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Assessment of surfactant adsorption in oil-based magnetic colloids

**Modesto T. López-López · Ana Gómez-Ramírez ·
Guillermo R. Iglesias · Juan D.G. Durán ·
Fernando González-Caballero**

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Abstract We describe in this paper different and complementary experimental methods for assessing the adsorption of surfactants on metal particles in oil-based suspensions. Two different kinds of particles are dispersed in mineral oil: iron microparticles and CoNi nanoparticles. The adsorption of oleic acid in the Fe/oil interface in diluted suspensions can be determined by obtaining the adsorption isotherm. In addition, we present a method based on the time evolution of the optical absorbance of suspensions, from which the existence of adsorption can be inferred. For concentrated suspensions, the used of optical methods is not recommended, since they are affected by a significant inaccuracy. We present here a useful alternative based on electromagnetic induction phenomena. The results obtained allow a more comprehensive knowledge of the aggregation process in concentrated suspensions. With the same purpose, a third group of experiments, based on rheological techniques, is carried out in Fe/oil and CoNi/oil concentrated suspensions. In these series of experiments, the effect of three surfactants (oleic acid, aluminum stearate and lecithin) is tested by measuring either the viscosity, or the magnetic field-induced yield stress of the suspensions. The combination of these series of experiments gives us valuable information about the most appropriate surfactant/carrier combination capable of imparting a high stability and a strong magnetorheological response in magnetic colloids.

Keywords Surfactant adsorption · Iron suspensions · Cobalt–Nickel suspensions · Magnetic colloids · Rheology

1 Introduction

The adsorption of surfactants or other additives in solid–liquid interfaces plays an essential role in many industrial processes, such as detergency, wetting, flocculation and dispersion (Drach et al. 2008; Mittal 1987; Rosen 1987; Sabah et al. 2002; Somasundaran 1985). Consequently, the evaluation of the adsorption of a given surfactant on the desired interface is required, before the industrial process is carried out. This evaluation is usually performed by obtaining the adsorption isotherm of the surfactant on the solid–liquid interface. Among other aspects, this isotherm gives us information about the amount of surfactant adsorbed per unit mass, the equilibrium concentration of surfactant and the saturation concentration, for a given temperature (Rosen 2004). However, in real systems adsorption of surfactants at interfaces is a complex process, strongly influenced by many factors, such as the properties of solids, solution ionic strength, surfactant composition, nature of solvent species, pH and temperature of the system, as well as dissolved mineral and biological species (Somasundaran et al. 1998). Then, an adsorption isotherm for each set of experimental parameters should be obtained before a process that is based on adsorption is executed. Unfortunately, obtaining adsorption isotherm is a tedious and very time-consuming task.

In this paper, we present some alternative methods to assess the adsorption of additives on solid–liquid interfaces. Although, these methods do not give precise information

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Prof. Waksmundzki always impressed me for his vitality and enthusiasm to confront new scientific challenges and for his compromise with the education of young scientists. Let this paper be a small piece of gratitude and honor to his Memory.

M.T. López-López · A. Gómez-Ramírez · G.R. Iglesias ·
J.D.G. Durán · F. González-Caballero (✉)
Departamento de Física Aplicada, Facultad de Ciencias,
Universidad de Granada, Campus de Fuentenueva s/n, 18071
Granada, Spain
e-mail: fgonzale@ugr.es

