Formation of Langmuir-Blodgett Films Containing Two-Dimensional Monoatomic Arrays of Rare-Earth Cations

Gennady B. Khomutov*

Faculty of Physics, M.V. Lomonosov Moscow State University, Moscow, 119899, Russia

SUMMARY: The work is focused on the preparation and characterisation of rare-earth containing stearic acid Langmuir-Blodgett (LB) films. Stearic acid monolayer behavior on the rare-earth containing aqueous subphase have been analyzed by thermodynamic measurements. The compression isotherm shape changed substantially under varying the anion type at the constant rare-earth cation content in aqueous subphase. The structure of formed multilayer rare-earth containing LB films was studied using small angle X-rays diffraction. The considerable structural defects in multilayer films were found when rare-earth chloride solution was exploited as aqueous subphase, caused presumably by electrostatic interactions at the monolayer surface under high binding of rare-earth cations. The use of monodentate complexones like acetic acid was proposed to form bulk phase quasi-neutral rare-earth complexes. The electroneutral ligand exchange reactions of such complexes with stearic acid monolayer allowed to neutralise monolayer surface under rare-earth cations binding and to form condenced monolayer below the triple-point temperature. The compression of such monolayer to the state of minimal compressibility and subsequent monolayer deposition resulted in the formation of high ordered LB films with high content of adsorbed multivalent rare-earth cations arranged in two-dimensional monoatomic arrays.

Introduction

Two-dimensional (2-D) structures are the physical limit in the creation of ultrathin metallic films of ultimately small thickness, corresponding to the dimensions of single atomic plane, and the development and study of literally 2-D and quasi-2-D systems are important from both a fundamental and an applied viewpoint. It is of particular interest for 2-D magnets investigations and for creation of new magnetic media with ultimately thin magnetic layers - 2-D monoatomic arays of magnetic metals. It is known, that surface metal layers often show properties different from the bulk metal. Due to the reduced dimensionality, the surface may exibit different magnetic properties from the bulk. A number of reports show experimental evidences that for the lanthanide surfaces a Curie temperature is higher for the surface than for the bulk$^{1)}$. This phenomenon was first observed for gadolinium$^{2)}$.

Langmuir monolayers of amphiphilic molecules at the gas-liquid interface and the corresponding Langmuir-Blodgett (LB) films on solid substrates have been studied for a long time as model objects for the investigations of physical properties of ordered 2-D, or nearly 2-D, systems. The stoichiometric chemical binding of metal cations from the water subphase to

CCC 1022-1360/98/$ 17.50

the surface of a floating Langmuir monolayer allows for the formation of mono- and multilayered LBfilms with adsorbed metal ions being ordered in integrated homogeneous two-dimensional arrays. Bound ions are adjacent to the planes of the polar heads of the amphyphilic molecules. It is possible to modify 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 nearly 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 formed as space ordered one atom thick planar layers of transition magnetic atoms, separated by the diamagnetic organic layers, were used for modelling and study of 2-D magnetic systems. One supposes that the ions should be close together to get strong interaction, and thus the minimum number of hydrocarbon chain seems desirable. Fatty acids and concretely stearic acid were used usually in such experiments.

The first investigations of magnetic properties of LB films with rare-earth cations revealed a new class of promising materials3). The giant nonlinear optical magnetic Kerr effect was observed for Gd-containing LB films4) and EPR studies gave evidence that these films possessed magnetic ordering up to rather high (500K) temperatures5). This work is focused on the preparation and characterisation of stearic acid LB films containing three-valent rare-earth cations. The monolayer behavior on the cation-containing water subphase was analyzed by thermodynamic measurements and structure of deposited multilayer rare-earth containing stearic acid LB films was studied by small angle X-rays diffraction.

Experimental details

All reagents used were G.R. grade and were commercially available. Water was purified by a Milli-Q system (Millipore Ltd.). Surface pressure-monolayer area isotherm (P-A isotherm) measurements and monolayer transfer to solid substrates were carried out on a full automatic conventional teflon through at 20 °C as described elsewere6). X-ray scattering experiments were performed with a multicrystal diffractometer on the base of powder "Rigaku D/max-RC" diffractometer (X-ray wavelength λ =1.5405 A, power of X-rays source 12 kW). The density distribution in specular reflection geometry normal to the surface (incident angle equal to scattering angle) was recorded at room temperature.

