Microemulsions and nanoemulsions applied to iron ore flotation

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ABSTRACT

The present work investigates the microflotation of hematite and quartz using microemulsion and nanoemulsion systems as well as alkyl ether monoamine solutions. This application is based on the ability of such systems to reduce interfacial tension, which favors their application in separation processes. In these systems, the collector was composed by alkyl ether monoamine (Flotigam EDA®), n-butyl alcohol, and kerosene. Corn starch with a high degree of purity was the depressant in the process. Results show that the performance of nanoemulsions is higher than those of the microemulsions and alkyl ether monoamine solutions; by simplifying and leading to an improvement of the process.

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1. Introduction

Iron ores used in the iron and steel industry must present a high metallic content of iron (Fe) and a low presence of contaminants, especially silica (SiO₂), alumina (Al₂O₃), and phosphorus (P). Nowadays, China is the world’s largest producer of iron ore (accounting for 45% of world’s production), followed by Australia and Brazil, respectively [1].

According to Clout and Manuel [2], Brazil has one of the largest iron ore reserves in the world, being one of the main producers of concentrates. Due to the scarcity of high-grade iron ore in nature, the obtaining of products with these characteristics is made possible through the application of concentration techniques in processing plants.

Filippov et al. [3] classified froth flotation as the most effective process in the production of iron concentrates, both technologically and economically. The flotation is a separation technique, which is based on surface properties (hydrophobic or hydrophilic character) of the mineral species present in the pulp [4]. It uses chemical additives to modify surface properties and maximize selective separation [5].

According to Thella et al. [6], the reverse cationic flotation is used mainly in the selective hydrobization of quartz (SiO₂), as ether amines and ether diamines are more selective and present greater solubility in water, acting as collectors in the process. Some reagents used as collectors can also work as frothing agents. The amines, when added at pH close
to 10, are in equilibrium between their ionic (collector) and molecular (fother) species [7], being used at this pH range in flotation processes. Flotation depressants are used to inhibit the adsorption of the collector onto the surfaces of the minerals, when its flotation is not desired, thus, enhancing the effect of collectors on the capture of a desired mineral. In this way, hematite ($\text{Fe}_2\text{O}_3$) can be concentrated through the depressant action of natural organic polymers, such as starch. Filipov et al. [8] reported that the adsorption of starch on hematite surface is ten times higher than that on quartz surface.

Schulman et al. [9] observed that certain mixtures of oil, water, surfactant, and co-surfactant produce homogeneous systems, even without a substantial input of mechanical energy. They named these systems as “microemulsion”. Microemulsions are systems composed by water, an organic solvent, a surfactant, and, occasionally, an alcohol as co-surfactant [10]. These systems are formed by small droplets of one liquid dispersed in a continuous phase, and differ from macroemulsions due to their long-term thermodynamic stability [11,12]. Microemulsions are used in several processes involving the concentration of metal ions, such as chromium, iron, zinc, lead, nickel, copper, and manganese [13].

Nanoemulsions can be formed by mixing a nonpolar phase, an aqueous phase, surfactants, and, sometimes, a co-surfactant. As observed, both colloidal systems can be prepared using exactly the same ingredients, but in different ratios. In general, a greater surfactant-to-oil ratio (SOR) is required to prepare a microemulsion. Nanoemulsions present a transparent or translucent appearance to the naked eye and are classified as oil-in-water (O/W) or water-in-oil (W/O) [14–16]. McClements [16] and Gupta et al. [17] reported the major differences between nanoemulsions and microemulsions. They considered for comparison: stability characteristics, droplet size range, particle structure, and fabrication method. Nanoemulsions are thermodynamically unstable, can be kinetically stable over long time scales, present 20–500 nm spherical droplets, and always require the input of some external energy to form a colloidal system. On the other hand, microemulsions are thermodynamically stable systems, present 10–100 nm spherical or lamellar structures, and are formed by self assembly. According to Forgiairini et al. [18], nanoemulsions present droplet size between microemulsions and classical emulsions. McClements [16] highlights the main methods used for identifying the systems formed: long-term storage; sample history (condition after stirring, heating or freezing cycle); particle shape; and particle size distribution. As nanoemulsions can be typically formulated using less surfactant concentrations than other colloidal systems, they are becoming increasingly more attractive economically [15,19].

Dantas et al. [20] proposed the application of nanoemulsion systems in enhanced oil recovery (EOR) operations. Nanoemulsions assist in crude oil recovery by reducing the adhesion force between the oil phase and the formation rock.

