In situ observation of maghemite nanoparticle adsorption at the water/gas interface

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Abstract. The adsorption of $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) nanoparticles at the aqueous solution/gas interface was investigated by x-ray reflectivity. Two different concentrations (0.07 g/L and 0.7 g/L) were probed. The x-ray reflectivities indicate the adsorption of nanoparticles at the liquid surface for the highly concentrated solution, while no nanoparticle adsorption could be detected at the surface of the low concentrated solution within several hours. The vertical electron density profile of the high concentration solution/gas interface indicates the formation of a low ordered monolayer of nanoparticles occupying only 6% of the interfacial region.

1 Introduction

Nanoparticle materials are frequently used in industry e.g. for the design of surface coatings and in the production of cosmetic articles. But they are also interesting candidates for the development of advanced materials with regard to magnetic, optic and electronic properties. For example magnetic nanoparticles encapsulated together with a pharmaceutical agent in an organic container can be transferred into the human body and locally discharged by a magnetic field [1, 2]. Of special interest is the arrangement of nanoparticles at interfaces which might be the first step in the production process of ordered monolayer film coatings. Thus, the investigation of nanoparticle arrangements at interfaces is an important topic of recently published works. Here the solid/liquid (e.g. see [3, 4]), liquid/liquid [5–7] and liquid/gas [8–12] interfaces were investigated using microscopy, spectroscopy and scattering techniques.

The small diameter of the particles which is on the order of a few nanometers makes the direct observation of adsorbed films structure at the liquid/gas interface difficult. Thus, transferring the adsorbed film on a solid substrate and subsequent investigation with microscopic techniques is a common way for further analysis [8]. In this work, the formation of a $\gamma\text{-Fe}_2\text{O}_3$ nanoparticle film at the liquid/gas interface is observed *in situ* by means of non invasive x-ray reflectivity.

The x-ray reflectivity technique is the ideal tool to investigate the adsorption of nanoparticles at liquid surfaces because of its sensitivity to the electron density contrast. For a detailed description of this method see e.g. [13–15]. In the first Born approximation the reflected intensity is given by the expression:

$$I(q_z) = R_F \left| \int \frac{\partial \rho_e(z)}{\partial z} e^{iq_z z} dz \right|^2, \quad (1)$$

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with the Fresnel reflectivity R_F , the wave vector transfer perpendicular to the samples surface q_z and the laterally averaged electron density contrast $\frac{\partial \rho_e(z)}{\partial z}$. The wave vector transfer q_z is given by $q_z = \frac{4\pi}{\lambda} \sin(\theta)$ with the wavelength λ and the angle of incidence θ .

2 Experiment

The x-ray reflectivity measurements were performed at the beamline BW1 at HASYLAB [16] using a Beryllium (002) monochromator and a liquid surface scattering diffractometer. The incidence photon energy was 9.5 keV. The γ -Fe₂O₃ nanoparticles were prepared in water (millipore quality) and were stabilized at pH 3.5 using HCl solution. The preparation has been described in detail in [8]. Two different nanoparticle concentrations (0.07 g/L and 0.7 g/L) were prepared. The zeta potential ξ and nanoparticle diameter d was measured using a Zetasizer NanoZS from Malvern Instrument Co. ξ was found to be $\xi = +35$ mV resulting in a long term colloidal stability. The diameter d was found to be $d = 8.3$ nm. The nanoparticle solution was placed in a Langmuir trough. In order to suppress air scattering the Langmuir trough was flushed with He during the measurements. X-ray reflectivities were recorded up to a maximum q_z value of $q_z = 0.7 \text{ \AA}^{-1}$ using a NaI scintillation detector for detection of the reflected photon beam. For data normalization the incoming photon flux was monitored by an ionisation chamber. Each reflectivity scan took about 35 minutes and was repeated several times in order to observe the evolution of the adsorption process. The highly concentrated solution was examined over a time period of 240 min and the low concentrated solution over a period of 360 min. For reason of comparison a reflectivity of the pure water/gas interface was recorded.