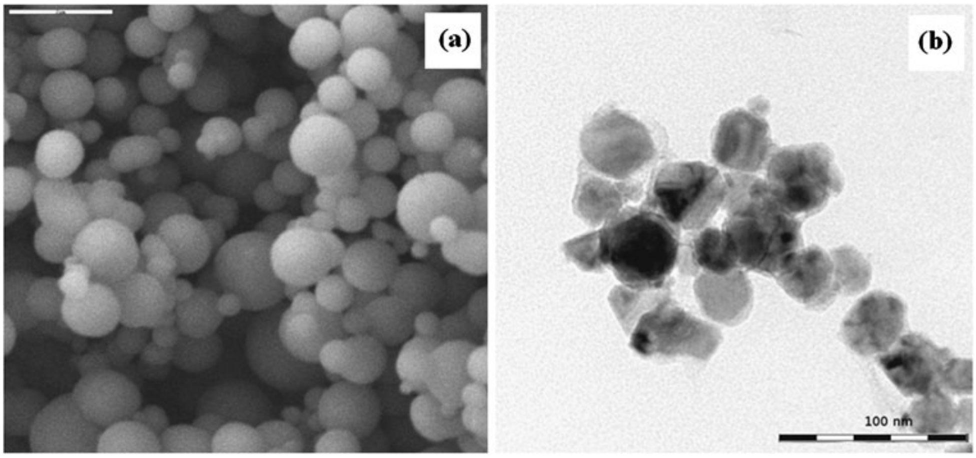

Fig. 1 Pictures of iron particles (**a**) and cobalt–nickel nanoparticles (**b**) obtained by SEM and HRTEM microscopy respectively. Bar length: (**a**) 2 μm; (**b**) 100 nm

about the amount of additive adsorbed, they are suitable for gaining valuable information on its effect on the macroscopic properties of the suspensions. An additional benefit of these methods is that they are easy and quick to carry out. Interestingly, we have found a quite good agreement between inferences based on the different methods and the experimental adsorption isotherm.

2 Experimental

2.1 Materials

Iron powder, obtained from carbonyl iron precursors, was supplied by BASF (Germany) and used without further treatment. The manufacturer indicates the following specifications: (i) chemical composition (wt.%): min. 97.5% Fe, 0.7–1.0% C; 0.7–1.0% N; 0.3–0.5% O; and (ii) density: 7.5 g/cm^3. The iron particles were spherical and polydisperse as observed by scanning electron microscopy (SEM) pictures. From pictures like that shown in Fig. 1(a), an average diameter of 930 ± 330 nm was estimated.

Cobalt-nickel (CoNi) particles were synthesized by reduction of ions in a liquid polyol, as described in Gómez-Ramírez et al. (2009). These particles were approximately spherical, as shown in the HRTEM micrograph in Fig. 1(b), with an average diameter of 24 ± 3 nm.

The specific surface area of the particles was measured by N_2 adsorption using the B.E.T multipoint method in a Quantasorb Jr. apparatus (Quantachrome, USA). We obtained 0.98 and 12 m^2/g for iron and CoNi particles, respectively.

Mineral oil (Fluka, Germany) was used as dispersing medium. Oleic acid (OA) (purity 90%), aluminum stearate (AlSt) (technical quality), and lecithin (BioChemika), all supplied by Sigma-Aldrich (Germany) were used as additives.

Suspensions were prepared as follows: (1) different additive-mineral oil solutions were prepared; (2) proper amounts of the metal powders were added to the selected oil solution in a polyethylene container; (3) the suspensions were shaken first by hand and then in an ultrasonic bath; (4) the previous step was repeated several times and then the sample was immersed in a Branson sonifier to ensure the required homogeneity; and (5) the sample was stirred (50 rpm; 24 h; 25 °C) to allow the adsorption of the surfactant on the particles in suspension.

2.2 Methods

The adsorption isotherm of oleic acid was obtained by means of absorbance measurements as follows: the optical absorbance was measured *vs.* oleic acid concentration for different oleic acid-mineral oil solutions and the data fitted to Beer law. For this purpose we used a Dinko Instruments spectrophotometer (model UV-VIS 8500, Spain) set at a wavelength $\lambda = 244$ nm, for which OA has a large absorbance (300 times higher than for the visible spectrum). Iron suspensions (solid volume fraction $\phi = 10\%$) with different initial OA concentrations were prepared and maintained under stirring for 24 h as described above. Then, the suspensions were placed on a powerful magnet to provoke the complete iron settling. Finally, the optical absorbance of the supernatant solutions was measured for estimating the OA equilibrium concentration after adsorption.

