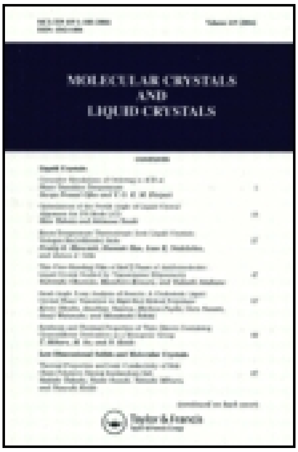

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Liquid Crystal Alignment on Langmuir-Blodgett Organosilicon Films

V. V. Belyaev [a], V. G. Mazaeva [b], M. V. Sobolevskii [b], I. G. Kokaulina [c] & A. S. Solomatin [a]

[a] Science & Education Center of Materials and Nanosystems Physical and Chemical Investigation, Moscow Region State University, Russia

[b] State Scientific Centre of Organoelement Chemistry and Technology, Moscow, Russia

[c] Moscow State Institute for Radio-Engineering, Electronics and Automation (Technical University), Moscow, Russia

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V. V. BELYAEV,[1] V. G. MAZAEVA,[2]
M. V. SOBOLEVSKII,[2] I. G. KOKAULINA,[3] AND
A. S. SOLOMATIN[1]

[1]Science & Education Center of Materials and Nanosystems Physical and Chemical Investigation, Moscow Region State University, Russia
[2]State Scientific Centre of Organoelement Chemistry and Technology, Moscow, Russia
[3]Moscow State Institute for Radio-Engineering, Electronics and Automation (Technical University), Moscow, Russia

Monomolecular films made by a Langmuir-Blodgett method with organosilicon compounds of different structure have been investigated. The monomolecular layer of alkyltriethoxysilane with more than eight carbon atoms in the chain can be transferred onto a glass substrate. Such film provides homogeneous LC alignment without rubbing.

Keywords Langmuir-Blodgett films; LC alignment; limiting area; organosilicon compounds; surface pressure

1. Introduction

Green technologies application in liquid crystal displays (LCD) development and production is an urgent task [1]. One of the key requirements for the green process is reduction of different functional layers deposition temperature and therefore power saving in the LCD manufacturing. Besides, using of less harmful chemicals reduces ecological impact onto the environment. Organosilicon compounds (OC) for LC alignment meet both green requirements mentioned [2,3]. They have coating temperature of 120°C–180°C which is significantly lower than polymerization temperature (200°C–450°C) of polyimides. The OC concentration in reagents is also very low (2–10%).

Nevertheless up-to-date intense development of flexible displays and e-paper imposes further reduction of the processing temperature. A Langmuir-Blodgett (LB) method can face this challenge because it is a room-temperature process as a rule. Additional merit of the LB technology is a deposition of monomolecular layers with different spatial structure of the substance and controlled layer thickness.

Address correspondence to V. V. Belyaev, Science & Education Center of Materials and Nanosystems Physical and Chemical Investigation, Moscow Region State University, Russia. Tel.: +7-495-7800950*1623; Fax: +7-499-2612228; E-mail: vic_belyaev@mail.ru

Applications of LB or Langmuir-Schaefer methods for rubbing-less LC alignment are described in [4,5]. Other applications of OC LB films are considered in [6–9].

The goal of the work is to investigate a method of creating monomolecular LB films of organosilicon compounds (OC) on which the homogeneous alignment of LC with different polarity can be achieved.

2. Experimental Methods

The LB films on the base of diphilic OC were made in a Micro Devices Technologies array. The equipment for formation and investigation of monomolecular films was manufactured by Special Design Bureau of R&D Institute of Physics Problems (Zelenograd, Russia).

Following conditions were used for the LB layers creation:

1. temperature 18°C–22°C,
2. pH = 6,
3. velocity of barrier movement $0.5\,\mathrm{mm\,s^{-1}}$,
4. holding time after solution deposition onto water surface 60 min.,
5. velocity of substrate extraction from water $0.1\,\mathrm{mm\,s^{-1}}$.