Results and discussion

The key step in formation of ionic layers in LB films is binding of water subphase cations to monolayer surface and subsequent deposition of cation-containing monolayer. The binding of multivalent cations to fatty acid monolayer is strongly dependent on ionic content and pH in aqueous phase. When amphiphilic molecules (for example long-chain fatty acids or lipids) are spreaded on the surface of water, they form monomolecular film and reduce the surface tension of the water by a quantity P (called monolayer surface pressure). The experimental compression isotherms of fatty acids usually show discontinuities and breaks in isotherm slope attributed to structural transitions of monolayer between 2-D gas, liquid expanded (LE), liquid condensed (LC) and solid phases7).

Fig. 1 shows the characteristic compression isotherms of stearic acid monolayer onto the aqueous subphase with different ionic content. Curve 1 on Fig.1 presents control P-A isotherm recorded when water subphase was used without any additions, pH = 5.4. The characteristic LC-solid phase transition in monolayer takes place as it follows from changes in P-A isotherm slope. Curve 3 and 4 are the P-A isotherms of monolayer onto the rare-earth chloride solution (pH = 5.5) These isotherms are compressed and shifted to the higher A region at large P values in comparison with control isotherm. Curve 5 shows the result of significant increase in gadolinium chloride concentration in aqueous subphase at the same pH value - the shift of corresponding P-A isotherm increased significantly and LC-solid state transition is still presented. Such P-A isotherm shift is characteristic for substantial increase in monolayer surface potential value. The curve 2 is compression isotherm recorded when gadolinium acetate solution at the same pH value was used. The slope of isotherm is sharp and monotonously smooth without any noticeble phase transitions, related to LE and LC phases. This P-A isotherm is corresponded to condenced monolayer below the triple-point temperature. Below the triple point temperature of the monolayer the 2-D molecular gas (vapor) condenses practically directly to the solid phase. It is known, that charging of monolayer surface shifts triple point significantly. The common features of curves 2 - 5 on Fig. 1 are the general decrease in compressibility and the collapse behavior. It is clear from Fig. 1 that the only change of negative counterion in rare-earth containing subphase from Cl^- to acetic acid causes dramatic changes in stearic acid Langmuir monolayer properties. The monolayer behavior on the surface of gadolinium acetate solution resembles that of monolayer when divalent cations are present in subphase.

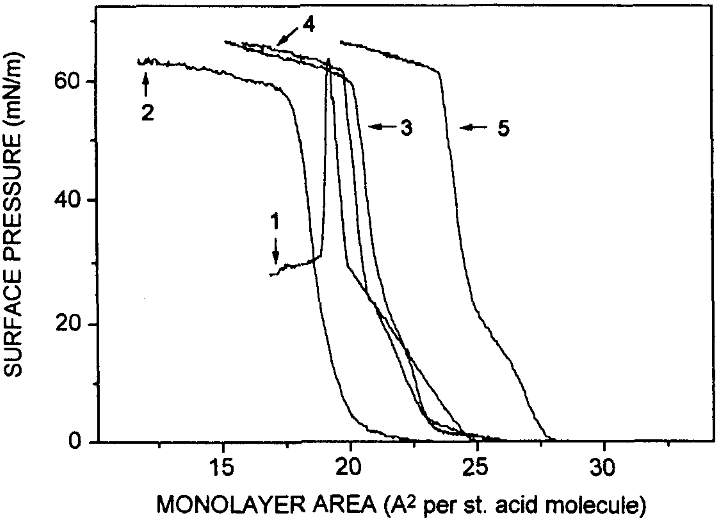

Fig.1: Surface pressure-monolayer area isotherms of stearic acid monolayer. Curve 1 = control isotherm on pure water subphase, pH = 5.5; curve 2 = 10^{-4} M gadolinium acetate in subphase, pH = 5.5; curve 3 = 10^{-4} M erbium chloride in subphase, pH = 5.5; curve 4 = 5×10^{-5} M gadolinium chloride in subphase, pH = 5.5; curve 5 = 3×10^{-4}M gadolinium chloride in subphase, pH = 5.5; Area is calculated per stearic acid molecule. T = 295 K.

In case of monolayers formed by molecules with dissociable head groups or when charged substances are adsorbed on monolayer surface from aqueous subphase, the electrostatic interactions at the interface are substantial part of monolayer free energy. As a result, the electrostatics at the interface influence the structure and the state of monolayer. The effect of electrostatic interactions on the monolayer surface pressure P value can be evaluated from thermodynamicGibbs free energy considerations. It was found that change in P due to the reversible charging of a monolayer at a fixed area in equilibrium with an aqueos subphase of a constant composition and temperature is[8]:

$$\Delta P = \int_0^{\varphi_o} \sigma d\varphi; \qquad (1)$$

where σ is the monolayer surface charge density; φ_o is electrostatic potential value at the interface. Simple electrostatic model assuming a uniform charge density on a planar interface and ions as point charges, known as Gouy-Chapmen theory of double layer, allowed to describe the change in ΔP = 37 mN/m at 21 A^2 per stearic acid molecule observed for the shift between P-A isotherms corresponding to curves 2 and 4 on Fig. 1. These evaluations give evidence that at compression extent corresponding to 21 A^2/stearic acid molecule, the classical electrostatic interactions determine the changes in P value and that monolayer surface is practically neutral when gadolinium acetate is present in aqueous phase. The change in monolayer free energy corresponding to obtained ΔP value is 4.95 kJ/mol stearic acid and is some 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 ΔP enhancement with the further decrease of monolayers area A. It was reported that changes in P value caused by divalent cations were significantly larger than predicted by calculations of free energy changes due to simple electrostatic interactions9). It points out that, as in our case, the hydration effects and specific interactions (including van der Waals, multipolar, hydrogen bonding, complexation etc.) besides the electrostatic effects can be involved when di- and multyvalent cations bind to monolayer.

X-rays diffraction technique is widely employed in investigations of structure of multilayer fatty acid LB films containing metal cations7, 10, 11). Fig. 2 shows the X-ray diffraction pattern in low angle range obtained from the multilayer rare-earth containing LB films fabricated under different ionic content in aqueos phase. On the diffractograms of LB films formed under the deposition of monolayer from the rare-earth chloride containing aqueous subphase (curves 1 and 2 on Fig. 2) one can see very broaden peak (~3.5 grad) and a number of narrow weak peaks. The close diffractogram was obtained for LB film fabricated by deposition of destroyed collapsed monolayer from gadolinium acetate solution (curve 3 on Fig. 2). The complex two-phase diffraction pattern with differently broaden peaks and rather low coherence length values can be interpreted as a result of disturbed layered structure of corresponding LB films. Curve 4 on Fig. 2 demonstrates a typical well-defined layered structure in the case of LB film formed using rare-earth acetate solution as a subphase. The width of either diffraction peak (~0.1 grad) yields a coherence length $D > 1000$ A. The layered structure period d was determined to be 52 A, two angstroms larger than for usual transition metal cations containing Y-type LB films.

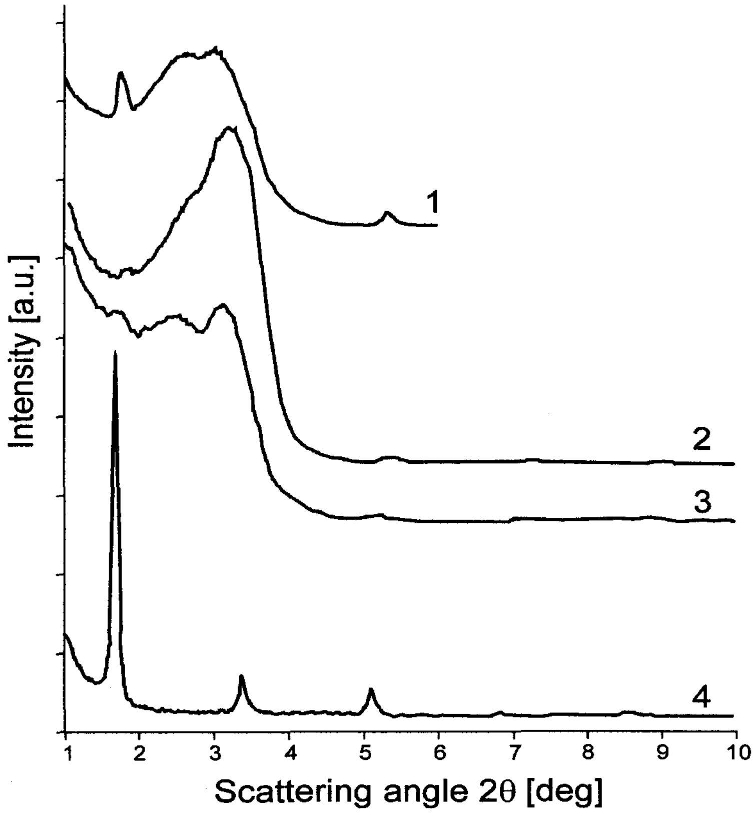

Fig. 2: X-rays diffractograms obtained in the θ - 2θ geometry from samples of the rare-earth containing multilayer LB films formed on the polished silicon substrate with natural oxide layer. Curve 1 = 50 monolayers, 10^{-4} M erbium chloride in subphase, pH = 5.5, deposition pressure 30 mN/m ; curve 2 = 50 monolayers, 10^{-4}M gadolinium chloride in subphase, pH = 5.5, deposition pressure 30 mN/m; curve 3 = 40 monolayers, 10^{-4} M gadolinium acetate in subphase, pH = 5.5, deposition pressure 60 mN/m (collapse); curve 4 = 50 monolayers, 10^{-4} M gadolinium acetate in subphase, pH = 5.5, deposition pressure 30 mN/m. For clarity, the curves are shifted towards each other by an order of magnitude in the y axis. T = 295 K.