The optical absorbance in diluted iron suspensions (1.25 g/L of Fe) was monitored using a Milton Roy spectrophotometer (model Spectronic 601, USA) at a wavelength $\lambda = 590$ nm. Square cuvettes with 1 cm light path were used; the center of the light beam struck the cuvette 1.5 cm above its bottom.

Settling rate in concentrated iron suspensions was monitored by means of an electromagnetic method. Detailed description of the experimental setup can be found in López-López et al. (2005a, 2006). Essentially, the method consists of measuring the electromotive force induced in a small sensing coil placed on the top of a test tube (1 cm in diameter) containing the suspension, which is subjected to an alternating magnetic field of low intensity. The electromotive force decreases as the particle concentration diminishes in the region of the tube surrounded by the sensing coil.

Rheological properties in the absence of magnetic field were measured using a Bohlin CS10 controlled stress rheometer (UK). The measuring system geometry was a vane-in-cup set (Bohlin V-25; vane diameter/height: 1.4 cm/3.0 cm; cup diameter/height: 1.5 cm/4.7 cm). Rheological properties in the presence of magnetic field were measured using a magnetorheometer (MCR300, Physica-Anton Paar, Austria). The measuring system geometry was a 20 mm diameter parallel-plate set for a gap width of 0.35 mm.

3 Results

As mentioned above, in this paper we present different methods that allow us to evaluate the adsorption of surfactants on the solid–liquid interface in colloidal suspensions. These methods are presented mainly for a reference colloidal suspension (metallic microparticles dispersed in oil) and only a few surfactants are tested. However, the methods could obviously be applied for other magnetic colloids and surfactants/polymers. Our reference starting point was a suspension of iron microparticles (10 vol.%) in different mixtures of oleic acid and mineral oil. The adsorption isotherm (see Fig. 2) was obtained as described in López-López et al. (2005b).

As observed, there is an initial sharp adsorption rise, which likely corresponds to the adsorption of the first monolayer of oleic acid. In fact, considering, as proposed by Rosensweig (1985), that an adsorption density of 2×10^{18} mol/m^2 corresponds to a 100% coverage by oleic acid molecules, we can estimate the number of statistical monolayers as shown in Fig. 2, which corroborate this assumption. In the oleic acid concentration range 3–8 mM, a pseudoplateau is observed, which is likely associated with the deposition of the second monolayer. Finally, for the largest concentrations studied, the adsorption becomes very intense as a consequence of multilayer deposition.

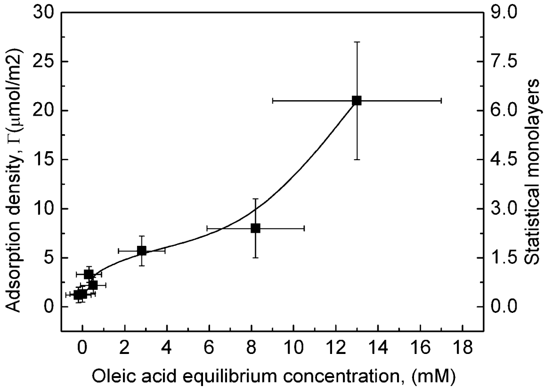

Fig. 2 Adsorption isotherm and number of statistical monolayers of oleic acid deposited on iron microparticles. Error bars represent the experimental uncertainties [Taken from López-López et al. (2005b)]

This is perhaps the most extended method of evaluation of the adsorption of a surfactant on the surface of a solid. However, in many cases scientists are more interested in obtaining or preventing from a given phenomenon (as for example, aggregation or corrosion) rather than in the precise knowledge of the amount of adsorbed additive on the surface of the particles. In these cases, it could be preferable to perform simple tests that inform us about the existence of adsorption and about the required amount of additive to reach a certain state.

