Original Article

Depressants in nanoemulsion systems applied to quartz and hematite microflotation

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\textbf{ABSTRACT}

Nanoemulsion systems were investigated in the microflotation of quartz and hematite. Four different depressants were used: Maizena\textsuperscript{®}, soluble starch, amidex, and amylose. The nanoemulsions comprise in a single stable phase varying amounts of water, kerosene, Flotigam EDA\textsuperscript{®} (collector), and n-butyl alcohol, allowing all flotation reagents to be added at the same time, reducing interfacial tension and favoring their application in the process. Micro flotation tests were performed in a modified Hallimond Tube and the zeta potential values of the minerals were determined in the presence and absence of reagents. Quartz floatability was not affected by depressants, even when concentrations of 100 ppm of depressant were used in the nanoemulsion. The determined isoelectric point of quartz (pH 2). High levels of hematite depression were obtained for all depressants (80\%–90\% depression). Quartz floatabilities of up to 95\% were achieved by using nanoemulsions in the process.

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1. **Introduction**

Iron ore is the main raw material used in the steel industry [1,2]. The depletion of its reserves throughout the world requires the use finely disseminated minerals. Processing methods such as gravity separation, magnetic separation, and flotation are widely used in the production of iron ores concentrates [3].

Cationic collectors and amines or amine derivatives are used to separate silicates, such as quartz, from iron oxides [4]. In the process, organic polymers, i.e. starch, play the roles of selectively flocculating and depressing hematite particles and other iron mineral constituents, keeping them concentrated in the un floated fraction [5].

Corn starch is largely used as a depressant for iron-containing minerals [6,7]. Starch consists mainly of amy-
lopectin and amylose, polysaccharides of monosaccharide α-D-(−)-glucopyranose [8]. Amylose is a linear molecule of 10^6–10^7 molecular weight which has helical behavior in solution. Amylopectin is a branched molecule consisting of several thousands of crosslinked amylose short chains having a molecular weight 10–100 times greater than the amylose. Most industrial starches contain 20–30% amylose, 70–80% amylopectin [9], between 1 and 2% oil, and between 7–8% protein [7].

The adsorption of polysaccharides has been addressed in several investigations [10–14]. Initially, hydrogen bonds between hydroxy groups were supposed to be the main interaction mechanism. Further studies, especially ones reporting advances in FTIR techniques, indicate that chemical adsorption occurs via complexation between hydroxylated metal ions on the mineral’s surface and polar groups in the polysaccharide.

Nanoemulsions are nanoscale-sized colloidal dispersions that are generally composed by surfactants, aqueous phase, and oil phase [15]. These systems can be produced by several methods, but they are typically prepared in a two-step process. Firstly, a microemulsion is obtained and then, it is converted into a nanoemulsion in a second step [16]. They present kinetic stability and transparent or translucent appearance [17]. Jaiswal et al. [18] considered nanoemulsions those with droplet sizes ranging from 10 nm to 1000 nm. Comparing with microemulsions and emulsions, the size of the dispersed droplets, high interfacial area, and the use of lower amount of active matter are the main advantages of using nanoemulsion.

This investigation addresses the floatability of hematite and quartz using nanoemulsion systems. Alkyl ether monoamine (Flotigam EDA®) and apolar oil (kerosene) were used as collectors. Maizena®, high purity grade corn starch (20–30% amylose), soluble starch (25–30% amylose), amidex (2% amylose), and pure amylose were the selected depressants.

2. Materials and methods

2.1. Materials

2.1.1. Mineral species

High purity samples of hematite, from Mina de Casa, Congonhas – MG, Brazil, and quartz, collected in Turmalina – MG, Brazil, were utilized. The minerals were comminuted in a porcelain mill. The microfluidation tests used the fraction in the size range -150 μm + 75 μm. The zeta potential determinations were conducted using the −38 μm fraction.

