Effect of anion type on monolayers and Langmuir–Blodgett films of gadolinium stearate

Gennady B. Khomutov [a,*], Alexander M. Tishin [a], Sergei N. Polyakov [b], Jakob Bohr [c]

[a] *Faculty of Physics, Moscow State University, Moscow 119899, Russia*
[b] *Institute of Nuclear Physics, Moscow State University, Moscow 119899, Russia*
[c] *Department of Physics, Technical University of Denmark, Building 307, DK-2800, Lyngby, Denmark*

Abstract

This work is focused on the preparation and characterization of gadolinium-containing stearic acid (SA) Langmuir–Blodgett (LB) films. SA monolayer behavior on the gadolinium-containing aqueous subphase has been analyzed by thermodynamic measurements. The compression isotherm shape changed substantially under varying anion type at the constant rare-earth cation content and pH in aqueous subphase. Those changes were ascribed to different monolayer surface charging under gadolinium binding. Small angle X-ray diffraction was used to study the structure of formed multilayer rare-earth-containing LB films. Considerable structural defects in multilayer LB films were found when gadolinium chloride solution was exploited as aqueous subphase for LB film formation, caused presumably by electrostatic interactions under charged monolayer deposition. The use of monodentate complexions like acetic acid residue was proposed to form bulk phase low-charged complexes with trivalent cations. The electroneutral ligand exchange reactions of such complexes with fatty acid Langmuir monolayer results in the formation of quasi-neutral trivalent cation complexes bound to the monolayer surface. This approach allowed effective neutralization of the monolayer surface under gadolinium binding and formation of condensed monolayer below the triple-point temperature. The compression and subsequent deposition of such monolayers resulted in the formation of highly ordered LB films with high content of adsorbed gadolinium cations arranged in two-dimensional (2-D) monatomic layers. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Langmuir–Blodgett films; Gadolinium; Monolayers

1. Introduction

The development of high technologies tends to direct physical and interdisciplinary investigations into the field of low-dimensional and nanometer-scale systems. Two-dimensional (2-D) structures

* Corresponding author. Tel.: + 7-95-939-3007; fax: + 7-95-939-1195.
E-mail address: gbk@bio383a.phys.msu.su (G.B. Khomutov)

are the physical limit in the development of ultra-thin metallic films of ultimately small thickness, corresponding to the dimensions of single atomic plane, and creation and study of literally 2-D and quasi-2-D systems are important from both a fundamental and an applied viewpoints. Controlling nano-scale morphology, arrangement and patterning is currently of principal importance in nanophase engineering and materials research.

Langmuir–Blodgett (LB) films have a number of attractive features concerning their use as model objects for the study of physical properties of ordered 2-D, or nearly 2-D systems. For example, the technique required for LB film formation is very simple when compared to that needed for epitaxial growth of ultrathin metal films. What is more, the effective approach to manipulate the growth kinetics and to force a smooth layer-by-layer growth in molecular beam epitaxy is the deliberate introduction of surfactants in the system [1]. It is possible to diminish and eliminate the effects a substrate can have on the layers of metal ions by a previous treatment of the substrate by deposition of a number of inert molecular monolayers. LB films containing bound metal cations are quasi-2-D systems with considerable freedom in molecular design, e.g. the distances between layers of metal ions, and the molecular and cationic composition and structure of the layers can be widely varied.

LB films of long-chain fatty acids and their various metal salts have been studied for a long time [2,3] and are perspective for device applications in several diverse areas including solid state molecular electronics, nanolithography, and different kinds of sensors [4]. The thermal, plasma and chemical treatment of LB films containing metal cations resulted in the formation of ultrathin metallic and oxidic layers [5–7]. LB films formed as space ordered one atom thick planar arrays of transition magnetic cations, separated by the nonmagnetic organic layers, is another field concerning the modeling and study of 2-D magnetic systems [8–15]. In particular, some of lanthanide ions have optical and magnetic properties very perspective for wide applications ranging from the probing in biological membrane systems [16] to planar metal-lorganic magnetic [17] and electrochromic materials [18].

The key step in the formation of LB films with metal ions being ordered in homogeneous 2-D arrays is the stoichiometric chemical binding of metal cations from the aqueous subphase to the monolayer surface and subsequent deposition of a cation-containing monolayer. Bound cations are adjacent to the planes of carboxylic groups of fatty acid molecules. It is known that ionic content and pH of the aqueous subphase is of principal importance in the fabrication of LB multilayers [2,3]. Presence of divalent cations significantly improves the processability of monolayers and structural characteristics of multilayer films [19,20]. The fatty acid monolayer behavior on the trivalent cations containing aqueous subphase is as a rule more complicated [21–24] and, correspondingly, monolayer deposition and formation of perfect LB films with high cationic content is in this case often a much more difficult task [25–27]. The properties of stearic acid (SA) Langmuir monolayer were reported as strongly dependent on pH and rare-earth cation concentration in the aqueous subphase [28]. The deposition of a SA monolayer from terbium chloride solution revealed changes from Y- to XY-type and LB films formed were characterized by structural inhomogeneities and reorganizations with time [29]. The investigations of monolayers and LB films of yttrium and rare-earth carboxylates revealed questions concerned with the optimum conditions for the deposition and cation-to-acid ratio in LB films formed. The ratio values of 1:3 [30–32], 1:2 [33,34] and 1:1.5 [5] were reported.

