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# Design and compressibility of Langmuir monolayers from organometallic nanocyclic complexes

H V Grushevskaya, N G Krylova, I V Lipnevich

Belarusian State University, 4 Nezavisimosti Ave., Minsk 220030, Belarus

E-mail: krylovang@bsu.by

**Abstract.** We propose to control design of organometallic conducting Langmuir monolayer by utilizing geometrodynamical approach. By means of this approach the compressibility of the monolayer, which consists of molecules of thiophene-pyrrole series oligomer with covalently bound hydrophobic alkyl chain, has been analyzed for different subphase with iron salts. It has been discovered that the monolayers are polymerized and turn into monolayers of nanocyclic organometallic coordination compounds at a two-dimensional phase transition of the first order.

## 1. Introduction

At present, conducting polymers are perspective materials for effective optimization of electrical and electro-chemical characteristics of nanosensors [1-3]. One of the promising directions to design ultra-thin films of metal-polymer compounds is their self-organized formation from metal complexes of macrocyclic coordination compounds [4]. The Langmuir – Blodgett (LB) technique is a nanotechnology to fabricate monolayers self-assembling on liquid-subphase surface in the process of a two-dimensional (2D) first-order phase transition from 2D gas up to condensed state of monolayer.

The consideration of monolayer compressibility  $\kappa$  can provide new information about thermodynamics and structural characteristics of the monolayers. The experimental determination of the surface compressional modulus ( $K$ ) in dependence on the area per molecule ( $A$ ) shows a nonlinear dependence  $K$  on  $A$  [5]. The  $K$  value reaches a maximum in two phase transition points and then decreases nearly to zero while the area per molecule decreases within the phase transition region named isotherm plateau.

However, the known procedures (e.g., [6]), which handle the statistical analysis of experimental data set for the monolayer compressibility  $\kappa$  in the whole region of surface pressure  $\pi$ , allow us to determine only the mean value of the compressibility coefficient – the "apparent" compressibility  $C'$  equals to  $1/K$  in relatively linear sections of the isotherms.

Besides this, as known [7-11], in the Langmuir monolayer one finds two-dimensional lattices of metal ions underneath the air–water interface and these lattices evolve in structure with pH, ion concentration, and time. Therefore, new methods for control of these monolayers states during time have to be developed. In this paper we use a geometrodynamical approach [12,13] to perform statistical analysis of compression isotherms for metastable Langmuir monolayers. It allows us to discover features of the compressibility coefficient  $\kappa$  based on experimental data concerning the 2D phase transitions of first order at different compression rates.

A goal of this paper is to study the compressibility of monolayer from coordination complexes of thiophene-pyrrole series oligomer on surface of different iron-salt subphases and propose a method for



design of LB-films according to features of monolayer-compressibility behavior at 2D phase transition of the first order.

## 2. Materials and methods

Salts  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  и  $\text{FeCl}_3$  (Sigma-Aldric, USA), hydrochloric acid, deionized water were used to prepare subphases. Monolayers and Langmuir – Blodgett films was formed from amphiphilic oligomer of thiophene derivatives: 3-hexadecyl-2,5-di(thiophen-2-yl)-1*H*-pyrrole (H-DTP, H-dithionilepyrrole). H-dithionilepyrrole was synthesized by a method proposed in [14].

All salt solutions have been prepared with deionized water with resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$ .

Iron-containing Langmuir monolayers are fabricated on an automated home-built Langmuir trough with controlled deposition on a substrate [15]. Hexan solution of DTP was dripped with the help of a micropipette on a liquid subphase surface. Langmuir monolayers were obtained by compressing of DTP molecules on air / aqueous subphase interface. Control of the surface tension was performed by a highly sensitive resonant inductive sensor. The Y-type transposition of monolayers on supports was performed by their vertical dipping. The complexes  $\text{Fe}(\text{II})\text{DTP}_3$  of high-spin  $\text{Fe}(\text{II})$  with thiophene-pyrrole ligands were synthesized by LB-technique at compression of H-dithionilepyrrole molecules on the surface of subphase with salts of three-valence Fe [15].  $\text{Fe}(\text{NO}_3)_3$  и  $\text{FeCl}_3$  solutions were used as subphases for the monolayer formation.