2.1.2. Nanoemulsion systems

To obtain the nanoemulsion systems, first microemulsion systems were obtained. They were composed by Flotigam EDA® (Clariant) as surfactant; kerosene (Petrobras) as oil phase; n-butyl alcohol (Pro-Analysis, 99%) as co-surfactant; and distilled water (Tecnal, TE-078) as aqueous phase. Four depressants were used in the experiments: modified corn starch (Maizena®), soluble starch, amidex, and amylose. They were added to the aqueous phase of the microemulsion at specific concentrations ranging from 10 to 100 ppm. The pH of nanoemulsion systems was adjusted prior to the flotation tests. Solutions were used at 0.5 M NaOH (CRQ, 98%) or HCl (Vetec, 37%). All reagents were used without further purification.

The titration methodology described by Bellocq and Roux [19] was used to obtain the microemulsion region inside the pseudoternary phase diagram. The maximum solubility point of the active substance (surfactant (C) + co-surfactant (S)) in the aqueous phase was determined. In a glass vial, 2 g of active material were weighed using a constant C/S ratio of 1, at room temperature (27 °C). The active material was titrated dropwise with the aqueous phase until the transition from cloudy to clear appearance. The flask was weighed and the amount of aqueous solution added to the system was determined. This point was called titration endpoint. To obtain the pseudoternary phase diagrams with the tested depressants, a depressant solution was used as aqueous phase (10 and 100 ppm, C/S = 1 ratio).

Eighteen mixtures (2 g) were titrated drop wise with the titrant solution until the system became clear: nine with different ratios of active matter + oil phase (10–90% by weight) and nine with varied proportions of depressant solution + oil phase (10–90% by weight). After titration, the flasks were weighed and the amount of titrant determined. The final amounts of aqueous phase, oily phase, and surfactant/co-surfactant phase (% by weight) were plotted in pseudoternary phase diagrams to determine the microemulsion region.

The nanoemulsions were obtained by microemulsion systems (MS) dilutions, according to the methodology described by Bellocq and Roux [19] and Gupta et al. [16]. All MS were composed by (wt %): 79.5% aqueous solution, 0.5% kerosene, 10% Flotigam EDA®, and 10% n-butyl alcohol, with a C/S ratio = 1. This MS composition was selected because it comprises a great amount of aqueous phase and a small amount of active matter. Firstly, microemulsion systems (100 mL) were obtained in a 150 mL beaker by adding the components in a two step process. In the first stage, the active material (co-surfactant+ surfactant) was mixed at 500 rpm for 10 min. In the second, the remaining components of the microemulsion were added (500 rpm, 10 min). A low energy methodology was employed in the preparation of nanoemulsion systems, adding slowly the desired depressant solution to the microemulsion system, under constant stirring (500 rpm). Five nanoemulsion systems with varying concentrations of surfactant were obtained (10, 25, 50, 75, and 100 ppm). The choice of nanoemulsion systems was based on the relationship between surface tension and surfactant concentration, always aiming a stable system.

The surface tension was measured using a Sensa-Dyne tensiometer (QC6000) at 27 °C. Real-time stabilities of nanoemulsion systems were verified by long-term (six months) storage tests, at 27 °C and natural light [20]. No phase separation was observed after long period of storage. Droplet sizes and particle size distribution (PSD) for microemulsion and nanoemulsions were obtained using a Nanotrac NPA252 (Microtac), in triplicate. Droplet sizes between 10–100 nm and the presence of only a single narrow peak were expected for the microemulsion. For nanoemulsions, droplets between 20–500 nm and single or multiple peaks may be observed which may be narrow or broad [21].
2.2. **Apparatus and calculations**

