ELSEVIER

Thin Solid Films 256 (1995) 186–191

thin solid films

Deposition of uniform fullerene films by LB technique

T. S. Berzina[a,*], V. I. Troitsky[a,*], O. Ya. Neilands[b], I. V. Sudmale[b], C. Nicolini[c]

[a] *Technobiochip, via Roma 28, 57030 Marciana, Italy*
[b] *Rigas Technical University, Azenes 14, LV-1048 Riga, Latvia*
[c] *Institute of Biophysics, University of Genoa, via Giotto 2, 16153 Genoa, Italy*

Received 28 February 1994; accepted 7 July 1994

Abstract

Deposition of uniform fullerene (C_{60}) films is carried out using the Langmuir–Blodgett (LB) technique. As an intermediate stage an LB film from a mixed monolayer of C_{60} and a specially selected surfactant compound is deposited. The surfactant compound used forms itself into amorphous uniform LB films and C_{60} molecules distribute homogeneously in this matrix. Another property of the surfactant compound is its solubility in hexane, in which C_{60} does not dissolve. One-component C_{60} film is obtained after treatment of the sample with hexane. To achieve this result mixtures of C_{60} with several compounds were studied and finally one of them was selected. Surface pressure–area isotherms were recorded to evaluate the degree of C_{60} dissolution in matrix monolayers. Deposited LB films were studied by optical microscopy, electron diffraction and transmission electron microscopy techniques to record changes of the structure and morphology under variation of the conditions and selection of the compounds. One-component C_{60} monolayers at the air–water interface as well as C_{60} films transferred with the horizontal lift technique were also investigated for interpretation of the data on mixed multilayers. Some features of the structure of the studied films are discussed.

Keywords: Deposition process; Electron diffraction; Electron microscopy; Langmuir–Blodgett films

1. Introduction

Fullerenes (C_{60}) [1] are compounds which promise very interesting applications. For example, alkali metal-doped fullerenes appear to be superconducting [2–4], while doped thin films become conducting [5]. Fullerenes embedded into lipid membranes act as efficient electron acceptors [6] and facilitate transport of electrons through a bilayer [7]. Employment of the Langmuir–Blodgett (LB) technique for deposition of highly organized fullerene thin films could reveal new technological possibilities. However, these are unusual for LB technique compounds. Obeng and Bard [8] studied the properties of C_{60} monolayers at the air–water interface and tried to deposit LB films. Although fullerene molecules concentrate at the air–water interface, deposition of uniform films of fullerene without the use of its modified derivatives is very problematic. One way to improve the quality of deposition is the dissolution of fullerene molecules in some surfactant matrix, done by Obeng and Bard using a matrix of arachidic acid. Octadecanol was also used [9] for the dissolution of C_{60} molecules, but this mixture does not form ideal monolayers at the air–water interface. Other attempts to deposit C_{60} LB films were made by Williams et al. [10], Nakamura et al. [11] and Long et al. [12]. However, monocomponent uniform fullerene LB films have not been deposited using the LB technique until now.

The structure of fullerenes has been investigated by X-ray diffraction [1, 13, 14], electron diffraction [1, 12] and scanning tunneling microscopy (STM) [15, 16] techniques. STM images of C_{60} samples show close packing of spherical molecules with lattice spacing of about 1.1 nm. X-ray diffraction studies at room temperature show that C_{60} molecules crystallize in a face-centered cubic (FCC) lattice with lattice spacing of 1.404–1.411 nm. The structure of the C_{60} LB films was investigated by STM, transmission electron microscopy and electron diffraction methods [17]. A FCC lattice with a unit-cell side of 1.420 nm was discovered.

Herein we present a method of producing uniform fullerene films in which an intermediate stage of the

---

*Permanent address: Zelenograd Research Institute for Physical Problems, 103460 Moscow, Russian Federation.

0040-6090/95/$9.50
SSDI 0040-6090(94)06278-1

deposition uses mixed monolayers of fullerene and a specially selected surfactant compound. To obtain a one-component fullerene film, surfactant compound matrix must be removed from the multilayer with a solvent acting selectively after the completion of the process.

2. Experimental details

Solutions of C_{60} and arachidic acid in benzene were prepared, as well as solutions of some donor and acceptor surfactant compounds listed below in benzene and in a mixture of chloroform with hexane (1:2). Concentrations of the initial solutions were 0.33 mg ml^{-1}. Appropriate volumes of these solutions were mixed to form monolayers of the C_{60} mixtures with the usual surfactant molecules in molar ratios from 0.5:2 to 1:1. In some experiments some amounts of chloroform and hexane were added to the solution of C_{60} to change the conditions of the compound spreading.

Study of surface pressure–area isotherms of the monocomponent and mixed monolayers and deposition of the LB films were performed with the LB MDT System (Russia). The C_{60} films were deposited by a horizontal lifting technique while a vertical lifting technique was used for the deposition of other compounds and mixed films. C_{60} monolayers were compressed for deposition up to a surface pressure of 40 $mN\ m^{-1}$. Deposition of the mixed monolayers was performed at surface pressure values of 25–40 $mN\ m^{-1}$ depending on the surfactant compounds used in the mixture. Usually a pressure of deposition was chosen that was 10–20 $mN\ m^{-1}$ lower than the collapse pressure. The speed of deposition by the vertical lift technique was 0.5 $cm\ min^{-1}$.

The morphology of the films deposited onto hydrophobic silicon and sapphire substrates was also examined with an optical microscope, LUMAM-I (Russia), at magnifications of up to 800. Silicon substrates were treated with dimethyldichlorosilane vapour and washed in hexane and acetone to make them hydrophobic. Sapphire substrates were irradiated with a wide electron beam at an accelerating voltage of 1 kV in a JEE-4C (Japan) vacuum chamber with a dose of approximately $10^{-4}\ C\ cm^{-2}$ at a pressure of 10^{-5} Torr. The thinnest film of polymerized vacuum oil grows on the substrate under the action of electrons and results in a hydrophobic surface. To control the quality of the film morphology 25–35 monolayers were usually deposited because at such thicknesses the changes in the interference colour of the film on a silicon substrate at the site of defective deposition are very strong and well distinguished.

Electron diffraction and electron transmission microscopy studies were carried out with electron microscope JEM-100C (Japan) at an accelerating voltage of 100 kV. The LB films consisting of 11–31 monolayers were deposited onto copper grids covered by collodion film 10–20 nm thick. To determine the spacings gold or bismuth thin films were evaporated on some samples.

