number of monolayers exceeds three) but in separate small jumps (a jump constitutes tunnelling accompanied by thermal excitation) through each monolayer in succession (Fig.9). In this model the current decreases exponentially with increase of the thickness of each monolayer separately but with increase in the number of identical monolayers it diminishes merely in accordance with a linear law. This conclusion is in full agreement with experiment[8,53]. The picture illustrated in Fig.9 becomes appreciably more complex when

account is taken of the curvature of the barrier due to the charges bound at the boundaries between the monolayers; this effect has been taken into account[54].

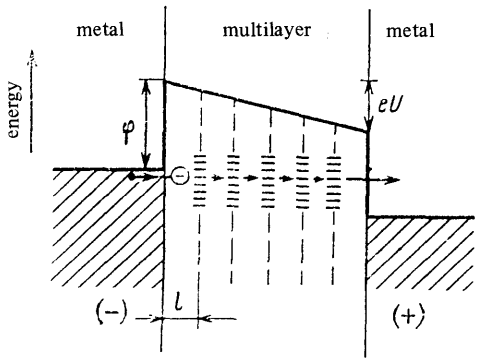


Figure 9. The jump mechanism of the electrical conduction in multilayers (l = thickness of monolayer).

Together with the jump conductivity, injected carriers associated with the emission of electrons from the electrode into the bulk of the multilayer via a contact potential barrier may make an appreciable contribution to the current[52]. This mechanism (the Schottky emission) can apparently explain the marked influence of the material of the terminals on the conductivity of the metal–Langmuir film–metal system. Nor can one rule out the possibility of the ionisation of the impurity molecules in the bulk of the multilayer by the electric field (the Poole–Frenkel mechanism)[52]. The latter effect may play a dominant role in relatively thick multilayers (tens of monolayers).

In the multilayers formed by molecules of substituted anthracene [see, for example, compound (VIII)], a sharp anisotropy of the electrical conductivity is observed. For the same electric field strength, the conductivity in the plane of the multilayer can exceed by 8 orders of magnitude the conductivity measured at right angles. The anisotropy has been explained[55] by a special type of packing of the molecules of compound (VIII) in the monolayer (like a deck of cards), which facilitates the transfer of electrons from molecule to molecule in the plane of the monolayer. However, one should also take into account the possibility of conduction via interlayer surface states, which has also been noted[8]. The passage of the current along the monolayer in the latter case does not require an activated electron jump through relatively wide barriers and the current should be significantly greater for the field directed along the plane of the monolayers.

The introduction of molecules with an extensive chain of conjugated bonds as impurities into the aliphatic acid monolayer increases the tunnel current for the monolayer. Such an experiment has been carried out[56] using carotenoic acid (XIII). Figuratively speaking, the molecules of this acid play the role of thin "conductors" which partially "short circuit" the aliphatic acid monolayer, because they have a free electronic level located below the energy level of an electron *in vacuo*, which facilitates electron tunnelling. In fact the molecules with conjugated bonds lower the height of the potential barrier for the tunnel transition. The molecules of azo-dyes (XII), whose conjugated chain is oriented at right angles to the plane of the monolayer, also influence the conductivity in a similar manner[31]. As stated above, adsorbed monolayers[43,57] can be "skeletised" by desorbing the dye molecules introduced into the monolayer beforehand. The resulting holes are responsible for the marked (approximately by an order of magnitude) increase of the tunnel current through the monolayer[51], although there is no short circuiting as a consequence of the holes being "overgrown" by a layer of the oxidised material of the electrode.

3. Inelastic Tunnelling and Tunnel Spectra

Direct proof of the tunnel mechanism for the flow of current through individual Langmuir layers is provided by the observation of the tunnel spectra of impurity states. Fig.10 illustrates elastic (1) and inelastic (2) electron tunnelling through a dielectric layer. In the latter case the tunnelling electron loses its energy on passing through the film, liberating a molecule of the main substance of the dielectric or impurity. Usually one is dealing with vibrational molecular excitations[58] and $W \cong 0.1$ eV, since the energies of the tunnelling electrons (in eV) do not exceed numerically the potentials (in volts) applied to the electrodes. However, electronic transitions with energies $W \cong 1-2$ eV can also be excited[59]; the loss of energy by the electron under these conditions gives rise to a small (~1%) anomaly on the voltage–current characteristic at an electrode potential $U = W/e$ (Fig.11*a*). If the $I-U$ curve is differentiated twice with the aid of an electronic circuit, the anomaly is revealed extremely clearly (Fig.11*b*). In the presence of a large number of varied energy states within the monolayer, the d^2I/dU^2 curve represents an elaborate spectrum of bands.

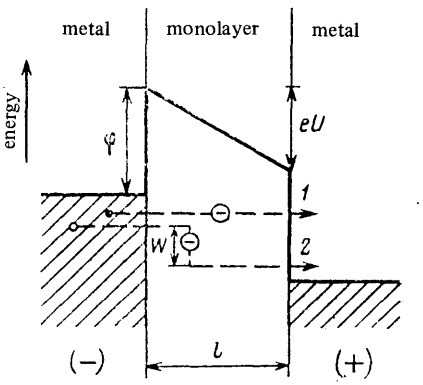


Figure 10. The elastic (curve *1*) and non-elastic (curve *2*) tunnelling of an electron through a monolayer.

The tunnel spectra can reflect the electronic structure not only of the dielectric but also the metal. In particular, the spectra reveal the energy gap characteristic of a superconductor, provided that even only one of the electrodes is a superconductor (the experiment was carried out below the critical temperature). Such observations have been made using the barium stearate monolayer as the dielectric layer[60]. The vibrational spectra of the stearic acid monolayer, obtained recently by tunnel spectroscopy, agree well with infrared and Raman spectra[61]. One cannot rule out the possibility that the method of tunnel spectroscopy will prove

suitable also for the investigation of the electronic spectra of molecules with conjugated bonds forming Langmuir or adsorption monolayers or behaving as impurities in the latter, since at low temperatures such monolayers do not undergo electrical breakdown at potentials up to 4 V,[51,60] while electronic spectra correspond to energies ≥ 1 eV.

A fairly detailed review of the electrical properties of Langmuir layers, including a discussion of the mechanisms of their electrical conduction and breakdown, has been published[62].

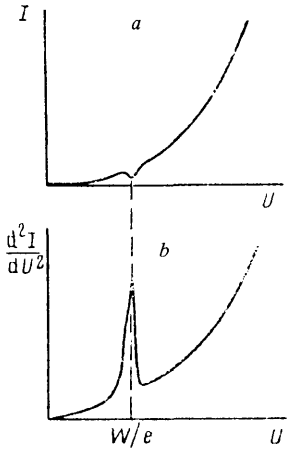


Figure 11. The determination of the characteristics of the tunnel "spectrum" with the aid of the differentiation of the voltage–current characteristic.

4. Asymmetric Structures and a Molecular Rectifier

If the electrodes with a multilayer structure are made from different metals, then in the case of symmetrical multilayers of the *Y* type (see Fig.5), a potential difference appears in the specimen as a consequence of different electronic work functions of the metals. Such a potential difference can arise even in the presence of identical (for example, aluminium) electrodes due to the different properties of the outside film on the lower and upper electrodes[63]. The potential difference due to the difference between the electronic work functions usually amounts to tenths of a volt. If approximately 200 such specimens are connected in series, then a potential of 50 V can be drawn from a battery obtained in this way[60].

It has been claimed[54] that the difference between the electron work functions leads to the electrical breakdown of sandwich structures even in the absence of an external field, provided that they consist of a single aliphatic monolayer between aluminium and barium electrodes.

Another type of asymmetry can be created by the successive deposition of monolayers of different compositions; the material of the electrodes can then be identical. For example, an unusual form of the tunnel voltage–current characteristic, corresponding to the passage of current through a three-layer structure in only one direction, has been predicted theoretically[64]. It is significant that in this case one of the monolayers must be formed by surface-active donor molecules and the other by acceptor molecules, so that the multilayer is in fact an analogue of a charge-transfer complex in which the donor and acceptor are separated by a narrow neutral bridge [the molecules of the autocomplexes (IX) are good models]. The electron current flows along the acceptor–neutral bridge–donor chain from one electrode to the other with non-elastic tunnelling in the neutral bridge. The reverse current is much smaller and the authors[64] thus predict a current rectifying effect.

So far as we are aware, there are no published experimental data concerning the observations of the predicted effect apparently owing to the difficulty of observing the tunnel current in a three-layer, i.e. relatively thick, structure. However, the rectifying effect has been noted for a photocurrent in asymmetric donor-acceptor multilayers[54]. The attempts to create specifically rectifying and subsequently also transistor multistructures may serve as classical examples of molecular architecture.

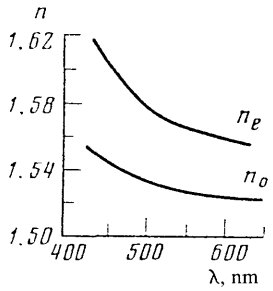


Figure 12. The dispersion curves for the refractive indices of cadmium arachidate[65].

