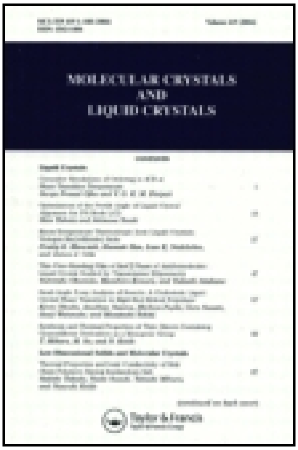

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Magnetic Langmuir-Blodgett Films

Carlos Lafuente [a] , Helene Soyer [a] , Serge Ravaine [a] , Christophe Mingotaud [a] & Pierre Delhaes [a]

[a] Centre de Recherche Paul Pascal-C.N.R.S., University of Bordeaux I, Avenue Schweitzer, 33600, Pessac, FRANCE

Version of record first published: 24 Sep 2006

To cite this article: Carlos Lafuente, Helene Soyer, Serge Ravaine, Christophe Mingotaud & Pierre Delhaes (1998): Magnetic Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 322:1, 91-98

To link to this article: http://dx.doi.org/10.1080/10587259808030205

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 91-98
Reprints available directly from the publisher
Photocopying permitted by license only

Magnetic Langmuir-Blodgett films

CARLOS LAFUENTE, HELENE SOYER, SERGE RAVAINE,
CHRISTOPHE MINGOTAUD, PIERRE DELHAES
Centre de Recherche Paul Pascal-C.N.R.S., University of Bordeaux I, Avenue
Schweitzer, 33600 Pessac, FRANCE

Received 6 April 1998; accepted 25 April 1998

Langmuir-Blodgett (LB) films containing various inorganic complexes were prepared using the so-called semi-amphiphilic approach where ions are adsorbed along a charged monolayer. The metal complexes are organized generally in monolayers within the LB films. The magnetic properties of such LB films are related to that of the inorganic molecules and present an anisotropic behavior in some cases. Those results emphasize the interest to control perfectly the molecular organization in order to build up new magnetic hybrid materials.

Keywords: Langmuir-Blodgett film, magnetism, inorganic complexes, hybrid material

INTRODUCTION

In the field of research concerning magnetic and electronic organized soft media, a special interest is devoted to organized thin films. To build up molecular layered structures, one of the most powerful tool is the Langmuir-Blodgett technique[1]. However, only few works have been devoted to magnetic LB films. They are based upon an ionic association between a metallic (and magnetic) cation and a long chain fatty acid or similar molecule. A pioneering work was published by Pomeranz et al[2] who have shown that manganese or iron stearate can form magnetic LB films. These authors have demonstrated that the ESR resonance line presents an anisotropic behavior which is characteristic of 2d dipolar interactions. Using similar strategy but more recently, Talham and coworkers[3] have described the realization of manganese octadecylphosphonate LB films with an in-plane structural organization as observed in the solid state. The spin susceptibility temperature dependence of the Mn^{2+} ions indicates a long range magnetic ordering and follows the expression for a quadratic layer Heisenberg AF.[4]

An alternative strategy based on a more sophisticated molecular engineering has been developed few years ago. Instead of using simple transition metals as the previous authors, inorganic complexes or inorganic molecular assemblies were organized in LB films by the semi-amphiphilic method. Such method is a generalization of the strategy employed with the metallic cations or various ionic organic molecules[5]. It must satisfy two basic requirements at the gas-water interface: equilibrium of the charge densities for the semi-amphiphilic association and adjustment of the respective molecular areas. Concerning the amphiphilic cations, insoluble layers can be built from ammonium, sulfonium or even phosphonium salts. For the magnetic part, the choice is guided by the type of involved ligands. The recent progresses in molecular magnetism have shown that magnetic interactions are indeed propagated through some extended bridging networks: the coupling between magnetic moments could then be propagated over relatively large distances[6]. In particular, new molecular ferro or ferri-magnets have recently been realized with heterobimetallic compounds using oxalate[7] and cyanide ligands[8].

In this paper, the formation and characterization of several hybrid inorganic/organic LB films are presented. Those well-defined multilayers exhibit various magnetic properties. They represent a new series of lamellar materials in which magnetic properties of the inorganic sheet can be combined with conducting, optical or electrochemical functions due to the organic part.

