



Froth flotation via microparticle stabilized foams

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ABSTRACT

There is a still growing interest in the recovery of rare earth elements due to their manifold industrial and technological applications. We present here a simple and effective method for the enrichment of micrometer sized La_2O_3 particles via microparticle stabilized foams. By using the short chain amphiphile (1-hexyl)trimethylammonium bromide (C_6TAB) foam that is generated by surface modified particles only can be generated. This technique allows a more selective and specific particle transport mechanism. The results are discussed in terms of surface charges and transport mechanisms. Furthermore, the effects of particle concentration, pH and amphiphile concentration are studied and evaluated.

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1. Introduction

Colloidal structures in a nonequilibrium state, i.e. systems that are kinetically hindered to minimize their surface energy, are nowadays implemented in manifold applications [1]. Among those, Pickering emulsions [2] and stimuli responsive Pickering emulsions [3–6] are prominent examples. In this context, foams stabilized by solid nano- or microparticles have attracted remarkable attention in recent years because of their unique foaming properties and the wide field of potential applications [7–9].

It is well-known that the combination of surfactant molecules with solid particles, which results in an adsorption at solid/liquid interfaces, can be used to either stabilize or destabilize foams [7,10,11]. However, it is only recently that foams solely stabilized by nanoparticles have been reported [12,13]. For example, Binks et al. investigated aqueous foams stabilized by silica nanoparticles with different hydrophobicity depending on the degree of silanization of surface silanol groups [12]. The case of foam stabilization with nanoparticles only, i.e. in the absence of surfactant is extremely delicate, but stable foams can be obtained in a narrow range of contact angles [14].

A very important case in applications is the case of mineral flotation. As reviewed by Fürstenau and Pradip, the most important parameter is the zeta potential and coverage of the particle by the

adsorbed surfactant layer [15]. Double and triple chain surfactants are of large usage due to their low *cmc*, and hence loss: mixtures of those, added to co-surfactants and modifiers can be used even in high volume fraction of particles as present in slurries produced from ores.

Further attempts have been made by surface lyophobicization of colloidal particles (e.g. Al_2O_3 , ZrO_2 , $\text{Ca}_3(\text{PO}_4)_2$) by short-chain amphiphilic molecules [16,17]. High volume macroscopic foams have been obtained, whereby the use of short-chain amphiphiles (<8 carbon atoms) is a key parameter of this approach. In this case, the initial concentration of microparticles is high, typically 35%, and a short chain amphiphile is used. The reduction in surface tension results from a combination of the one due to surfactant covered particles and the one induced by the surfactant introduced in high concentration. Gonzenbach and co-workers have shown that stable foams with up to 85% of air were produced by this route [16]. In this work, we examine the diluted regime, when the particle concentration in the bulk is low, typically of less than 1 g/l, fifty times less than in other cases; This is to evidence the influence of particles adsorbed on the surface. In a film even of the order of 0.01–0.1 μm , the amount of microparticles adsorbed on the air–water interface is larger than that of particles in the bulk of the foam film. The situation of low initial microparticle concentration is therefore adequate to investigate separation effects.

In froth flotation science and industry one generally distinguishes between ion flotation [18–22] and particle flotation [23–26]. Ion flotation is a separation process involving the adsorption of a surfactant and counterion at an air/water interface. In simple ion flotation, a continuous gas flow is applied to an aqueous

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solution comprising ions and an ionic surfactant of opposite charge of the ion to be concentrated. The surfactant carrying the oppositely charged ion is then concentrated in the foam phase, which is collected. In enhanced ion flotation allowing a more selective ion extraction either complexing agents [27,28], e.g. macrocyclic ligands [29] or chelating surfactants [30] have been implemented. Very recently, further attempts have also been made by using pulsed ultrasound for the generation of foam for ion flotation experiments [31]. The existence of molecularly clean foams has been proposed, since foam was generated by sono-induced nucleating bubbles. The approach opens a new field of applications of ultrasound among classical ones in nanoscience and material science [32–34]. For the froth flotation of nano- and micrometer sized particles typically ionic surfactants are used that on the one hand adsorb at oppositely charged particles and on the other hand effect the foam formation [25,26]. However, many factors, among those are particle size, surfactant, gas flow rate affect the flotation efficiency and selectivity [26]. The surfactant also plays a crucial role, since foam is also formed in absence of “lipophilized” particles allowing transport. When using surfactants to create the foam, where the particles should be enriched, the central problem that the foam is not generated by the particles themselves results in a lack of efficiency and selectivity. Furthermore, it is then difficult to determine the endpoint of a flotation experiment.