IV. THE OPTICAL PROPERTIES OF MONOLAYERS AND MULTILAYERS

1. Reflective Indices

Langmuir films are specially interesting from the standpoint of the creation of multilayer structures for the investigation of various interference phenomena, because the thickness of a single monolayer is rigorously fixed (it amounts to 24.5 Å for barium stearate, for example[1]). Numerous studies have been made on the optical properties of multimolecular layers formed by aliphatic acid salts[1,3]. The ellipsometric method, measurements of optical transmission and reflection, interferometry and, recently, the integral-optical technique have been widely used for this purpose[10]. The optical anisotropy of multilayers has been reliably established: the refractive index for light with its polarisation vector in the plane of the multilayer (n_o) is always less than the refractive index for polarisation whose direction coincides with the normal to the film (n_e). The optical anisotropy for cadmium arachidate for example, is fairly considerable ($\Delta n = n_e - n_o \cong 0.04$). Virtually no systematic studies of the frequency dispersion of n_e and n_o have been made and reliable data are available only for cadmium arachidate multilayers (Fig.12)[65].

There exist two possibilities of adjusting n_e and n_o to prespecified values at a particular wavelength. Firstly, by varying the composition of the buffer solution, it is possible

to obtain films of salts of different metals (Cd, Ba, Mn) alternatively films made up of aliphatic acid molecules with different lengths of the hydrocarbon chain can be used. The presence of atoms of heavier metals then increases both refractive indices n_o and n_e, while an increased hydrocarbon chain length entails mainly an increase of n_e. The pH of the buffer solution also plays a significant role, determining the concentration of the metal ions in the Langmuir film[10]. It is possible to introduce various dyes into multilayers of aliphatic acids and their salts, which also alters the refractive indices. The second method consists in the skeletisation of Langmuir films. The formation of "holes" on a molecular scale lowers the values of n_e and n_o in proportion to the area occupied by these "holes". Both methods are promising for the specific construction of interference coatings, integrated optical elements, etc.

2. The Waveguide Properties of the Films

It is known that the light beam propagated in any medium with a refractive index n_1 undergoes total internal reflection at the boundary with another optically less dense medium ($n_2 < n_1$) if the angle of incidence exceeds a critical value. A light beam introduced into a thin film at a certain angle is therefore propagated along the film as in a waveguide, undergoing repeated internal reflections at the boundaries of the film with air or another medium satisfying the condition $n_2 < n_1$. This phenomenon makes it possible to achieve extremely compact (film) optical elements used in modern integrated optics[66].

The possibility of the specific variation of the refractive indices and the clear-cut determination of their thickness make Langmuir films extremely convenient materials for such purposes. The main difficulty consists in obtaining defect-free films of high optical quality, since otherwise the light beam propagated along the film is to a large extent scattered by defects, losing its intensity. The best results have been obtained currently on cadmium stearate films[10,21]. Such a film (with the refractive indices $n_o = 1.53$ and $n_e = 1.56$ at a wavelength $\lambda = 633$ nm) is deposited on a quartz support ($n_2 = 1.4571$) and is covered on top by a liquid layer of isostearic acid ($n_3 = 1.4573$). Light is introduced into the film with the aid of a prismatic device and is propagated along it with a decay of 1 dB per cm of the length of the film (i.e. is attenuated by a factor of 10 over a distance of 10 cm).

The introduction of additional monolayers absorbing light in a particular spectral range as a result of the presence of surface-active dyes makes it possible to achieve the isolation of specific spatial[67] or spectroscopic[68] components of the radiation.

Langmuir films are also used as external plates of waveguide films, made, for example of glass or poly(methyl methacrylate)[65]. In this case the geometrical properties of the beam in the waveguide (modal composition) contain information about the refractive indices of Langmuir films consisting of a small number of monolayers. The method based on the measurement of the decay of surface electromagnetic waves propagated along the boundary between dielectric and metal is even more sensitive to the optical characteristic of individual monolayers. Such waves can be excited by visible[68] or infrared[69–71] radiation.

3. Molecules "in front of a Mirror"

Molecular architecture leads to an interesting possibility of investigating a wide variety of optical interference effects. In fact we can achieve the alternation of light emitting, reflecting, and absorbing layers in accordance with a predetermined plan with a rigorous specification of their thickness in each case. If the thicknesses of the corresponding layers are comparable to the wavelength of the light, it is possible to observe a whole range of new phenomena determined by the interference and diffraction of light[3].

Suppose, for example, that a light beam is incident on a metallic mirror surface (Fig.13). The reflected wave interferes with the incident wave, giving rise to a standing wave whose nodes and antinodes are located at fixed points in space. We now imagine that a molecule of a fluorescent dye is placed at different distances from the mirror surface. Then the molecules located at the antinodes of the standing wave will fluoresce strongly, while those which are at the nodes will not fluoresce at all. Such an experiment makes it possible to discover the location of the nodes of the standing wave, which depends on the phase of the beam reflected from the mirror. Classical experiments of this kind were performed as early as the past century by Drude and Nernst using photographic emulsions as indicators of the intensity (i.e. the square of the amplitude) of the standing wave. Using Langmuir films, such experiments can be carried out with a much higher degree of accuracy.

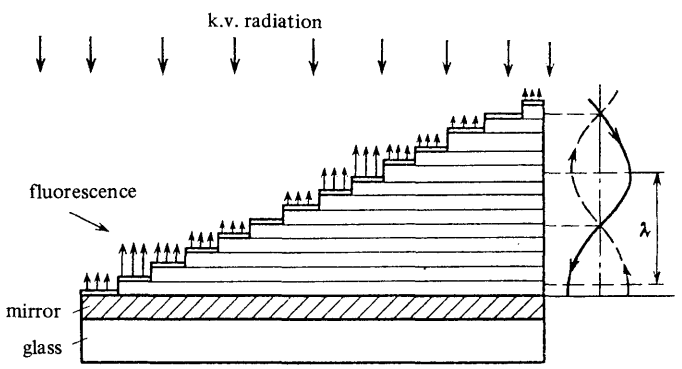


Figure 13. The Kuhn "ladder". Each "step" consists of 20 stearic acid monolayers. One of the monolayers of the fluorescent dye covers all the "steps" at once. The antinodes of the standing light wave (see the scheme on the right) are visualised with the aid of fluorescence; the fluorescence intensity is represented conventionally by the length of the vertical arrows[2].

Fig.13 illustrates the scheme of Kuhn's experiment[2]. Monolayers, for example of cadmium arachidate, were deposited on a silver mirror on a glass support in such a way that each successive monolayer occupied a smaller area than the preceding one; this results in the formation of a "ladder" of monolayers. A single monolayer of a surface-active fluorescent dye [for example, compound (VI)] is then deposited on the entire multistructure. The illumination of the multilayer from above with ultraviolet light at $\lambda = 366$ nm leads to the appearance of a very attractive striped fluorescence pattern of the dye on those sections of the "ladder" which correspond to the antinodes of the standing wave[72].

The light emitted by the fluorescent molecules located at a certain distance from the mirror can also be involved in the interference. The character of the interference then

depends on the nature of the emitter. An electric dipole, a magnetic dipole, an electric quadrupole, etc. are known to be capable of emitting. Each fluorescence band of the dye is associated with its intrinsic emitter so that there is a possibility of the transformation of the complex fluorescence spectrum of the dye as a result of interference effects. An example of such change in the spectrum is illustrated in Fig.14[3]. The dibenzoyloctane complex of europium (XIV) forms a monolayer separated from a gold mirror by a definite number of cadmium arachidate monolayers. The entire multistructure is immersed in an immersion liquid in order to avoid reflections from its surface. The complex fluoresces on excitation with ultraviolet light. Fig.14 shows that simple reflection from the mirror alters the form of the spectrum. This implies that the weak fluorescence band with a maximum at 592 nm cannot, in contrast to the band at 615 nm, be attributed to an electric dipole emitter[3]. The proximity of the molecular emitter to the metallic mirror leads to yet another remarkable effect: the fluorescence decay time begins to depend on the distance from the mirror. As a consequence of the interference of the waves, this dependence is oscillatory; when the emitter is in the immediate vicinity of the mirror ($0 < d < 500$ Å), the decay time tends to zero asymptotically.

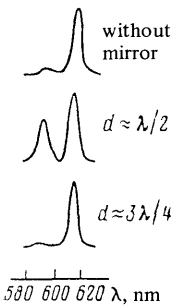


Figure 14. The fluorescence spectrum of a europium complex as a function of the distance d of the molecular emitters from the gold mirror.

By alternating the Langmuir monolayers with metallic mirrors sputtered *in vacuo*, it is possible to create a superlattice having two periods, one of which is equal to the thickness of a single monolayer and the other is equal to an arbitrarily specified distance between the metallic mirrors. The spectroscopic properties of such superlattices agree with theoretical calculations[22].

Numerous other examples of interference effects observed in the optical transmission and interaction of light for different positions of the absorbing or luminescent monolayer in a multimolecular structure have been quoted in reviews[2,3]. The method of specific construction of such multilayers makes it possible to elucidate the nature of the electronic oscillators in molecules.

4. The Dichroism of Dyes

The anisotropy of the refractive indices of Langmuir films was mentioned above. We shall consider the question of the orientation of the chromophoric chains of dye molecules which either form these films or have been introduced into monolayers of aliphatic acids as admixtures. In the usual method of the transfer of monolayers from the surface of water onto a glass or metallised surface, the monolayer or the multistructure on a solid surface is isotropic relative to the rotation of the specimen around the normal z to the layer; the z axis is the only distinct axis. When dyes are introduced into such a multilayer, light is absorbed regardless of the direction of its polarisation if the beam is incident rigorously at right angles to the surface of the multilayer.