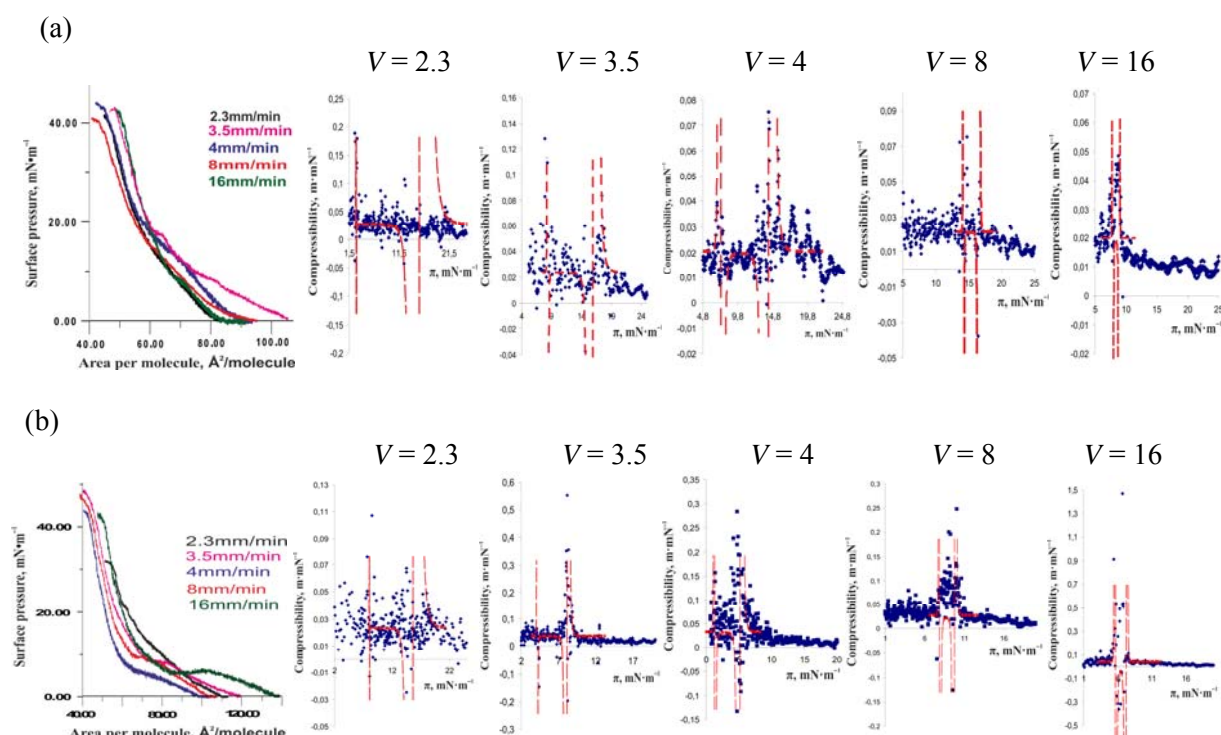
Spectral studies in visible range were carried out using a confocal micro-Raman spectrometer Nanofinder HE (“LOTIS-TII”, Tokyo, Japan–Belarus) by laser excitation at wavelength 532 nm and spectral resolution equals 0.1 nm.

Valent states of transition metal centers in coordination-complexes, from which iron-containing LB-monolayers are formed, have been detected by Mössbauer spectroscopy. Mössbauer spectra were registered in transmission geometry at room temperature utilizing spectrometer MS2000 with source of  $^{57}\text{Co}/\text{Rh}$  (40 mCu). All isomer shifts are represented relative to  $\alpha\text{-Fe}$ .