3. Results and discussion

A surface pressure–area isotherm of the C_{60} dissolved in benzene (Fig. 1) shows an area per molecule of about 0.30 nm^2 as reported previously [10, 12]. This value suggests the formation of a layer at the air–water interface with an average thickness approximately equal to that of three monolayers because the area per C_{60} molecule in an ideal monolayer calculated from structural data [12–14, 17] cannot be less than 0.87 nm^2. Initial unsatisfactory spreading of the compound seems to be the main reason for such a small value. Indeed, when observing the surface of water in reflected light after solvent evaporation, non-uniform colored areas of the film were noticeable. Consequently, the observed area per molecule of 0.30 nm^2 cannot be characteristic of a monolayer, as in the case of fatty acid salts. When, for example, a 1:2 (v:v) mixture of benzene and hexane is used, the area per molecule increases by 2–3 nm^2 even though C_{60} is insoluble in hexane. Addition of chloroform also changes this value. The area per molecule depends on the conditions of solvent evaporation, on the duration of pause before compression and, probably, on the dose of solution used. Thus, on the one hand, different values of the area per molecule reported previously [10, 12, 17] are not surprising, but on the other hand, the usual selection method of technological conditions cannot significantly improve the spreading of C_{60} monolayers.

One-component C_{60} monolayers could be prepared only by a horizontal lifting technique. Optical microscopic observation of films deposited onto silicon sub-

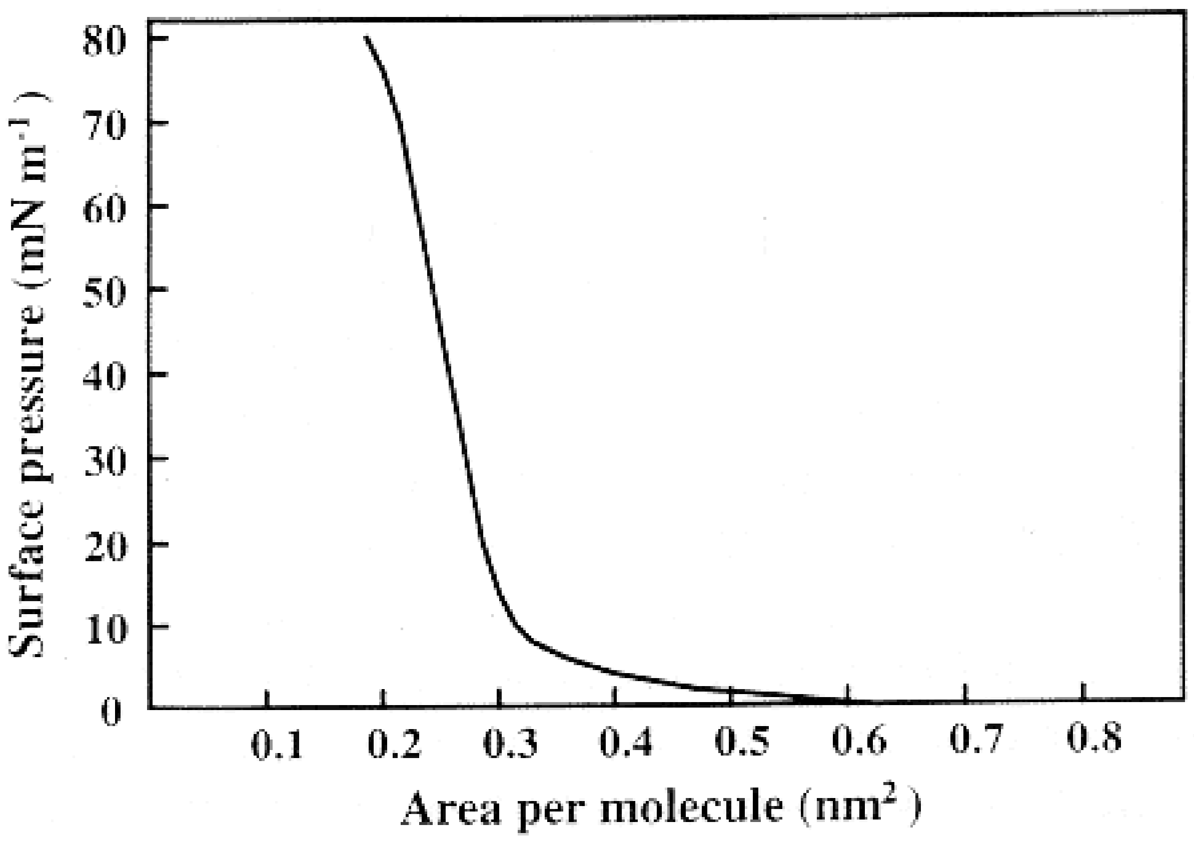

Fig. 1. Surface pressure–area isotherm of C_{60} layer spread at the surface of distilled water. Solution in benzene at a concentration of 0.33 mg ml^{-1}.