The OC have been selected among the substances studied by us recently for LC orientation by the adsorption method [2,3,10,11]. Following OC have been investigated:

1. alkyltriethoxysilane (ATEOS) $C_nH_{2n+1}Si(OC_2H_5)_3$, n = 3–16,
2. methylalkyldiethoxysilane (MADEOS) $(CH_3)(C_nH_{2n+1})Si(OC_2H_5)_2$, n = 6, 8, 10,
3. strengthened hexaalkylcyclotrisiloxane (HACTS) $[(C_nH_{2n+1})_2SiO]_2$, n = 1, 2.

The substances studied were solved in toluene, isopropyl alcohol or dodecane.

Typical dependence of the surface pressure expressed in $\mathrm{mN\ m^{-1}}$ *vs* area per one molecule in the layer expressed in Å^2 (π-S isotherms) is shown in Figure 1 for an

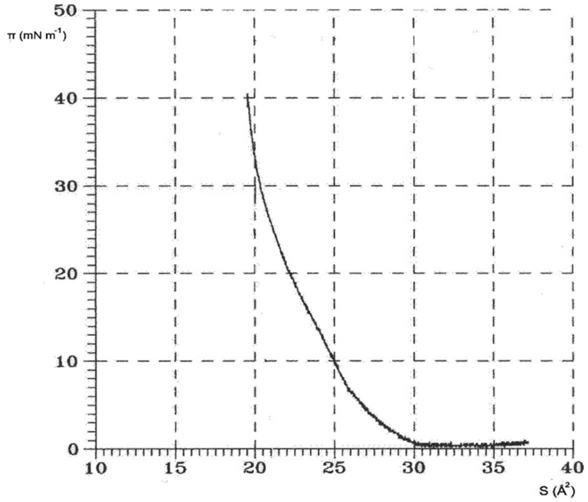


Figure 1. π-S isotherm of cetyl alcohol $C_6H_{13}OH$.

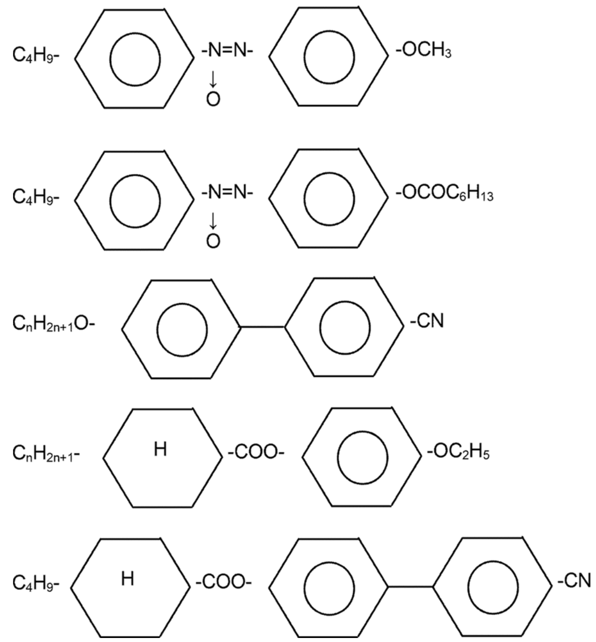


Figure 2. LC components of the LC materials ZhK-440 and ZhK-1282.

organic substance cetyl alcohol $C_6H_{13}OH$ on the water surface. The area per one molecule in the ultimate monolayer is determined by an extrapolating the π-S dependence to the zero surface pressure. In every curve the limiting left point corresponds to the surface pressure in an ultimately compressed layer. The accuracy of the surface pressure measurement is of order of 0.2 $mN\ m^{-1}$. The area per one molecule in the ultimately compressed layer reduces when the substance concentration on the water surface increases.

To coat the OC hydrophilic glass substrates have been washed out by different methods so that the substrate was wet by water completely.