A very simple approach to evaluate the influence of surfactant adsorption on the settling behavior of diluted colloidal suspensions is to monitor the time-evolution of their optical absorbance. For example, the adsorption in our reference system could be evaluated in this way. Thus, Fig. 3 shows the optical absorbance measured for suspensions containing 1.25 g of iron per liter of suspension (volume fraction approx. 0.02%).

As observed in Fig. 3, in all cases the optical absorbance tends to decrease as time increases, which is reasonable considering the large size and density of the dispersed particles. However, three different regions can be distinguished: (i) at low oleic acid concentration (≤ 3 mM) there is not any appreciable effect of surfactant adsorption on the absorbance vs. time curve. This could be interpreted either as an incomplete covering of the particle surface by the surfactant or as a failure of the coating to prevent from undesired aggregation. (ii) At oleic acid concentration of 30 mM, A_n decreases faster, which is an indication of the modification of the particle surface by the surfactant molecules. Namely, oleic acid molecules are able to prevent by steric repulsion the formation of particle aggregates, which existed in the absence of surfactants. The observed behavior is just a consequence of the fact that individual particles settle faster than aggregates. (iii) At the highest oleic acid concentrations (> 600 mM) the absorbance decreases very slowly because of the formation of very big, loose flocculi (visible even with naked eyes), which settle at very low rate. Thus, this region could be associated to the formation of flocculate iron–oleic acid structures.

Therefore, this method provides information not only about the existence of adsorption, but also about the ability of the surfactant to work as an effective dispersant of flocculant agent.

Nevertheless, the adsorption in dilute and concentrate suspensions could be rather different. Firstly, for a similar

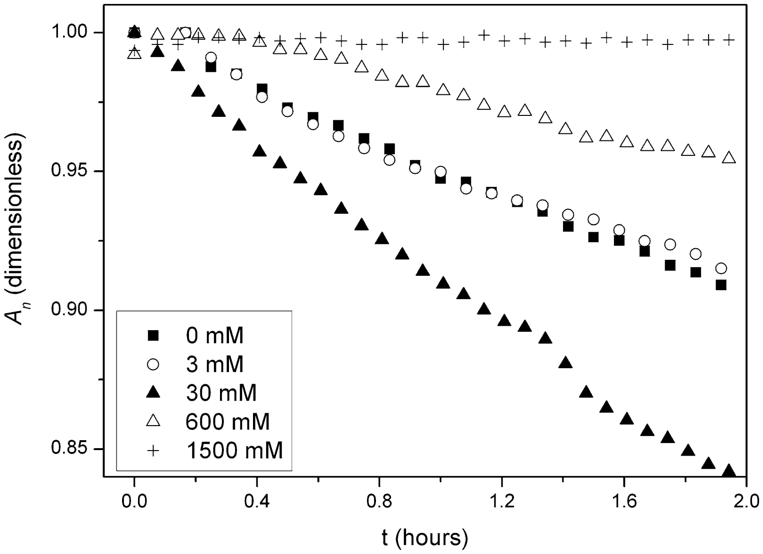

Fig. 3 Normalized absorbance $An(= A/A_0)$ vs. time for suspensions of iron microparticles (1.25 g Fe per liter of suspension) dispersed in mineral oil. Initial concentration of surfactant (oleic acid) is indicated in the figure

