



Liquid–liquid phase transfer of magnetite nanoparticles – Evaluation of surfactants

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ABSTRACT

Because of the large surface area of colloids interface effects are dominant in contrast to volume effects. The study presents experimental results of the direct transfer of magnetite nanoparticles from an aqueous to a non-miscible organic phase. The starting point is a water-based colloid that is synthesized through a precipitation reaction. The transfer is based on the adsorption of surfactants onto the particle surface at the liquid–liquid interface. While penetrating the liquid–liquid interface, the particles are covered with surfactants and a partial de-agglomeration is initiated. The intention is to produce a stable organic colloid, which has important applications in industry. The optimized process parameters for the successful phase transfer process, the adsorption reactions at the liquid–liquid interface and the stabilization of primary particles in the organic phase are demonstrated.

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1. Introduction

Colloidal nanoparticle systems in non-aqueous liquids are required for several applications such as magnetic fluids for gaskets or magnetic cushions [1], self-organizing coatings of surfaces and composite materials [2–4]. A precipitation reaction in an aqueous phase is the preferred way to synthesize inorganic nanoparticles. The application occurs in the organic phase. Consequently, the particles have to be transferred after synthesis from the liquid aqueous phase to a liquid non-aqueous phase. The state of the art for the phase transfer of microscale particles is a redispersion step after filtration and thermal drying. This strategy cannot be applied for nanoparticulate systems, because quality and functionality [5] of the particles are affected by an exposition to the gas phase (e.g., irreversible agglomeration, oxidation and sintering).

One promising approach to avoid these negative consequences is the direct phase transfer of nanoparticles through a defined liquid–liquid interface (Fig. 1). The liquid aqueous phase is instable, because of the salt concentration and resulting zeta potential. Thus the agglomeration of the nanoparticles occurs in the liquid aqueous phase. It is the first fundamental step in the process mechanism of the phase transfer. Through sedimentation the agglomerates are transported to the liquid–liquid interface. At the interface surfactant molecules from the organic phase

adsorb on the particles. The adsorption of surfactant changes the surface properties of the particles from hydrophilic to hydrophobic and provides the wetting of the particles by the organic phase. The strong repulsive potential of the adsorbed molecules leads to a partial de-agglomeration of the particles, a physicochemical dispersion and has a stabilizing effect on the particles to prevent further agglomeration within the organic phase [6]. The dispersed and functionalized particles move away from the phase interface by sedimentation so that a stable colloid forms, a so-called organosol.

Systematic investigations of the phase transfer of nanoparticles have been conducted on gold and silver hydrosols [7–12], which are synthesized via a reduction reaction at low concentrations (10^{-3} to 10^{-5} g/l). After synthesis the hydrosol is stabilized either with an adsorbed hydrophilic surfactant or by electrostatic repulsion. For the phase transfer the receiving liquid phase contains a second surfactant [11,13,14]. In this case vigorous shaking or stirring is used for the mass transport of the particles to the liquid–liquid interface. During this process an emulsion is generated, because of the surface activity of the surfactant [12]. These undesired effects require further processing to break the emulsion in order to separate the phases again.

The surfactant concentration in the organic phase is a very important parameter [15], because it determines the adsorption process and thus whether the phase transfer occurs or not. For a successful direct phase transfer it is essential to have a high pH value in the aqueous phase as well as a threshold concentration of surfactant in the organic phase. This allows the particles to become hydrophobic.

In addition to the threshold concentrations of the surfactant there is an optimal concentration for the stabilization of primary particles. This concentration is high enough to allow the surfactants e.g. fatty

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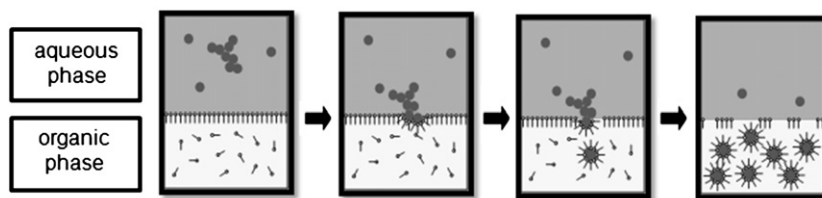


Fig. 1. Fundamental steps in the process mechanism of the phase transfer.

acids to disintegrate agglomerates into primary particles after phase transfer and to form stable colloids.

2. Material and methods

The magnetite nanoparticles are synthesized by a precipitation reaction. The materials, which are used for it, are described in Section 2.1 and the production process is explained in Section 2.2.

2.1. Materials

Iron(II)sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), linoleic- and ricinoleic acid are purchased from Fluka. Iron(III)chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ammonium hydroxide (26% NH_3) and oleic acid (technical grade) are from Riedel de Haen. We use dichloromethane (DCM) from Roth and ammonium chloride and ammonium sulphate from KMF. The fatty acids caprylic-, lauric-, myristic-, palmitic- and stearic acid are purchased from Aldrich. All chemicals are used as received.