Rare earth elements in general and lanthanum oxide (La_2O_3) in particular have nowadays diverse industrial and technological applications. La_2O_3 exhibits many attractive properties for diversified applications, such as catalysis [35,36], optical filters [37] and non-volatile memory cells [38]. Various techniques for the enrichment of rare earth elements from sludge have been developed including fractional crystallization and precipitation, respectively, ion exchange with chelating agents and liquid–liquid extraction [39]. However, these methods are either time consuming, expensive, or large amounts of chemicals and solvents are needed. We present here a simple and efficient method for the enrichment of La_2O_3 from an aqueous dispersion that has great potential to be extended to other oxide minerals. We investigate in this work microparticle flotation in the diluted case by using micrometer sized oxide particles with a high degree of polydispersity in combination with a short-chain amphiphilic molecule with weak foaming properties, which may be termed Pickering flotation mechanism. The foam is generated by particles only, allowing a more efficient and specific particle flotation. The present study clearly reveals the great potential of particle stabilized foams for flotation processes with respect to particle transport properties and efficiency.

2. Results and discussion

Surface charges of mineral oxide surfaces in aqueous solution generally arise from the protonation or deprotonation of the surface hydroxyl groups. Hence, both sign and magnitude of the surface charge depend on the pH of the solution. The pH value, at which charge neutrality is reached, i.e. the relative population of positively and negatively charged sites on the metal oxide surface is equal, is termed the point of zero charge (PZC). The PZC is therefore one key parameter for the flotation of oxide minerals since the surface charge delimits the adsorption of a collector and hence the flotation efficiency [15]. La_2O_3 represents a typical rare earth mineral oxide; the evolution of its ξ -potential in aqueous solution in dependence of the pH value is visualized in Fig. 1a. Within $10.5 \leq \text{pH} \leq 12.0$, the surface is significantly negatively charged, while below $\text{pH} \leq 9.5$ a positively charged particle surface has been found. Within $9.5 \leq \text{pH} \leq 10.5$ a charge reversal could be observed resulting in an isoelectric point of IEP = 10.1, which agrees reasonably well with the value of IEP = 10.4 reported in the literature for hydrous La_2O_3 [40].

Upon exposure of a hydrophilic metal oxide surface to a solution containing amphiphilic molecules, the amphiphile adsorbs at the oppositely charged surface. The degree of adsorption depends on the mineral surface being oppositely charged with respect to the charge of the amphiphile head-group. There are two main factors that make such an adsorption favorable: first, an electrostatic attraction between the charged amphiphile headgroup combined with the entropic effect of counter-ion release and second, a hydrophobic effect, i.e. hydrophobic attraction between the hydrocarbon chains of the amphiphile used. We have chosen the cationic short-chain amphiphile (1-hexyl)trimethylammonium bromide (C_6TAB) as agent to hydrophobize the mineral oxide surface for several important reasons: first, the cationic headgroup is predestined to adsorb on a negatively charged surface; second, it exhibits a high solubility in water combined with a high critical micelle concentration ($\text{cmc}(\text{C}_6\text{TAB}) = 0.99 \text{ mol L}^{-1}$) [41]. Its cmc value is high compared to its longer chain homologues, e.g. the cmc of 1-hexadecyltrimethylammonium bromide (C_{16}TAB) is higher by a factor of about 1000 ($\text{cmc}(\text{C}_{16}\text{TAB}) = 9.7 \times 10^{-4} \text{ mol L}^{-1}$); [42] the high cmc value prevents rehydrophilization of the particles (owing to amphiphile double layer formation) over a wide concentration range. Third, the foaming properties of C_6TAB in aqueous solution are marginal. Using a “low-foaming” amphiphile is opposed to the conventional approach used in ion flotation, since it is generally accepted that efficient ion flotation requires the generation of stable foams induced by the surfactant used [20]. By contrast, in flotation of La_2O_3 we found that C_6TAB adsorbed at the negatively

