Biocompatible Magnetite Nanoparticles at the Air/Water Interface

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In the last decade, the iron oxide nanoparticles, known as SuperParamagnetic Iron Oxide Nanoparticles (SPION), have received a significant attention from the scientific world due to their applicability in a variety of domains. In the biomedical field [1], the iron oxide nanoparticles are very useful as drug delivery systems, as magnetic resonance imaging contrast enhancers (clinical diagnosis), as inflammation response or anti-cancer agents, for labeling and cell separation. These NPs are very attractive for medical purposes due to their unique features, such as their large surface/volume ratio, which allows them to bind, adsorb or carry compounds such as drugs, proteins, enzymes or antibodies, which can be then directed to a special tissue or organ using an external magnetic field, or can be heated in alternating magnetic fields for use in hyperthermia.

The system studied in the present work is completely different from the iron oxide NPs already studied at the air-water interface. It consists of a monodisperse population of Fe₃O₄ cores with a diameter of 6.4 nm, which are grafted with catechol-terminated copolymers of 2-(2-methoxyethoxy) ethyl methacrylate (MEO₂MA) and oligo(ethylene glycol) methacrylate (OEGMA) [2]. The NPs were named Fe₃O₄@MEO₂MA₉₀-co-OEGMA₁₀, 90 and 10 representing the molar fractions of MEO₂MA and OEGMA, respectively. It is important to highlight the fact that these NPs are dual dispersible. Due to the presence of oligo(ethylene glycol) side groups on the surfaces, the Fe₃O₄@MEO₂MA₉₀-co-OEGMA₁₀ NPs can be dispersed in water, exhibiting a high colloidal stability against salt, and in the same time, they can be well dispersed in organic solvents, like chloroform, ethanol or toluene.

Due to the fact that the NPs can be dispersed both in water and chloroform, the NPs films have been prepared either by adsorption of the NPs from the aqueous bulk solution or by spreading them at the interface from a chloroform solution. Dispersed in water, the Fe₃O₄ NPs adsorb at the air/water interface. Using a concentration of 1.5·10⁻³ mg/ml, a constant surface pressure value of approximately 23 mN/m is reached after 20 h. Compression/expansion isotherms of Langmuir layers formed by spreading are shown in Figure 1.

![Figure 1: Compression/expansion isotherms of a NPs layer prepared by spreading (starting coverage 3.89·10⁻⁴ mg/cm²) on Milli-Q Millipore water at 20 °C.](image)

By compression, a significant increase of the surface pressure is observed until a value of approximately 25 mN/m. This is the critical pressure (πₜ) of the NPs film. During further compression, a plateau region appears at which the surface pressure increases only slightly up to a maximum value of 27 mN/m. It is very important to highlight that no hysteresis of the compression/expansion isotherms is observed when the interfacial film formed by spreading is compressed to surface pressures below the critical pressure of the Langmuir layer. This suggests
that no loss of the NPs from the interface occurs by compression. Therefore, we can calculate the interfacial concentration of NPs corresponding to the critical pressure. The critical concentration amounts to \((7.7 \pm 0.6) \times 10^{-4}\) mg/cm\(^2\). This value is in good agreement with the NPs’ interfacial concentration of \(8.2 \times 10^{-4}\) mg/cm\(^2\) which can be calculated considering that all the NPs of the aqueous solution adsorb at the air/water interface. This shows that the adsorbed particles are trapped at the interface and do not exchange with the subphase. Comparing the compression/expansion isotherms, a pronounced hysteresis was observed. The question arises whether the NPs form an irreversible multilayer film on top of the water surface or are squeezed out from the interface and re-dispersed into the aqueous bulk above the critical pressure. In order to distinguish between the two possible scenarios, we further investigated the NPs Langmuir film \textit{in situ}, using the X-Ray fluorescence technique at BW1, and also after the transfer onto a solid support by using Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM) (Figure 2, left).

The X-ray fluorescence Fe K\(\alpha\) (6.4 keV) and Fe K\(\beta\) (7.06 keV) lines, obtained for a NPs film compressed to 25 mN/m (in the plateau region), are shown in Figure 2, middle. The presence of Fe, and therefore of the Fe\(_3\)O\(_4\) NPs, at the air/water interface is confirmed by the characteristic peaks. Moreover, the AFM image presented in Figures 2, left, confirms also the presence of the NPs at the interface, revealing at the same time a lack of special arrangement of the metallic cores. The AFM measurements indicate that these NPs form monolayers but not multilayers.

In order to prove that upon compression to surface pressures above the critical pressure the NPs are squeezed out from the interface into the aqueous subphase, the following experiment was performed. A layer of NPs was formed on the right side of the one barrier Langmuir trough (Figure 2, right) by spreading. By using two surface pressure microbalances (W1 and W2), we were able to measure at the same time the surface pressure on both sides of the barrier. After compressing the film to a minimal surface area, the barrier was stopped in this position for 110 min. Then the barrier was compressed to the left side of the trough (expansion of the right side). An increase in the surface pressure on the left side and a decrease of the surface pressure on the spreading area was measured. AFM measurements of samples prepared by the Langmuir-Schaefer technique from the left side of the barrier proof the presence of NPs desorbed from the right compartment and adsorbed to the left compartment. Moreover, the enrichment of the left compartment with the iron oxide NPs was proved by measuring \textit{in situ} X-Ray fluorescence spectra at different surface pressures. An increase of the intensity of the characteristic Fe K\(\alpha\) and Fe K\(\beta\) X-ray fluorescence peaks upon compression of the adsorption layer can be seen.

References