The LC alignment by the LB OC films was studied in cells filled in with NIOPIK (Russia) LC materials ZhK-440 (a mixture of weak-polar butyl-methoxy and butyl-hexanoyloxy azoxybenzenes with $<\varepsilon> \sim 5.5$and $\triangle\varepsilon \sim -0.5$) and ZhK-1282 (a mixture of polar alkyl- and alkoxycyanobiphenyls and weak-polar Demus and Grey ethers with $\triangle\varepsilon \sim +10$) (Fig. 2).

To determine the type of the alignment the cell was positioned between two crossed polarizers. The dark field of view corresponds to homeotropic (vertical) LC alignment, and the bright field of view corresponds to homogeneous planar LC alignment. The validity of such approach has been confirmed by accurate measurement of LC pretilt angle on OC aligning coatings deposited by the adsorption method [3,11].

3. Results

The π-S isotherms have been measured for ATEOS with the alkyl chain length from 3 to 16 carbon atoms (Fig. 3). Compounds with more than 8 carbon atoms in the

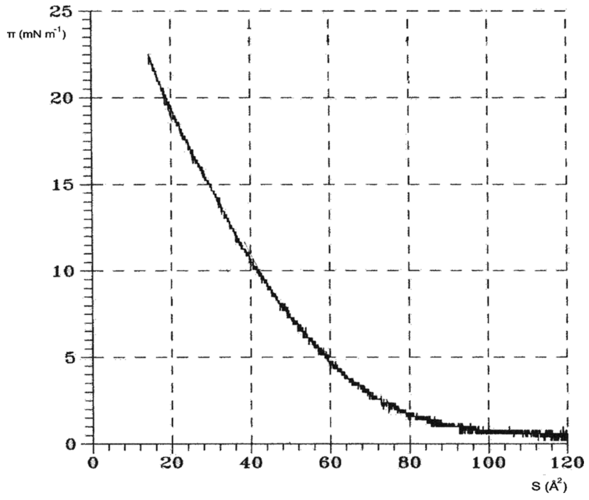


Figure 3. π-S isotherm of decyltriethoxysilane $C_{10}H_{21}Si(OC_2H_5)_3$, amount 0.0260 mg on the water surface.

chain are suitable for the LB method. The values of both area per one molecule in the ultimately compressed layer and surface pressure for different solvents and amount of the substance on the water surface are listed in Table 1.

The ATEOS surface pressure dependences differ significantly from those for organic surface active substances (SAS). They have lower steepness and very low surface pressure in the ultimate monolayer (10–13 mN m^{-1} against 40 mN m^{-1} for cetyl alcohol). The area per one molecule in the ultimate monolayer depends on the solvent, number of carbon atoms in the alkyl chain and the amount of the substance on the water surface. For hexadecyltriethoxysilane $C_{16}H_{33}Si(OC_2H_5)_3$ an inflection point on the π-S isotherm is obtained in vicinity of the ultimately compressed layer.

The π-S dependences for MADEOS are similar (Table 1). However for MADEOS the values of the area per one molecule and the surface pressure at the same amount of the substance on the water surface are lower than for ATEOS.

At the first time we have found that multiple cycles of compression-tension of the DTEOS monolayer on the water surface with pH = 6–7 do not result in the monolayer collapse (a brittle destruction specific for organic SAS) with sharp decrease of the surface pressure; on the π-S isotherms a weak expressed inflection point appears. Hence the monolayer transfer onto the substrate is to make at the surface pressure $\leq$12 mN m^{-1}. In such manner we have transferred the monolayer from water to the glass at $\pi = 10$ mN m^{-1} and the substrate movement from water. The best solvent for this procedure was a 50%:50% vol. mixture of toluene with isopropyl alcohol.

