



Three-dimensional aggregation of fullerene C₆₀ at the air–water interface

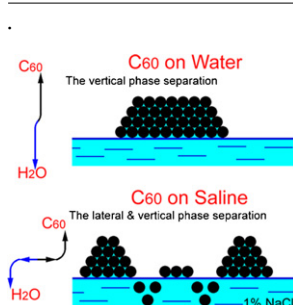
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HIGHLIGHTS

- Using cyclohexene as a spreading solvent, we prepared the highly homogeneous 2D system C₆₀–H₂O.
- On water, the system suffers the vertical phase separation into the C₆₀ polylayers and free water.
- On saline, the holed and pitted C₆₀ polylayers arise because of the lateral phase separation.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper seeks to get a mechanistic insight into homomolecular aggregation of fullerenes in low-dimensional systems. For this purpose, the forced aggregation of fullerene C₆₀ on two subphases (pristine water and aqueous 1% NaCl solution) has been studied by analysis of the compression curves and Brewster angle microscopy (BAM). The analysis indicates that the highest ordered structure being achievable upon multi-cycle compression is the C₆₀ hexalayer. The lower aggregation stages are directly observable by BAM. The floating layers are stated to be organized as a binary colloid system C₆₀–H₂O, where the C₆₀ component behaves as a guest initially but becomes a host towards the tetralayer stage. In turn, the H₂O component inhibits the structural collapse and promotes the smooth vertical growth of the C₆₀ aggregates. The polylayers exhibit a variety of morphological features, both aggregated species and structural defects, whose evolution is discussed in terms of the vertical and lateral phase separation.

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1. Introduction

Homomolecular aggregation of fullerenes in colloid solutions is a widely studied phenomenon. However, despite impressive experimental works were performed [1–5], it is difficult to link the proposed aggregation models [6] with solution-deposited thin films, whose structural features are determined by nanoscale interfacial effects during solvent evaporation [7–9]. Besides, the homoaggregation is known to occur in parallel with solvation of the fullerene molecules [10]. The latter interaction is more exothermic [11] but oddly was not included in the said models.

An instructive experimental approach to the fullerene aggregation in thin films is the Langmuir–Blodgett (LB) technique. Indeed, the layers at the air–water interface are supposed to be solvent-free, while the impact of water on the target interaction C₆₀–C₆₀ can be rationalized in the fine frameworks of the hydrophobic hydration concept (see the work [12] and references therein). The floating C₆₀ layers were a subject of intensive experimental studies over the Nineties [13] and the findings have been converted into the physico-mathematic model [14]. According to this model, the C₆₀ monolayer is stabilized by three direct contacts C₆₀–C₆₀ and transforms into the bilayer when only one or two contacts take place. All data serving as a basis of this model were acquired on the floating layers deposited from benzene. This solvent clings to the C₆₀ molecule [15] and hence unwillingly evacuates from the C₆₀-covered water surface. As a consequence, the benzene-deposited

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