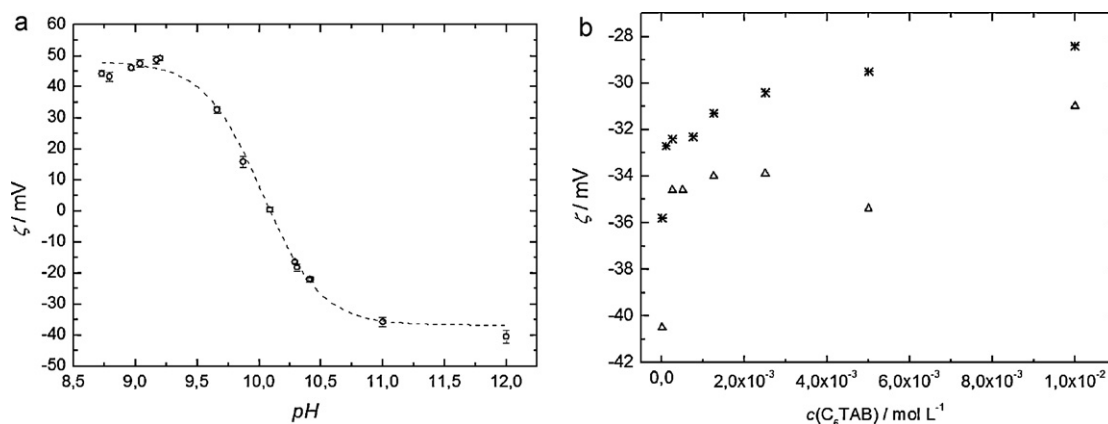


Fig. 1. (a) Zeta potential of La_2O_3 particles ($\rho(\text{La}_2\text{O}_3) = 0.5 \text{ g L}^{-1}$) in absence of C_6TAB (\circ), dotted line is a visual aid. (b) ξ -Potential of La_2O_3 particles ($\rho(\text{La}_2\text{O}_3) = 0.5 \text{ g L}^{-1}$) in presence of C_6TAB at pH = 11 ($*$) and pH = 12 (Δ), respectively.