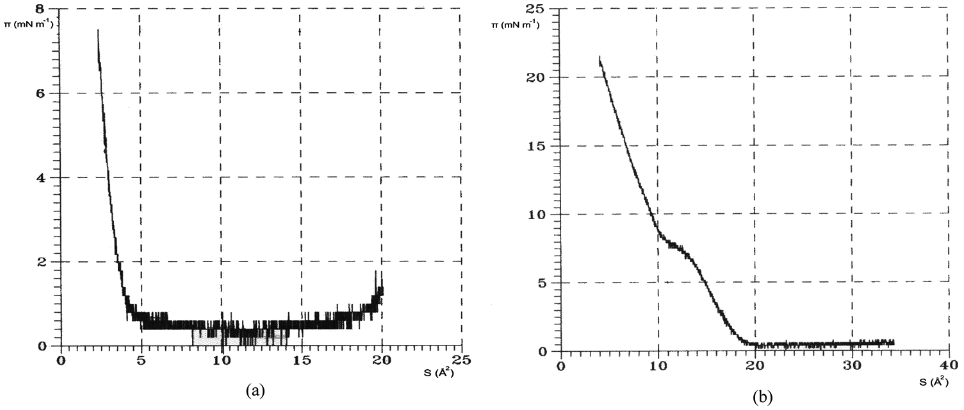
A computer modeling gave a value of the monolayer transfer coefficient for the chosen process conditions equal to 1. An attempt of the DTEOS multilayer formation failed; the second layer transfer coefficient was less than 0.2. Possible reason is easy mutual sliding of the layers.

A single monolayer DTEOS film on the glass substrate without electrode coating gives LC aligning effect without rubbing. For both ZhK-440 and ZhK-1282 a well-homogeneous planar alignment is observed. The same effect for the adsorption method is achieved only at additional mechanical rubbing.

Table 1. Dependence of the area per one molecule in the monolayer and the surface pressure on both ATEOS and MADEOS amount on the water surface

Substituent R	Substance amount on the water surface, mg	S_{lim}, Å^2	π_{max}, mN m^{-1}	Solvent
$RSi(OC_2H_5)_3$				
$C_{16}H_{33}$	0.0088	145	12	Isopropyl alcohol
	0.0177	70	12	Isopropyl alcohol
	0.0266	60	13	Isopropyl alcohol
	0.0088	160	8	Dodecane
	0.0266	62	13	Dodecane
$C_{10}H_{21}$	0.0052	180	5	Isopropyl alcohol
	0.0078	120	14	Isopropyl alcohol
	0.0260	60	13	Isopropyl alcohol
	0.0087	200	10	Dodecane
	0.0174	150	11	Dodecane
C_8H_{17}	0.0088	125	6	Isopropyl alcohol
	0.0263	42	11	Isopropyl alcohol
$RSi(CH_3)(OC_2H_5)_2$				
C_6H_{13}	0.025	26	12	Isopropyl alcohol
	0.1	9	7	Isopropyl alcohol
C_8H_{17}	0.02	42	10	Isopropyl alcohol
	0.03	30	10	Isopropyl alcohol
$C_{10}H_{21}$	0.00768	122	10	Isopropyl alcohol
	0.0128	80	11	Isopropyl alcohol
	0.25	58	14	Isopropyl alcohol

We have also found at first time a hysteresis behavior at the monolayer compression and following tension. The π-S dependence at the second compression almost repeats the curve at the tension. The second compression monolayer is easier to transfer onto the substrate.



(a)

(b)

Figure 4. π-S isotherm of hexamethylcyclotrisiloxane and hexaethylcyclotrisiloxane.

At the same conditions the HACTS have been investigated. They are not diphilic substances because both hydrophilic and hydrophobic parts are not combined in one molecule. However on the water surface the HACTS molecules can be arranged with their alkyl substituents to aerial phase and with siloxane groups to water. In Figure 4 surface pressure isotherms of hexamethylcyclotrisiloxane and hexaethylcyclotrisiloxane (HMCTS and HECTS, respectively) are shown. The π-S isotherms are different for the substances with different substituents. In the HECTS isotherm there are two well-expressed regions of the surface pressure growth. The first part in the area range from 19 to 13 Å^2 can be determined by a change of molecular conformation. The further surface pressure increase starts from the limiting area of 13 Å^2. For the HMCTS the surface pressure growth begins from 5 Å^2 and the dependence has no specific inflection points.