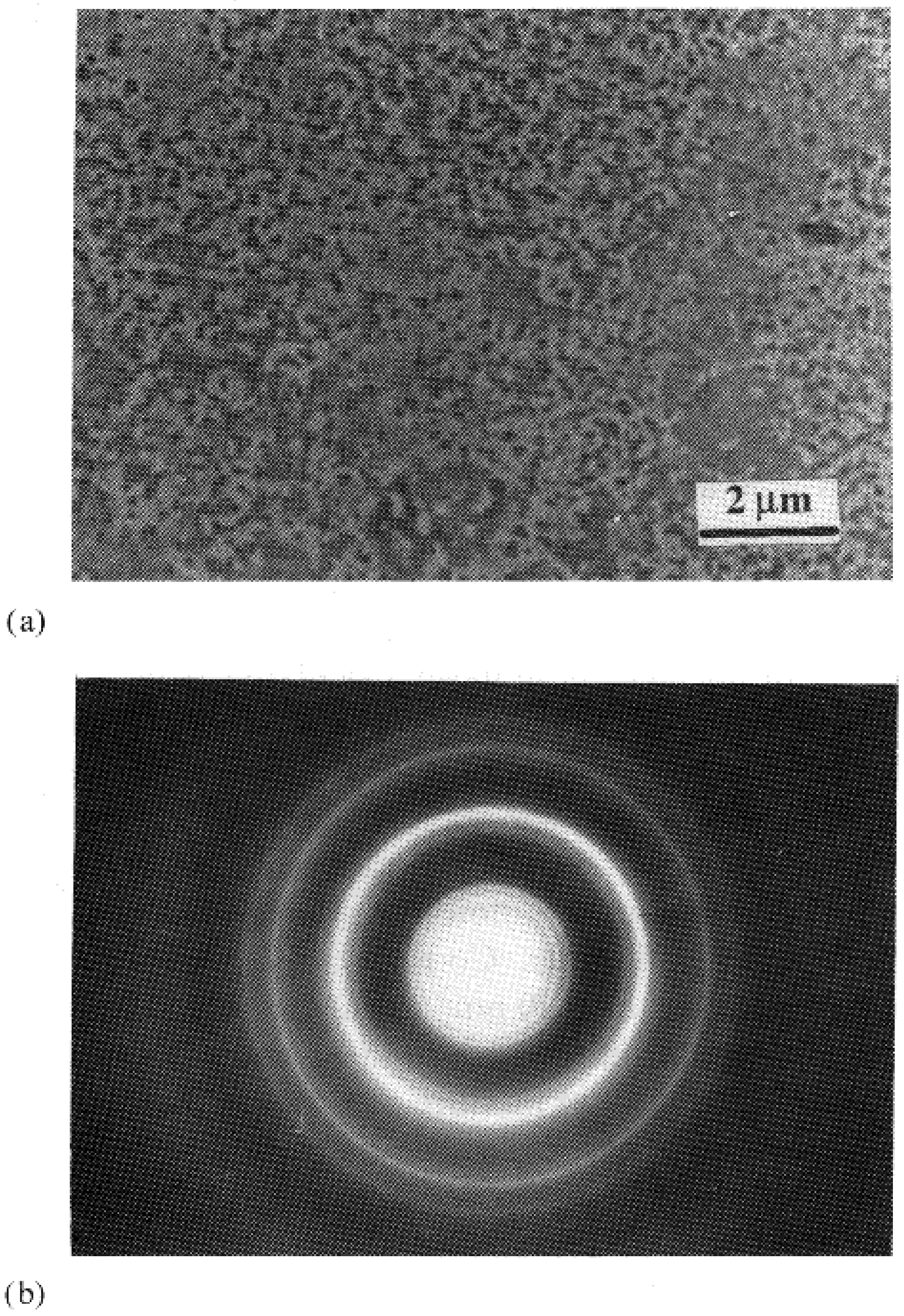

Fig. 2 Electron micrograph (a) and electron diffraction pattern without tilting the sample (b) of the C_{60} film deposited by the horizontal lift technique after compression up to 40 mN m^{-1}. Fifteen successive touchings of the surface in the areas separated by a grid.

strates shows non-uniform macroscopic areas caused by poor deposition. The crystallites that form the film can also be detected at high magnification. Typical patterns are demonstrated by the transmission electron micrograph (Fig. 2a) of the film on the collodion substrate. Here crystalline aggregates 100–400 nm in size are seen. The average dimensions of crystallites forming both aggregates mentioned above and areas between them of 30–40 nm can be derived from the widths of rings in the electron diffraction pattern (Fig. 2b) of the same sample.

Spacings corresponding to this electron diffraction pattern (Table 1) give a FCC lattice with a unit-cell side of 1.410 ± 0.007 nm. A preferred orientation of the crystallites with respect to the surface is not observed, as evidenced from tilting the sample up to an angle of 55°. Therefore, a polycrystalline structure is probable. However, *hkl* indices of the reflections shown in Table 1 and corresponding to the rings in Fig. 2b submit to the rule $k = l$ with the exception of the *620* reflection. Textures with an orientation of {111} planes preferably parallel to the substrate are possible under such conditions. If the mosaic angle is not too small this fact may be undetectable when tilting the sample because of the high symmetry of the cubic lattice and overlapping of arcs formed by different reflections. The appearance of a weak ring with spacing of 0.226 nm can be explained by the presence of a small amount of crystallites oriented in some other manner, which is quite possible according to the results [17] obtained with high-resolution electron microscopy. Therefore, the possibility of a texture arising cannot be ruled out and, in fact, it is reasonable because of the orienting influence of the substrate.

Table 1
Electron diffraction data for the C_{60} films deposited by the horizontal lift technique

Spacings (nm)	*hkl*	Spacings (nm)	*hkl*
0.814	*111*	0.289	*422*
0.707	*200*	0.267	*511*
0.407	*222*	0.254	*044*
0.354	*400*	0.226	*620*
0.323	*133*	0.205	*444*

Following the method proposed by Obeng and Bard [8], mixed monolayers of the C_{60} with different compounds were studied at the air–water interface. The films were then transferred onto the substrates. When arachidic acid was used as a matrix for dissolution of C_{60} molecules, precipitation of C_{60} crystalline aggregates always occurred independent of processing conditions and the mixture compositions. Electron microscopy studies show that the morphology of the films is similar to that shown in Fig. 2a but with a lower concentration of the C_{60} crystallites. To increase the solubility of the C_{60} molecules in the matrix, surfactant donor compounds were used since C_{60} has been shown to be an electron acceptor when photoexcited [6] and the interaction with donor molecules could be stronger than that with fatty acid molecules.

When using the mixtures of C_{60} with hexadecyl-bis(ethylenedithio)-tetrathiafulvalene ($C_{16}H_{33}$-BEDT-TTF) (Fig. 3a) a considerable decrease in the concentration of C_{60} crystallites in the deposited film was observed, although the morphology remained poor. The poor morphology can be explained by an unsatisfactory spreading of the $C_{16}H_{33}$-BEDT-TTF at the air–water interface [18] as well as by the tendency of this compound to crystallize. This essentially pushes out the C_{60} molecules from the crystallites. Nevertheless, the comparison of the surface pressure–area isotherms for the $C_{16}H_{33}$-BEDT-TTF monolayers with those for the mixtures of $C_{16}H_{33}$-BEDT-TTF and C_{60} shows that a more homogeneous distribution of the C_{60} molecules in this matrix takes place with respect to distribution in the arachidic acid monolayer. For example, when a mixture of C_{60} with $C_{16}H_{33}$-BEDT-TTF in a 1:2 molar ratio was used (Fig. 4) approximately 23% of the