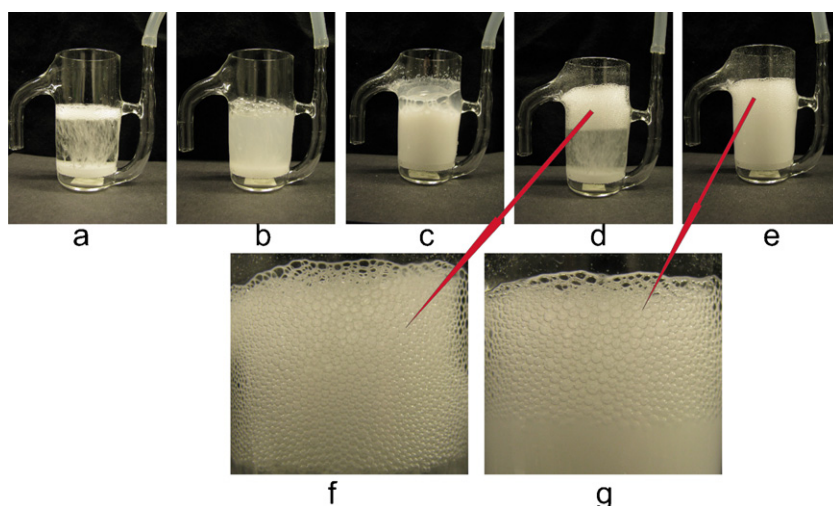


Fig. 2. Photos of aqueous solutions of 30 mL total volume at a gas flow rate (N_2) of 0.3 L min^{-1} for (a) $c(C_6\text{TAB}) = 5 \times 10^{-3} \text{ mol L}^{-1}$ demonstrating the marginal foaming properties of $C_6\text{TAB}$ in water; (b) $\rho(\text{La}_2\text{O}_3) = 0.3 \text{ g L}^{-1}$, $\text{pH} = 12$; (c) $\rho(\text{La}_2\text{O}_3) = 1.3 \text{ g L}^{-1}$, $\text{pH} = 12$; (b) and (c) clarify the negligible foaming properties of particles in water; (d) $\rho(\text{La}_2\text{O}_3) = 0.3 \text{ g L}^{-1}$, $\text{pH} = 12$, $c(C_6\text{TAB}) = 5 \times 10^{-3} \text{ mol L}^{-1}$; (e) $\rho(\text{La}_2\text{O}_3) = 1.3 \text{ g L}^{-1}$, $\text{pH} = 12$, $c(C_6\text{TAB}) = 5 \times 10^{-3} \text{ mol L}^{-1}$; (f) and (g) represent a scale-up of the foam phase of (d) and (e), respectively; (d)–(g) clearly verify the existence of particle stabilized foams.

charged La_2O_3 surface results in microparticle stabilized foams and that the low foaming properties of $C_6\text{TAB}$ in water without particles (cp. Fig. 2a), allows an efficient particle transport during a flotation experiment. In Fig. 1b, the evolution of the ξ -potential at a given particle concentration and pH value ($\text{pH} = 11$ and $\text{pH} = 12$, respectively) with increasing $C_6\text{TAB}$ concentration is shown. The resulting curves represent typical saturation curves. For example at $\text{pH} = 12$, the ξ -potential increases from $\xi \sim -41 \text{ mV}$ up to $\xi \sim -33 \text{ mV}$ until a saturation is reached at $c(C_6\text{TAB}) \sim 4 \times 10^{-3} \text{ mol L}^{-1}$, which is still far below its cmc value. A still quite negative value of the ξ -potential is necessary to avoid particle agglomeration and flocculation during the flotation process. By contrast, for $C_{16}\text{TAB}$ a positive value of the ξ -potential has been determined even at low surfactant concentrations (ξ -potential was positive for $c(C_{16}\text{TAB}) \geq 10^{-4} \text{ mol L}^{-1}$, details are given in Fig. S3 in the Supporting Information). Consequently, we have chosen for the following experiments a fixed pH value ($\text{pH} = 12$) and $C_6\text{TAB}$ concentration ($c(C_6\text{TAB}) = 5 \times 10^{-3} \text{ mol L}^{-1}$) while the amount of particles was varied. The idea of generating microparticle stabilized foam by using short-chain amphiphiles is not new and has already been reported in literature [13,16]. In this study, we apply and transfer this concept to the flotation of rare earth oxide microparticles, starting from extremely diluted solutions. The use of foam stabilized by particles only allows to effectively transporting particles from a continuous aqueous phase into foam that is generated solely by surface modified particles. The foaming behavior in the presence and absence of particles is exemplified in the different photographs of Fig. 2. The pictures in Fig. 2 have been taken at a constant gas (N_2) flow to visualize the different foaming behavior in presence and absence of particles and/or short-chain amphiphiles, respectively. From the ξ -potential measurements it could be deduced that at a given particle mass concentration of $\rho(\text{La}_2\text{O}_3) = 0.5 \text{ g L}^{-1}$ saturation of the particle surface is reached far below the cmc value of $C_6\text{TAB}$ (compare Fig. 1b). For a $C_6\text{TAB}$ concentration of $c(C_6\text{TAB}) = 5 \times 10^{-3} \text{ mol L}^{-1}$ ($cmc(C_6\text{TAB}) = 0.99 \text{ mol L}^{-1}$) in water the foaming after 1 min is marginal, as visualized in Fig. 2a. This negligible foaming was also observed for samples, where defined particle mass fractions ($\rho(\text{La}_2\text{O}_3) = 0.3 \text{ g L}^{-1}$ and $\rho(\text{La}_2\text{O}_3) = 1.3 \text{ g L}^{-1}$) have been dispersed in water after the same time interval and constant N_2 flow, as can be seen in Fig. 2b and c, respectively. By contrast, the combination of the same particle mass fractions and $C_6\text{TAB}$ concentration after the same time interval and N_2 -flow rate leads to the formation of stable

foam, as shown in Fig. 2d–g. These observations strongly support the fundamental idea that the foam is stabilized by surface modified particles only. Therefore, the question of the mechanism of the formation of foam in the presence of microparticles a short-chain amphiphile arises.