4. Discussion

The significant difference of the surface pressure isotherms of ATEOS and cetyl alcohol is determined by molecular structure of the substances. The results obtained can be explained by examining molecular conformations of the alkoxysilanes studied on the interface surface and chemical reactions running during formation of the LB organotriethoxysilane monolayer. In initial process phase the subphase surface area is big, and the amount of the substance on the surface is small, then the carbohydrate substituents of the molecules have horizontal orientation on the water surface. During compression by the movable barrier the molecules do not form a dense packed layer with vertical orientation of the alkyl groups in relation to the subphase. Reasons are relatively small substituent's length, weak cohesion between the substituents and steric effects of the ethoxy groups which can be hydrolyzed in part.

Schemes of reactions which can take place in the LB organotriethoxysilane monolayers formations are discussed in [12].

To explain the data presented in Table 1 the area occupied by the OC molecule on the water surface was calculated with using of following geometry. The alkyltriethoxysilane molecule can occupy two ultimate positions (Fig. 5).

1. All three oxygen atoms are directed to the water surface.
   In this case the area per one OC molecule is approximately defined by the area of the triangle which is the base of the pyramid formed by the –Si-O- bonds and the area of three rectangles projected from the ethoxy groups rests onto the water surface. The S_1 value is the same for all ATEOS.
   The area per one MTEOS molecule is less by the area occupied by one ethoxy group.
2. Two oxygen atoms and the alkyl substituent are directed to the water surface

The area S_2 is approximately defined by the area of the tetragon formed by the alkyl substituent and three ethoxy groups. The area value depends on the substituent sizes.

The area per one MADEOS molecule is less by the area occupied by the -CH_2-CH_3 group.

In Table 2 values of ultimate areas occupied by the OC molecule on the water surface are presented.

Comparison of calculated and experimental data presented in Tables 1 and 2 is in favor of a suggestion on a tilted position of the molecules in the ultimately

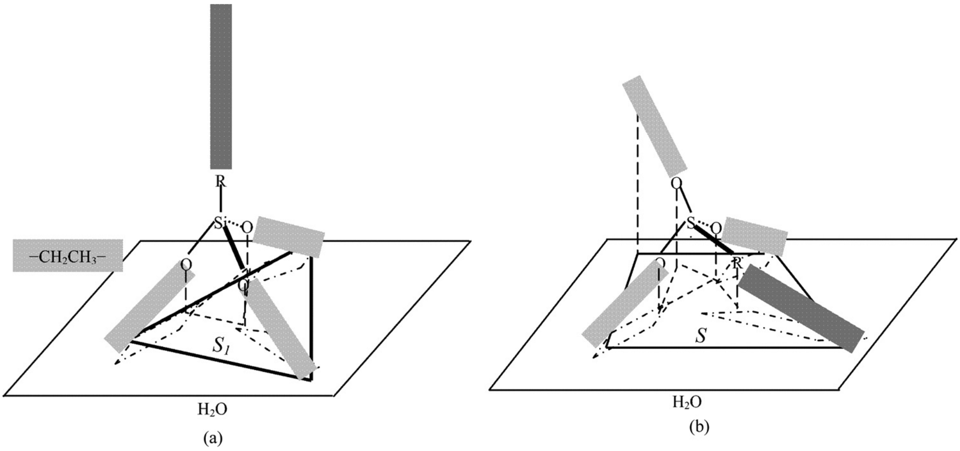


Figure 5. Two ultimate positions of the ATEOS molecule on the water surface for a calculation of area S_1 or S_2 occupied by the OC molecule.

compressed layer owing to exceeding interaction between the water and hydrogen bonds in the hydrocarbon substituent over the interaction between the alkyl substituents themselves.