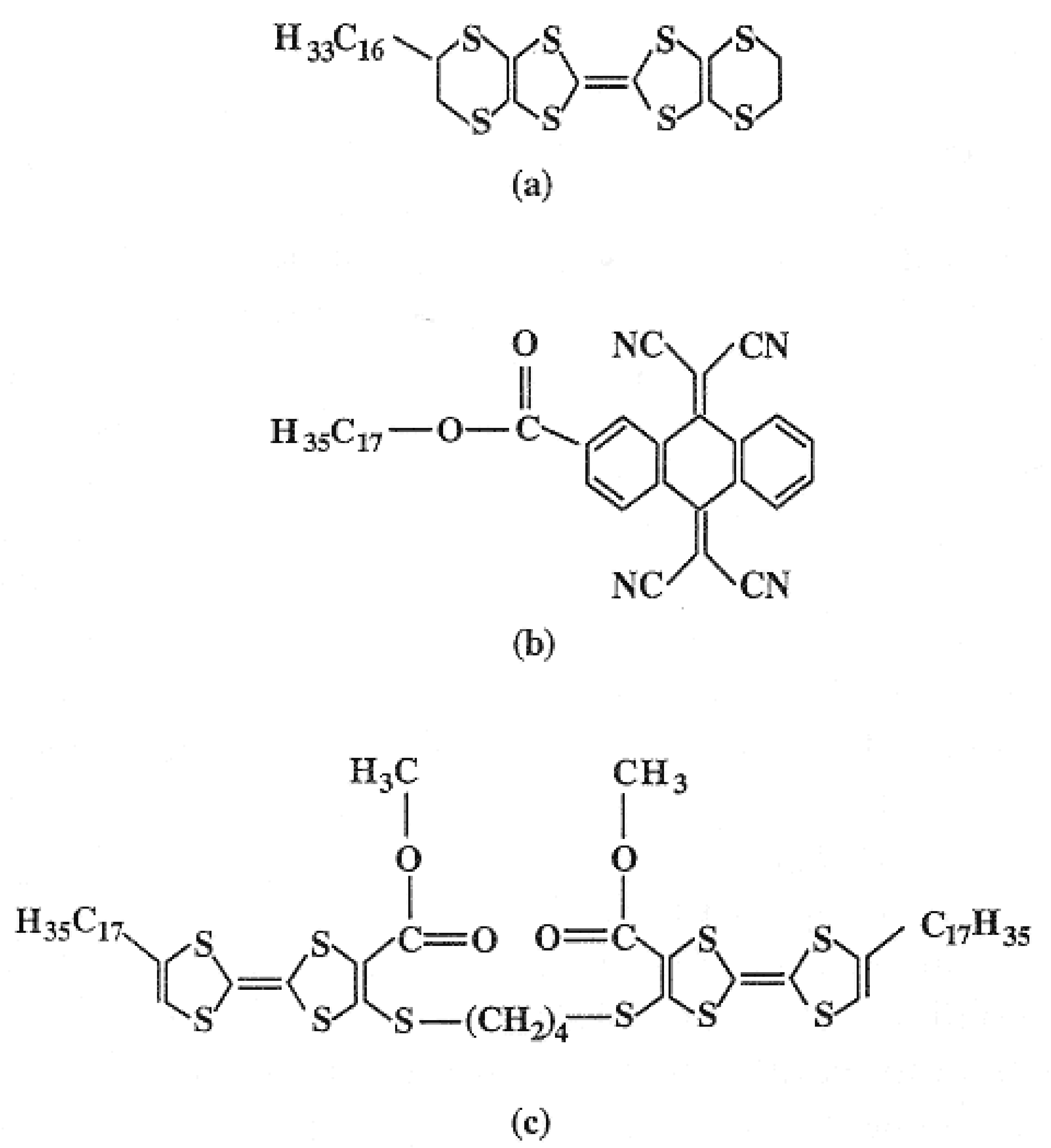

Fig. 3. Chemical formulae of $C_{16}H_{33}$-BEDT-TTF (a), $C_{17}H_{35}$-OC-TCNAQ (b), and SURF (c) molecules used for deposition of mixed LB films with C_{60}.