3 Data analysis and discussion

The reflectivities of the water/gas interfaces were refined using the Parratt algorithm [17]. The roughness of the water surface was found to be $\sigma_{\text{H}_2\text{O}} = (2.7 \pm 0.1) \text{ \AA}$ which is in good agreement with the surface roughness obtained by capillary wave theory [15]. A normalized reflectivity of a water/gas interface is shown in figure 1 (open circles). The refinement of the reflectivities taken for the aqueous nanoparticle solutions interface was proceeded in two steps. The data were first refined using a simple model of the pure interface or one adsorbed layer of nanoparticles. This simple model provides only an estimation of the layer thickness and electron density ρ since the layer may be not well ordered. In order to improve the quality of the refinement an iterative algorithm was applied which modulates the electron density profile stochastically [18]. The resulting electron density profiles are displayed also in figure 1. As shown in figure 1 a,c all reflectivities taken from the low-concentrated solutions can be explained without the assumption of an adsorbed layer of γ -Fe₂O₃ nanoparticles. Only a very small, non-significant change in the surface roughness to $\sigma_{\text{Fe}_2\text{O}_3} = (3.0 \pm 0.2) \text{ \AA}$ was observed.

The high-concentrated nanoparticle solution shows a different behaviour. After 90 min changes in the reflectivity curve at low angles were observed which grow to a drastic change after 240 min as shown in Fig. 1(b). The corresponding electron density profile is displayed in figure 1(d) and shows an increase of the electron density at the liquid/gas interface. This increase indicates the formation of an approximately 8 nm thick monolayer of nanoparticles. The gradual increase of electron density, which starts approximately 200 $\text{\AA}$ below the liquid surface, suggests a sporadic formation of locally restricted bi- or multilayer islands. Surface potential measurements show that the adsorption process is saturated at this state. For further analysis the average electron density in the interfacial region was extracted by an integration over the first 8 nanometers below the liquid surface leading to $\bar{\rho}_{\text{exp}} = 0.40 \text{ e/\AA}^3$. The assumption of dense packed layer of spherical nanoparticles (two dimensional hexagonal packing, 60% volume fraction of the particles) leads to an average density of $\bar{\rho}_{\text{th}} = 0.97 \text{ e/\AA}^3$. Thus only a small fraction of 6% of the available interface volume is occupied by the nanoparticles. This finding is in agreement with other studies using hydrophilic nanoparticles with low contact angles which report weak adsorption too (for an overview see [19]).

Fig. 1. Top: Reflectivities normalized by R_F a: of the low-concentrated solution (0.07 g/L) after 60 minutes (diamonds) and 360 minutes (squares). b: and high-concentrated solution (0.7 g/L) after 60 minutes (diamonds) and 240 minutes (squares). For comparison the normalized reflectivity of the water/gas interface is shown (open circles). The solid lines display the refinement of the reflectivities. Bottom: electron density profiles obtained by the refinement of the reflectivities for c: low concentrated solution (solid line) and water (dashed dotted line) interface, (d) high concentrated solution (solid line) and water (dashed line) interface.

This behaviour can be explained in principle by the discussion of surface energy and particle – particle and particle – surface interactions. Applying Young’s equation for the calculation of the change ΔE in surface energy leads to [10]

$$\Delta E = -\pi r^2 \gamma_{\text{liq}} (\cos(\beta) - 1)^2 \quad (2)$$

with the surface tension of the liquid γ_{liq} , the radius of the nanoparticle r and the contact angle β . For the system maghemite/water the contact angle β is $\beta = 12^\circ$ [20] leading to $\Delta E = -0.24 k_B T$ per particle. Thus one maghemite nanoparticle which reaches the liquid/gas interface should stay there because the surface energy is reduced. The prediction of stability and structure of a completely adsorbed nanoparticle film at a liquid surface is a non trivial task. Calculations in the framework of the DLVO (Derjaguin Landau Verwey Overbeek) theory [10] show that the particles should not form a stable film at the liquid/gas interface because of repulsive electrostatic and van der Waals interactions. Only if dipolar interactions between the particles, mainly caused by an asymmetric arrangement of ions on the nanoparticles surface, are taken into account, stable films are predicted (for a detailed overview see [21]). Here the concentration of dipoles near the interface steers the height of a sorption barrier which prevents the formation of stable films. A deficit of dipoles raises the barrier and prevents the adsorption. This property can qualitatively explain the concentration dependence of the adsorption process observed and discussed in this work.