2.2. Precipitation of magnetite nanoparticles

The magnetite nanoparticles are produced by co-precipitation of an aqueous solution of iron(III)chloride hexahydrate and iron(II)sulphate heptahydrate with a molar ratio of $\text{Fe}^{3+}/\text{Fe}^{2+} = 2:1$. The iron solution is precipitated by a 20% excess of the ammonium hydroxide solution.

The precipitation process is done by vigorous stirring in a flask. The iron salts are dissolved in de-ionized water and heated to 70 °C. The amount of ammonium hydroxide is quickly added to the solution. This produces a suspension containing deep black magnetite nanoparticles with a primary particle size of 15 nm and a solid content of 20 g/l. Finally the suspension is stirred for another 20 min at 70 °C to evaporate any dispensable ammonia.

2.3. Experimental setup for phase transfer

To perform the liquid–liquid phase transfer an aqueous phase of 0.02 mass-% ammonia is used. The organic phase is dichloromethane with different fatty acids at maximum concentrations up to 350 mmol/l. At first 15 ml of aqueous suspension is laminated on top of 15 ml of the organic phase. The phase transfer itself is carried out in a laboratory scale centrifuge (Hettich Universal 30 F) at 1000 rpm (145 $\times g$) for 60 min. After that the aqueous phase is removed and samples are taken to determine the magnetite content in the organic phase. The determination is done by the chemical reduction of magnetite into iron, dissolving the iron in water and measuring the iron content by atomic emission spectroscopy (AES). Also for the centrifugation process of the organic phase to remove the big aggregates the laboratory scale centrifuge (Hettich Universal 30 F) at 5000 rpm (3626 $\times g$) was used for 20 min. The zeta potential has been measured in the diluted aqueous phase and the particle sizes for the volume distribution have been determined in the organic phase using Malvern Instruments Zetasizer Nano ZS.

3. Results and discussion

The phase transfer experiments show a strong dependency on the ammonia concentration in the aqueous phase (Fig. 2). At ammonia concentration below 10^{-4} mass-% no phase transfer occurs, because the particles settle within the aqueous phase, accumulate and form a solid layer above the liquid–liquid interface. At ammonia concentrations above 10^{-2} mass-% the particles are hydrophobized at the interface by adsorption of the surfactant and transferred completely into the organic phase. Within the concentration interval of 10^{-4} to 10^{-2} mass-% there is a transition region where a partial phase transfer takes place. In this region one part of the particles is transferred and the other part is held back at the liquid–liquid interface.

The determination method of the transfer yield (AES) led to standard deviations of 10%. This applies for Fig. 4 and 5 also. The zeta potential in the aqueous phase is negative at all ammonia concentrations. For low ammonia concentrations the zeta potential is close to the point of zero charge at around pH 6. The standard deviation of the zeta potential is around 5%. The pH of the aqueous suspension is increasing according to the addition of ammonia as expected. A complete phase transfer occurs above pH 8.5. As the measuring of the pH values is very definite the standard deviation amounts to 2%.

The formation of a white layer in the organic phase up to a completely white organic phase can be observed at high ammonia concentrations of approximately 10 mass-% (Fig. 3a). This layer has a negative effect on the quality of the phase transfer. Further centrifugation leads to a kind of phase inversion: The aqueous phase then contains the described white layer (Fig. 3b). Nevertheless the determination of the magnetite content in the organic phase after centrifugation process confirms a phase transfer yield of 100%. The white phase originates from the reaction of ammonia with the fatty acid forming the ammonium salt of the fatty acid, e.g. an oleate. The ammonium salt of the fatty acid leads to the formation of an emulsion of the two liquid phases. This effect is known from the generation of an emulsion during the phase transfer by vigorous shaking [11,16].

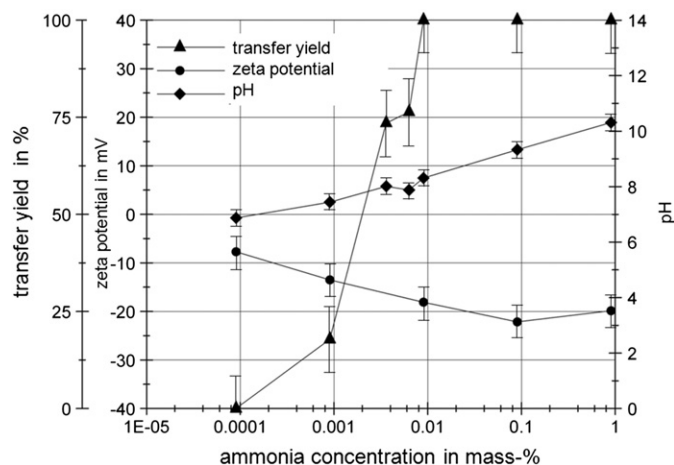


Fig. 2. Quantification of the influence of ammonia on the phase transfer with ricinoleic acid.

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