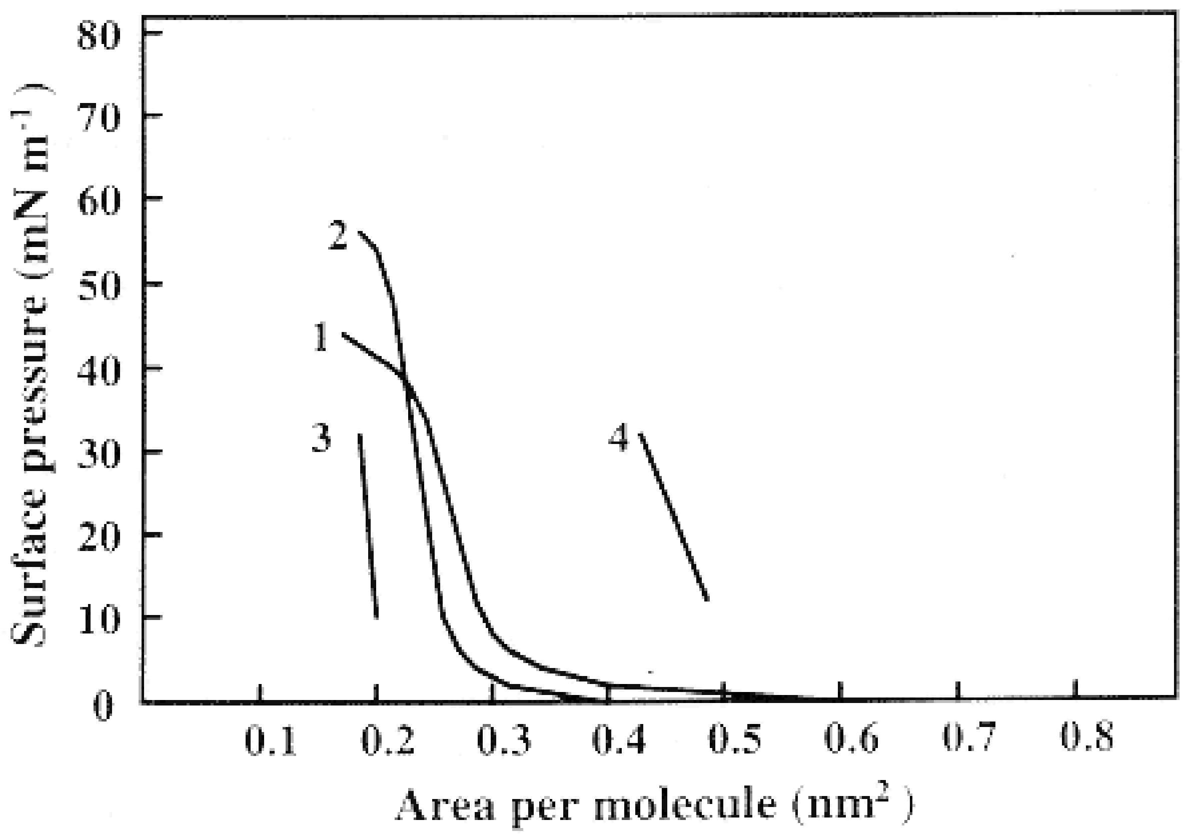

Fig. 4. Surface pressure–area isotherms of $C_{16}H_{33}$-BEDT-TTF monolayer (1) and mixed monolayer of C_{60} with $C_{16}H_{33}$-BEDT-TTF in the molar composition of 1:2 (2) spread at the surface of pure water from a solution of benzene, chloroform and hexane mixture. Lines 3 and 4 show the disposition of the isotherms under the condition of complete elimination of C_{60} molecules from the monolayer (3) and under the condition of ideal dissolution of the latter in the matrix (4).

monolayer area is occupied by C_{60} molecules. This was determined from the area per molecule of a $C_{16}H_{33}$-BEDT-TTF monolayer of 0.31 nm^2 and average area per molecule in the mixed monolayer of 0.27 nm^2. If ideal dissolution takes place, C_{60} molecules must occupy 58% of the monolayer surface if we assume that the area per C_{60} molecule is 0.87 nm^2. To examine the degree of dissolution of the C_{60} molecules in the matrix, we can introduce the parameter $v = S_{C60}/S_{max}$, where S_{C60} and S_{max} are the real and maximum possible areas occupied by C_{60} molecules in the mixed monolayer respectively. The value of $1 - v$ shows the proportion of the total number of molecules that are pushed out from the monolayer, or segregated in big crystallites, or form the second row of C_{60} molecules in the monolayer, and so on. In the example above $v = 0.22$. In our experiments with an arachidic acid matrix v did not exceed 0.1.

A small addition of heptadecyloxycarbonyltetracyanoanthraquinodimethane ($C_{17}H_{35}$-OC-TCNAQ) acceptor (Fig. 3) in the $C_{16}H_{33}$-BEDT-TTF monolayer considerably improves the spreading of the latter and suppresses, to some extent, the tendency to crystallize [18]. Owing to this property the use of such a complex matrix may homogenize the distribution of the C_{60} molecules. The monolayers formed from the mixture of C_{60} with $C_{16}H_{33}$-BEDT-TTF and $C_{17}H_{35}$-OC-TCNAQ molecules in the ratio of 1:2:0.2 were studied at the air–water interface and in transferred films. The portion of the monolayer area occupied in this case by C_{60} molecules is 26% (Fig. 5) whereas for ideal dissolution it must be equal to 53% and $v = 0.32$. A transmission electron microscopy study of the deposited films confirms that precipitation of the C_{60} crystallites, in spite of the morphology of the layer, is considerably better than in the previous experiments.

To improve the dissolution of C_{60} a surfactant donor compound shown in Fig. 3c (SURF), which forms amorphous LB films, was used. The dissolution of the C_{60} molecules in such a monolayer was very good. The surface pressure–area isothem in Fig. 6 shows that for a 1:2 mixture of C_{60} with SURF, v equals 0.72. A uniform, amorphous film is deposited using a monolayer of this mixture as indicated by the transmission