The dispersion of La_2O_3 particles in an aqueous solution and the addition of NaOH until a basic pH ($\text{pH} = 12$ in the following experiments) is reached, leads to the deprotonation of surface hydroxyl groups and the particle surface becomes then negatively charged. Afterwards, $C_6\text{TAB}$ molecules are added in excess, followed by the adsorption of the positively charged amphiphile head-group at the oppositely charged particle surface. Consequently, the outer layer of the particle becomes more hydrophobic due to the short hydrocarbon chain. These surface modified particles promote an effective stabilization of a liquid/gas interface. The surface modified particles adsorb at the gas bubbles due to their partially hydrophobic character and are transported to the top of the device. Foam bubbles are formed, where the film at the liquid/gas interface is stabilized by the surface modified particles. Note that neither the bare particles nor the short-chain amphiphile ($C_6\text{TAB}$) alone promote the formation of stable foam (compare Fig. 2). Noteworthy, the adsorption of the surface modified particles at the liquid/gas interface stabilizes the interfacial film resulting in microparticle stabilized foam. Consequently, the particles are significantly enriched in the foam phase compared to the bulk solution.

This enrichment in the foam phase forms the basis of an efficient particle separation from the bulk solution, the foam phase is collected, until stable foam is no longer maintained indicating that the maximum amount of particles for a given experimental setup has been collected. This approach is an additional advantage of the exertion of a short-chain amphiphile with low foaming properties compared to the application of long-chain surfactants, where the endpoint of a flotation experiment is difficult to be determined.

After having shown the ability to form microparticle stabilized foams their efficiency for a flotation experiment remains to be discussed. Van Hee et al. have recently demonstrated that the flotation efficiency of protein coated polystyrene is significantly influenced by particle size and particle aggregation [24]. In this study, the particle concentration was chosen as a variable to assess the optimum conditions for a flotation experiment.

In Fig. 3, the flotation efficiency, e.g. the mass transport of particles that has been found in the foam phase is

compared to its initial mass concentration ($\rho(\text{La}_2\text{O}_3)_{\text{initial}}$). On the ordinate is shown the weight percentage of La_2O_3 extracted in the foam phase, given by the mass of La_2O_3 ($m(\text{La}_2\text{O}_3)_{\text{foam}}$) (collected in the foam phase, divided by the initial mass of La_2O_3 ($m(\text{La}_2\text{O}_3)_{\text{initial}}$) multiplied by 100 ($\text{wt}\%(\text{La}_2\text{O}_3)_{\text{extracted in foam}} = (m(\text{La}_2\text{O}_3)_{\text{foam}}/m(\text{La}_2\text{O}_3)_{\text{initial}}) \times 100$). For particle mass concentrations $\rho(\text{La}_2\text{O}_3)_{\text{initial}} \leq 1 \text{ g L}^{-1}$ flotation efficiencies of around 80% could be obtained. At higher particle concentrations $1 \text{ g L}^{-1} \leq \rho(\text{La}_2\text{O}_3)_{\text{initial}} \leq 2.5 \text{ g L}^{-1}$ the efficiency significantly decreased until a plateau was reached ($\rho(\text{La}_2\text{O}_3)_{\text{initial}} > 3 \text{ g L}^{-1}$), where the flotation efficiency was below 10%. Note that the particles possess a high degree of polydispersity with sizes in the micrometer range. Consequently it was not possible to obtain convenient results by means of dynamic light scattering. First a light scattering experiment suffers from the sedimentation during each measurement step and second the samples were opaque (compare Fig. 2) in the concentration regime used. However, the results indicate that at high particle concentrations an agglomeration of particles is likely to occur and particles are no longer efficiently enriched and stabilized at the liquid/gas interface, probably because gravity and sedimentation then plays a more important role. Fig. 3 yields information about the mass of particles that have been transported in the foam phase and about the efficiency of particle transport. However, in Fig. 3, there is no information about the amount of water that has been transported with the particles in the collected foam phase.