There is a number of fundamental physical and chemical problems connected with the formation of highly ordered integrated LB films with high content of multivalent cations. Interface electrostatic and hydration effects, hydroxide formation, specific binding and complexation of ions, intermolecular and interlayer interactions, structural relaxation and reorganization processes are of principal importance. The questions of the present study were the features of aqueous Gd complexes interactions with a SA monolayer and the exploration of possibilities to create highly-ordered fatty acid LB films with 2-D layers of condensely packed trivalent rare-earth cations. In this work we describe the changes in the compression

isotherm of a SA monolayer on the gadolinium-containing aqueous subphase, caused by variations in anion nature at the constant rare-earth cation content and pH value in the subphase. We also report the results of structural characterization of corresponding gadolinium-containing SA LB films formed, carried out by the small angle X-rays diffraction technique. The conditions necessary to form highly integrated and ordered mono- and multilayered rare-earth-containing LB films are discussed.

2. Experimental section

All reagents were G.R. grade and were commercially available. SA (CH_3–$(CH_2)_{16}$–COOH), Gd-chloride, Gd-acetate and acetic acid (C_2H_3COOH) were obtained from Serva and used without further purification. Water was purified by a Milli-Q system (Millipore). Surface pressure–monolayer area isotherm measurements and monolayer transfer to solid substrates were carried out on a full automatic conventional Teflon trough at 21°C as described elsewhere [35]. Langmuir monolayers were formed by spreading a chloroform solution of SA (2×10^{-4} M) on the surface of purified water or onto the aqueous subphase containing 1×10^{-4} M Gd salt solution. pH of aqueous subphase was 5.5. After complete solvent evaporation and cation binding equilibration (≈ 15 min) the floating monolayer on the aqueous subphase was compressed by a mobile Teflon barrier at a speed ≈ 3 Å^2 per molecule of SA per min. The compression isotherms recorded with compression rates ranging from 1 to 9 Å^2 per molecule of SA per min were reproducible. Monolayers were then transferred to various solid substrates at a constant pressure (≈ 30 mN m^{-1}), temperature (21°C) and dipping speed (3 mm min^{-1}) using the conventional vertical dipping method. Gadolinium-containing LB films with a different number of Gd layers were formed. The polished silicon (with a native oxide layer, 0.3–0.5 nm thick) and quartz plates were used as a substrate material when multilayer films were formed. Inductively coupled plasma-emission spectroscopy with an ICAP-61

setup was used for chemical analysis of the LB films formed. Small-angle X-ray scattering experiments were performed with a modified 'Rigaku D/max-RC' diffractometer (X-ray wavelength $\lambda = 1.5405$ Å, power of X-ray source 12 kW).

3. Results and discussion

3.1. Monolayer compression isotherm analysis

The formation of highly ordered Langmuir monolayer and multilayer LB films using LB technique requires an appropriate monitoring and control of the corresponding monolayer at the surface of aqueous subphase. The compression of the monolayer (and corresponding decrease in monolayer area A) results usually in a decrease of the surface tension value γ by a quantity π (monolayer surface pressure). The experimental compression isotherms of fatty acid monolayers show discontinuities and breaks in isotherm slope attributed to structural transitions of the monolayer between 2-D gas, liquid expanded (LE), liquid condensed (LC) and solid phases [2,3].

Fig. 1 shows the observed characteristic compression isotherms of SA monolayer onto the aqueous subphase with different ionic content. Curve 1 on this figure presents the control π-A isotherm recorded when the water subphase was used without any additions, pH = 5.5. The characteristic LC–solid phase transition in the monolayer takes place as follows from changes in π-A isotherm slope. Curve 2 is the π-A isotherm of the monolayer on the gadolinium chloride solution (concentration of GdCl$_3$ was 1×10^{-4} M, pH = 5.5). The isotherm became compressed and shifted to the higher A region at large π values in comparison with the control isotherm. But the LC–solid state transition is still present. The analogous behavior of arachidic acid monolayer on the GdCl$_3$ containing subphase (concentration 1×10^{-4} M, pH = 5.86) was reported in [30] and on the YCl$_3$ solution (1×10^{-5} M, pH ≈ 5.8) in [31]. Such a π-A isotherm change correlates usually with substantial increase in the surface electrostatic potential value. Curve 3 is a compression isotherm recorded when a gadolinium acetate so-

lution of the same concentration (1×10^{-4} M GdAc$_3$) and the same pH value (pH = 5.5) was used. This π-A isotherm corresponds to a condensed monolayer below the triple-point temperature. The slope of the isotherm is large and monotonously smooth without any noticeable phase transitions, related to LE and LC phases. Below the triple point temperature of the monolayer the 2-D molecular gas condenses practically directly to the solid phase. It is known, that charging of the monolayer surface shifts the triple point significantly. Thus, the triple point for a stearylamine monolayer on an acidified subphase (monolayer surface is protonated and charged positively) is $\approx 13°C$, while on unacidified (neutral surface) it is 45°C [36]. The common features of curves 2 and 3 on Fig. 1 are the general decrease in compressibility and the collapse behavior. We have evaluated the compressibility of
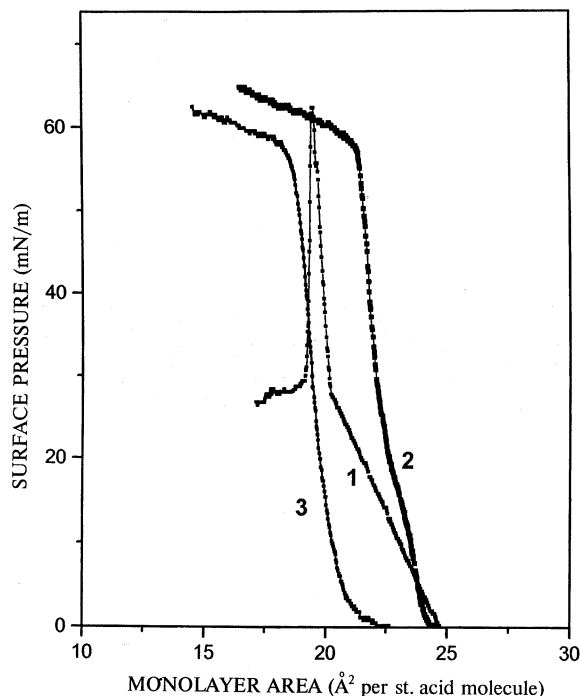

