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From dispersed nanodiscs to thin films of layered organic material via reversible swelling

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Abstract

We show that nanodiscs stabilized with polymers order and pile up on a surface upon drying. The resulting surface films with an average thickness of one micron are made of collapsed cohesive layers with smectic long-range order. This occurs with and without plastifying stabilizing polymer and produces crevasses. The stacked discs undergo a two-to-three-dimensional crystallization while bottom layers close to the surface fuse and produce infinite bilayers. Small angle X-ray scattering experiments demonstrate that excess polymer is segregated from the crystalline stack. Water adsorption isotherms show that reversible swelling of the excess polymer does not destroy the compact stack of partially fused nanodiscs collapsed parallel to the surface. In the absence of chemical binding, the stacks of layered nanodiscs can be removed by simple washing with pure water. AFM, TEM and SEM experiments demonstrate that presence of crevasses is quenched by the presence of a plastifying polymer.

Keywords: Catanionic; Surfactant mixtures; Thin layers; Osmotic pressure; Adsorption isotherm

1. Introduction

Depositing onto a surface a thin (<1 mm) dense layer of protective material is of primary importance in the field of lubrication and corrosion-control. Most wide-spread strategy is to use polymers, starting from the molten state or "bad-solvent" condition. In principle, starting from a flat object with high aspect ratio and low thickness gives the best results in surface protection for a given amount of material. Having this complete tiling of the surface in mind, several types of disc shaped colloids have been studied and are in use for covering surfaces: clays, i.e. inorganic layered silicates [1]; aluminium oxide platelets, basis of paints for the car industry [2]; organic "bicelles", disc-shaped micelles made from surface active lipids or peptides [3]. Recently, a new type of nanodisc has been described [4]. These are made with crystalline bilayers made from alternated anionic and cationic surfactants, a class of mixture of surface-active agents designed as "catanionics" [5]. Their rigidity is of the order of one mega-Pascal [6] and they can be stabilized by the addition of some peculiar polymers [7]. A review about physical properties of catanionic nanodiscs is available [8].

The main difficulty when manipulating asymmetric flat colloids with the aim of making compact layers is to avoid several very general behaviours: Onsager transitions producing microphase separated pastes [9] and formation of highly swollen gels when colloids touch by edges, making "house of cards". By using catanionic nanodiscs, the house-of-cards local microstructure structure is not favorable, since – unlike clay and aluminium platelets – edges of the catanionic nanodiscs are hydrophilic and highly charged. The Onsager transition occurs without any attraction, but can be quenched by the repulsion between the discs.

The aim of this work is to explore the possibility of making sub-micronic thin films starting from stabilized nanodiscs by means of controlled drying on a chemically inert surface. The drying of dilute solutions of colloids produces complex

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figures such as rings of material, patterns in the interior of the droplet or in some favorable cases large superstructures [10–14]. The details of the final morphology are determined by the competition between off-equilibrium phenomena, such as capillary flow or solvent density fluctuation, in conjunction with colloid–colloid or colloid–substrate interaction [10,11]. At a larger scale, the propagation of cracks can be studied if the deposited layer is thick enough, e.g. in the case of more concentrated colloidal solutions [15]. In the case of composites of inorganic platelets and polymer deposited onto flat substrates, the anisotropic particles have been shown to orient preferentially along the substrate [16]. Here, we focus on rigid discs made of organic materials embedded in an organic matrix. We report AFM, SEM, water adsorption isotherms and grazing incidence on thin films deposited on glass. On drying a drop of the samples containing a know amount of nanodiscs, three different organizations of the layers of discs may a priori be formed:

(A) When a droplet of the disc sample is placed on a thin, clean substrate and allowed to dry, the formation of a columnar organization of discs is a possibility, as seen from the side view (Fig. 1a). In this case, a few discs are shown to be attracted to the hydrophilic substrate and form the first layer, upon which more discs build up in a regular, upward direction. The organization takes place in such a manner that the discs align themselves more along the sides than the edges. If the discs arrange in the columnar organization, they are more compact and can slide over each other better than other possible organizational forms. However, since "defects" occur, there are some discs that rest edge-on against the sides of other discs and hence, there are some gaps in the organization of the discs. The circles in the inset diagram represent the stacks of discs when viewed from the top. This diagram shows the hexagonal close packing structure of the discs when they are arranged in a columnar organization. When discs are put together in a confined area, the best possible form of lattice structure is the hexagonal close packing. It is expected that discs form "Chinese hats" on the top on drying.