Quartz and hematite microflotation tests were performed, with nanoemulsions containing the four types of depressants at different concentrations, in a 320-mL modified Hallimond tube, originally designed by Hallimond and modified by Fuerstenau et al. [22]. A magnetic stirrer was used to promote the mixing of reactants in suspension without occurrence of hydrodynamic drag, at flow rate of 60 mL/min to ensure efficient operation of the apparatus (Fig. 1). The pH of the mineral sample (1.0 g) and nanoemulsion (V = 100 mL) was adjusted to the required value. The volume of the tube was completed, and the system was conditioned for 5 min under constant stirring. After this period, air was bubbled through the porous plate, located at the base of the Hallimond tube for 1 min at a constant flow rate. The floated fraction was oven dried at 100 °C until constant weight. The initial weight \( m_i \) and that of the floated fraction \( m_f \) were used to calculate the floatability.

\[
\text{Floatability (\%) = } \frac{(m_f)}{(m_i)} \times 100
\]

The following conditions were investigated:

- hematite floatability as a function of depressant concentration and type using a nanoemulsion system with 30 ppm of collector, at pH 10;
- quartz floatability as a function of collector and depressant concentrations in the nanoemulsion system, at pH 10, aiming at verifying the formation of amine/starch complexes.

The samples were also analyzed by the electrophoresis technique. Zeta potential curves of the minerals were determined with use of the Zeta Meter ZD3-D-G 3.0+ equipment.

Aqueous suspensions were prepared with the mineral, electrolyte (NaCl 58.44 ppm) and the reagents, collector and depressant, in the nanoemulsion. The top size of samples was 38 μm. The decantation time in solution was approximately 3 h, in order to analyze only particles in the size range <10 μm. The pH range from 2 to 12 was investigated using NaOH or HCl solutions. The reagents were used in the lowest possible amount, avoiding a significant increase in the ionic strength of the solution, which would decrease the reliability of results. Experiments were done in triplicate and results are presented as mean values. Samples results with standard deviation greater than 5% were discarded and re-analyzed, in order to obtain reliable results.

3. **Results and discussion**

3.1. **Pseudoternary phase diagrams**

In order to obtain nanoemulsion systems with varying proportions of depressants, pseudoternary phase diagrams, for each depressant under study, were constructed to obtain the microemulsion area, verifying whether the depressant dosage modifies microemulsion stability.

The C/T ratio = 1 was fixed in the process and the concentration of Maizena®, soluble starch, amidex, or amylose in aqueous solution were studied for values of 10 and 100 ppm (Fig. 2). No significant change was observed in the microemulsion area, allowing concluding that these additives can, in this concentration range, be added to the system without impairing its stability.

3.2. **Microflotation**

Hematite floatability curves for nanoemulsion systems with 30 ppm collector and varying concentrations of the four depressants tested, at pH 10, are shown in Fig. 3.

The results indicate that all four polysaccharides in the nanoemulsion acted as hematite depressants, amidex being the most effective due to its high amylpectin content. Pavlovic and Brandão [12] studied the depressant effect of corn starch and its amylese and amylpectin components on hematite and quartz surfaces by infrared spectroscopy, adsorption isotherms, and microflotation tests. All the carbohydrates enhanced the hydrophilic character of hematite.

Quartz floatability curves with nanoemulsion containing collector and depressant as a function of collector concentration, at pH 10, are presented in Fig. 4.

Negative effects on quartz floatability were not detected over the entire range of collector and depressant concentrations analyzed. The use of nanoemulsions, even at low collector concentrations, provided high floatability for quartz, regardless of the presence of varying amounts of amylese in the structure of the depressant.

Other authors have shown different results suggesting the formation of clathrates with the surfactant due to the helical structure of the starch. Somasundaran [23] and Takagi and Isemura [24] explained that clathrate formation occurs mainly.
Fig. 2 – Pseudoternary phase diagrams for systems composed by the depressor aqueous solution (10 and 100 ppm), kerosene, Flotigam EDA®/n-butyl alcohol.
Nanoemulsion collector and depressant systems did not show tendency to clathrate formation, even when the depressant used was constituted mainly by amylose, probably due to the stability of this compound, being able to preserve the collecting power of the surfactant.

3.3. Zeta potential

The zeta potential of quartz was determined by the electrophoresis method in suspensions with 58.44 ppm of NaCl. The results are shown in Fig. 5.