On the other hand, chromophoric chains of the dye can be distributed in different ways, being oriented on average either at right angles to the support or in the plane of the support. The situation which is actually realised may be elucidated by studying the anisotropy of the absorption of light for layers placed at a certain angle relative to the incident beam (examples are presented in Fig.15). In the molecule of the azo-dye (XV) the alkoxy-"tail" is attached to the azo-system in the *para*-position and the entire molecule is oriented at right angles to the plane of the monolayer. Correspondingly light polarised in the plane of incidence (with an electric vector e_1—see the insert Fig.15) is absorbed more strongly than the light with the vector e_2 in the perpendicular plane, since in the former case there is a component parallel to the conjugation chain of the molecule (Fig.15*a*). The broad absorption band with $\lambda_{max} \cong 500$ nm in Fig.15*b* is associated with the polymethine dye (XVI) whose chromophores are located in the plane of the support. In this case the light with the vector e_2, also located in the plane of the support, is absorbed more intensely. The additionally introduced azo-dye (XII), absorbing in the region of $\lambda \cong 415$ nm, has a dichroism with a different sign (the absorption shoulder in the short-wavelength region is weaker), which corresponds to the perpendicular orientation of the chromophore, as in the case illustrated in Fig.15*a*. The perpendicular orientation of the chromophores has been observed also for other dyes without alkyl tails introduced as admixtures into Langmuir aliphatic acid multilayers[72]. The same orientation of the chromophores of the azo-dyes (XII) in a monomolecular layer on the surface of water (i.e. before its transfer to the support) has also been established[32].

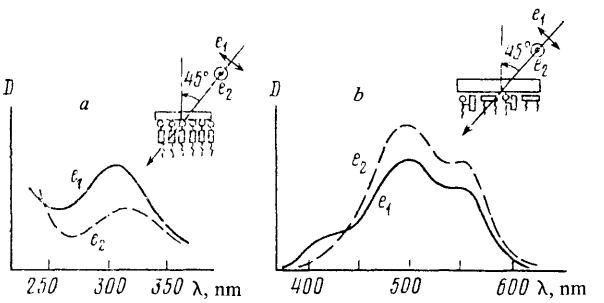


Figure 15. The dichroism of dyes with different orientations of chromophores: *a*) perpendicular orientation for the azo-dye (XV) with R = SO_2NH_2;[73] *b*) spectra of mixed monolayers of the azo-dyes (XII) and the polymethine dye (XVI) with the chromophore oriented parallel to the support[31]. The inserts illustrate the geometry of the experiment; the rectangles represent molecular chromophores.

A remarkable example of dichroism of another type has been demonstrated in a study[33] where an anisotropic surface (the cleavage plane of crystalline gypsum) was used as the support for the deposition of monolayers. In this case the molecules of the surface-active dyes (VI) and (XVII) are distributed with the chromophores not located simply in the plane of the support but along a specific direction on this plane which coincides with the orientation of one of the crystal axes of gypsum. The dichroism of such monolayers and multilayers can be easily observed also when the beam is incident at right angles to the specimen (Fig.16). The light polarised parallel to the *a* axis of the gypsum crystal is absorbed much more intensely, which indicates the orientation of the chromophore of the dye (XVII) precisely along the *a* axis. The above study[33] thus leads to the possibility of molecular architectural design in all three dimensions.

Theoretical studies of the optical properties of absorbing multilayers require allowance for the anisotropy of the refraction and absorption of light; for monoaxial structures (with an isolated *z* axis), such studies have been carried out[74,75]. For three-dimensional structures, it is necessary to employ the mathematical apparatus of the theory of crystal optics.

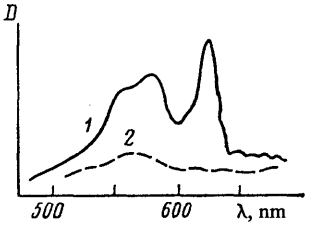


Figure 16. The dichroism of the dye (XIV) on the cleavage plane of crystalline gypsum; the polarisation vector is parallel (curve *1*) and perpendicular (curve *2*) to the *a* axis[33].

5. Spectroscopic Characteristics

Depending on the concentration of the dye in the monolayer of the surface-active substance, the type of packing of the chromophores in the monolayer, and the presence or absence of an influence of the neighbouring monolayers, the absorption and fluorescence spectra of the dye undergo significant changes, which are due primarily to the formation of different associated species. Fig.17 illustrates the transformation of the absorption spectrum of the dye (XVIII) with increase of its molar concentration in the monolayer of cadmium arachidate from 1:100 to 1:1, The increase of the intensity of the absorption band of the dimers (460 nm), associated with the suppression of the absorption band of the monomer, is clearly seen.

A further increase in the concentration of the dye (for example, its employment in a pure form without admixture of aliphatic acids) leads to an even more notable aggregation effect. Fig.16, for example, shows clearly a narrow absorption peak (λ = 625 nm), usually attributed to the parallel packing of the chromophores of the "brickwork" type (*J*-aggregate). The vibrations of the electronic oscillators of individual molecules take place in phase and are added together ensuring an intense absorption of light in a narrow spectral range.

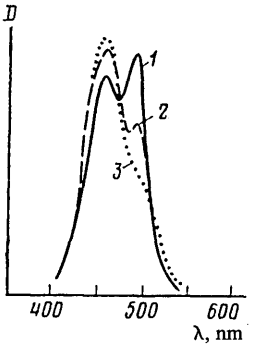


Figure 17. The equilibrium between the monomers (λ_{max} = 490 nm) and dimers (λ_{max} = 460 nm) of the dye (XVIII) in a monolayer of cadmium arachidate for different molar ratios of the two components: 1) 1:100; 2) 1:10; 3) 1:1.[2]

The spectroscopic properties of a dye in a monolayer are influenced by the molecule of the same or another dye in a neighbouring monolayer. The extent of this influence is determined by the distance between the corresponding chromophores. For example, if one monolayer contains the dye (VII) and another the dye (XVIII), mentioned above, and their chromophores are separated by alkyl chains, then the overall absorption spectrum of the two dyes constitutes a simple superposition of their individual spectra. On the other hand, if the chromophores of these two dyes are in contact, the overall spectrum is appreciably modified, i.e. exciton effects arise[2]. In a number of instances the fluorescence spectra of such systems with chromophores in contact show broad long-wavelength bands due to the formation of excited dimers (excimers). The effects of the interaction of the molecules (particularly those of chlorophyll) in neighbouring monolayers are easily observed also in the infrared absorption spectra[76].

An interesting example of the dependence of the absorption spectrum of Langmuir multilayers on the polarisation of light is presented in Fig.15*a*. For light with the polarisation e_1, the absorption maximum is displaced towards shorter wavelengths compared with the maximum for the polarisation e_2. This is caused, on one hand, by the interaction of static molecular dipoles with one another and, on the other hand, by the deviations from the ideal orientation of the molecules of the azo-dye in the multilayer. Then the light with the polarisation e_1 "selects" the molecules oriented on average along the normal to the layer and that with the polarisation e_2 "selects" molecules which have deviated from the ideal orientation. If the static dipole moments of the ground (μ_g) and excited (μ_e) states of the dye molecule are different [for the azo-dye (XV) their difference is $\Delta\mu = \mu_e - \mu_g \cong 3$ D[77]], then the spectral shift is proportional to the product $\mu_g\Delta\mu$ and depends on the angular scatter of the molecular orientations[73].

6. The Transmission of Excitation Energy and the "Photon Funnel"

One of the most impressive achievements of molecular architectural design has been the elucidation of the mechanisms for the transmission of excitation energy from one molecule (of a sensitiser or energy donor) to another (energy acceptor). This question has a long history and is extremely important in practice, because the development of methods for the sensitisation of photographic and other photosensitive materials depends on its solution.

The simplest mechanism for the transfer of energy from one molecule, excited by a light quantum, to another, unexcited molecule involves radiative transfer in which the acceptor molecule simply absorbs the light emitted by the luminescent donor molecule. In thin Langmuir films this mechanism hardly operates because of the weak absorption of light by one or several dye monolayers. The second possible mechanism involves Förster energy transfer; this mechanism operates when the acceptor molecule is at a short distance from the donor molecule. It is known that in the nearest region, i.e. at distances $R \ll \lambda$, the electric field of the emitting dipole decreases in proportion to R^{-3}. In this region the electric wave has not yet been formed, although the energy of the alternating electric field can be transmitted to a neighbouring oscillator. Such energy transfer has come to be regarded as non-radiative, although the probability of this process is proportional to the degree of overlap of the luminescence band of the donor and the absorption band of the acceptor. The third, also non-radiative, mechanism of energy transfer with the aid of exciton excitations is possible only for close packing of the donor and acceptor molecules.