(B) The second possibility is the 'House of Cards' organization (Fig. 1b). The Collapsed 'House of Cards' organization contain a large amount of water and has poor performance in protecting the surface (except if "moistening" is the effect at aim). In this case too, some discs are attracted to the charged substrate and form the first layer. More discs build in the upward direction on this initial layer but in such a manner that few discs rest edge-on on the initial layer of discs and are supported by other discs. More discs then come onto the discs that rest edge-on and are seen to be positioned side-on. If the discs arrange in the collapsed 'House of Cards' organization, the packing is less compact than in the columnar organization. The discs have orientational order and there are fluctuations about the mean value of tilt angle. Therefore, the discs follow a nematic type of orientational order. The average thickness measured is greater than the average thickness expected from compaction hypothesis. The flat

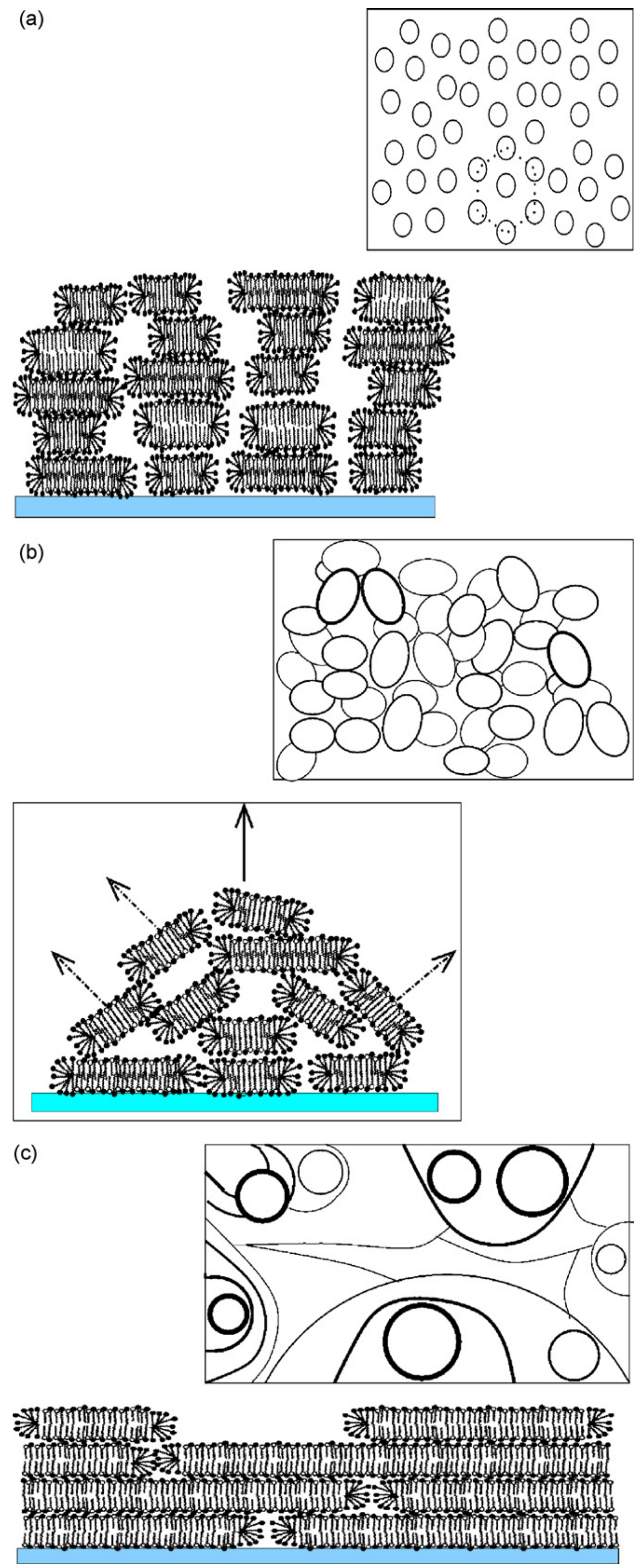

Fig. 1. (a) Columnar organization of discs (cross-sectional view), inset, the top view. (b) 'House of Cards' organization of discs (cross-sectional view), inset, the top view. (c) 'Merging from the Edges' organization of discs (cross-sectional view); inset, the top view.