Fig. 1. Surface pressure–monolayer area isotherms of SA monolayer. Curve 1, control isotherm on pure water subphase, pH = 5.5; curve 2, 1×10^{-4} M gadolinium chloride in subphase, pH = 5.5; curve 3, 1×10^{-4} M gadolinium acetate in subphase, pH = 5.5. Area is calculated per molecule of SA. $T = 294$ K.

the SA monolayer on aqueous subphases studied using the formula for surface compressional modulus [2]:

$$K^s = -A \times (\partial \pi / \partial A)_T$$

where A is the molecular area in the film. It was found that K^s value for pure SA monolayer (derived from curve 1) in solid state ($\pi = 35$ mN m^{-1}) is ≈ 1125 mN m^{-1}. Maximal K^s values for monolayer on GdCl$_3$ solution was 870 mN M^{-1} and on gadolinium acetate-containing subphase was ≈ 700 mN m^{-1} (at $\pi \cong 35 \div 40$ mN m^{-1}). However the slopes of those compression isotherms ($\partial \pi / \partial A$ value) were very close. These data give evidence that the structure and effective mechanical construction of SA monolayer with bound Gd^{3+} cations in solid state can be close, independent of the anionic content of aqueous subphase, but the observed shift of compression isotherms on chloride and acetate solutions is the result of electrostatic interactions.

It is clear from Fig. 1 that the only substitution of negative counterion in gadolinium-containing subphase from Cl$^-$ to acetic acid residue causes dramatic changes in SA Langmuir monolayer properties. The monolayer behavior on the surface of a gadolinium acetate solution resembles that of a monolayer when divalent cations are present in the subphase.

Using the LB vertical dipping method two different sets of Gd-containing LB films were formed. The first type of films was obtained with the use of gadolinium chloride solution as subphase (concentration of GdCl$_3$ 1×10^{-4} M, pH = 5.5). Only few layers were deposited with the transfer ratios close to 1 and further deposition tended to XY-type and decreased transfer ratios. On the contrary, when Gd-acetate solution was used as the aqueous subphase (concentration of GdAc$_3$ 1×10^{-4} M, pH = 5.5), Y-type depositions were successful and reproducible. Such multilayer LB films had good interference color uniformity.

In order to establish the quantity of gadolinium ions incorporated into LB films a chemical analysis of the samples with the use of inductively coupled plasma-emission spectroscopy was carried out. In LB films formed with GdAc$_3$ solution

as subphase, the gadolinium content was established to be ≈ 1.5 SA molecules per gadolinium cation. This value corresponds to that obtained in [5] for yttrium arachidate LB films and was in agreement with our estimations derived from the analysis of EPR spectra of LB films formed when gadolinium was in a paramagnetic state [14,15]. The layer area per gadolinium ion in the LB film was evaluated to be 14.9 $Å^2$. Assuming a hexagonal structure of the Gd monolayer it corresponds to a lattice parameter of 4.1 Å, which is only slightly larger than that for bulk metallic Gd (3.64 Å).

A large number of experiments have been carried out to study metal ion interactions with molecular surfaces of monolayers and membranes but often little is known about the interface structures formed under these interactions. The binding stoichiometry of cations to negatively charged carboxylic groups of monolayer is usually proposed to correspond to 1:1 for a monovalent and 1:2 for a divalent cation [37]. However, several authors have suggested the formation of positively charged 1:1 complexes between COO^- and divalent cations [38,39]. The formation of basic soaps at pH close to where the metal hydroxides begin to precipitate was also proposed [40]. Cation binding may become complicated and enhanced by nonelectrostatic interactions and cation complexation. Multi-valent cations in water solutions form a number of differently charged aquatic complexes which can include $(OH)^-$ and other water phase components. The binding parameters of Gd^{3+} and its complexes with a SA monolayer are not definitely established at present. But it is known that ion-binding constants for rare-earth cation adsorption to model membranes are two orders of magnitude higher than binding constants for divalent cation binding to the same molecular surfaces [41]. It was reported that a SA monolayer was already completely converted to the neutral soap form at the $TbCl_3$ content in water subphase as small as 1×10^{-6} M [42]. Measurements of the surface potential value by vibrating plate method revealed substantial difference ($\approx$ 200 mV) in monolayer surface potential recorded at pH 5.7 for SA monolayer on $TbCl_3$ and $MnCl_2$ solutions at high enough cation concentrations (10^{-5} M for Tb^{3+} and 10^{-2} M for divalent cation) [42]. It is important that the character of surface potential-cation concentration dependencies was principally different for trivalent cation (Tb^{3+}) and for divalent cation (Mn^{2+}). For divalent cation surface potential value monotonously decreased to zero with the increase of cation concentration, but for rare-earth cation the potential value decreased to minimum value (≈ 200 mV) at concentrations $\approx 5 \times 10^{-6}$ M and then increased with further $TbCl_3$ concentration growth [42]. One can interpret this results as the well-known formation of neutral 1:2 complexes between bound divalent cation and two SA molecules (and resulting neutralization of monolayer surface) and overcharging of monolayer surface under the binding of trivalent rare-earth cations.