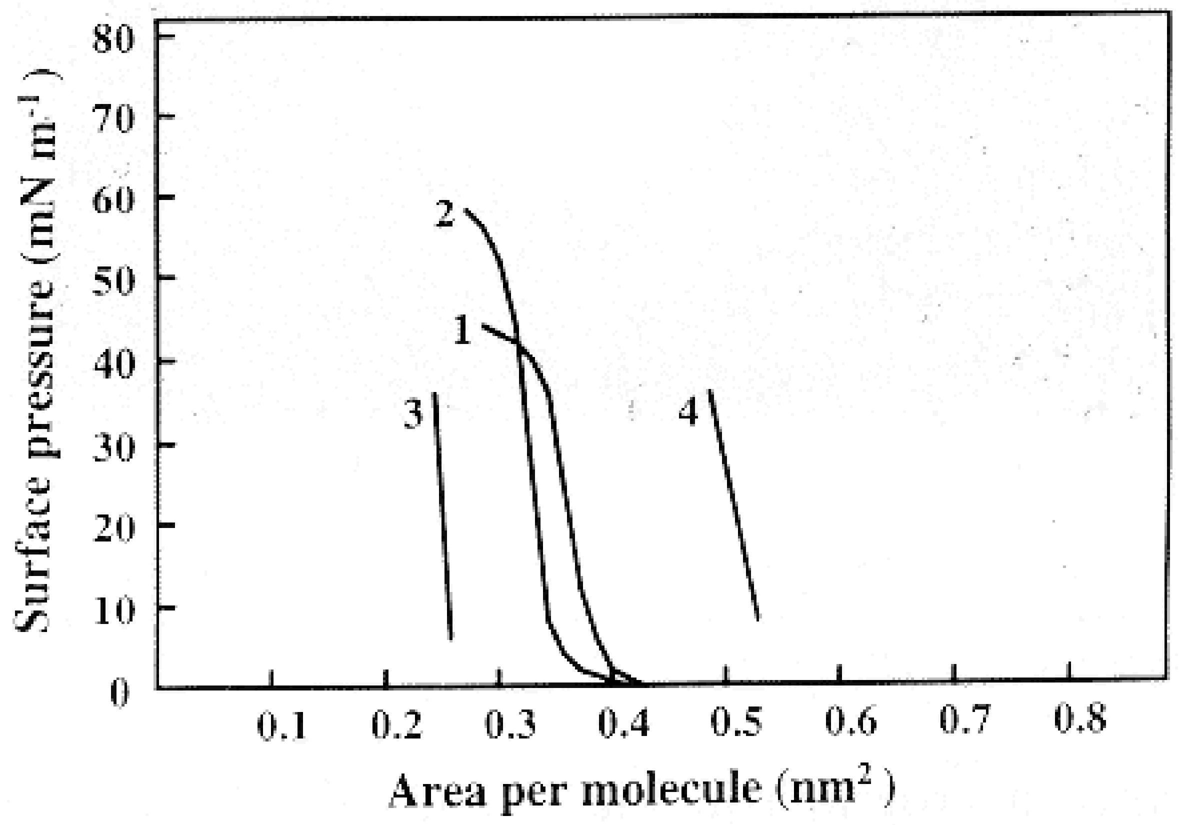

Fig. 5. Surface pressure–area isotherms of $C_{16}H_{33}$-BEDT-TTF monolayer with the addition of $C_{17}H_{35}$-OC-TCNAQ acceptor in the molar ratio of 1:0.1 (1) and mixed monolayer of C_{60} with $C_{16}H_{33}$-BEDT-TTF and $C_{17}H_{35}$-OC-TCNAQ in the molar ratio of 1:2:0.2 (2) at the surface of pure water. The compounds are dissolved in a mixture of benzene, hexane and chloroform. The meaning of lines 3 and 4 is the same as in Fig. 4.

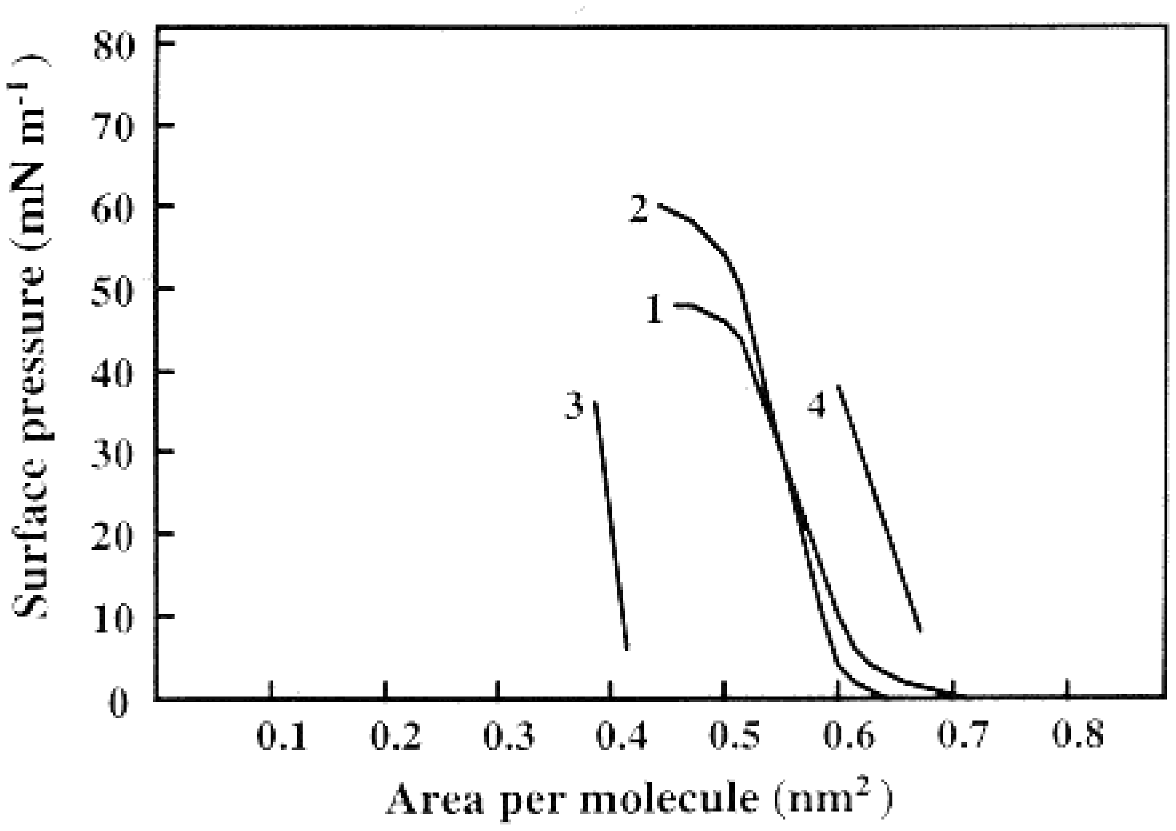

Fig. 6. Surface pressure–area isotherms of the SURF monolayer (1) and mixed monolayer of C_{60} with the SURF in molar composition of 1:2 (2) spread at the surface of pure water from the solution in benzene. The meaning of lines 3 and 4 is the same as in Fig. 4.