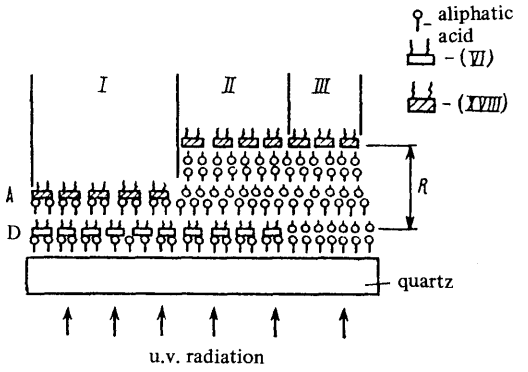


Figure 18. The scheme of Kuhn's experiment[2] designed to elucidate the mechanism of the transmission of excitation energy from the molecules of the sensitiser D to those of the acceptor A.

Fig.18 illustrates the scheme of Kuhn's experiment[2] designed to elucidate the mechanism of energy transfer between monolayers. A monolayer of sensitiser molecules D is deposited on a transparent quartz support (the insulating monolayer of aliphatic acids plays an auxiliary role). The oxacyanine dye (VI) mixed with cadmium arachidate was used for the molecules D. The monolayer of acceptor molecules A [the dye (XVIII) mixed with cadmium arachidate] is separated from the sensitiser layer by several cadmium arachidate monolayers. The number of these monolayers can be varied at will. Illumination of the sensitiser through the support by ultraviolet light leads to the following picture. On the right-hand side (III), where there is no sensitiser, the field of observation is dark, since the acceptors do not absorb the ultraviolet light. In region II, where the acceptor molecules are at a long distance from the monolayer of D molecules, the blue fluorescence from sensitiser molecules absorbing ultraviolet light, is observed. The molecules of the acceptor A absorb little of the fluorescence of the donor D, which is itself weak, and this hardly alters the spectral composition of the latter. In region I the acceptor molecules fluoresce intensely in the yellow part of the spectrum. They clearly receive energy from the molecules of the donor D by a non-radiative process. By altering the number of monolayers separating the D and A monolayers and by measuring the fluorescence intensity of the acceptor A, it is possible to test the theory developed for the Förster mechanism. Fig.19 illustrates the corresponding curve (curve *1*)[3]. Evidently the resonance non-radiative energy transfer is effective over distances of ~ 50–100 Å and less.

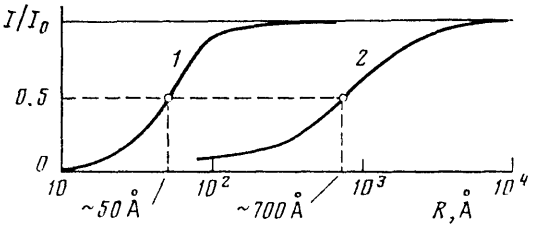


Figure 19. Dependence of the fluorescence intensity of the acceptor molecules on the distance R between the acceptor monolayer and the sensitiser monolayer (in Fig.18) (curve *1*) and between the acceptor molecules within a single monolayer (in Fig.20) (curve *2*).

Extensive studies on the mechanism of the excitation energy transfer through dielectric monolayers, carried out by Kuhn et al.[2] and Drexhage[3], confirm the validity of the Förster mechanism not only for dielectric dipolar oscillators but also for emitters of the type of a magnetic dipole and an electric quadrupole. The non-radiative energy transfer can occur from both singlet and triplet states of the sensitiser[78].

An absolutely different situation obtains when the acceptor molecule, with a structure similar to that of the donor molecule, is introduced into a continuous monolayer formed by the donor molecules. As already stated, the close packed chromophores (in the given instance of the donor molecules) form ordered assemblies which collectively absorb and emit light within narrow spectral ranges (*J*-aggregates). The acceptor molecules introduced into the same monolayer effectively absorb the energy of the *J*-aggregates, transforming it into the emission of their intrinsic luminescence. Fig.20 illustrates the fluorescence spectrum of a mixed monolayer in which there is only one acceptor molecule (trimethine and pentamethine surface-active cyanine dyes[79]) for each 250 sensitiser molecules. Despite the sharp difference between the donor and acceptor concentrations, the fluorescence intensity from the long-wavelength band (acceptor band) is almost the same, while at liquid nitrogen temperature it is

actually higher than from the short-wavelength band of the donor. This demonstrates that the energy of the light absorbed by a large number of donor molecules is concentrated at a single acceptor molecule, i.e. the principle of the "photon funnel" is realised.

Exactly the same experiment has been carried out recently with the dyes (VI) and (VII) as the donor and acceptor respectively[5]; the concentration of the molecules of the dye (VII) in the monolayer of the dye (VI) was varied. The fluorescence intensity of the acceptor molecules was plotted against the average distances between them (see Fig.20 and curve *2* in Fig.19). Fig.19 shows that in this case the characteristic distance from which the acceptor collects energy is ~ 700 Å and the number of donor molecules forming the "photon funnel" is 5×10^4. This figure agreed with the exciton mechanism of energy transfer: during its lifetime ($\sim 10^{-9}$ s), the exciton executes ~ 10^4 jumps from molecule to molecule and gives up its energy to the acceptor molecule if the latter is encountered in its path[6].

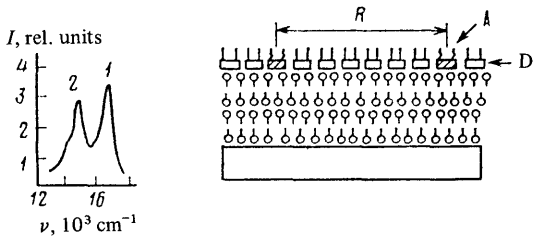


Figure 20. The fluorescence spectrum of a mixed monolayer of donor and acceptor molecules: 1) spectral maximum of the donor; 2) spectral maximum of the acceptor.

Experiments in recent years have shown that the principle of the "photon funnel" discussed above plays a key role in the mechanism of photosynthesis, where one trapping molecule collects the energy from ~ 300 chlorophyll molecules[6].

V. EFFECTS DUE TO "SPONTANEOUS" POLARISATION

1. "Spontaneous" Polarisation#

A completely new trend in molecular architectural design is the creation of asymmetric structures without an inversion centre. A whole series of new properties appear in such structures. We have already spoken of the idea of creating a molecular rectifier; in the next section we shall discuss vectorial electron transfer under the influence of light and now we shall consider the question of the presence of a permanent dipole moment per unit volume of a monolayer or multilayer, i.e. "spontaneous" polarisation *P*.

Turning to Fig.5, we may note that, in the presence of a longitudinal molecular dipole moment μ in the surface-active molecules, layers of type *X* and *Z* should have an overall dipole moment $P = \mu n$, where $n = N_A \rho / M$ is the number of molecules per unit volume (ρ is the density and *M* the molecular weight). In layers of type *Y*, where the overall dipole moments of the monolayers are compensated, $P = 0$. The numerical value of the polarisation for layers of types *X* and *Z* is $P \cong 10^6$ C cm^{-2} for $\mu = 6$ D and $M = 400$ g mol^{-1}.[23] In the experimental determination of the "spontaneous" polarisation, it is necessary to overcome at least two difficulties. Firstly, it is necessary to obtain layers of type *X* or *Z*, which cannot be always achieved; in particular, the molecules of aliphatic acids tend to be arranged in layers of type *Y* whatever the method of deposition. Secondly, the "spontaneous" polarisation, equal to the surface charge density on the multilayer, is usually compensated by the free charges due to the conductivity of the specimen or other leakages. It is therefore possible to measure experimentally not the absolute value of *P* but the changes in it, for example, when the temperature (pyro-effect) or pressure (piezo-effect) is altered. The value of *P* can also be calculated in terms of the molecular dipole, provided that there is an independent method of checking the state of orientation of these dipoles (for example, on the basis of the linear Stark effect—see below). The estimate of *P* quoted above has been obtained[23] by the last method for the azo-compound (XV).

2. The Pyro- and Piezo-Effects

The pyroelectric effect was first observed on *X*- and *Z*-type multilayers of the azo-compounds (XV) and substituted benzenes (XIX)[80]. In order to observe the effect, multilayers consisting of 10–100 monolayers were illuminated by pulses from a laser at a wavelength $\lambda = 1.06$ μm. Light was absorbed in a semi-transparent aluminium electrode and heated the multilayer. A potential pulse then arose on the electrodes, characterised by the pyro-coefficient $\gamma = dP/dT$. The sign of this pulse was the opposite of that for multilayers of the *X* and *Z* types; on layers of the *Y* type, the pyrosignal was not observed. This fact and also the kinetics of the increase and fall of the signal made it possible to establish its pyroelectric nature. The calculated value of γ for a 100-layer structure of the *X* type [compound (XV)] with R = SO_2NH_2 is 3×10^{-10} C cm^{-2} K^{-1}, which is lower approximately by an order of magnitude than the pyro-coefficient of film pyroelectrics[114].

The piezoelectric effect can be observed by a very clear procedure using the repeated reflections of a sound wave in a glass support on which a multilayer of the *X* or *Z* type has been deposited[23]. This wave can be obtained by the optoacoustic method, provided that the glass (for example, an SZS-21 light filter) absorbs the pulse of the laser emission at a wavelength $\lambda = 1.06$ μm. The resulting acoustic wave and its frequent repetitions (echo) excite in the multilayer the piezoeffect pulses, which can be observed on an oscilloscope screen using sputtered metallic electrodes, one of which has been deposited on glass (under the layer) and the other on the multilayer. The signs of the piezo-effect are different for layers of the *X* and *Z* types; the effect has not been observed on layers of the *Y* type.