EXPERIMENTAL SECTION

Dimethyldioctadecylammonium bromide (DODA) was obtained from Kodak and used without further purification. Chloroform (HPLC grade from Prolabo) was used as spreading solvent. The water of the subphase was a Millipore Q-grade water with a resistivity higher than 18 MΩ.cm.

Built-up films have been obtained by the vertical lifting method using a home-made LB trough working at room temperature under a continuous dried nitrogen flow[9]. After each increase of the surface pressure, waiting time allows the system to reach its equilibrium. Steps of 2 mN/m were usually chosen. Films were transferred onto optically polished calcium fluoride or zinc selenide for infrared measurements, onto optically polished glass substrate for X-ray experiments and onto diamagnetic mylar sheet for SQUID experiments.

Infrared (IR) spectra were recorded on a FTIR 750 Nicolet spectrometer. Linear dichroism was used in order to determine the molecular orientations in LB films[10].

X-ray diffraction experiments were performed with an INEL curve detector associated with an IBM computer for peak assignments.

For electrochemical experiments, an Autolab PGSTAT 20 potentiostat (from Ecochemie) was used.

The magnetic susceptibility was measured with a Quantum Design MPMS-5 SQUID magnetometer between 2 and 300 K. Experimental conditions were the same as those already described[11].

RESULTS AND DISCUSSION

Langmuir film

As already described in the literature[9,12], the isotherm (see figure 1) on pure water suggests that the DODA monolayer is in an expanded state at the interface because of the high repulsion between the charged polar heads. Figure 1 demonstrates that the compression isotherm of DODA is strongly modified when, for example, the $K_3Fe(CN)_6$ complex is dissolved in the aqueous subphase. In a first stage, the Π-A curve is shifted toward the smaller areas per molecule and at the same time the curve is steeper at the end of the compression. When the concentration in ions reaches ca 10^{-6} M, maximum density is found for the Langmuir film at a given surface pressure. Then, any further increase in the complex concentration induces an increase in the molecular areas. Such type of behavior has been already reported for other inorganic ions[9] and is related to the adsorption process of the ions along the charged Langmuir film.

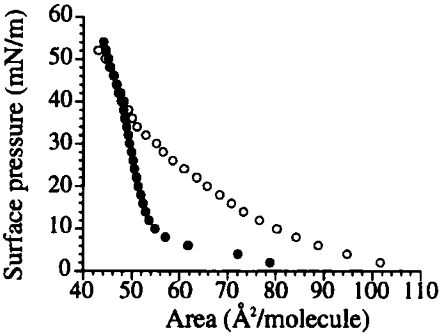

FIGURE 1 Compression isotherm of DODA on pure water (open circle) and on a 10^{-6} M $K_3Fe(CN)_6$ solution (full circle).

Langmuir-Blodgett film

Whatever the inorganic ions may be, the transfer of the monolayer from the interface onto a solid substrate is easily performed when the molecular density in the film is high enough[9,13]. The transfer is generally Y-type. These LB films were characterized by complementary techniques such as infrared spectroscopy, X-ray diffraction and magnetic susceptibility measurements.

Infrared linear dichroism

Besides the bands assigned to the CH_2 stretching or scissoring vibrations of DODA alkyl chains, bands associated with the complexes are clearly visible in the IR spectra of the LB films. Compared to values in KBr pellet, these vibration bands in LB films are narrower and somewhat shifted. They demonstrate that the inorganic molecules are indeed trapped within the LB film. Furthermore, when the infrared electrical field is not parallel to the plane of the substrate, a splitting of the bands associated with the complex is generally observed in the DODA LB film (see figure 2). This dichroism proves that the complexes have a particular organization within the LB films. The electrostatic interactions with the charged lipids are certainly responsible for such orientation or/and distortion of the complexes in the multilayers.