Negative values of the zeta potential were obtained for quartz in the pH range of 2–11. The isoelectric point (PIE) of the quartz was determined at pH 3.0, which is consistent with the literature values for quartz pH 2–3 [25-28].

Curves of zeta potential of quartz in suspensions with Flotigam EDA® and nanoemulsion at concentrations of 30 ppm and 50 ppm are illustrated in Fig. 6. As expected, being NaCl an indifferent electrolyte [29], its ions are not specifically adsorbed onto quartz and the isoelectric point (IEP) coincides with the point of zero charge (PCZ). The zeta potential curve for quartz in amine nanoemulsion at 30 and 50 ppm showed that the addition of amine promotes a reduction of the zeta potential modulus in the studied pH range. Increase in the pH of the isoelectric point of the quartz was also observed. In the absence of amine, the isoelectric point occurred at pH 2. Adding nanoemulsion with 30 ppm of amine, the isoelectric point reached pH 5, and at 50 ppm a value of pH 6 was attained, indicating the occurrence of adsorption of the collector onto

due to the housing of the surfactant molecule inside the amylose helices, impairing the performance of the collector in the flotation.

Pinto et al. [10], in their study on the effects of amylose and amylpectin on oxyminerals, observed a trend of quartz depression at low concentrations of amine and starch (approximately 1 ppm and 10 ppm, respectively). However, they attributed the fact to low amine concentration.

Fig. 3 – Hematite floatability as a function of depressant concentration and type in the nanoemulsion (Nanoemulsion with 30 ppm of Flotigam EDA®, pH 10).

Fig. 4 – Quartz flotability with nanoemulsion containing collector and depressant as a function of collector concentration for (a) Maizena®, (b) Soluble Starch, (c) Amidex, and (d) Amylose.
the mineral surface. The positive charge of amine contributes
to the decrease of the negative charge presented by the quartz
in the exclusive presence of indifferent electrolyte.

Fig. 7 shows the results of zeta potential determinations of
quartz in nanoemulsion containing concentrations of 50 ppm
of amine and 100 ppm of depressants.

The surface charge of mineral particles is greatly influenced
by the pH of the solution [30,31]. The zeta potential of quartz
became less negative for pH values above 6. Somasundaran
[23] showed evidence of increased adsorption on the mineral
surface in the presence of starch, and of starch in the presence
of collector, thus, contributing to the observed decrease of the
zeta potential modulus. Starch should in fact be co-adsorbed
at the quartz/solution interface in association with amine.

Similar results were obtained by Yin et al. [32] in their study
on the separation of quartz and hematite using magnetite.
The negative zeta potential value for each of the three minerals
increased nearly linearly with increasing pH from the
isoelectric point up to pH 12.

Feng et al. [33], studying the mechanism of interaction of
magnesium ions with cassiterite and quartz surfaces and their
response to flotation separation, showed that the zeta potential
of magnesium ion-treated quartz was less negative within
the pH range investigated. The extent of change in negativity
of zeta potential of mineral particles increased with increasing
pulp pH, and the maximum value was found within the
pH range from 8.6 to 11.7. The authors believe that the results
may be related to the adsorption of magnesium species onto
quartz surfaces.

4. Conclusions

The study showed that nanoemulsions can be used in the
microflotation of quartz and hematite. Some of the main
conclusions are summarized below:

(i) Even at low concentrations of amine and depressants it
was possible to achieve high flotabilities of quartz;
(ii) All depressants introduced into the nanoemulsion sys-
tems were efficient to promote hematite depression;
(iii) No significant effects were observed by the presence
or absence of amylose in depressants showing that
clathrate formation does not occur in nanoemulsion sys-
tems applied to reverse cationic flotation.

The proposed methodology is an innovation in the con-
centration of iron ores and opens the way for the use of
nanoemulsions in this field.

Conflicts of interest

The authors declare no conflicts of interest.

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