3. The Linear Stark Effect

The observation of the spectral shift (linear in terms of the field) of the electronic absorption band in an external electric field constitutes a powerful quantitative method for the investigation of the polar structures of Langmuir films.

More precisely, we are dealing with macroscopic polarisation due to the process involved in the preparation of the multilayers.

Suppose that a molecule has a dipole moment μ_e in the excited state which does not coincide with the dipole moment in the ground state μ_g, i.e. $\Delta\mu = \mu_e - \mu_g \neq 0$. The ground and excited energy levels in an electric field **E** are then displaced by $\mu_g\mathbf{E}$ and $\mu_e\mathbf{E}$ respectively and the shift of the absorption band is $\Delta h\nu = (\mu_e - \mu_g)E$ (for simplicity it is assumed that the field is directed along the μ_e, μ_g, and $\Delta\mu$ vectors). The direction of the spectral shift is determined by the sign of $\Delta\mu$. If the molecular dipoles in the film lie in one direction, the shift of the absorption band of the film corresponds to the shift of the absorption band of the molecule. Otherwise, the spectral shifts towards long-wavelengths and short-wavelengths are averaged out owing to the scatter of the angles between the directions of the vectors **E** and $\Delta\mu$. The spectral shift of the band in an electric field implies an alteration of the optical transmittance at the specified wavelength. The amplitude of the relative change in the transmittance $\Delta T/T$ is proportional to $\langle\cos\theta\rangle$, where θ is the angle between the vectors $\Delta\mu$ and **E**. In the experimental observation of the linear Stark effect (Fig.21), the electric field vector is usually directed along the normal to the film. If the direction of the vector $\Delta\mu$ coincides with the molecular axis, as happens for the azo-compounds (XV), then the angle θ is the angle of deviation of the molecular axis from the normal. Thus the amplitude $\Delta T/T$ is a measure of the approach of the molecules to the ideal orientation (in which $\langle\cos\theta\rangle = 1$).

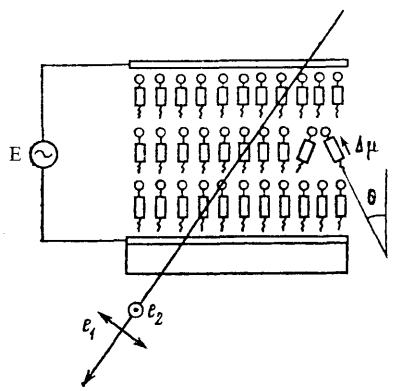


Figure 21. Measurement of the linear Stark effect for a multilayer structure. The molecules of compound (XV) have a chromophoric azo-system (rectangles) and an acceptor group R (circles). There is a transparent SnO_2 electrode on a quartz support and a semitransparent aluminium electrode on top of the multilayer.

Fig.21 illustrates the experimental arrangement designed to observe the linear Stark effect in a multilayer of the *Z* type formed by the azo-compounds (XV)[23]. The polarisation of the light can be of any kind provided that the molecules are scattered at angles θ; otherwise light with the usual polarisation is not absorbed. The changes in the optical transmittance of the film following the application of an external field are illustrated in Fig.22. The $\Delta T/T$ spectrum has the same form as the $dD/d\lambda$ spectrum if one disregards the slight ($\Delta\lambda \cong 10$ nm) mutual shift of these curves due to the different forms of the averaging of the optical and electro-optical contributions by the individual molecules[81]. The value of $\langle\cos\theta\rangle$ is calculated from the $\Delta T/T$ amplitude.

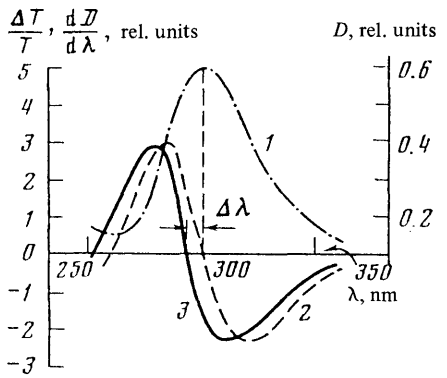


Figure 22. Curves representing the optical density *D* (curve *1*), its first derivative with respect to the wavelength $dD/d\lambda$ (curve *2*), and the $\Delta T/T$ Stark effect signal (curve *3*) for an *X*-type multilayer of compound (XV) with R = $SO_2N.(C_2H_5)_2$.[81]

The $\Delta T/T$ Stark signals for films of the *X* and *Z* types have opposite signs; on *Y* layers, the $\Delta T/T$ amplitude is approximately 30 times lower and is due to the incomplete compensation of the dipole moments of the neighbouring monolayers[23].

We may note that the combination of the dichroism[73] and the linear[81] and quadratic[82] Stark effect methods makes it possible to estimate not only $\langle\cos\theta\rangle$ for Langmuir films but also the next three terms in the expansion of the orientation distribution function of the molecules ($\langle\cos^2\theta\rangle$, $\langle\cos^3\theta\rangle$, and $\langle\cos^4\theta\rangle$)[82]. Measurements of the linear Stark effect together with the pyro- and piezo-effects convincingly demonstrate the polar structure of films of the *X* and *Z* types.

4. Generation of the Second Harmonic of the Light and the Photogalvanic Effect

The polar structure of layers of the *X* and *Z* types must lead to a further two effects which have not so far been observed experimentally. Firstly, symmetry considerations allow in the given instance the generation of the second harmonic of the light via a dipole mechanism (we are dealing with the doubling of the frequency of a powerful light beam). Secondly, intramolecular charge transfer from the donor substituent to the acceptor (for example in azo-compounds) should lead to a potential difference between the electrodes of the multistructure illustrated in Fig.21 when the latter is illuminated (the photogalvanic effect). This potential difference should be proportional to $\Delta\mu$ and to the number of molecules excited by the light with wavelength corresponding to the intramolecular charge transfer band, which is in its turn proportional to the light intensity and to the lifetime of the molecules in the excited state.

VI. PHOTOELECTRIC AND PHOTOCHEMICAL PROPERTIES

1. Electron Transfer

The study of the photoelectric and photochemical properties of artificial multimolecular structures is perhaps the most important trend in molecular architectural design. This concerns the modelling of the processes involved in photosynthesis, the photolysis of water, the creation of solar energy converters, etc. The key factor in all these problems is the achievement of a directed (vectorial) electron transfer from one molecule to another.

The vectorial electron transfer under the influence of a light quantum is modelled by a two-layer structure formed by a monolayer of electron-donating dye molecules and the monolayer of electron accepting molecules (Fig.23)[6]. The thiacyanine dye (VII) can serve as the donor and the bipyridylium salt (XX) (viologen) can serve as the acceptor. When this two-layer system is illuminated by light at wavelengths corresponding to the absorption band of the donor molecules, the excited electron, raised to the highest level of the donor molecule, can tunnel through the dielectric layer to the highest unoccupied level of the acceptor molecule. This transfer can be observed by the quenching of the fluorescence of the donor. The transmission of energy via the mechanisms discussed in the previous section is ruled out in this instance, since compound (XX) has no absorption bands in the spectral region of the fluorescence of the dye (VII). The intensity of this fluorescence depends very markedly on the distance between the chromophoric chains of the donor and acceptor molecules. Thus in case *1* (Fig.23) the fluorescence is quenched completely, in case *2* it diminishes approximately by a factor of two, and in case *3* it hardly changes.

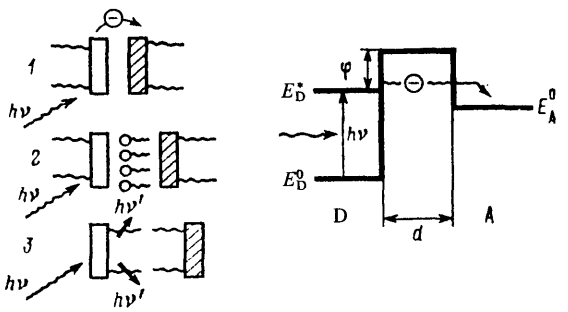


Figure 23. Electron transfer from the photoexcited state of the donor molecule to the highest unoccupied orbital of the acceptor molecule. Open rectangles—electron donor molecules; filled rectangles—electron acceptor molecules; ν' = fluorescence frequencies; in case (2) there is an intervening layer of aliphatic acid molecules[6].

Such a pronounced dependence of the fluorescence intensity on the thickness of the dielectric layer is consistent with the tunnel mechanism of electron transfer through the potential barrier. Experiments in which the width of the tunnel barrier, i.e. the thickness of the aliphatic monolayer, illustrated in scheme *2* (Fig.23), was altered by replacing one aliphatic acid homologue by another (the number of carbon atoms increased from 14 to 22) served as a quantitative confirmation of this postulate[5,6]. The fluorescence intensity diminished exponentially in conformity with the theory of tunnel currents (Fig.24).

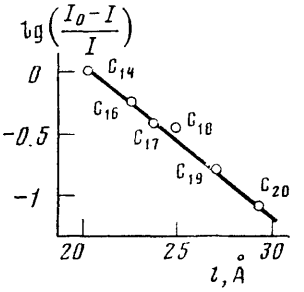


Figure 24. The quenching of the fluorescence intensity of the donor I as a function of the thickness of the tunnel barrier; I_0 = intensity in the absence of a layer of acceptor molecules[6].