According to electroneutrality considerations, three SA molecules are necessary to compensate the $+3$ charge of the Gd^{3+} ion. It is known that in multivalent cation-containing LB films the cation content can exceed the stoichiometric value for simple salt formation. The iron content in ferric arachidate multilayer LB films was 3.5 times higher than the stoichiometric value [10]. A charge discrepancy analogous to the one for LB films was observed in ferric stearate powders and ascribed to the presence of hydroxides in the material [43]. The electroneutral stoichiometry of the gadolinium content in the LB film would have corresponded to a ratio of the three SA/Gd. The established ratio of 1.5 SA/Gd in the LB film formed implies that initially the quantity of gadolinium cations bound to the Langmuir monolayer on the aqueous subphase surface was also correspondingly high. Such overstoichiometric saturation binding should definitely result in the overcharge of the floating monolayer. Taking into account the charge of the Gd^{3+} cation and established binding ratio, the surface charge density in this case should be the one positive elementary charge per SA molecule.

In case of monolayers formed by molecules with dissociable head groups or when charged

substances are adsorbed on a monolayer surface from the aqueous subphase, the electrostatic interactions at the interface can be a substantial part of the monolayer free energy. As a result, the electrostatics at the interface influence the structure and the state of the monolayer. The effect of electrostatic interactions on the monolayer surface pressure π value can be evaluated from thermodynamic Gibbs free energy considerations. It was found that the surface pressure change $\Delta\pi_{el}$ due to the reversible charging of a monolayer at a fixed area in equilibrium with an aqueous subphase of a constant composition and temperature is [44]:

$$\Delta\pi_{el} = \int_{0}^{\varphi_0} \sigma \, d\varphi \tag{1}$$

where σ is the monolayer surface charge density; φ_o is the electrostatic potential value at the monolayer surface. A simple electrostatic model assuming a uniform charge density on a planar interface and ions as point charges, known as Gouy–Chapman theory of the double layer, was widely used for quantitative descriptions of surface electrostatic phenomena in biological and model membranes and monolayers [44–48]. The generalized Gouy equation of this theory is [46]:

$$\sigma = \{2\varepsilon\varepsilon_o kT\Sigma_i n_i(\infty)[\exp(-z_i e\varphi_o/kT) - 1]\}^{1/2} \tag{2}$$

where σ is the monolayer surface charge density; φ_o is the electrostatic potential value at the interface; ε and ε_o are dielectric constant of water and vacuum, respectively; k is Boltzmann's constant; T is absolute temperature; $n_i(\infty)$ is the space density (number per unit volume) of ion i in the bulk phase whose charge is $z_i e$. The summation includes all ions present in the aqueous phase. Gouy–Chapman theory neglects water–water, water–ion and other interactions in the interfacial region where molecular and hydration fields can play a significant role. Electrostatic models which allow for the effects of interfacial hydration predict the electrostatic potential value near the surface to increase owing to the

water binding to the surface and the effective interfacial dielectric constant being much smaller than the bulk value [41]. It means, that the real surface charge density can be lower at the same surface potential value if the effective interfacial dielectric constant is correspondingly small. Thus, evaluations obtained with the use of Gouy–Chapman theory can serve as the low limit of surface potential values and the difference of calculated and experimentally determined quantities can reflect contributions of hydration effects to the electrostatic interactions at the studied surface.

We carried out calculations based on the Gouy–Chapman model to evaluate the pure electrostatic part in π value difference $\Delta\pi$ between curves 2 and 3 in Fig. 1. The σ values were determined for different monolayer area A with the use of the obtained stoichiometry $+1e$ per SA molecule. In experiments with diluted gadolinium chloride and acetate solutions we did not adjust the final pH value in the aqueous phase after gadolinium salt was dissolved. This pH value was as a rule ≈ 5.5 and close to pH value of pure water used (pH ≈ 5.6). It allowed us to suppose that the only ions presented in the aqueous phase were Gd^{3+}, A^-, H^+ and OH^-, where A^- is the acid residue of the gadolinium salt. Thus, molar concentrations of ions present in the aqueous phase were: Gd^{3+} (10^{-4} M), A^- (3×10^{-4} M), H^+ ($10^{-5.5}$ M), OH^- ($10^{-8.5}$ M). Using Eq. (2) the φ_o value was obtained for every σ value. We also carried out calculations for the ionic content in the aqueous phase where half of the gadolinium cations were present in a form of doubly positively charged complexes like $\{Gd^{3+}(OH)^-\}^{2+}$. The φ_o value was found to be practically the same because the term of the main value in Eq. (2) is one corresponding to A^-. Combining Eq. (1) and Eq. (2) yields an expression for monolayer surface pressure difference between charged and neutral state (or, in general, between two charged states). For gadolinium solution used in our experiments and for ion molar concentrations as space density of charged components this equation becomes:

$$\Delta\pi = (2\varepsilon\varepsilon_0)^{1/2}(RT)^{3/2}$$

$$(10^{-3}/F)\int_0^{\phi 0}\{A[\exp(-3\phi)-1]+3A[\exp(\phi)-1]$$

$$+B[\exp(-\phi)-1]+C[\exp(\phi)-1]\}^{1/2}\mathrm{d}\phi$$
$$(3)$$

Here ϕ is the normalized potential $F\varphi/RT$, F is the Faraday constant, R is the gas constant. This integral can be solved numerically. Introducing the constants $A = 10^{-4}$, $B = 10^{-5.5}$, $C = 10^{-8.5}$, used for determination of the φ_o value, the numerical integration gives the value of $\Delta\pi_{el}$. The equality $\Delta\pi = \Delta\pi_{el}$ was found to be valid for $A = 22$ Å^2 per SA ($\sigma = +1e/22$ Å^2, $\varphi_o = 330$ mV, $\Delta\pi_{el} = 37.4$ mN m^{-1}). This values correspond to the difference in π values at $A = 22$ Å^2 per SA for compression isotherms of SA monolayers on the gadolinium acetate and gadolinium chloride solutions (Fig. 1). These evaluations can give evidence that at monolayer compression extent corresponding to 22 Å^2 per SA, the classical electrostatic interactions can determine the changes in π value and that the monolayer surface is practically neutral when gadolinium acetate is present in the aqueous phase. The change in monolayer free energy corresponding to the obtained $\Delta\pi_{el}$ value is 4.95 kJ mol^{-1} SA and is a little lower than the values of typical hydrogen bond energies. The possible different dependencies of chemical potential of monolayer molecules and complexes on the compression extent and different corresponding structural changes and hydration effects in the interface region could result in $\Delta\pi$ enhancement with a further decrease of the monolayer area A.

The changes in the π-A isotherm of an ionized monolayer caused by the water subphase ionic content variations were described earlier for mono- and divalent ions with the Gouy–Chapman model [44,47,48]. The effects were interpreted as increase in surface charge density in the case of monovalent cations and as screening and compensation (under binding) of negative surface charges by divalent cations. The observed changes in π value caused by divalent cations were significantly larger than predicted by calculations of free energy changes due to simple electrostatic interactions. It points out that, as in a case of trivalent cations studied in present work, the specific interactions (including van der Waals, multipolar, hydrogen bonding, hydration, complexation, etc.) besides the electrostatic effects can be involved when di- and multivalent cations bind to the monolayer. Divalent cations condense the monolayer, decrease the π value of LE–LC phase transition in lipid monolayers and even eliminate this transition thus transferring the monolayer to the state below the triple point [47]. Analogous effects are found to be characteristic for monolayers on gadolinium acetate containing an aqueous phase at the pH used. It is known also, that the presence of divalent cations in the aqueous phase significantly improves the processability of monolayers under deposition and the structural characteristics of multilayer LB films [19,20]. We have found the principal improvement in monolayer deposition when Gd acetate salt was used instead of chloride (at the same concentration and pH value). We also observed that LB films formed by monolayer deposition from the gadolinium acetate-containing aqueous subphase had a much more perfect layered structure (see below).

On the basis of π-A isotherm and chemical analysis data it is possible to suppose that the binding of gadolinium to a SA monolayer is determined mainly by Gd^{3+}–SA interactions, and the close structures are formed when chloride or acetic acid ions are present in solution. The Gd^{3+} ion can bind with at least two SA molecules and crosslink the monolayer carboxylic groups at the interface. The main reason of differences between properties of a SA monolayer on gadolinium chloride and acetate-containing aqueous subphases and corresponding Gd-containing LB films is the positive charge of the monolayer surface in the former and the quasi-neutrality in the last case. Our model of the phenomenon is based on the changes in interfacial electrostatics when chloride was replaced by acetic acid residue in the gadolinium-containing aqueous phase. The high Gd^{3+} binding causes overcharging of the monolayer on GdCl$_3$ solutions. The acetic acid residue is known as effective monodentate complexion and being present in subphase

can form rather electroneutral complexes with Gd^{3+} cations. The acetic acid and SA have the same carboxylic group that promotes the exchange reactions between these ligands. The quasi-electroneutral ligand exchange reactions of such complexes in this case result in the formation of quasi-neutral complexes of Gd^{3+} with SA and acetate at the monolayer surface (possibly OH^- can take part in such complexes depending on the local surface pH value).

The important question is the formation of Gd^{3+} cation complexes with hydroxide. The electronic structure of Gd is seven electrons of the unfilled 4-f orbital located inside and screened by the higher 5-s and 5-p orbitals. This is the reason for low ability of rare-earth cations to form covalent bonds because electron pairs of ligands can't be allocated at cation free 4-f orbitals. So the rare-earth cations form complexes with a mainly ionic (electrostatic) nature of bonds. It is known that multivalent cations of transition metals in water solutions easily form complexes with OH^- like $\{M^{n+}(OH^-)_m\}^{+n-m}$ where m is pH and cation concentration dependent. There is a cation specific pH value above which metal hydroxides begin to precipitate. The metal hydroxides often form dimeric, oligomeric, polymeric and aggregative 3-D structures. Rare earth cations are characterized by a significantly reduced affinity to metal hydroxides formation in comparison with trivalent cations of other metals (Fe^{3+}, Cr^{3+}, Al^{3+}, V^{3+}, etc.). This is due to the relatively large sizes of rare-earth cations, weak electrostatic interactions between such cations and OH^-, and low ability to covalent bond formation. The available data make it possible to suppose that Gd-hydroxide formation in a bulk phase is substantial at pH values > 7 [49]. Hydroxide-complexes of lanthanides are ionic in nature and its stability decreases with the number of ligands bound. Therefore if, for example, the equilibrium aqueous phase complex like $\{M^{3+}(OH)^-\}^{2+}$ of rare-earth metal M cation binds to the SA monolayer surface, the OH^- group will be lost and the possible resulting surface complexes can only be $\{M^{3+}(SA)_n^-\}^{+3-n}$, where $1 \leq n \leq 3$ because the