In microemulsion and nanoemulsion systems, the presence of a nonpolar phase is important for the flotation process. Studies show that several hydrophobic minerals can be concentrated in flotation processes by using a nonpolar agent alone or in association with a surfactant. As an example, one can describe the flotation of molybdenite [21], in which 200–250 g of oil per ton of ore fed are employed. In the flotation of graphite, kerosene is used as a collector reinforcer and pine oil as a foaming agent. The mixture of ether amine and diesel oil was also used industrially in the cationic reverse flotation of iron ore [7]. In calamine ore flotation the use of diesel oil as an amine chain extender has been reported [22]. Diamines associated with kerosene have shown good results in mineral flotation processes [23].

This work addresses the floatability of hematite and quartz using ether monoamine solutions, microemulsion and nanoemulsion systems. These systems were used aiming to simplify the flotation process by introducing in a single phase the conventional flotation agents. The systems used alkyl ether monoamine solution (Flotigam EDA®) and apolar oil (kerosene) as collectors, and high purity corn starch as depressant.

## 2. Materials and methods

### 2.1. Materials

**2.1.1. Mineral species**

The mineral species used were hematite, supplied by Mina de Casa de Pedra (CSN Mineração, Congonhas – MG, Brazil) and quartz, collected in the town of Turmalina (Minas Gerais, Brazil). The mineral samples consisted of well-formed crystals with dimensions around 5 cm. Initially, the samples were fragmented with the aid of a hand hammer to reach top size of 0.5 cm. An agate mortar was used to produce particles with sizes in the range of $\pm 150$ to $\pm 75$ $\mu$m. Results of chemical analyses by X-ray fluorescence (XRF) are shown in Table 1, indicating that the purity degree satisfies the requirement for the experimental runs.

**2.1.2. Microemulsion and nanoemulsion systems**

The chemicals used for microemulsion and nanoemulsion obtaining were: alkyl ether monoamine system (surfactant; Flotigam EDA® – Clariant), high purity corn starch (depressant), kerosene (oil phase; Petrobras), n-butyl alcohol (co-surfactant; Pro-Analyis, 99%), and distilled water (aqueous phase; Tecnal, TE-078), used without any additional purification. For pH adjustment of microemulsion and nanoemulsion systems, before flotation tests, 0.5 M NaOH (CRQ, 98%) and 0.5 M HCl (VETE, 37%) solutions were used.

The microemulsion region inside the pseudoternary phase diagram was determined by titration. First, the maximum solubility point of the active matter (surfactant (C) + co-surfactant (S)) in the aqueous phase was determined. In a glass vial, 2 g of active matter was weighed using a constant C/S ratio, varying from 0.5 to 4, at room temperature ($27^\circ$C). The active matter was titrated dropwise with the aqueous phase until obtaining the transition from cloudy to clear appearance. The vial was weighed and the amount of aqueous solution added to the system was determined at this titration endpoint. The titrant solution was prepared by adding 10 wt% water beyond the endpoint. Nine blends (2 g) with different ratios of active matter + oil phase (10–90 wt%) and nine blends of aqueous phase + oil phase (10–90 wt %) were titrated dropwise with the titrant until reaching a clear appearance. The vials
containing the systems were weighed and the amount of titrant was determined. The pseudoternary phase diagram was thus, constructed by plotting the amounts of aqueous phase, oil phase, and surfactant/co-surfactant phase used in each experiment. In order to obtain the pseudoternary diagrams with corn starch, a corn starch solution was used as aqueous phase (100 and 1000 ppm; C/S ratio = 1). The microemulsion systems (MS) used to perform quartz and hematite microflotation experiments were composed by (wt%): (i) 85.5% water, 0.5% kerosene, 7% Flotigam EDA, and 7% n-butyl alcohol, C/S ratio = 1; and (ii) 79.5% water, 0.5% kerosene, 10% Flotigam EDA, and 10% n-butyl alcohol, C/S ratio = 1. These microemulsion systems were selected because they comprise a great amount of aqueous phase and a small amount of active matter.