In the case of the methylhexyldiethoxysilane the molecules overcreeping with the second layer formation may take place.

The data in Table 1 show a dependence of the limiting area per the molecule or the chain in the layer on the substituent length at the same substance amount on the water surface. So, at the silane amount ~0.026 mg the limiting area per the molecule is small length of the carbohydrate substituent:

1. Condensation of molecules in the monolayer with vertical orientation of long substituents.
2. Overcreeping of a part of molecules during compression.

The isotherms of hexadecyltriethoxysilane differ from the isotherms of ethoxysilanes with shorter alkyl group. The appearance of the inflection point on the HDTES isotherm is owing to an increase of the molecules cohesion in the ultimate monolayer and an increase of its rigidness with the chain length increase. If the

Table 2. Ultimate areas occupied by the OC molecule

R	S_1, Å^2	S_2, Å^2
	$RSi(OC_2H_5)_3$	
C_8H_{17}	34	68
$C_{10}H_{21}$	34	77
$C_{16}H_{33}$	34	99
	$(CH_3)RSi(OC_2H_5)_2$	
C_6H_{13}	24	51
C_8H_{17}	24	59
$C_{10}H_{21}$	24	67

substituent at the silicon atom will increase up to $C_{18}H_{37}$ then it is to expect an appearance of a condensed solid rigid monolayer.

The solvent influences weakly on the isotherm type for big amount of the substance on the water surface. However in the Table 1 it is shown that for small amounts (0.0088 mg of HDTES and 0.0078 mg of DTES) of the substance in dodecane bigger values of the limiting area and smaller surface pressure take place. It can be owing to a solvent's traces between the molecules' islands.

A necessary condition of creating the LB films of given thickness and orientation is the formation of a true equilibrium monolayer. In correspondence to Crisp recommendations [13] the monolayer is both true and equilibrium if reproducible π-S dependences are obtained in the process of the monolayer deposition from different solvents. Hence the limiting area per the molecule in the monolayer should not depend on these parameters.

Our investigation of the isotherms of the ATEOS with carbon atoms number in the substituent up to 16 has shown that the substances form liquid monolayers on the water surface. The alkyl substituents in the monolyaers are positioned at an angle in relation to the surface as the values of the limiting area in organotriethoxysilanes are equal to $32\,\text{Å}^2$ [26].

The cetyl alcohol forms the true solid monolayer on the water surface. Its limiting area per the molecule is close to the value of the cross section for organic SAS molecules ($\sim 20.5\,\text{Å}^2$), i.e., a rigid monolayer is formed with the strictly vertical position of organic chains.

The hysteresis existence in the monolayer compression-tension cycle can be explained by the appearance of a stable structure under compression. The structure arises owing to hydrolysis and condensation, it is not destroyed under tension.

Both HACTS and ATEOS behavior on the water under compression differs strongly. Firstly, the surface pressure increase begins at very small values of the area per one molecule. It can be owing to the following factors:

1. Overcreeping of molecular layers with the formation of a thin liquid film,
2. Polymerization of cyclotrisiloxanes and formation of big aggregates during the time before the layer compression owing to HACTS high reaction ability.

Secondly, the π-S isotherms are different for the substances with different substituents (Fig. 4). Such behavior discussed above is not typical for the monolayer structure.

5. Conclusions

1. Planar homogeneous LC alignment without rubbing has been obtained on the monomolecular decyltriethoxysilane film.
2. The LB conditions of monomolecular ordered DTEOS layers formation have been found and investigated. They are as follows:
    - temperature 20 ± 4°C,
    - water pH = 6,
    - solvent: a 50%:50% vol. mixture of toluene with isopropyl alcohol,
    - substance amount on the water surface ~ 0.02 mg,

- surface pressure ~10 mN m^{-1},
- the second compression monolayer is transferred onto the substrate during its extraction from water.

3. The LB technology is not applicable to form the monolayer HACTS structure at conditions studied.

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