In Fig. 4, the particle mass concentration in the foam phase ($\rho(\text{La}_2\text{O}_3)_{\text{foam}}$) versus $\rho(\text{La}_2\text{O}_3)_{\text{initial}}$ is visualized. At around $\rho(\text{La}_2\text{O}_3)_{\text{initial}} = 1 \text{ g L}^{-1}$ a maximum concerning the particle mass concentration in the foam phase was found. This can be interpreted that at this concentration the maximum amount of particles was present in the liquid/gas interface combined with rather low amounts of water. Therefore, we suggest the existence of an optimal flotation concentration, where the particles are closest to each other at the liquid gas interface without being aggregated in a manner that the gravity plays an important role. Considering further a flotation efficiency of around 80% at $\rho(\text{La}_2\text{O}_3)_{\text{initial}} = 1 \text{ g L}^{-1}$, this interpretation appears to be plausible.

Note that at high initial mass concentrations of La_2O_3 ($\rho(\text{La}_2\text{O}_3)_{\text{initial}} > 3 \text{ g L}^{-1}$) the particle mass concentration in the foam phase is significantly lower compared to the liquid phase. If particles aggregate at high initial mass concentrations of La_2O_3 they are heavier and hence adsorb less effectively at a gas bubble. Therefore, the probability that a particle aggregate is transported to the top

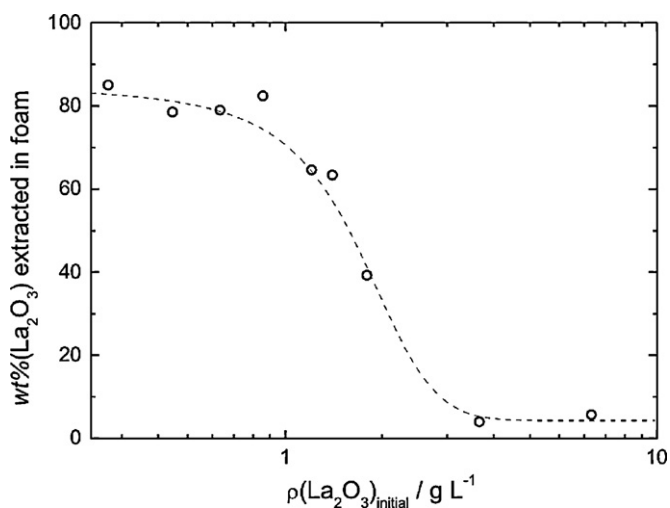


Fig. 3. Froth flotation efficiency as a function of the initial La_2O_3 mass concentration ($\rho(\text{La}_2\text{O}_3)_{\text{initial}}$), dotted line represents a visual aid.

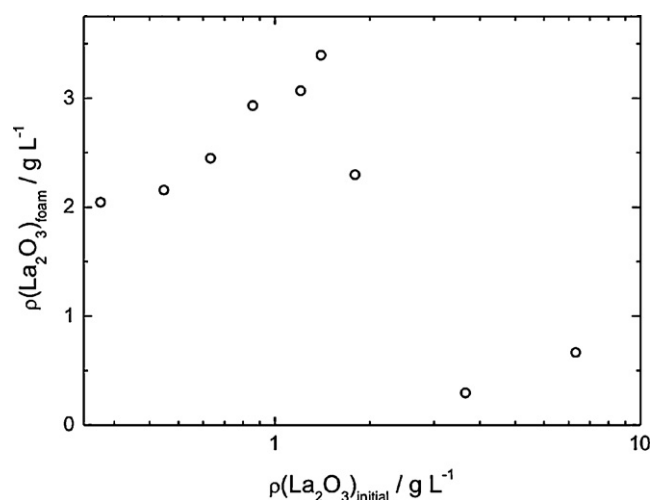


Fig. 4. Mass concentration of La_2O_3 in foam phase ($\rho(\text{La}_2\text{O}_3)_{\text{foam}}$) versus ($\rho(\text{La}_2\text{O}_3)_{\text{initial}}$) indicating the existence of an optimum flotation concentration.

of the flotation vessel and then stabilizes foam bubbles there is reduced, since gravity plays a more important role. This observation can be of great importance for an experiment where two types of particles (i.e. two different mineral oxides) shall be selectively enriched in either the foam phase or the remaining phase.