## 3. Thermodynamical analysis

Typical experimental dependences of the surface pressure  $\pi$  upon the area per molecule  $A$  (compression  $\pi - A$ -isotherm) for DTP-monolayer fabricated on surfaces of  $\text{Fe}(\text{NO}_3)_3$  - and  $\text{FeCl}_3$  - containing subphases are shown in figure 1. As one can see, the phase transition occurs in a monolayer formed on  $\text{FeCl}_3$  subphase at less surface pressure value than in a monolayer formed on subphase with  $\text{Fe}(\text{NO}_3)_3$ . The corresponding dependences  $\kappa(\pi)$  at different compression rates  $V$  have been approximated by theoretical curves, as represented in figure 1 (red dashed lines). The phase-transition width  $\Delta\pi_{\text{pht}}$  is determined as a difference between two singular points on a theoretical curve. In figure 2 dependences of  $\Delta\pi_{\text{pht}}$  on compression rates  $V$  are shown for monolayers fabricated on  $\text{FeCl}_3$  - and  $\text{Fe}(\text{NO}_3)_3$  -containing subphases.  $\Delta\pi_{\text{pht}}$  is seen to decrease with increase of  $V$ , at that, this dependence behaves as  $1/V^3$ .  $\Delta\pi_{\text{pht}}$  was established to be larger for the monolayer formed on subphase with  $\text{Fe}(\text{NO}_3)_3$  than for the monolayer formed on subphase with  $\text{FeCl}_3$ . In contrast to a model system of Van der Waals gas type, the theoretical dependence of compressibility on  $\pi$  changes a sign twice and, consequently, describes metastable state well. Thus, a range of values of surface pressure, at which phases coexist due to their instability, diminishes with rise of the compression rate  $V$  and, consequently, the plateau degenerates into a tricritical point. Respectively, increase of the rate  $V$  results in the monolayer turns into a glass-like state of a supercooled liquid state type.

In Table 1 values of the monolayer compressibility, which were determined according data in figure 1, are represented for the Langmuir monolayers before the phase transition, in the phase transition state and for the LB-monolayer after the phase transition. As one can see, though before the phase transition the compressibility values for monolayers fabricated on subphases with  $\text{Fe}(\text{NO}_3)_3$  are lower than for  $\text{FeCl}_3$  at all  $V$ ,  $\kappa$  values after the phase transition are larger for  $\text{Fe}(\text{NO}_3)_3$  than for  $\text{FeCl}_3$ . The compressibility  $\kappa$  of monolayers after the phase transition is 3-5 times lower than before phase transition. Thus, a structure of the monolayer formed on the subphase with  $\text{FeCl}_3$  is the more rigid one.



**Figure 1.**  $\pi - A$ -isotherms (left) and dependences of compressibility  $\kappa$  on surface pressure  $\pi$  at different compression rates  $V = 2.3, 3.5, 4.0, 8.0, 16.0$  mm/min (right) in first-order 2D-phase transition for monolayers fabricated on subphases with  $\text{Fe}(\text{NO}_3)_3$  (a) and  $\text{FeCl}_3$  (b). Symbols denote experimental data processing results, dashed red curves are the theoretical predictions.

**Table 1.** The value of Langmuir-monolayer compressibility formed on  $\text{Fe}(\text{NO}_3)_3$  - and  $\text{FeCl}_3$ -containing subphases at different compression rate before, at, and after first-order phase transition (PT).

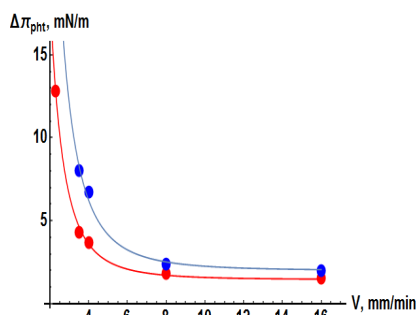
Compression rate, mm/min	Compressibility, m/N					
	before PT		at PT <sup>a</sup>		after PT	
	$\text{Fe}(\text{NO}_3)_3$	$\text{FeCl}_3$	$\text{Fe}(\text{NO}_3)_3$	$\text{FeCl}_3$	$\text{Fe}(\text{NO}_3)_3$	$\text{FeCl}_3$
2.3	33±10	45±16	24±11	25±15	8.5±1.0	9.0±1.9
3.5	34±10	47±16	24±10	30±15	8.6±1.0	7.4±0.9
4.0	20±3	50±20	20±4	30±19	8.0±0.4	7.6±1.9
8.0	23±3	35±7	22±3	25±9	11.0±1.5	8.8±1.4
16.0	19±5	40±20	19±4	30±15	6.7±0.4	6.2±1.1