4 Summary

X-ray reflectivities were taken from maghemite nanoparticle solutions surfaces at two different concentrations. While the low concentrated solution shows no adsorption of nanoparticles the high concentrated solution shows the formation of a nanoparticle monolayer. The density profiles indicate a low packed layer in which only 6% of the accessible volume is occupied by the nanoparticles. This result is qualitatively in accordance with theoretical treatments of the adsorption process.

We acknowledge HASYLAB/DESY, member of the Helmholtz Association (HGF), for provision of light source facilities. We would like to acknowledge the Bundesministerium für Bildung und Forschung (BMBF project nos. 05KSPE1 and 05KSPEA) and the Deutsche Forschungsgemeinschaft (DFG project no. TO 169/12-1) for financial support.

References

1. A. Shukla, P. Degen, H. Rehage, J. Am. Chem. Soc. **129**, 8056 (2007)
2. P. Degen, A. Shukla, U. Boetcher, H. Rehage, Coll. Polym. Sci. **286**, 159 (2008)
3. J.D. Fisk, M. Rooth, A.M. Shaw, J. Phys. Chem. C **111**, 2588 (2007)
4. T. Takahashi, A.S. Dimitrov, K. Nagayama, J. Phys. Chem. **100**, 3157 (1996)
5. J.-P. Abid, M. Abid, C. Bauer, H.H. Girault, P.-F. Brevet, J. Phys. Chem. C **111**, 8849 (2007)
6. Y. Lin, A. Böker, H. Skaff, D. Cookson, A.D. Dinsmore, T. Emrick, T.P. Russell, Langmuir **21**, 191 (2005)
7. Y.-K. Park, S.-H. Yoo, S. Park, Langmuir **23**, 10505 (2007)
8. Y.S. Kang, D.K. Lee, C.S. Lee, P. Stroeve, J. Phys. Chem. B **106**, 9341 (2002)
9. L.-H. Chen, A. Dudek, Y.-L. Lee, C.-H. Chang, Langmuir **23**, 3123 (2007)
10. J.-W. Hu, G.-B. Han, B. Ren, S.-G. Sun, Z.-Q. Tian, Langmuir **20**, 8831 (2004)
11. K.S. Mayya, M. Sastry, Langmuir **14**, 74 (1998)
12. P. Piranski, Phys. Rev. Lett. **45**, 569 (1980)
13. B.M. Ocko, X.Z. Wu, E.B. Sirota, S.K. Sinha, M. Deutsch, Phys. Rev. Lett. **72**, 242 (1994)
14. S.K. Sinha, E.B. Sirota, S. Garoff, H.B. Stanley, Phys. Rev. B **38**, 2297 (1998)
15. M. Tolan, *X-ray Scattering from Soft Matter Thin Films*, Vol. 148 (Springer, Berlin, 1999)
16. R. Frahm, J. Weigelt, G. Meyer, G. Materlik, Rev. Sci. Instrum. **66**, 1677 (1995)
17. L.G. Parratt, Phys. Rev. **95**, 359 (1954)
18. M.K. Sanyal, S. Hazra, J.K. Basu, A. Datta, Phys. Rev. B **58**, R4258 (1998)
19. B.P. Binks, Curr. Opinion Coll. Interf. Sci. **7**, 21 (2002)
20. C. Galindo-Gonzalez, J. de Vicente, M.M. Ramos-Tejada, M.T. Lopez-Lopez, F. Gonzalez-Caballero, J.D.G. Duran, Langmuir **21**, 4410 (2005)
21. F. Martınez-Lopez, M.A. Cabrerizo-Vylchez, R. Hidalgo-Alvarez, J. Coll. Interf. Sci. **232**, 303 (2000)