3. Experimental

3.1. Chemicals

(1-Hexyl)trimethylammonium bromide (Alfa Aesar, 98%) and lanthanum(III) nitrate hexahydrate (Alfa Aesar, 99.9%) were used without further purification.

3.2. La_2O_3 microparticle preparation and characterization

La_2O_3 has been prepared by the calcination of the corresponding nitrate hexahydrate salt at 700°C according to the literature [43,44]. X-ray powder diffractograms revealed a hexagonal close packing (Fig. S2 in the Supporting Information). Prior to each experiment, the colorless powder was dispersed in deionized Millipore water and sonicated for 5 min with a power density of 21 W cm^{-2} (Ultrasonic Processor VCX 505, Sonics & Materials, Inc., USA, 20 kHz, 12 mm tip-diameter) resulting in polydisperse micrometer sized particles (SEM in the Supporting Information, Fig. S1).

3.3. ξ -Potential measurements

pH values were adjusted by the addition of diluted NaOH (1N TitriPUR, Merck) under stirring, the pH was measured using a pH meter (WTW microprocessor pH meter). The ξ -potential was determined in DTS 1060C cells using a ZetaSizer Nano (Malvern Instruments), equipped with a laser operating at 533 nm.

3.4. Flotation experiments

The flotation experiments have been performed using a home-built flotation vessel as visualized in Fig. 2. The flotation vessel was built up with an inner diameter of 4 cm and a height of 8 cm, a G4 glass frit has been used to obtain a homogeneous dispersion of the gas feed from the bottom of the glass vessel. La_2O_3 was weighed in the appropriate amount in a glass vessel, followed by the addition of 25 mL of water and sonicated. Afterwards, the pH was adjusted and C_6TAB (from a stock solution of $c(\text{C}_6\text{TAB}) = 50 \times 10^{-3} \text{ mol L}^{-1}$)

was added and filled with water to give a final C_6TAB concentration of $c(C_6TAB) = 5 \times 10^{-3} \text{ mol L}^{-1}$ and an overall volume of 30 mL. The mixture was then transferred into a flotation vessel (cp. Fig. 2) and a continuous N_2 flow of 0.3 L min^{-1} was applied. The foam phase was collected until no more foam overflow occurred. Afterwards, the amount of foam was determined from precise weight measurements, followed by several centrifugation steps (water, ethanol, acetone) and the bare particles dried at 80°C for 2 h to determine the mass of particles collected.

4. Concluding remarks

In conclusion, we demonstrated that adsorption of short-chain amphiphiles to oppositely charged metal oxide surfaces yields microparticle stabilized foams, which are appropriate for an effective froth flotation of these particles. Furthermore, it was exemplified that the flotation efficiency and the maximum particle packing density are a function of initial concentration. The main advantage of flotation via these microparticle stabilized foams is that no additional foaming agent is necessary that may affect both efficiency and selectivity. It should be stressed that La_2O_3 was a model system, however, we believe that this concept can be extended to other rare earth metal oxides that also differ in their isoelectric points and hence, not only an effective, but also a selective enrichment may be possible using this concept. We basically want to attain one important goal with this study, namely the proof of concept that foams stabilized by surface modified rare earth oxide microparticles only can be used for an effective flotation, separation and preconcentration of these particles. We believe that this concept can be extended to many other nano- and microparticles and is therefore of interest for manifold applications. The next step will be to exemplify that a flotation of two types of particles can be used to separate two types of particles from each other, and to investigate the influence of microparticle concentration of the quantity of air entrapped in the foam, thus giving access to the average thickness of the foam film collected.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2012.04.024>.

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