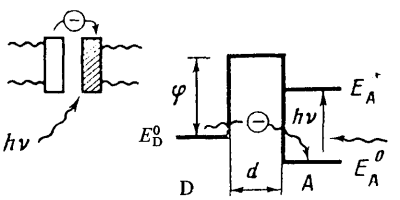


Figure 25. Electron transfer on photoexcitation of the acceptor molecule. Open rectangle—electron donor molecule; filled rectangle—electron acceptor molecule[6].

The degree of quenching of the donor fluorescence depends not only on the width of the barrier but also on the relative positions of the energy levels of the donor and acceptor. In particular, a decrease in the ionisation potential of the donor increases the probability of the electron tunnelling and enhances the quenching effect[83]. The quenching intensifies also on formation of *J*-aggregates by the donor molecules[84].

A second example of photoinduced electron transfer is illustrated in Fig.25. In this case light excites the acceptor molecule and the electron passes from the highest occupied orbital of the donor molecule to a liberated site in the lowest level of the acceptor. Examples of such electron-donating and electron-accepting molecules are provided by compounds (XXI) and (XXII) respectively. In this case the electron transfer from compound (XXI) to (XXII) is monitored by observing the quenching of the fluorescence of the dye (XXII)[2,6].

2. The Electron "Pump"

The photoinduced vectorial electron transfer from the donor to the acceptor molecule, illustrated in Fig.23, is accompanied by the reverse (dark) process, involving the

tunnelling of the electron through the barrier from A to D. However, the two schemes can be combined (Figs. 23 and 25) by exciting with light the dye which serves as an electron acceptor in relation to one molecule and at the same time as an electron donor in relation to another. Such a scheme is illustrated in Fig. 26. The molecule of the surface-active compound (XXIII) can be conveniently employed as the photosensitive species. The photoinduced electron transfer to the acceptor—the distearylbipyridylium salt (XX)—takes place when a monolayer of these molecules is illuminated. The lost electron is replaced by an electron from the dye-source [the leuco-form of the dye Stearylene Blue (XXIV)].

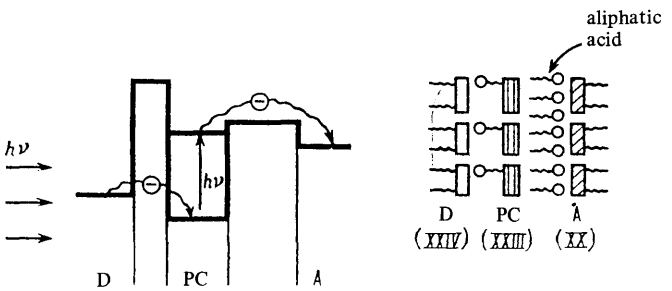


Figure 26. Schematic illustration of the "electron pump"; D = electron source molecule; PC = photocatalyst; A = electron acceptor molecule.

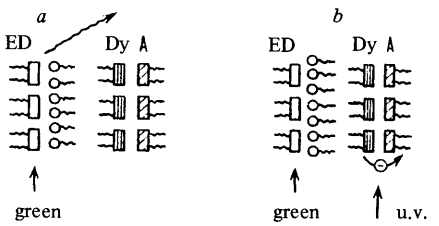


Figure 27. Illustration of the combined effect of the electron phototransfer from the dye Dy to the acceptor A and of the excitation energy transfer from the energy donor ED to A.

Thus the multistructure illustrated in Fig. 26 effects a two-stage electron transfer from the source molecule S to the acceptor molecule; the intervening layer plays the role of the photocatalyst PC. As a result of such transfer, the energy of the electron increases. Consequently this structure effects the pumping of electrons from lower energy levels to higher levels, i.e. plays the role of a molecular "pump" for electrons.

The operation of this "pump" can in principle be monitored by the appearance of the oxidised (blue) form of the dye (XXIV) or the reduced form (also blue) of viologen (XX). However, this is difficult to achieve experimentally. A more effective method of detecting the viologen radical involves the observation of the quenching of the fluorescence of special molecules (energy donors) added to the multistructure and chosen in such a way that their fluorescence band coincides with the absorption band of the viologen radical. Then, in the absence of electron transfer in the dye–acceptor (viologen) pair (Fig. 27*a*), the energy donor (ED) fluoresces under the influence of visible light, for example, in the red region. Illumination of the dye Dy with ultraviolet light leads to electron transfer from the dye molecule to the acceptor, whereupon viologen is converted into a radical which also absorbs light in the red part of the spectrum. The non-radiative (Förster) mechanism of energy transfer from ED to A begins to operate, which is indeed observed experimentally as the quenching of the red fluorescence of the energy donor[5].

3. Photoconductivity and Photo-e.m.f.

The vectorial phototransfer of an electron can be investigated also by a purely electrical method involving the measurement of the photocurrent in an external circuit for different polarities of the field applied to the specimen or the photo-e.m.f. induced in the electrodes of the specimen.

A fairly large number of studies have been made of the photoconductivity of Langmuir films sensitised by dyes. The physical mechanism of the primary process involving the appearance of a photoelectron in the specimen has been considered[85] in relation to a multilayer structure into which a monolayer containing molecules of quinquethienyl (X), whose electronic oscillators are perpendicular to the plane of the layers (Fig. 28), was introduced. The monolayer of quinquethienyl is located among the layers of cadmium arachidate and its position (more precisely its coordinate x) can be varied at will. A potential U, which "inclines" the potential energy diagram for the system, is applied between the mercury and aluminium electrodes. Under the influence of light, electrons pass from the highest occupied orbital of the quinquethienyl molecule to the lowest unoccupied orbital; hence the electrons tunnel across the barrier (or pass through it) and appear in one of the bound energy states on the surface between neighbouring cadmium arachidate monolayers (Fig. 9). Next electrons move to the positive electrode via the jump mechanism considered in Section III. The first stage in overcoming the barrier limits the photocurrent. If the ionisation potential of quinquethienyl is ϕ_0 before the application of the external electric field, then it is clear from simple geometrical considerations that in the electric field it falls to $\phi = \phi_0 - eU(L/2d)$, where L is the length of the molecules of compound (X). The current in the external circuit should be proportional to the probability of the escape of electrons from the quinquethienyl molecules to the positive electrode [i.e. to the factor $\exp(-\phi/kT)$] and the time taken to traverse the distance x. Indeed the exponential increase of the current with increase in the potential and the linear dependence on the position of the layer of compound (X) in the multistructure have been observed experimentally[85]. Other results[86] also confirm the model under consideration.

In structures of the type illustrated in Fig. 28 it is possible to observe not only a transverse (across the multilayer) but also a longitudinal (in the plane of the layers) component of the photoconductivity. This can be done with the aid of photosensitisers of a new type incorporating the rhodanine fragment (XXV)[87]. The photoconductivity of the longitudinal type exceeds by 2–3 orders of magnitude the transverse component and its temperature variation is of a different type, which agrees with the jump model of the transverse conduction considered previously and the non-active mechanism of the longitudinal conduction[8].

The transverse photoconductivity can be greatly increased by employing, instead of the simple sensitiser shown in Fig.28, a more complex, "photosynthetic" system[88] consisting of monolayers of an electron acceptor and donor and a "molecular conductor" between them[31,54]. Such "construction" of the sensitiser makes it possible to increase the probability of its photoionisation. The corresponding multistructure and energy diagram are shown in Fig.29.

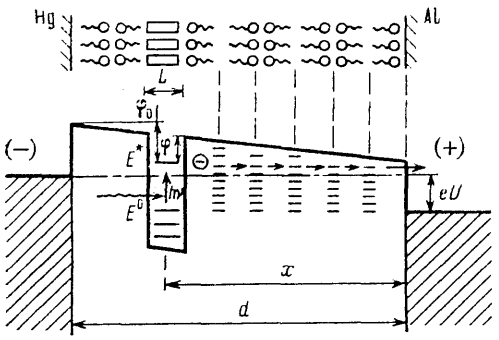


Figure 28. Model elucidating the mechanism of photoconduction in a cadmium arachidate multilayer sensitised by a monolayer of quinquethienyl (X)[85].

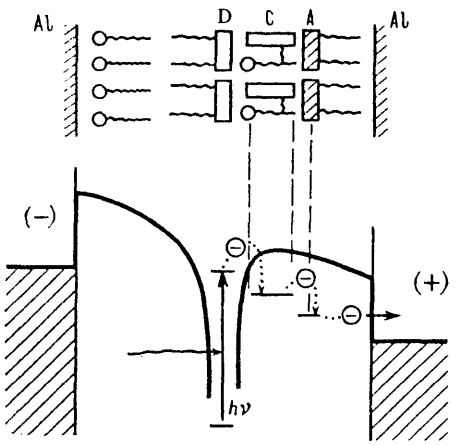


Figure 29. Model elucidating the electronic transitions in the donor D—molecular-conductor C—acceptor A—positive electrode system[54].