To produce the nanoemulsion system, the microemulsion system described in item (ii) was diluted to achieve the desired concentration of surfactant, in accordance with the methodology described by Belloq and Roux [24]. First, the microemulsion systems (100 mL), with and without corn starch, were obtained in a 150-mL beaker by adding the components in a two-step process. In the first step, the active matter (co-surfactant + surfactant) was mixed at 500 rpm for 10 min. Then, in the second step, the remaining components of the microemulsion were added (500 rpm, 10 min). In order to obtain the nanoemulsion, a low-energy methodology was employed. Water was added slowly to the microemulsion system, under constant stirring (500 rpm). Five nanoemulsion systems with varied surfactant concentrations were obtained (10, 25, 50, 75, and 100 ppm). The choice of nanoemulsion system was based on the relationship between surface tension and surfactant concentration, always looking for a stable system. Surface tension was measured by using a SensaDyne tensiometer (QC6000), at 27 °C. The nanoemulsion systems real-time stabilities, with and without corn starch addition, were checked by long-term storage tests (six months), at 27 °C and natural light [25]. After a long period of storage, phase separation could not be observed. Droplet size and particle size distribution (PSD) for microemulsions and nanoemulsions were obtained by using a Nanotrac NPA252 (Microtac), in triplicate. Droplet sizes between 10 and 500 nm and the presence of only a single narrow peak are expected for microemulsions. For nanoemulsions, droplets size in a wider range between 20 and 500 nm and single or multiple peaks that may be narrow or broad could be observed [16].

2.2. Experimental methods and conditions, apparatus, and calculations

Microflotation tests were carried out in a 320-mL modified Hallimond tube, originally designed by Hallimond and modified by Fuerstenau et al. [26]. A magnetic stirrer was used to promote complete mixture of reagents in suspension, without occurrence of hydrodynamic drag, at a constant air flow rate (60 mL/min), to ensure an efficient operation of the apparatus. Fig. 1 illustrates a schematic diagram of the experimental apparatus and how the addition of materials was performed. In the experimental runs, quartz and hematite were used separately with a collector solution, microemulsion and nanoemulsion systems with and without the addition of depressant and/or pH modifiers. The pulp’s pH, mineral sample (1.0 g), and collector solution, microemulsion or nanoemulsion sample (V = 100 mL) were adjusted to the required conditions/values and, then, conditioned for 5 min under constant stirring. After stirring, air was bubbled through the porous plate, located at the base of the Hallimond tube, for 1 min (60 mL/min). Table 2 summarizes the operating conditions used in the experiments, and Table 3 shows experimental conditions, compositions, droplet sizes, and PSD of systems used in the microflotation tests. The floated product

<table>
<thead>
<tr>
<th>Table 1 – X-ray fluorescence analyses of hematite and quartz samples.</th>
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<tr>
<td></td>
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<tr>
<td>---------------------</td>
</tr>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>90.883</td>
</tr>
<tr>
<td>SiO₂</td>
</tr>
<tr>
<td>96.988</td>
</tr>
</tbody>
</table>

**Fig. 1 – Schematic diagram of the microflotation cell with indication of the addition of materials.**
$m_f$ (after dried in an oven at 100 °C to constant weight) and the initial mass $m_i$ were used in the calculation of floatability, according to Eq. (1):

Floatability (%) = \left( \frac{m_f}{m_i} \right) \times 100 \tag{1}

### 3. Results and discussion

#### 3.1. Pseudoternary phase diagrams

The objective of this study was to evaluate the behavior and changes in the microemulsion region when the flotation reagents are added to the aqueous phase and, thus, to verify that all reagents required for the flotation tests can be assembled in a single phase. Fig. 2 presents the pseudoternary diagrams, obtained using four different cosurfactant/surfactant (C/S) ratios: (a) C/S = 0.5; (b) C/S = 1.0; (c) C/S = 2.0; and (d) C/S = 4.0.

The analysis of the pseudoternary phase diagrams reveals that the co-surfactant/surfactant ratio has an influence in the size of the microemulsion region, and shows that for high C/S ratios (2 and 4) there is a significant decrease in the microemulsion region. The Winsor I (WI) region shown in the plots is formed by an oil-in-water (o/w) microemulsion in equilibrium with an oil phase in excess [27]. The Winsor I region is not desirable for this study, considering that it contains an oil phase in excess. Thus, the ratio C/S = 1 was chosen because it presented a large Winsor IV region without high consumption of surfactant, as compared with C/S = 0.5, despite presenting similar regions.

Fig. 3 shows the pseudoternary phase diagrams obtained with the addition of the depressant agent (high purity corn starch) in the aqueous phase. In this study, the C/S ratio was set at 1 (C/S = 1) and the concentration of corn starch in aqueous solution was set at 100 (Fig. 3(a)) and 1000 ppm (Fig. 3(b)). No significant change was observed on the area of the microemulsion region. This is an important

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**Table 2 – Operating conditions used in the microflotation experiments.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral sample</td>
<td>1 g</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>5 min</td>
</tr>
<tr>
<td>Flotation time</td>
<td>1 min</td>
</tr>
<tr>
<td>Compressed air flow</td>
<td>60 mL/min</td>
</tr>
<tr>
<td>Granulometry</td>
<td>−150 to +75 μm</td>
</tr>
<tr>
<td>Microemulsion volume</td>
<td>100 mL</td>
</tr>
</tbody>
</table>