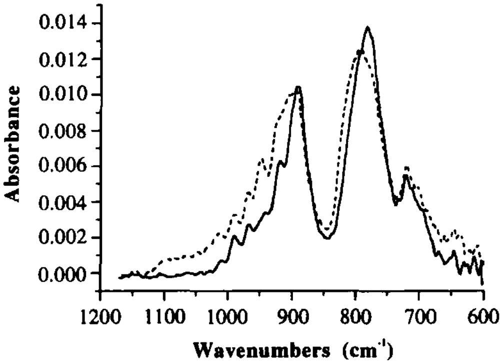

FIGURE 2 Infrared spectra of a $K_6[SiMn(H_2O)W_{11}O_{39}]$/DODA LB film. The angle between the plane of the substrate and the electric field is either 0° (solid line) or 60° (dashed line).

X-ray diffraction

A variable number of Bragg peaks is observed in the diffractogram both depending on the structure of the inorganic ion and of the positively charged lipid. Layer thickness of the LB films can then be evaluated. Taking into account the tilt angle of the alkyl chains (evaluated by IR dichroism) and the length of the lipid, thickness of each inorganic layer in LB can be estimated and compared to crystallographic data of complex crystals. Such comparison demonstrates that the inorganic anions generally form monolayers of anions within the LB film (see figure 3)[9,13].

Magnetic susceptibility

Because of the average large distance and the lack of superexchange pathways between the magnetic centers, interactions between metal complexes should be negligible within the LB film. The experimental χ.T product is indeed similar in the LB film and in powder (see figure 4). This proves that the metal complex structure is not strongly modified within the multilayer architecture.

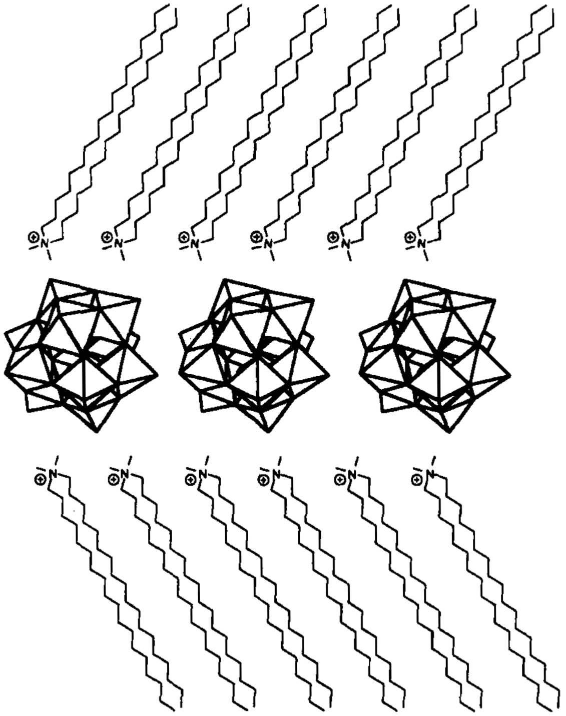

FIGURE 3 Schematic organization of Keggin polyanions in a LB film.

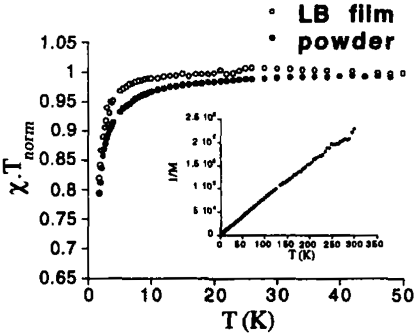

FIGURE 4 Plot of χ.T (normalized value) versus temperature of the $K_6[SiMn(H_2O)W_{11}O_{39}]$ polyanion in powder (open circles) and in LB film (full circles).

Depending on the exact nature of the complexes, several magnetic behaviors were recorded, varying from a simple Curie law to strong deviations from such law (see figure 5)[14]. Ferromagnetic LB films have even been obtained[15].

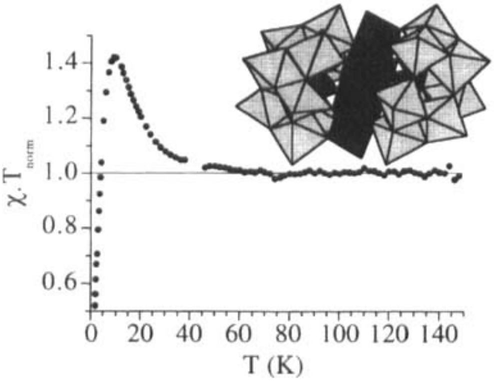

FIGURE 5 Plot of χ.T (normalized value) versus temperature for a LB film based on a $K_{10}[Co_4(H_2O)_2(PW_9O_{34})_2]$ polyanion.