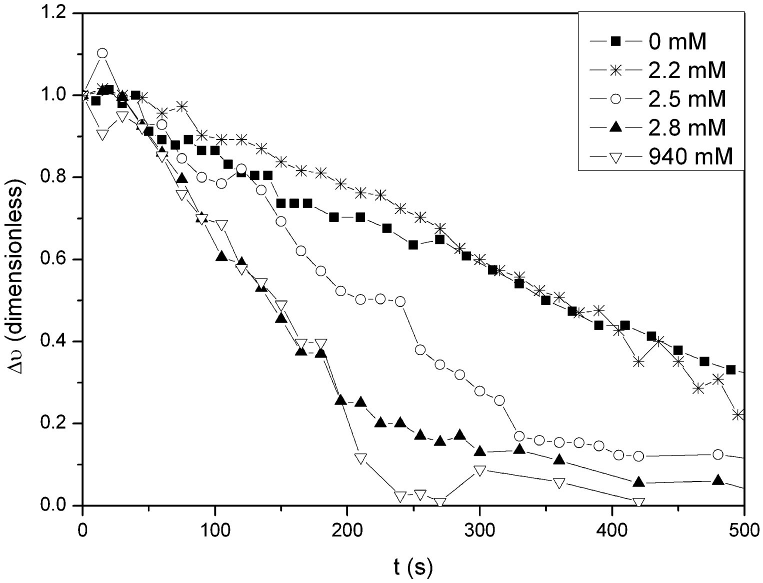

Fig. 4 Normalized electromotive force, $\Delta\upsilon$, as a function of time for suspensions of iron microparticles (10 vol.%) in mineral oil. Initial concentration of surfactant (oleic acid) is indicated in the figure

initial surfactant concentration, the adsorption density will be much smaller in the latter case due to the much higher interfacial area. Consequently, we should not expect to reach the region associated to the formation of iron–oleic acid flocculi. Secondly, when dealing with concentrated suspensions, optical methods cannot be applied to monitor the settling behavior. To overcome this problem, we present here several methods that can be used in concentrate suspensions.

The first one is based on monitoring the settling rate of the particles in suspension, and can be only used for suspensions of magnetic particles. The existence of adsorption in our reference suspension has also been analyzed using this method. As an example, Fig. 4 shows the results for an iron concentration of 10 vol.%. The y-axis corresponds to the normalized electromotive force, which is defined as:

$$\Delta\upsilon = \frac{V(t) - V(t \to \infty)}{V(t = 0) - V(t \to \infty)} \qquad (1)$$

where $V(t)$ is the instantaneous electromotive force, $V(t \to \infty)$ is the electromotive force in the stationary state, and $V(t = 0)$ is the initial electromotive force. Similarly to Fig. 3, there is an overall trend of the curves to decrease with time, which is associated to the settling of the dispersed particles. Note that at not very high solid content, $\Delta\upsilon$ is approximately proportional to the volume concentration of magnetic particles in the area surrounded by the sensing coil (López-López et al. 2005a).

As observed, settling happens at the slowest rate for the suspension without surfactant. As mentioned above, this could be explained by considering that without surfactant, particles aggregate forming large flocculi that sediment slowly due to friction with the walls of the tube and colli-

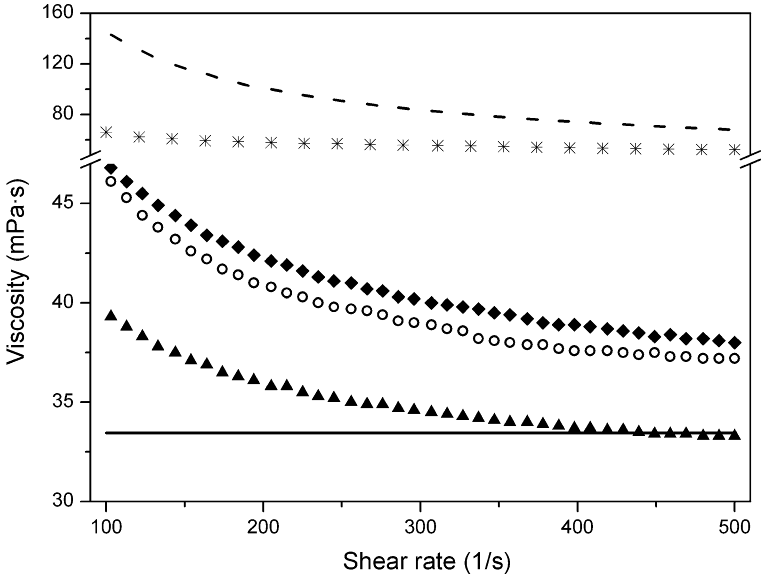

Fig. 5 Viscosity as a function of shear rate for suspensions containing 10 vol.% of iron particles dispersed in mineral oil. Surfactant concentration and name are: *dashed line*: no surfactant; $*$: 2.2 mM oleic acid; $\circ$: 2.8 mM oleic acid; ♦: 21 mM AlSt; ▲: 2.5 mM lecithin; *continuous line*: Batchelor's formula