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**Table 3 – Experimental conditions and composition of systems used in the microflotation experiments.**

<table>
<thead>
<tr>
<th>pH effect of systems on the microflotation process</th>
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<tbody>
<tr>
<td>n-Butyl alcohol</td>
</tr>
<tr>
<td>Flotigam EDA®</td>
</tr>
<tr>
<td>Kerosene</td>
</tr>
<tr>
<td>Droplet size</td>
</tr>
<tr>
<td>PSD</td>
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<table>
<thead>
<tr>
<th>Analysis of quartz and hematite floatability with collector solution and nanoemulsion</th>
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</thead>
<tbody>
<tr>
<td>Collector solution</td>
</tr>
<tr>
<td>Concentration (ppm)</td>
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<td>5–50</td>
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</table>

<table>
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<tr>
<th>Analysis of hematite depression with corn starch</th>
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</thead>
<tbody>
<tr>
<td>n-Butyl alcohol</td>
</tr>
<tr>
<td>Concentration (ppm)</td>
</tr>
<tr>
<td>30</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Analysis of different concentrations of amine and corn starch in quartz floatability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanoemulsion</td>
</tr>
<tr>
<td>Concentration (ppm)</td>
</tr>
<tr>
<td>10–100</td>
</tr>
</tbody>
</table>
Fig. 2 – Pseudoternary diagrams of systems composed by aqueous phase, n-butyl alcohol/Flotigam EDA®, and kerosene at different ratios of co-surfactant/surfactant (C/S). (a) C/S = 0.5; (b) C/S = 1; (c) C/S = 2; (d) C/S = 4.

Fig. 3 – Pseudoternary diagrams of systems composed by cornstarch solution, n-butyl alcohol/Flotigam EDA®, and kerosene for depressant concentrations of (a) 100 ppm and (b) 1000 ppm.
observation, once this additive can be combined to the system, in the studied concentration range, without affecting its stability negatively.

In order to obtain the nanoemulsions, an aqueous-phase rich microemulsion point (79.5% water, 0.5% kerosene, 10% Flotigam EDA®, and 10% n-butyl alcohol) was selected and dilutions were made to obtain the concentration of surfactant desired for each study [28].

3.2. pH effect of microemulsion and nanoemulsion systems on the microflotation process

Microemulsions used for quartz and hematite micro flotation had 14% and 20% C/S ratio, and 0.5% kerosene. Distilled water was used as aqueous phase. The compositions were chosen and varied in order to provide a response regarding the influence of the surfactant percentage on the microemulsion and to favor the contact between collector and mineral species, promoting the hydrophobicity of quartz. Another important feature is that the chosen microemulsion is located in the water-rich region, thus, consuming small amounts of surfactant, co-surfactant, and oil phase. The pH of the microemulsion was varied, covering a range from 5 to 12.

Fig. 4 illustrates the results obtained and shows that the highest levels of quartz and hematite floatability were achieved at pH 10 (natural microemulsion pH), reaching recoveries of 50% for quartz with C/S ratio = 14% and 70% for C/S ratio = 20% (Fig. 4(a)). For hematite, Fig. 4(b), the results using 14% and 20% C/S ratios were 32% and 53%, respectively. A significant decrease in floatability was observed at higher pH values, a region where the molecular species of the collector is predominant. This behavior was expected as amine adsorption occurs in response to the electrostatic mechanism. On the other hand, it is essential to mention that the addition of pH modifier agents does not impair the stability of the microemulsion. The C/S ratio for obtaining the nanoemulsions and performing the following studies was set at 20%.

Fig. 5 shows the effect of the pH of the nanoemulsion containing 30 ppm of Flotigam EDA® on floatability. The floatability of both, quartz and hematite, increases with the pH, up to a maximum at pH 10 (region where the ionic and molecular strengths of the collector coexist in equilibrium), with floatability of 93% for quartz and 40% for hematite, falling drastically for higher pH values. Nanoemulsions enhance the selectivity between quartz and hematite, a finding that had not yet been reported in the flotation literature.

3.3. Analysis of quartz and hematite floatability with surfactant solution and nanoemulsion

This study was intended to evaluate the effect of collector solutions (conventional method) and nanoemulsions on the floatability of quartz and hematite for surfactant concentrations ranging from 5 to 50 ppm. Fig. 6 shows the results. In the absence of corn starch, amine adsorbs both on quartz and on hematite surfaces. However, in the case of quartz (Fig. 6(a)), the maximum floatability was achieved at 30 ppm of amine, reaching 93% floatability for surfactant solution and nanoemulsion. It should be noted that floatability levels close to 90% were observed for nanoemulsions even at low surfactant concentrations (5 ppm).