Finally, the average of the χ.T product for high temperature should be proportional to the quantity of metal complexes trapped in the LB films. Comparing this mean value together with the results in powder, an estimation of the amount of magnetic ions was made. Knowing the number of layers deposited onto the substrate, the transfer ratio and the area per molecule at the transfer surface pressure, calculation of the number of lipid molecules is straightforward. Then, the ratio between the metal complexes and the positively charge lipids was easily evaluated. Its value is found close to the complex charge, suggesting that the electroneutrality between the inorganic complexes and the lipid parts is respected. However, one can not totally rule out that small H^+ or K^+ cations could be adsorbed with the anions in order to fulfill the electroneutrality within the multilayers.

Outside the magnetism, the hybrid multilayers may have various interesting properties. For example, electrochromism can be observed in those LB films (see figure 6). Indeed, using a conducting ITO substrate, electrochemistry is easily performed on such material. The reduction or oxidation of the inorganic layers induces a reversible change in the optical absorption of the LB films.

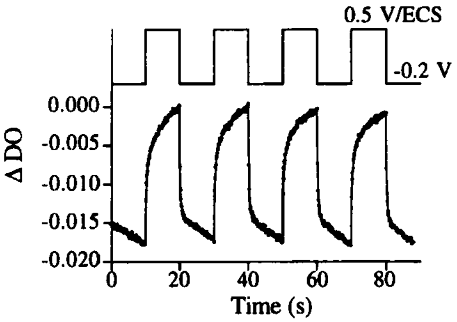

FIGURE 6 Changes in the optical density of a particular hybrid LB due to oxidation/reduction electrochemical cycles.

Therefore, those new hybrid multilayers represent new opportunities to develop original optical, magneto-optical or magneto-conducting devices.

References

[1.] A. Ulman, *Introduction to ultrathin organic films* (Academic Press, Boston, 1991), pp 442.
[2.] M. Pomerantz, F. W. Dacal and A. Segmuller, *Phys. Rev. Lett.* , **40**, 246 (1978).
[3.] H. Byrd, J. K. Pike and D. R. Talham, *J. Am. Chem. Soc.* , **116**, 7903 (1994).
[4.] C. T. Seip, H. Byrd and D. R. Talham, *Inorg. Chem.* , **35**, 3479 (1996).
[5.] H. Kuhn, *Thin Solid Films* , **178**, 1 (1989).
[6.] O. Kahn, *Molecular magnetism* (VCH, New-York, 1993).
[7.] S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gutlich and A. Hauser, *Inorg. Chem. Acta* , **216**, 65 (1994).
[8.] T. Mallah, S. Thiebaut, M. Verdaguer and P. Veillet, *Science* , **262**, 1554 (1993).
[9.] M. Clemente-Leon, B. Agricole, C. Mingotaud, C. J. Gomez-Garcia, E. Coronado and P. Delhaes, *Langmuir* , **13**, 2340 (1997).
[10.] M. Vandevyver, A. Barraud, A. Ruaudel-Teixier, P. Maillard and C. Gianotti, *J. Colloid Interface Sci.* , **85**, 571 (1982).
[11.] M. Clemente-Leon, C. Mingotaud, B. Agricole, C. J. Gomez-Garcia, E. Coronado and P. Delhaes, *Angew. Chem. Int. Ed. Engl.* , **36**, 1114 (1997).
[12.] J. Marra, *J. Phys. Chem.* , **90**, 2145 (1986).
[13.] M. Aiai, J. Ramos, C. Mingotaud, J. Amiell and P. Delhaes, *Chem. Mater.* , in press (1998).
[14.] M. Clemente-Leon, C. Mingotaud, C. J. Gomez-Garcia, E. Coronado and P. Delhaes, *Thin Solid Films* , in press (1998).
[15.] C. Mingotaud, C. Lafuente, J. Amiell and P. Delhaes, submitted.