<sup>a</sup> Values of compressibility are determined in the middle between the two singular points of the theoretical curves

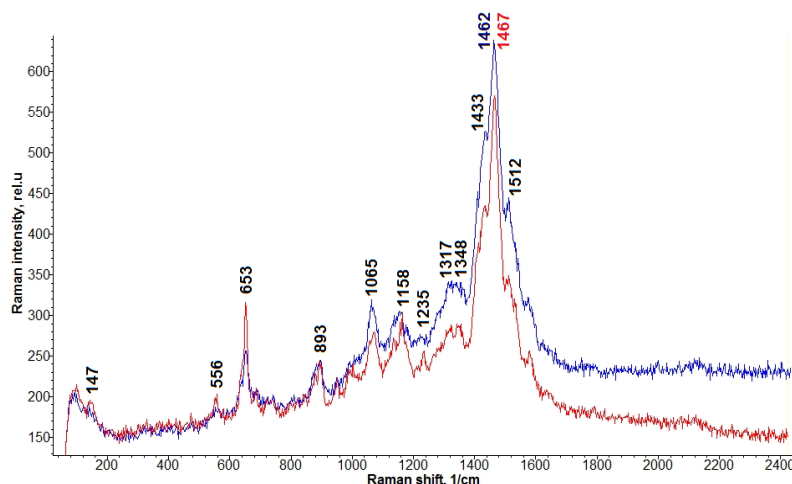
#### 4. Raman spectroscopy of Fe-containing LB-films

In figure 3 Raman spectra of 5 LB-DTP-monolayers fabricated on  $\text{Fe}(\text{NO}_3)_3$  - and  $\text{FeCl}_3$  -containing subphases are shown. In [3] characteristic molecular vibrations observed in the Raman spectrum of 5-, 7-monolayer LB-DTP-film formed on subphase with  $\text{Fe}(\text{NO}_3)_3$  have been examined. At fabrication of

LB-monolayer on subphase with  $\text{FeCl}_3$  narrowing of all Raman lines is observed that evidence the weaker interaction of the metal centers with surroundings. Intensities of Raman bands  $556\text{ cm}^{-1}$ ,  $653\text{ cm}^{-1}$  (ring in-plane deformation) and  $1235\text{ cm}^{-1}$  (CH-bending) for LB-films formed on  $\text{FeCl}_3$ -containing subphase increase. Besides this, intensification of spectral band  $1158\text{ cm}^{-1}$ , being characteristic for Cl–O vibration, is registered. Shift of 2-subst pyrrole Quadrant stretch Raman band into high-frequency region (from  $1462$  to  $1467\text{ cm}^{-1}$ ) is observed.



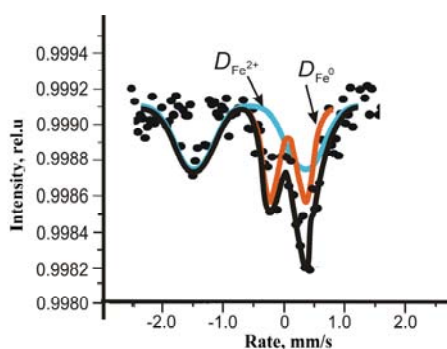
**Figure 2.** The dependences of phase transition width value  $\Delta\pi$  on compression rate  $V$  for Langmuir monolayers formed on  $\text{Fe}(\text{NO}_3)_3$  - (blue) and  $\text{FeCl}_3$  - containing (red) subphases.



**Figure 3.** Raman spectra of 5 monolayer LB-DTP-films formed on  $\text{Fe}(\text{NO}_3)_3$ - (blue) and  $\text{FeCl}_3$ -containing (red) subphases at compression rate  $4\text{ mm/min}$ . Pressure of LB-film deposition  $\pi$  was  $25\text{ mN/m}$ . Excitation by green laser at wavelength  $532\text{ nm}$  and laser power  $5.4\text{ mW}$ . Accumulation time was  $1\text{ s}$ .