existence of neutral or +1-charged surface mixed complexes of M^{3+} with SA and hydroxide in this case should inevitably mean the existence of equilibrium aqueous phase complexes like $\{M^{3+}(OH)_2^-\}^{1+}$ and $\{M^{3+}(OH)_3^-\}^0$. The last complex form insoluble aggregates and precipitates in water and the $\{M^{3+}(OH)_2^-\}^{+1}$ complex exists only in a narrow pH region immediately contiguous to the pH value where metal hydroxides begin to precipitate [33]. As a result, the binding of rare-earth cations to a monolayer on the solution in which rare-earth cations form complexes mainly with the hydroxide (as in the case of $GdCl_3$ solution) can cause the positive charging of monolayer surface and poor deposition in a wide pH range right up to the beginning of metal hydroxide precipitation. The only way to obtain the electroneutral monolayer with maximal, in this case, trivalent metal-to-acid ratio 1:3, good transfer to substrate and perfect layered structure of corresponding LB films is to use lowered concentrations of trivalent metal salts, as was showed for YCl_3 in [31]. With $TbCl_3$ in an aqueous phase, good SA monolayer deposition and LB films quality was obtained for low $TbCl_3$ concentrations ($< 1 \times 10^{-5}$ M) [41], while for concentration 0.5×10^{-4} M $TbCl_3$ the transition from Y- to XY-type deposition and structural inhomogeneities and reorganizations with time in LB films formed were observed [29].

According to the Boltzmann equation, for the equilibrium concentration of any charged species $C_i(x)$ in the local region (x), where the local electrical potential value is φ_x, one obtains:

$$C_i(x) = C_i(\infty)\exp\{-z_iF\varphi_x/RT\} \qquad (4)$$

Here $C_i(\infty)$ is the concentration of species i in the bulk phase, where the electrical potential value is 0. Correspondingly, for local surface concentrations of H^+ ions it follows [50]:

$$pH_s = pH_b + F\varphi_0/(2,3 \times RT) \qquad (5)$$

where pH_s is the pH value at the interface, pH_b is the pH value in the bulk phase. For a φ_0 value of 330 mV and $pH_b = 5.5$, as were evaluated before, the pH_s value is ≈ 11. This rather high pH_s value (obviously higher than the pH value of the beginning of Gd hydroxide precipitation range) points
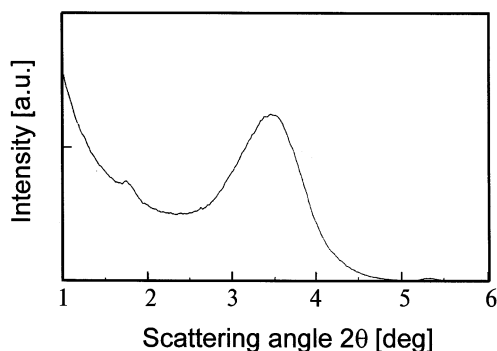
Fig. 2. X-ray diffractogram of LB film (35 bilayers) formed by the deposition of SA monolayer from gadolinium chloride containing aqueous subphase (1×10^{-4} M gadolinium chloride in subphase, pH = 5.5) on the surface of polished silicon substrate with natural oxide layer. $T = 294$ K.
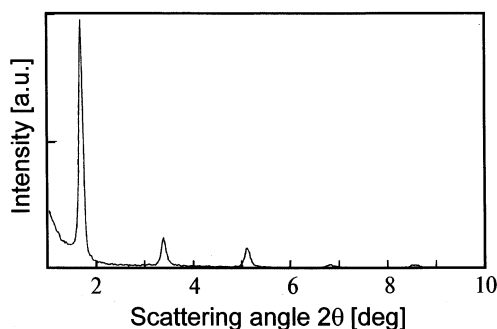

Fig. 3. X-ray diffractogram of LB film (35 bilayers) formed by the deposition of SA monolayer from gadolinium acetate containing aqueous subphase (1×10^{-4} M gadolinium acetate in subphase, pH = 5.5) on the surface of polished silicon substrate with natural oxide layer. $T = 294$ K.

out to the possibilities of bound Gd-hydroxide formation at the interface due to the high local surface basification when the number of bound Gd^{3+} is exceeding substantially electroneutral stoichiometry 1:3 Gd/SA. This effect can be the reason for the changes in the monolayer surface polarity properties and eventually in the deposition character as was pointed out in [51].

We suppose, that the electrostatic interactions of charged surfaces under multilayer LB film formation procedure, and the gadolinium hydroxide formation at the interface can be the reasons for the differences in monolayer deposition features and structures of LB films formed

when gadolinium chloride and gadolinium acetate solutions were used. In gadolinium acetate solution bulk phase quasi-electroneutral complexes can interact with SA monolayer surface and the electroneutral ligand exchange reactions in this case should result in the formation of practically neutral monolayer with high surface density of Gd complexes. Using this approach we obtained the LB films with gadolinium content as high as 1:1.5 Gd/SA. It seems possible to obtain ordered LB films with even higher cation content using surfactants and complexions with other charged groups as, for example, orthophosphoric acid derivatives.