sions. When a high enough oleic acid content (> 2.2 mM) is added, significant changes are observed. This could, of course, be associated to the progressive covering of the iron surface by oleic acid, which prevents from particle aggregation. No further change of the sedimentation behavior is obtained for oleic acid concentrations higher than 2.8 mM and, consequently, this could be associated to a complete coverage of the iron surface by oleic acid at this concentration. Note that this value of oleic acid concentration is well-related with data shown in Fig. 2.

The weakest point of this method is the fact that it can only be used for suspensions of magnetic particles. An appropriate option for suspensions of non-magnetic particles is the use of rheological methods. In this paper we present a rheological alternative to evaluate the adsorption of surfactants on the surface of suspended particles. This method is based on the prediction for the viscosity of suspensions of hard and slightly deformable particles. For example, in the case of spherical particles, the viscosity is given by Batchelor's formula (Batchelor 1977):

$$\eta_r \equiv \frac{\eta}{\eta_0} = \left(1 + 2.5\phi + 6.2\phi^2\right) \tag{2}$$

In this equation, η is the viscosity of the suspension, η_0 the viscosity of the carrier liquid, η_r the relative viscosity, and ϕ the volume fraction of spherical particles. Equation (2) holds approximately up to $\phi \leq 0.10$ (Barnes et al. 1998). For higher order in ϕ and for particles of any shape the empirical Krieger–Dougherty equation can be used (Krieger and Dougherty 1959; Larson 1999). Experimentally, it is observed that the more flocculated the suspension the higher its viscosity. Therefore, since the adsorption of a surfactant on a surface modifies its physicochemical properties, the state of flocculation of a suspension must change when a surfactant is adsorbed on the dispersed particles. Depending on the compatibility of the surfactant and the liquid carrier, adsorption gives rise to an increase or a decrease of the suspension viscosity. For example, for our reference suspension, since oleic acid has affinity towards mineral oil, we expect a decrease of the viscosity as the concentration of oleic acid is increased up to the point where particle surface is completely coated. This is actually the case (see Fig. 5): for a suspension containing 10 vol.% of iron particles, the minimum value of the viscosity is already obtained for 2.8 mM of oleic acid, in agreement with data of Figs. 2 and 4. In addition, this method allows us to compare the adsorption efficiency of different additives. For example, in Fig. 5 we also show some results for suspension of iron particles (10 vol.%) in mineral oil, either with lecithin or aluminum stearate (AlSt) in solution. Note that the concentrations of AlSt and lecithin used in these experiments (21 mM AlSt, 2.5 mM lecithin) are also the minimum required to provoke the maximum effect in experiments like those shown in Fig. 4 for oleic acid.

As observed, it is possible to reach the same state of dispersion with oleic acid and aluminum stearate (i.e. it is possible to give a similar adsorbed coating with both surfactants), whereas with lecithin a viscosity value closer to Batchelor's prediction is obtained. It can, therefore, be concluded that lecithin works as the most efficient surfactant for preventing particle aggregation in Fe-mineral oil suspensions. Then, with this method we obtain the following pieces of information: (i) oleic acid, lecithin and aluminum stearate adsorb on iron oxides in mineral oil; (ii) all of them show the required compatibility towards the carrier liquid.