In the example given, the rectangular potential well for the electron-donating dye [the indocarbocyanine dye (XXVI)] has been replaced by the more realistic Coulombic potential. The tunnel or thermoactivated electron transfer from the photoexcited state of the donor to the free orbital of the acceptor (XX) is facilitated by the presence of the "molecular conductor" C containing the conjugated chain of the azochromophore of compound (XII). The presence of this chain decreases the width of the potential barrier which must be overcome by the electron tending to enter the acceptor and then the electrode. At any rate, the absence of the molecules of C decreases the photocurrent by an order of magnitude[54]. The change in the polarity of the applied potential results in an appreciable difference in the photocurrent. Since the electrodes are the same in the given instance, this partial "rectification" of the current is caused exclusively by the asymmetry of the "photosynthetic" unit.

The artificially created asymmetry of the multilayer is a necessary attribute required to obtain a photoelectromotive force at the electrodes when the latter are illuminated. Artificial membranes immersed in the solution were used previously to obtain a photo-e.m.f., the opposite surface of the membrane being in contact with solutions of different types. Photo-e.m.f.'s of the order of fractions of a volt were achieved in this way following the illumination of membranes by light from standard light sources[89,90]. Approximately the same photo-e.m.f.'s have been observed also on asymmetric Langmuir multilayers[54,91]. Here an additional factor promoting an increase of the photo-e.m.f. is the use of asymmetric electrodes made, for example, of metals having different electron work functions[54] or using oxide films, the photo-e.m.f.'s reaching several volts in the latter case[92].

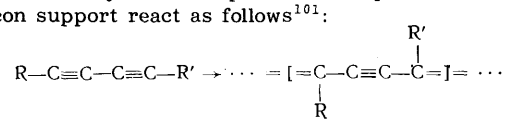
4. Photochemical Aspects

There exist fairly numerous publications devoted to the study of the photochemical reactions in monolayers on the surface of water and also in Langmuir multistructures. Their detailed consideration is outside the framework of this review. We shall only note some of the trends which are closest to the idea of molecular architectural design. In particular, photochromic compounds are of special interest for the creation of artificial structures modelling optical memory devices. The surface potential and the area per molecule in monolayers of surface-active photochromic compounds change under the influence of illumination, which can be measured with the aid of the Wilhelmy balance[93,94].

Extensive studies on various photochemical reactions in Langmuir monolayers and multilayers have been carried out in Whitten's laboratory (see, for example, Refs.95—98). The formation of photodimers and excimers, photochemical oxidation and reduction processes (particularly those involving porphyrins), the photoisomerisation of olefins, the photochemical reactions of ketones and surface-active styrene derivatives, and other reactions[12] have been investigated. It was found that the structure of the monolayer has a decisive influence in many instances not only on the rate of reaction but also on the type of final products. As a rule, products whose structure is compatible with the symmetry of their environment are preferred. It has been noted[97,99] that compounds bound in the Langmuir matrix can serve as more effective reagents and also as catalysts of chemical reactions than the compounds in an isotropic solution.

Special mention should be made of polymerisation reactions in solid Langmuir films. Their investigation was begun comparatively recently[100], but important practical results for a whole series of different compounds have already been obtained[10-12]. Ultraviolet radiation, electron beams, and γ-radiation (in particular that from a ^{60}Co source) have been used to initiate polymerisation in multilayers.

The polymerisation of diacetylene derivatives (V) can serve as an example. Under the influence of ultraviolet light, the Langmuir monolayers of compound (V) deposited on a quartz or silicon support react as follows[101]:



The structure of the monolayer, determined by X-ray diffraction, does not change significantly under these conditions. In general the polymerisation process occurring within the plane of a single monolayer does not as a rule involve the molecules of another layer, which extends the scope of molecular architectural design, permitting the successive deposition of polymer layers made up of different compounds.

An interesting example of a compound which polymerises under the influence of an electron beam is ω-tricosenoic acid. The molecules of this compound in the Langmuir monolayer are oriented at right angles to the support and their cross-linking at the site of the rupture of the unsaturated bond takes place within the plane of the monolayer. The stable multilayers used as electron resists are obtained by this method[102].

A survey of studies of polymerisation in monolayers and of the preparation of monolayers and multilayers directly with the aid of polymer molecules has been published recently[12].

VII. PROBLEMS OF MOLECULAR ARCHITECTURAL DESIGN: REALITY AND PROSPECTS

Molecular architectural design, i.e. the creation of complex molecular assemblies with a predetermined architecture, leads to boundless possibilities for their applications in a wide variety of branches of science and engineering if one disregards technical difficulties. Only some of them are illustrated in the scheme below but the advances in molecular architectural design have already been significant; the corresponding literature sources are indicated in the subsection on technical applications.

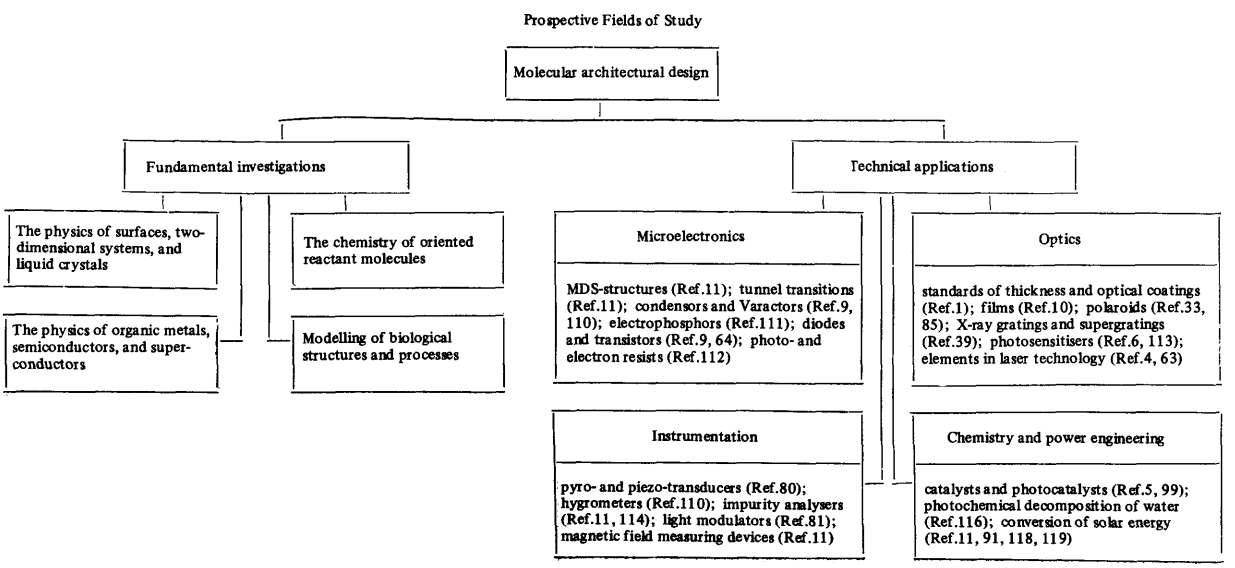
1. Fundamental Investigations

Evidently a monolayer resting on the surface of water or transferred onto a solid support can serve as an excellent model of a two-dimensional condensed medium. Studies of the structures of such monolayers have become particularly urgent now that impressive advances have been made in the theory of phase transitions in three-dimensional bodies and the general development of statistical physics of condensed media is directed towards the study of media with a reduced dimensionality. A number of investigations[27,30,122] can serve as examples. The study of the surfaces of solids and liquids also belongs to this field.

Problems concerning the structural organisation of a single monolayer and the correlations in the packing of molecules in neighbouring monolayers, which are in contact with one another, have a direct bearing on the physics of smectic liquid crystals[103] and can be solved with the aid of model systems such as Langmuir layers. On the other hand, a number of ideas in the physics of liquid crystals, concerned, for example, with the explanation of the mechanism of ferroelectricity, can be successfully transferred to the physics of membranes and artificial monolayers and multilayers[104].

In the future molecular architectural design will become a standard procedure for the investigation of a wide variety of processes occurring in organic solids. We have already spoken of the advances in the spectroscopy of complex organic molecules and various associated species, about the mechanisms of the transfer of excitation energy, etc. (Section IV). With the aid of Langmuir films, it is possible to investigate also other exciton processes, in particular, the interaction of excitons with the surface of a crystal, with admixtures, or with metallic electrodes[7,105,106].

It is known that the relative positions of the donor and acceptor fragments of molecules (in the form of stacks, columns, etc.) plays a decisive role in the exciton mechanism of the superconduction in organic crystals. Such structures can be built up in principle on the basis of Langmuir films. Experiments with anthracene derivatives indicate a "stacked" structure of multilayers, leading to a pronounced anisotropy of the electrical conductivity[34]. A similar structure is also characteristic for example, of quinquethienyl layers[85]. Donor–acceptor two-layer systems, formed, for example, by the surface-active analogues of compounds such as tetrathiofulvalene and tetracyanoquinodimethane (TTF–TCNQ complexes), as well as other compounds of this type, which do not form crystals with a suitable structure[9], are of undoubted interest for the physics of organic metals and superconductors.



There is no necessity to mention that chemical and physicochemical reactions involving reactants whose molecules are rigorously oriented in space provide the experimenter with a greater "degree or freedom" than do experiments with isotropic solutions. Clearly in the oriented state it is possible to involve new molecular fragments in the reaction. For such chemical reactions, one can use various boundaries (between the monolayer and the support, between the monolayer and the external environment, and also the boundary between the monolayers)[99]. As already stated, it is thereby possible to alter not only the rates of the reactions but also their products (an example is provided by the formation of a silver mirror at the interface between a monolayer and water[107]).