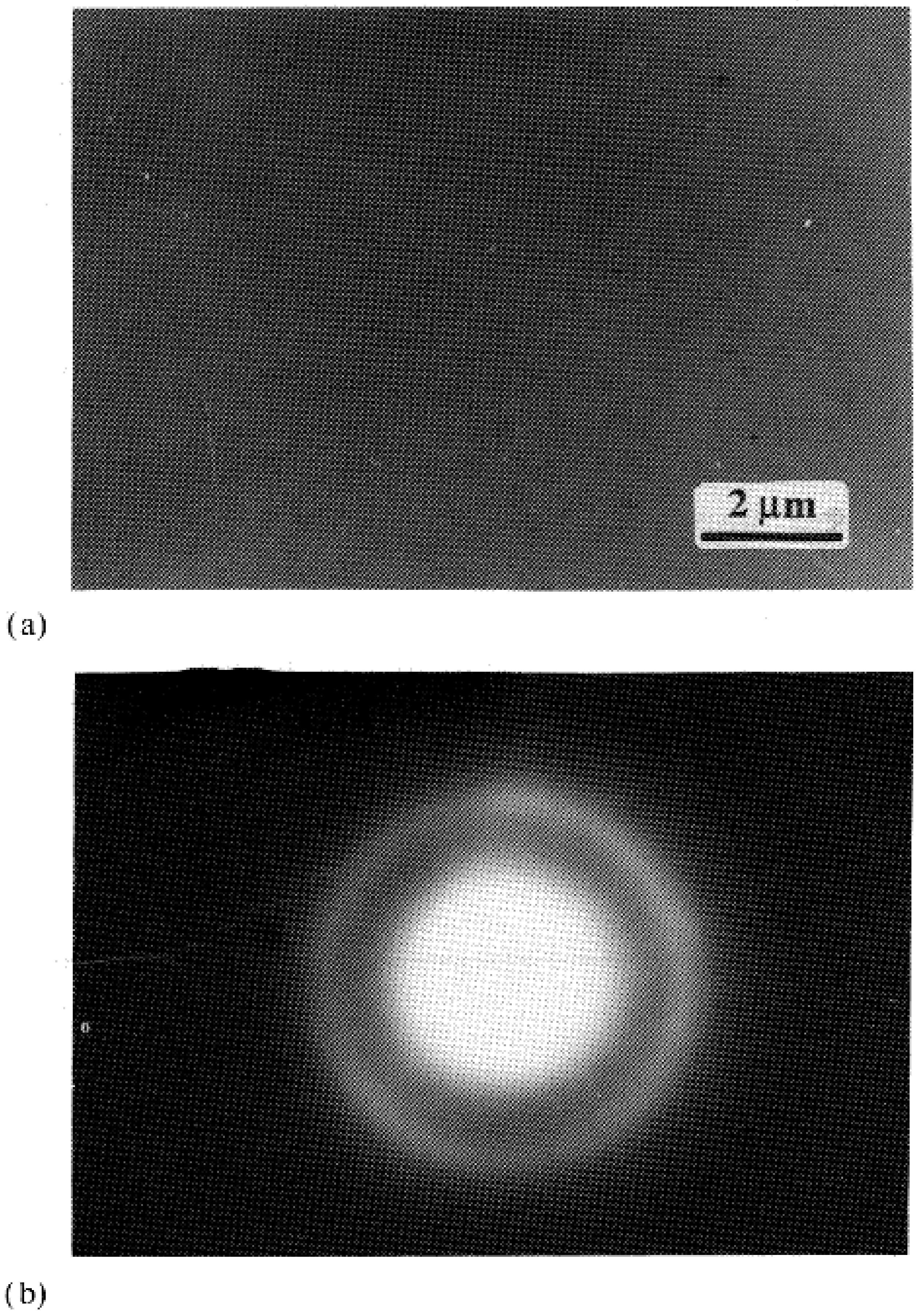

Fig. 7. Electron micrograph (a) and electron diffraction pattern (b) of 25 monolayers of C_{60} mixture with SURF in molar ratio of 1:2. Surface pressure of deposition, 32 mN m^{-1}.

electron micrograph in Fig. 7 and electron diffraction pattern in Fig. 7b. A very low surface concentration of precipated crystallites is sometimes evident, which can explain the deviation of ν from 1. However, decreasing the C_{60} content in the mixture did not alter this. From experiment, the highest content of the C_{60} molecules at which very homogeneous multilayers can be deposited is a ratio of approximately 1:2. The value of ν can also decrease due to a penetration of some part of the C_{60} molecules into the tails of the SURF molecules, which is possible since changing of conformation of SURF can easily occur and the dimension of the $-S-(CH_2)_4-S-$ bridge is comparable with the diameter of the C_{60} molecule. In this case, the increase of average area per molecule will not be proportional to the area per C_{60} molecule. Such a penetration is also in agreement with the supposition of donor–acceptor interaction because in this case donor groups of SURF and C_{60} molecules should be closely packed. Unfortunately, we could not obtain evidence of charge-transfer complex formation, although IR spectra of the films have been recorded.

Orientation of the C_{60} crystallites that precipitate in the mixed film is very specific. Spacings (Table 2) corresponding to the electron diffraction pattern (Fig. 8) from such an area of the film show the assembly of crystallites with the planes {*321*} and {*941*} to be preferably parallel to the substrate plane. When tilting the sample, obvious features of the texture with the axis normal to the layer plane are observed. This may result from a packing of the SURF molecules. In the (*321*) plane, for example, C_{60} molecules form a lattice with periods of 2.23 and 1.73 nm and with an angle between corresponding vectors of 105°. The area of such a cell is

Table 2
Spacings in the structure of C_{60} crystallites incorporated into the mixed film of C_{60} and SURF compounds

Spacings (nm)	Probable sets of *hkl* indices	
	I	II
0.323	$1\bar{3}3$	$1\bar{3}3$
0.291	$2\bar{4}2$	$\bar{2}42$
0.193	$4\bar{6}0$	
0.172		$0\bar{2}8$
0.161	$0\bar{4}8$	$\bar{2}\bar{6}6$
0.145	$4\bar{8}4$	$\bar{4}84$