A similar rheological method that can be used to evaluate the adsorption of an additive consists of analyzing the redispersibility of a suspension after storage. Detailed infor-

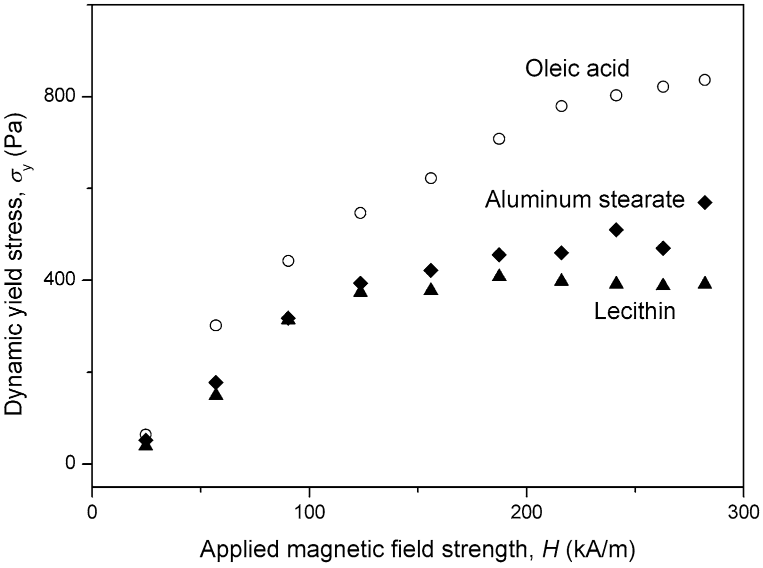

Fig. 6 Dynamic yield stress as a function of the applied magnetic field strength for suspensions of CoNi nanospheres (10 vol.%) in mineral oil. The concentration of surfactants is similar to those in Fig. 5

mation about experimental techniques to measure the redispersibility can be found in López-López et al. (2006).

Let us finally present another rheological alternative that can be used only with suspensions of magnetizable particles—known as magnetorheological (MR) suspensions. MR suspensions are characterized by the remarkable property of changing their rheological behavior (increase of viscosity, appearance of high yield stress) upon application of magnetic fields. This behavior is known as MR effect. The typical rheograms (shear stress plotted vs. shear rate) shown by MR suspensions are perfectly characterized by a Bingham plastic equation (Bossis et al. 2002; Larson 1999):

$$\sigma = \sigma_y + \eta_{pl}\dot{\gamma} \tag{3}$$

In this equation, σ is the shear stress, σ_y the dynamic (Bingham) yield stress, η_{pl} the plastic viscosity, and $\dot{\gamma}$ the shear rate. Usually, the strength of the MR effect is characterized by the value of the dynamic (Bingham) yield stress. In many cases, the adsorption of additives can also be inferred by the strength of this effect. For example, in Fig. 6 we show the values of the dynamic yield stress for suspensions of CoNi nanospheres (10 vol.%) in mineral oil, as a function of the applied field strength.

As observed, the yield stress increases with the applied magnetic field, as expected for MR suspensions. Let us now focus on the effect of the different surfactants on the yield stress. As can be seen, there is not any noticeable difference among the yield stresses for the suspension stabilized with aluminum stearate and the suspension stabilized with lecithin, whereas the highest values of the yield stress are obtained for the suspension stabilized with oleic acid. This suggests that dispersion was much better when oleic acid was used as surfactant. Therefore, we can conclude that in oil media, the adsorption on CoNi alloys of oleic acid is more efficient than that of lecithin or aluminum stearate.

4 Conclusions

The stability and rheological behavior of suspensions consisting of magnetizable micro- o nanoparticles dispersed in oil media is strongly controlled by the adsorption of surfactants on the solid/liquid interface. The adsorption of surfactants compatible with the mineral oil employed in this work as carrier liquid, such as oleic acid, aluminum stearate, or lecithin, hinders the aggregation of the particles and the appearance of big flocculi. Consequently, surfactants play a fundamental role in the performance of magnetic colloids in different technological applications. In the major part of these applications, highly concentrated suspensions are used and, consequently, the evaluation of the surfactant concentration needed to achieve the best colloidal stability is not free of a significant degree of uncertainty. For this reason, the combination of several experimental techniques to assess the adsorption process is recommended.