3.2. X-ray diffraction measurements

Besides the cationic content needed, the principal requirements to LB films formed are the structure order and integrity. X-rays diffraction in the low angle range (SAXS) was employed to detect the periodic structure of LB films formed. This method is widely used in investigations of the structure of multilayered fatty acid metal cation contained LB films [2,11,52,53]. Figs. 2 and 3 show the SAXS patterns obtained from the fabricated multilayer LB films. In all cases, several Bragg reflections were observed. One can determine the layer spacing d according to the Bragg formula:

$$n\lambda = 2d \sin \theta$$

where n is the order of the reflection peak, λ denotes the wavelength and θ the maxima of the Bragg peaks. In the diffractogram of the LB film formed by deposition of monolayer from the gadolinium chloride-containing water subphase (Fig. 2) one can see a very broad peak ($\approx 3.5°$, $W_{1/2} = 0,794°$) and a number of narrow weak peaks ($W_{1/2} = 0.2°$). The width $W_{1/2}$ of any reflection peak is connected with the physical limit of the region of coherent scattering. The positional coherence length D can be evaluated from the line width of the diffraction peaks using Scherrer's formula [54]. The phase responsible for the broad peak at 3.5 grad is characterized by a D value of 110 Å. The phase

giving narrow diffraction peaks has a D value ≈ 500 Å. The complex two-phase diffraction pattern with different broad peaks and rather low coherence length values can be interpreted as a result of a disturbed layered structure of Gd–LB films formed using a gadolinium chloride solution as a subphase. This structure consists of a layered phase with period $d \approx 48$ Å and another disordered phase with single peak of $d \approx 25.2$ Å. The characteristic structure period d for different divalent metal cations stearate Y-type LB films is 50 Å [2,53]. The close d value was obtained for LB multilayers of Fe(III) stearate deposited on Si substrates [55]. The layered phase in 'chloride' Gd-containing LB film has a d value more close to the period of pure SA–LB film and powder (≈ 47 Å) which implies that this phase corresponds to regions of Y-type layers without Gd ions with very low reflectivity. In Fig. 2, 99% of the integral reflection intensity is corresponds to the phase with the broad peak at 3.5°. This phase can originate from 3-D Gd-hydroxide polymeric clusters and/or X-type disordered Gd LB film (taking into account the characteristic geometric parameter ≈ 25 Å for this phase). These results are in qualitative agreement with the data on the AFM study of fatty acid LB films formed by monolayer deposition from subphase with trivalent rare-earth cation chloride solution $\approx 10^{-4}$ M concentration that such LB films have rather nonuniform and nonplanar morphology [29,30].

Fig. 3 demonstrates a well-defined layered structure in the case of Gd LB film formed using gadolinium acetate solution as a subphase (35 Gd layers). For this LB film several narrow Bragg reflections were observed. The number of registered peaks was determined only by original X-ray beam intensity. The width of either diffraction peak ($\approx 0.1°$) yields a coherence length $D > 1000$ Å. The layered structure period d was determined to be 52 Å, 2 Å larger than for usual divalent metal cations stearate Y-type LB films. A similar d value (52.8 Å) was observed in [53] for magnesium stearate LB films and was explained by inclusion of bound water into the LB film structure. It is possible to propose the formation of electroneutral planar complexes which can include H_2O, OH^- and acetic acid molecules, because the only negatively charged substances in this solution are acetate and hydroxide anions. Since the OH^- ion is much smaller than the carboxylic group COO^- of SA and the acetic acid molecule, the presence of hydroxide in the structure can result in close packing of gadolinium ions in LB film layers. At present the detail chemical and physical structure of the Gd layers region in Gd-containing LB films is unclear and another fine techniques have to be exploited to elucidate it.

4. Conclusions

The properties of a SA Langmuir monolayer on the gadolinium-containing aqueous subphase have been studied under variations in anion type at a constant rare-earth cation content and pH value in the aqueous subphase. We proposed that interface electrostatic interactions caused changes in the floating monolayer behavior, deposition type and resulting in structural defects in the corresponding LB films. The use of monodentate charged weak complexions like acetic acid residue was proposed to form bulk phase quasi-neutral complexes with trivalent metal cations. The electroneutral ligand exchange reactions of such complexes with fatty acid monolayer results in the formation of neutral multivalent cation complexes at the monolayer surface. This approach allowed neutralization of the monolayer surface under Gd^{3+} binding and formation of a condensed monolayer below the triple-point temperature. The compression and subsequent deposition of such a monolayer resulted in the formation of highly ordered LB films with high content of adsorbed multivalent rare-earth cations arranged in 2-D layers.

References

[1] M. Copel, M.C. Reuter, E. Kaxiras, R.M. Tromp, Phys. Rev. Lett. 63 (1989) 632.

[2] G.L. Gaines, Insoluble Monolayers at Liquid-Gas Interfaces, Wiley, New York, 1966.

[3] B.P. Binks, Adv. Colloid Interface Sci. 34 (1991) 343.

[4] G.G. Roberts, Langmuir-Blodgett Films, Plenum Press, New York, 1990.

[5] D.T. Amm, D.J. Johnson, T. Laursen, S.K. Gupta, Appl. Phys. Lett. 61 (1992) 522.

[6] D.M. Shah, W.K. Chan, R. Bhat, H.M. Cox, N.E. Schlotter, C.C. Chang, Appl. Phys. Lett. 56 (1990) 2132.

[7] T. Faldum, W. Meisel, P. Guetlich, Fresenius J. Anal. Chem. 353 (1995) 723.

[8] M. Pomerantz, Surf. Sci. 142 (1984) 556.

[9] C.T. Seip, G.E. Granroth, M.W. Meisel, D.R. Talham, J. Am. Chem. Soc. 119 (1997) 7084.

[10] E. Giesse, G. Ritter, M. Schurr, H. Voit, Nuovo Ciménto Soc. Ital. Fis. D 18 (1996) 305.

[11] S.A. Yakovenko, V.V. Kislov, V.V. Erokhin, A.Yu. Potapov, G.B. Khomutov, Z Phys. Chem. 66 (1992) 1028.

[12] N. Rozlosnik, D.L. Nagy, E. Giesse, D. Brandl, R. Buder, Mol. Cryst. Liq. Cryst. Sci. Technol. A 262 (1995) 1645.

[13] F. Bonosi, G. Gabrielli, G. Martini, Colloids Surf. A 72 (1993) 105.