Molecular architectural design is perhaps of greatest interest for the modelling of various biological processes, in particular the primary stages of photosynthesis. The attempts to model the molecular antenna (or "photon funnel"[5,79]) and also the fundamental photocatalytic electron transfer from a donor to an acceptor[5,6,108] and the replication of information at the molecular level[7] can be regarded as entirely successful. Other model biological studies, including the modelling of the self-organisation of matter[109], are apparently tasks for the immediate future.

2. Technical Applications

The incorporation of molecular architectural design in technology proceeds mainly via four pathways (Fig.30). Microelectronics, where Langmuir films can already be used in commercially produced instruments, can apparently be placed in the first place. This applies primarily to the dielectric layers in metal–dielectric–semiconductor structures, for example, field effect transistors, where the current flowing through the semiconductor is controlled by the electric potential of the metallic electrode separated from the semiconductor by a thin dielectric layer. In field effect transistors based on silicon, the natural oxide layer plays the role of the dielectric. Other semiconductors (for example, InP or CdTe) do not have an oxide film and an additional layer of dielectric with a high electrical strength is essential. Langmuir multilayers, for example, those based on polymerised diacetylenes (a layer with a calibrated thickness and consisting of several tens of monolayers is usually employed) are used as layers of this kind[11].

Ultrathin Langmuir multilayers (with a thickness equivalent to 1–4 monolayers) are also used as tunnel junctions in "cold cathodes" employing the properties of the contact between a photoconductor and a metal. A Schottky potential barrier is usually formed on such contacts. Under the influence of light, a photo-e.m.f. is generated at the site of contact between the semiconductor and the metal and the structure itself becomes an effective converter of light energy into electrical energy. The use of an additional (tunnel) dielectric layer between the metal and the semiconductor improves the efficiency of the conversion of light energy into electrical energy. Thus the efficiency of the "cold cathode" on *n*-type cadmium telluride increases by a factor of 1.4 when two monolayers of the substituted anthracene (VIII) are deposited on the semiconductor[11].

By virtue of their high electrical strength and the possibility of the preparation of films with a rigorously specified and very small thickness, Langmuir monolayers and multilayers are extremely convenient dielectrics for the preparation of high capacitance condensers. The capacitance reaches 0.1 $\mu F\ cm^{-2}$ for the field strength corresponding to breakdown, $\sim 3 \times 10^6\ V\ cm^{-1}$.[110] Condensers whose capacitance is altered under the influence of an external field (Varactors) can also be prepared on the basis of Langmuir films[9].

The unusual type of molecular packing in Langmuir films makes it possible to achieve a high luminescence and electroluminescence (arising from the application of an electric field) quantum yields in them[34,111]. Electrophosphors based on Langmuir films can prove promising for the creation of electroluminescent devices for the reproduction of information (digital displays, panels, flat television screens, etc.). The formation of donor–acceptor multilayers, the employment of surface-active complexes and autocomplexes with charge transfer, and the preparation of solid multilayers based on radical-ion salts will probably lead in the near future to the creation of molecular current rectifiers and more complex transistor structures[9,64].

Quite definite advances have been made in the field of the formation with the aid of Langmuir monolayers of high-resolution photo- and X-ray-resistors.

A sensitivity to an electron beam to within $5 \times 10^{-7}\ C\ cm^{-2}$, for a contrast reaching 2 and a spatial resolution of ~ 600 Å, has been achieved recently on the basis of polymerisable ω-tricosenoic acid films[112]. It was noted that the electron resists obtained by the Langmuir Blodgett technology also exhibit a high resistance to plasma and an effective adhesion to aluminium.

The application of Langmuir films in optics (Fig.30) is based primarily on the possibility of varying their refractive indices for a rigorously specified film thickness. Hence arises the possibility of creating optical thickness standards[1], optical coatings, and interference filters as well as X-ray diffraction gratings[39] and supergratings. It has been noted[9] that X-ray gratings based on multilayers could be particularly useful in the future for the creation of lasers operating in the X-ray range.

The marked dichroism of Langmuir monolayers formed by surface-active dyes, particularly in the aggregated state[33,85,108], makes it possible to employ these structures for the creation of effective film polarizers. The selective absorption of light by dyes can be used also in the development of film layers for the isolation of specific spectral components of radiation (the selection of modes)[63], the generation of ultrashort pulses[4], etc. One may also expect that the non-linear optical properties of polar multilayers will find fairly extensive applications in the immediate future.

Langmuir films are of great interest for integrated optics. They can be used for the creation of both waveguide elements themselves and the outer plates of such devices. The technique of the preparation of multilayers makes it possible to construct the necessary refractive index profile across an integrated optical structure. A fairly high optical quality of such structures (decay of light waves smaller than 1 dB per cm of the path traversed for film thicknesses up to 5000 Å) has already been achieved[10].

The transmission of excitation energy and vectorial electron transfer can be used successfully for the sensitisation of traditional photographic materials. Experiments with silver bromide crystals have shown that AgBr is sensitised as a result of electron transfer from an excited dye monolayer[6,7]. The presence of an electrical acceptor suppresses the sensitisation effect. Specially constructed multilayers on the surface of a photosensitive crystal make it possible to achieve simultaneously the transfer of energy from one dye to another (via the "photon funnel" mechanism), which gives up an electron in its turn to the crystal[113]. This leads to an extremely effective sensitisation of the photographic process.

A new method of recording and replication of information at the molecular level, recently proposed by Kuhn[7], is of

special interest for engineering. Recording on Langmuir films can be achieved with the aid of an electron beam, which induces a photochemical process. The rerecording of information from one monolayer to another is effected by contact procedures similar to the replication of ribonucleic acid in cell chromosomes.

On the other hand, the first attempts to create pyroelectric elements on the basis of polar multilayers led to pyrocoefficients of ~ 10^{-10} C cm^{-2} K^{-1},[80] which is only an order of magnitude lower than the corresponding values for the best film pyroelectrics[114]. In view of the low dielectric constants, which increase the quality factor for pyroelectric materials, one can regard the further development of pyroelectric radiation transducers based on Langmuir multistructures as extremely promising. This applies also to piezoelectric transducers.

There is reason to believe that the linear Stark effect, observed in polar films of surface-active dyes[81], will prove useful in the development of fast acting thin-film light modulators. It has also been suggested that tunnel transitions in Langmuir monolayers be used for the creation of highly sensitive magnetic field measuring devices[11].

Instrument engineering is in acute need of highly sensitive transducers permitting the analysis of low concentrations of admixtures of various gases, water vapour, ionic impurities in solutions, etc. The development of hygrometers based on cadmium behenate multilayers with a gold film electrode permeable to water molecules has been reported[110]. The capacitance of such a structure depends on the amount of water which has diffused through the gold electrode. Selectivity with respect to various impurities can be ensured with the aid of specially constructed multilayers deposited on the open surface of a field effect transistor sensitive to extraneous impurities[115]. The multilayers can also include various biologically active molecules which ensure the selective transport of impurity molecules (for example, via the mechanism of the action of ionophores in membranes).

Reports already exist concerning the creation of instruments detecting gases such as ammonia, carbon monoxide, and hydrogen[11,111].

The possibilities of molecular architectural design in chemistry and power engineering have been assessed very optimistically. The advantages of specific synthesis on Langmuir matrices have already been pointed out. We shall now consider the results of modern studies in the conversion of solar energy into electrical energy. One of the ways of achieving such conversion is photochemical decomposition of water into oxygen and hydrogen; certain surface-active metal complexes can then be used as photocatalysts. A successful attempt at the photochemical decomposition of water with the aid of a monolayer of a ruthenium complex has been reported[116], but subsequent studies[83,117] revealed a number of fundamental difficulties. Another procedure for the conversion of energy consists in the creation of solar batteries by analogy with semiconducting p–n junctions[88]. The Schottky barriers were already mentioned above. In addition, one can employ solid Langmuir multilayers formed by electron-donating and electron-accepting compounds[54,91] as well as electrolytic cells in which the Langmuir monolayers are deposited on a solid support with an optically transparent electrode. In the former case (chlorophyll *a* combined with quinones) the efficiency of the conversion reaches hundredths per cent for a photocurrent quantum yield of the order of several tenths per cent[91]; in the second version (a layer of chlorophyll on an SnO_2 electrode) the photocurrent quantum yield can reach 12–16%.[118,119] The corresponding efficiency of the energy conversion is lower by more than an order of magnitude than the efficiency characteristic of semiconductor solar batteries. However, it is noteworthy that the Langmuir layers are very cheap and technologically convenient. The latter factor is extremely significant when one considers the necessity to "collect" solar energy from large areas. Furthermore, one can employ the principle of the "photon funnel" for the collection of light energy with the aid of a combination of dyes in an energy converter incorporating an electrolytic cell. This should yield an appreciable gain in the efficiency of the conversion[120,121].

In conclusion of the review we emphasise that molecular architectural design is now entering the period of its vigorous expansion and we are justified in expecting from this new field new scientific discoveries and important practical applications.

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