At least, two groups of experiments can accomplish this recommendation. The first group is appropriate for diluted suspensions: (a.i) adsorption isotherms, and (a.ii) sedimentation profile monitored by optical techniques. The second group, addressed to concentrated suspensions, consist of: (b.i) measurements of the electromotive force generated in a coil that surrounds the suspension as the particles settle, and (b.ii) analysis of the (magneto)-rheological behavior of suspensions.

In this work, the combination of these different experimental approaches is shown as a useful way to state which is the best surfactant and its optimal concentration in each case. To be precise, in suspensions of iron microparticles dispersed in mineral oil, the addition of lecithin seems the best option. In suspensions of CoNi nanospheres dispersed in mineral oil, the magnetorheological results demonstrate that oleic acid works as the optimal surfactant in order to reach the highest magnetorheological effect, which usually is the main objective in the formulation of these magnetic colloids.

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References

Barnes, H.A., Hutton, J.R., Walters, K.: An Introduction to Rheology. Elsevier, Amsterdam (1998)

Batchelor, G.K.: Effect of Brownian-motion on bulk stress in a suspension of spherical-particles. J. Fluid Mech. **83**, 97–117 (1977)

Bossis, G., Volkova, O., Lacis, S., Meunier, A.: Magnetorheology: fluids, structures and rheology. In: Odenbach, S. (ed.) Ferrofluids, pp. 202–230. Springer, Berlin (2002)

Drach, M., Andrzejewska, A., Ciesla, J., Narkiewicz-Michalek, J.: Theoretical description of aggregation of cationic emini surfactants in the bulk solution and on the silica surface. Adsorption **14**, 629–638 (2008)

Gómez-Ramírez, A., López-López, M.T., Durán, J.D.G., González-Caballero, F.: Influence of particle shape on the magnetic and magnetorheological properties of nanoparticle suspensions. Soft. Matter. **5**, 3888–3895 (2009)

Krieger, I.M., Dougherty, T.J.: A mechanism for non-Newtonian flow in suspensions of rigid spheres. Trans. Soc. Rheol. **3**, 137–152 (1959)

Larson, R.G.: The Structure and Rheology of Complex Fluids. Oxford University Press, New York (1999)

López-López, M.T., de Vicente, J., Bossis, G., González-Caballero, F., Durán, J.D.G.: Preparation of stable magnetorheological fluids based on extremely bimodal iron-magnetite suspensions. J. Mater. Res. **20**, 874–881 (2005a)

López-López, M.T., de Vicente, J., González-Caballero, F., Durán, J.D.G.: Stability of magnetizable colloidal suspensions by addition of oleic acid and silica nanoparticles. Colloids Surf. A **264**, 75–81 (2005b)

López-López, M.T., Zugaldía, A., González-Caballero, F., Durán, J.D.G.: Sedimentation and redispersion phenomena in iron-based magnetorheological fluids. J. Rheol. **50**, 543–560 (2006)

Mittal, K.L. (ed.): Surface and Colloid Science in Computer Technology. Plenum, New York (1987)

Rosen, M.J.: Surfactans in Emerging Technologies. Dekker, New York (1987)

Rosen, M.J.: Surfactants and Interfacial Phenomena. Wiley, Hoboken, New Jersey (2004)

Rosensweig, R.E.: Ferrohydrodynamic. Cambridge University Press, Cambridge (1985) p. 48

Sabah, E., Turan, M., Celik, M.S.: Adsorption mechanism of cationic surfactants onto acid- and heat-activated sepiolites. Water Res. **36**, 3957–3964 (2002)

Somasundaran, P.: Energetics of Adsorption at Interfaces. In: Mohan Rao, M. et al. (eds.) Thermodynamics and Kinetics of Metallurgical Processes. The Indian Institute of Metals, Calcutta (1985)

Somasundaran, P., Shrolri, S., Huung, L.: Thermodynamics of adsorption of surfactants at solid–liquid interface. Pure Appl. Chem. **70**, 621–626 (1998)