[14] G.B. Khomutov, Yu.A. Koksharov, A.M. Tishin, New class of magnetic materials: rare-earth containing Langmuir–Blodgett films as planar magnets, in: Preprint N5/ of Faculty of Physics, Moscow State University, Moscow, 1996, p. 1996.

[15] A.M. Tishin, Yu.A. Koksharov, J. Bohr, G.B. Khomutov, Phys. Rev. B 55 (1997) 11064.

[16] C.H. Evans, in: E. Frieden (Ed.), Biochemistry of the Lanthanides, Plenum, New York, 1990.

[17] J. Bohr, S.A. Gudoshnikov, Yu.A. Koksharov, O.V. Snigirev, A.M. Tishin, G.B. Khomutov, Int. Patent Appl. PCT/RU97/00150, priority date 6 September, publication number WO98/10442 of 12.03.98.

[18] M.L. Rodriguez-Mendes, R. Aroca, J.A. DeSaja, Chem. Mater. 4 (1992) 1017.

[19] D.J.M. Linden, J.P.K. Peltonen, J.B. Rosenholm, Langmuir 10 (1994) 1592.

[20] J.B. Peng, J.B. Ketterson, P. Dutta, Langmuir 4 (1988) 1198.

[21] R. Aveyard, B.P. Binks, N. Carr, A.W. Cross, Thin Solid Films 188 (1990) 361.

[22] M.R. Buhaenko, R.M. Richardson, Thin Solid Films 159 (1988) 231.

[23] M.R. Buhaenko, J.W. Goodwin, R.M. Richardson, Thin Solid Films 159 (1988) 171.

[24] M. Simovic, L.j. Dobrilovic, J. Radioanal. Chem. 44 (1978) 345.

[25] B.M. Abraham, J.B. Ketterson, K. Miyano, A. Kueny, J. Chem. Phys. 75 (1981) 3137.

[26] K. Blodgett, J. Am. Chem. Soc. 57 (1935) 1007.

[27] Y. Ando, T. Hiroike, T. Miyashita, T. Miyazaki, Thin Solid Films 278 (1996) 144.

[28] J. Peltonen, M. Linden, H. Fagerholm, E. Gyorvary, F. Eriksson, Thin Solid Films 242 (1994) 88.

[29] E. Gyorvary, J. Peltonen, M. Linden, J.B. Rosenholm, Thin Solid Films 284,285 (1996) 3684.

[30] C. Fink, J. Hassmann, B. Irmer, G. Saemann-Ischenko, Thin Solid Films 263 (1995) 213.

[31] P. Ganguly, D.V. Paranjape, M. Sastry, S.K. Chaudhari, K.R. Patil, Langmuir 9 (1993) 487.

[32] M. Schurr, D. Brandl, Ch. Tomaschko, Ch. Schoppmann, H. Voit, Thin Solid Films 261 (1995) 271.

[33] D.J. Johnson, D.T. Amm, T. Laursen, S.K. Gupta, Thin Solid Films 232 (1993) 245.

[34] V.V. Arslanov, T.V. Zotova, I.A. Gagina, Colloid J. 59 (1997) 603.

[35] G.B. Khomutov, S.A. Yakovenko, T.V. Yurova, V.V. Khanin, E.S. Soldatov, Supramol. Sci. 4 (1997) 349.

[36] K.J. Stine, D.T. Stratmann, Langmuir 8 (1992) 2509.

[37] M. Losche, C. Helm, H.D. Mattes, H. Mohwald, Thin Solid Films 133 (1985) 51.

[38] S. McLaughlin, N. Mulrine, T. Gresalfi, G. Vaio, A. McLaughlin, J. Gen. Physiol. 77 (1981) 445.

[39] J.M. Bloch, W. Yun, Phys. Rev. A 41 (1990) 844.

[40] J.A. Spink, J.V. Sanders, Trans. Faraday Soc. 51 (1955) 1154.

[41] G. Cevc, Biochim. Biophys. Acta 1031 (1990) 311.

[42] M. Linden, J.B. Rosenholm, Langmuir 11 (1995) 4499.

[43] M. Pomerantz, A. Aviram, A.R. Taranko, J. Appl. Phys. 53 (1983) 7960.

[44] Th.A.J. Pains, Philips Res. Rep. 10 (1955) 425.

[45] G.B. Khomutov, S.A. Barguth, Russ. J. Plant Physiol. 36 (1989) 1066.

[46] S. McLaughlin, in: F. Bronner, A. Kleinzeller (Eds.), Current Topics in Membranes and Transport, Academic Press, New York, 1977, p. 71.

[47] C.A. Helm, L. Laxhuber, M. Losche, H. Mohwald, Colloid Polym. Sci. 264 (1986) 46.

[48] J.A. DeSimone, J. Colloid Interface Sci. 67 (1978) 381.

[49] C.F. Baes, R.E. Mesmer, The Hydrolysis of Cations, Wiley, New York, 1976.

[50] G.B. Khomutov, Z Phys. Chem. 64 (1990) 1153.

[51] J.F. Stephens, J. Colloid Interface Sci. 38 (1972) 557.

[52] L.A. Feigin, Yu.M. Lvov, V.I. Troitsky, Sov. Sci. Rev. A Phys. (Lond.) 11 (1989) 285.

[53] U. Hohne, H. Mohwald, Thin Solid Films 243 (1994) 425.

[54] A. Guinier, X-ray Diffraction, W.H. Freeman, San Francisco, 1963.

[55] M. Prakash, J.B. Peng, J.B. Ketterson, P. Dutta, Thin Solid Films 146 (1987) L15.