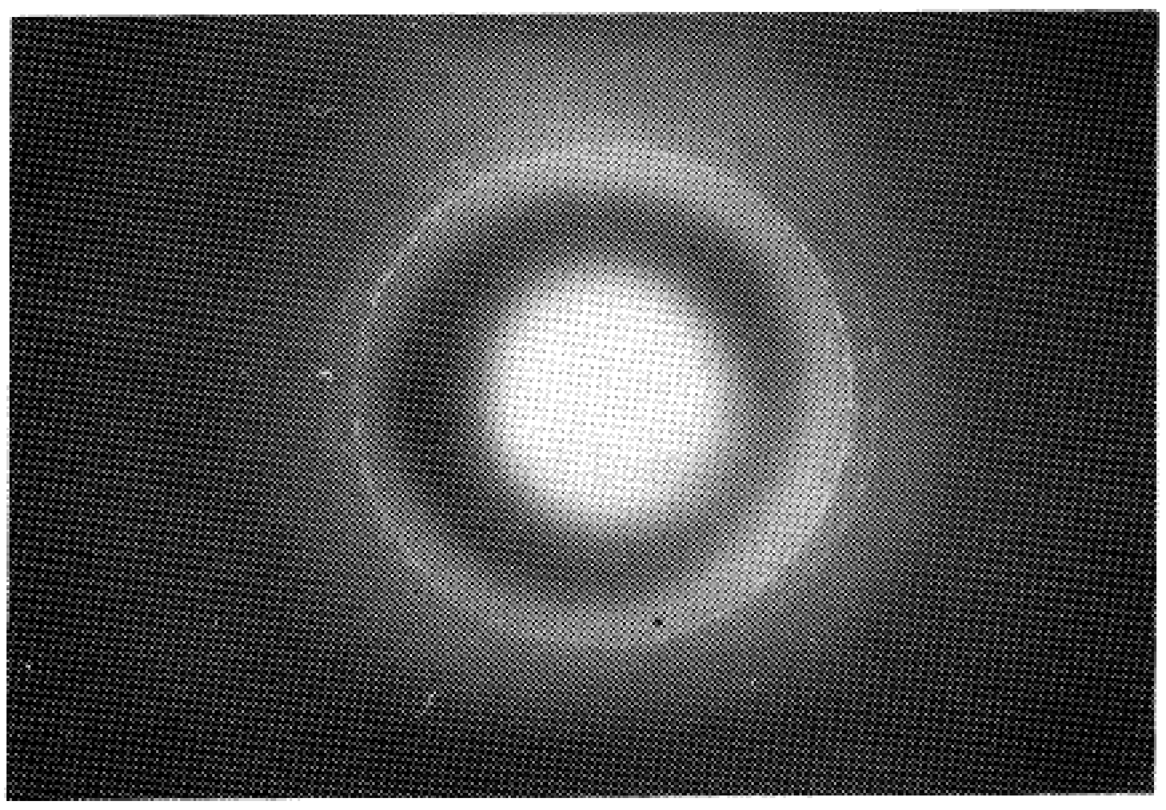

Fig. 8. Electron diffraction pattern from the area of 25 monolayers of the C_{60} mixture with SURF in molar ratio of 1:2 with precipitated C_{60} crystallites. Surface pressure of deposition, 32 mN m^{-1}.

equal to 3.72 nm^2, which compares quite well with the area per six SURF molecules.

It is important to note that the SURF compound is soluble in hexane, whereas C_{60} is not. After treatment of the sample by hexane the thickness of the film decreases and monocomponent C_{60} film remains on the substrate. It is interesting that no crystallization of C_{60} takes place and a very uniform amorphous C_{60} film is formed. Electron microscopic images show that the morphology is exactly the same as that before the treatment. No changes in film morphology and structure occur even if the sample is kept in hexane over several days. It is speculated that recrystallization is suppressed because the diffusion of C_{60} molecules is restricted by the matrix molecules. Removal of the SURF molecules and translation of the C_{60} towards the substrate occur simultaneously. This retards the lateral motion of the molecules. A similar result was obtained for other two-component LB films [19]. Thus, such a method of preparation of uniform films can be applied to many surfactant compounds, which do not form high quality multilayers.

4. Conclusions

Uniform amorphous C_{60} films can be deposited with the use of the LB technique. The film preparation procedure is carried out in the following manner. First, a surfactant compound for formation of mixed monolayers with C_{60} is selected so as to achieve homogeneous distribution of the C_{60} molecules in the monolayer. The LB film of the compound itself must be uniform and amorphous. An additional requirement is its solubility in some solvent that does not dissolve the C_{60} fraction. Then an LB film of C_{60} mixture with the selected compound is deposited onto the substrate. Finally, the sample is treated with the solvent acting selectively on the matrix molecules. Monocomponent uniform C_{60} film remains on the surface of the substrate after such treatment.

References

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature, 347* (1990) 354.

[2] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature, 350* (1991) 600.

[3] M. J. Rosseinsky, A. P. Ramirez, S. H. Glarum, D. W. Murphy, R. C. Haddon, A. F. Hebard, T. T. M. Palstra, A. R. Kortan, S. M. Zahurak and A. V. Makhija, *Phys. Rev. Lett., 66* (1991) 2830.

[4] K. Taigaki, I. Hirosawa, T. W. Ebbsen, J. Mizuki, Y. Shimakawa, Y. Kubo, J. S. Tsai and S. Kuroshima, *Nature, 356* (1992) 419.

[5] R. C. Haddon, A. F. Hebard, M. J. Rosseinsky, D. W. Murphy, S. J. Duclos, K. B. Lynos, B. Miller, J. M. Rosamilia, R. M. Fleming, A. R. Kortan, A. J. Muller, R. H. Eick, S. M. Zahurak, R. Tycko, G. Dabbagh and F. A. Thiel, *Nature, 350* (1991) 320.

[6] K. S. Hwang and D. Mauzerall, *J. Am. Chem. Soc., 114* (1992) 9705.

[7] K. S. Hwang and D. Mauzerall, *Nature, 361* (1993) 138.

[8] Y. S. Obeng and A. J. Bard, *J. Am. Chem. Soc., 113* (1991) 6279.

[9] J. Milliken, D. D. Dominguez, H. H. Nelson and W. R. Barger, *Chem. Mater., 4* (1992) 252.

[10] G. Williams, C. Pearson, M. R. Bryce and M. C. Petty, *Thin Solid Films, 209* (1992) 150.

[11] T. Nakamura, H. Tachibana, M. Yumura, M. Matsumoto, R. Azumi, M. Tanaka and Y. Kawabata, *Langmuir, 8* (1992) 4.

[12] C. Long, Y. Xu, F. Gou, Y. Li, D. Xu, Y. Yao and D. Zhu, *Solid State Commun., 82* (1992) 381.

[13] P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich and K. Holezer, *Nature, 351* (1991) 632.

[14] P. Meiney, J. E. Fischer, A. R. McGhie, W. Komanow, A. M. Denenstein, J. P. McCauley, Jr. and A. B. Smith, *Phys. Rev. Lett., 66* (1991) 2911.

[15] J. R. Wilson, G. Meijer, D. S. Bethune, R. D. Johnson, D. D. Chambliss, M. S. deVries, H. E. Huziker and R. H. Wendt, *Nature, 348* (1991) 621.

[16] J. L. Wragg, J. E. Chamberlin, H. W. White, W. Krätschmer and K. Huffman, *Nature, 384* (1991) 623.

[17] P. Wang, M. Shamsuzzoha, X.-L. Wu, W.-J. Lee and R. M. Metzger, *J. Phys. Chem., 96* (1992) 9025.

[18] T. S. Berzina, S. L. Vorobyova, V. I. Troitsky, V. Yu. Khodorkovsky and O. Ya. Neilands, *Thin Solid Films, 210/211* (1992) 317.

[19] S. V. Ayrapetiants, T. S. Berzina, S. A. Shikin and V. I. Troitsky, *Thin Solid Films, 210/211* (1992) 261.