For hematite (Fig. 6(b)), the floatability reached around 55% for 30 ppm amine solution. For nanoemulsion system, values around 38% were observed at this amine concentration. The largest floatability of quartz is due to its affinity for the collector ion (amine) which, in every pH range, presents more negative surface charge than hematite.
Fig. 6 – Floatability of quartz (a) and hematite (b), as a function of amine concentration, with collector solution and nanoemulsion, at pH = 10.0.

Fig. 7 – Floatability of hematite as a function of depressant concentration in the nanoemulsion with 30 ppm amine Flotigam EDA® at pH = 10.0.

3.4. Analysis of hematite depression with corn starch

Fig. 7 shows the results for microflotation tests using hematite and amine (30 ppm) in nanoemulsion system, with corn starch depressant in concentrations ranging from 0 mg/L to 100 mg/L. This concentration was sufficient to promote the maximum floatability, as one can observe from the results shown previously.

Corn starch present in the system acts as a hematite depressant, yielding a 26% floatability level. A sharp effect cannot be observed as the nanoemulsion already reduces significantly the floatability (in the absence of depressant).

3.5. Analysis of different concentrations of amine and corn starch in quartz floatability

Fig. 8 shows the results of the microflotation tests for quartz using Flotigam EDA®, as collector in a nanoemulsion. Corn starch was used as depressant at different concentrations.

One can observe that higher concentrations of starch and amine increase quartz depression. Corn starch with approximately 25% amylose enhanced quartz depression significantly. The greatest quartz depression can be explained by the ability of starch to form clathrate with amine through its helical structure. Pattanaik and Venugopal [23] showed that the ionization of fatty acids, phosphates, and other minority constituents of corn starch may generate negative charge under basic pH conditions. Statistically, this negative charge, according to Partridge and Smith [29], can be attracted to the positive charge of amine, favoring the formation of clathrate.

Shrilimahi et al. [30] investigated the interaction between ether monoamine and amylose using determinations of contact angle, bubble attachment time, quartz crystal microbalance with dissipation monitoring (QCM-D), and molecular dynamics simulation (MDS). The authors suggested that the formation of clathrate is responsible for the impaired floatability of quartz, corroborating the findings of Lima et al. [31].

Conclusively, Table 4 shows a comparison of the main results obtained in the floatability tests using microemulsions and nanoemulsion systems. The microemulsion was able to float 70% quartz and 55% hematite while the nanoemulsion floated 90% quartz and 30% hematite using lower surfactant concentration (30 ppm).
Table 4 – Quartz and hematite floatability using microemulsion and nanoemulsion systems at pH 10 (natural pH of the systems).

<table>
<thead>
<tr>
<th></th>
<th>Microemulsion</th>
<th>Nanoemulsion</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Concentration (ppm)</td>
<td>Floatability (%)</td>
</tr>
<tr>
<td>n-Butyl alcohol</td>
<td>100,000</td>
<td>30</td>
</tr>
<tr>
<td>Flotigam EDA®</td>
<td>100,000</td>
<td>30</td>
</tr>
<tr>
<td>Kerosene</td>
<td>5,000</td>
<td>0.0015</td>
</tr>
<tr>
<td>Corn starch</td>
<td>–</td>
<td>25</td>
</tr>
<tr>
<td>Quartz</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>Hematite</td>
<td>55</td>
<td>30</td>
</tr>
</tbody>
</table>

4. Conclusions

Nanoemulsions, compared to microemulsions and collector solutions, have the potential to be used in the quartz and hematite microflotation process. Some of the main conclusions of the study are summarized below:

i. The microemulsion region is affected by the C/S ratio and is not affected by the addition of corn starch to the aqueous phase, even at high concentrations.

ii. The use of kerosene in emulsified systems showed promising results for the process and improved the stability of microemulsions and nanoemulsions without compromising flotation efficiency.

iii. The use of corn starch did not alter the stability of microemulsion and nanoemulsion systems and allowed 74% hematite depression for nanoemulsions containing 75% of depressant and 30 ppm of Flotigam EDA®.

iv. Nanoemulsion was able to achieve quartz floatability above 90% using lower surfactant concentration.

These results represent an innovation in iron ore concentration and pave the way for the use of nanoemulsions in this field, improving the simplicity and efficiency of processes, reducing the cost associated with the use of surfactants, and optimizing the variables to obtain high iron grades with low silica content.

Conflicts of interest

The authors declare no conflicts of interest.

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