The related resuls were reported in[12)] where deposition of monolayer from terbium chloride solution revealed changes from Y- to XY-type and LB films formed were characterized by structural nonhomogeneities and reorganizations with time. We proposed that the interface electrostatic interactions caused the changes in the state of fatty acid monolayer onto the rare-earth multivalent cations containing aqueous subphase and monolayer deposition type. Those interactions also resulted in structural defects in corresponding LB films formed. The use of monodentate complexones like acetic acid was proposed to form bulk phase quasi-neutral rare-earth complexes. The electroneutral ligand exchange reactions of such complexes with stearic acid monolayer results in the formation of quasi-neutral rare-earth complexes bound to monolayer surface. The area density of bound rare-earth cations incorporated in LB film can be obtained high enough. For example, distances between the Gd cations in planar layers in stearic acid LB film are comparable with characteristic distance of atoms in bulk gadolinium4). Such a structure of rare-earth containing LB films can promote two-dimensional magnetic ordering phenomenon in this material5).

Conclusion

It has been shown that the state of fatty acid Langmuir monolayer on the rare-earth containing aqueous subphase and the structure of corresponding multilayer LB film are dependent substantially on the anion type of dissolved rare-earth salt. The structural disorder analogous to monolayer collapse structures was found in multilayer LB films when rare-earth chloride solution was exploited as aqueous subphase, caused presumably by electrostatic interactions under deposition of monolayer with high binding of rare-earth cations to monolayer surface. The approach based on the use of monodentate complexones like acetic acid allows to neutralize monolayer surface under rare-earth cations binding and subsequent LB film formation thus giving possibility to obtain high ordered LB films with high content of adsorbed multivalent rare-earth cations arranged in two-dimensional monoatomic arrays.

Acknowledgment

The X-rays scattering diffractograms were gratefully obtained with the help of Prof. S.N. Polyakov, Institute of Nuclear Physics, Moscow State University. I thank to Dr. Yu.A. Koksharov, Dr. A.M. Tishin, Prof. O.A. Aktsipetrov and Prof. J. Bohr for intensive and effective collaboration. This work was supported by Russian Fund for Basic Researches (Grant 96-03-33766a).

References

1) P.A. Dowben, D.N. McIlroy, "*Surface magnetism of the lanthanides*", Handbook on the Physics and Chemistry of Rare Earths, Vol. 24, ed. by K.A. Gschneidner, Jr and L.Eyring, Elsevier Science, New York 1997, p. 1-46

2) C. Rau, *J.Magn. & Magn mater.* **30** 141 (1992)

(3) G.B. Khomutov, Yu.A. Koksharov, and A.M. Tishin, *"New Class of magnetic materials: rare-earth containing Langmuir-Blodgett films as planar magnets"*, Preprint N5/1996 of Faculty of Physics, Moscow State Univ., Moscow, 1996, p.1-28.

(4) O.A. Aktsipetrov, A.A. Fedianin, G.B. Khomutov, T.V. Murzina, A.M. Tishin, J. Bohr, *La Revue de Mmetallurgie*, SF2M, Journees d'Automne ,Ja 1997, p. 146

(5) A.M. Tishin, Yu.A. Koksharov, J. Bohr and G.B. Khomutov, *Phys. Rev. B* **55**, 11064 (1997)

(6) G.B. Khomutov, T.V. Yurova, S.A. Yakovenko, V.V. Khanin, E.S. Soldatov, *Supramolecular Science* **4**, 349 (1997)

(7) G.L. Gaines, *"Insoluble monolayers at liquid-gas interfaces"*, John Willey: New York 1966.

(8) Th.A.J. Pains, *Philips Res. Rep.*, **10**, 425 (1955)

(9) M. Losche, C.A. Helm, H.D. Mattes and H. Mohwald, *Thin solid films* **133**, 51 (1985)

(10) S.A. Yakovenko, V.V. Kislov, V.V. Erokhin, A.Yu. Potapov, and G.B. Khomutov, *Z. Phys. Chem.* **66**, 1028 (1992)

(11) L.A. Feigin, Yu.M. Lvov, V.I. Troitsky, *Sov. Sci. Rev. A. Phys. (London)*, **11**, 285. (1989)

(12) E. Gyorvary, J. Peltonen, M. Linden, J.B. Rosenholm, *Thin Solid Films*, **284-285**, 3684 (1996)