## 5. Mössbauer spectroscopy

To establish a structure of studied supramolecular compound, it is important to find out a valent state of metal center. Mössbauer spectrum of a sample of nanoporous anodic alumina (nanopore diameter is  $10\text{ nm}$ ) coated by iron-containing 13-monolayer LB-DTP-film formed on subphase with  $\text{Fe}(\text{NO}_3)_3$  is shown in figure 4.



**Figure 4.** Mössbauer spectrum of iron-containing 13-monolayer LB-film of dithionilepyrrole.

As one can see, two doublets are observed in Mössbauer spectrum of 13-monolayer LB-film of dithionilepyrrole. One of them  $D_{\text{Fe}^{2+}}$  is registered at rate  $\nu$  about  $1.6\text{ mm/s}$ , and another doublet  $D_{\text{Fe}^0}$  – at rate  $\nu$  about  $0.3\text{ mm/s}$ . These values of  $\nu$  is close to  $\nu$  equals  $1.7\text{ mm/s}$  and  $0.4\text{ mm/s}$ , which are characteristic for doublets of paramagnetic ion  $\text{Fe}^{2+}$  in oxide of metal alloy  $\text{FeCoZr}$  and

superparamagnetic  $\text{Fe}^0$  in non-oxidized FeCoZr, respectively [16]. The broadened lines  $D_{\text{Fe}^{2+}}$  in figure 4 evidence interaction of iron ions with dielectric 2D matrix. Vice versa, the narrowness of  $D_{\text{Fe}^0}$  doublet lines in figure 4 means that reduction of the Fe atoms is accompanied by the exit of these atoms from LB-monolayer plane.

Organometallic complexes, which contain S, can reduce  $\text{Fe}^{3+}$  up to  $\text{Fe}^0$  [17-19]. Due to this Mössbauer spectrum indicates that complexification of high-spin ion  $\text{Fe}^{2+}$  with S in quasi-two-dimensional parts of LB-film (with 7 monolayers and less) proceeds. According to the Mössbauer spectrum in figure 4, an interlayer interaction in thick LB-film (with 9 monolayers and more) leads to partial reduction of  $\text{Fe}^{2+}$  up to  $\text{Fe}^0$ . It allows to assume that an iron ion coordinated by six sulphur atoms of three from six H-dithionilepyrrole residues to form a hexagon.

Thus, the Mössbauer spectroscopy analysis of the iron-containing DTP-LB-film consisted of 13 LB-monolayers shows that ions  $\text{Fe}^{3+}$  in compressed metal-aromatic complexes of DTP can turn into high-spin bivalent state Fe(II) and be reduced up to  $\text{Fe}^0$ .

## 6. Discussion and conclusion

According to foregoing data, the monolayers are polymerized and turn into monolayers of nanocyclic organometallic coordination compounds with a mixing valent state. Figure 5 shows schemes of the LB-monolayers of Fe-DTP-complexes in high-spin Fe(II) and low-spin Fe(III) states. As one can see, Fe(III)DTP<sub>3</sub> complexes have planar structure in opposite to dome-shaped structure of Fe(II)DTP<sub>3</sub> complexes. As provided by the compressibility analysis and the data of Raman spectroscopy, one can conclude that the value of mixing valent state of iron in LB-monolayers formed on  $\text{FeCl}_3$ -containing subphase tends to one of high-spin state, while a mixing valent state of iron in monolayers formed on  $\text{Fe}(\text{NO}_3)_3$ -containing subphase is closer to one of low -spin state.



**Figure 5.** Schemes of LB-monolayer of Fe(II)DTP<sub>3</sub> (a) and Fe(III)DTP<sub>3</sub> (b) complexes.

So, the method of experimental isotherm analysis utilizing geometrodynamics approach has been proposed to estimate the compressibility of metastable Langmuir monolayers. This method allows to find out the monolayer features, which determine the design of ultrathin LB-film after its deposition on a support.

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