Short communication

Reverse froth flotation of magnesite ore by using (12-4-12) cationic gemini surfactant

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ABSTRACT

The cationic gemini surfactant 1,4-bis(dodecyl-N,N-dimethylammoniumbromide)butane (BDDAB) was tested as a possible collector in the reverse froth flotation of magnesite ore. This novel type of collector was compared with its conventional monomeric equivalents: primary dodecylamine (DA) and tertiary dimethyldodecylamine (DDA). Electrokinetic measurements documented a strong effect of the synthesized gemini surfactant on the zeta potential of quartz. The effect of the three collectors declined in the following order: BDDAB > DA > DDA. Laboratory froth flotation tests confirmed an improved collecting ability of the gemini surfactant compared to both the conventional collectors. The desilication efficiency declined in the following order: BDDAB > DA > DDA. The results obtained with the lowest concentration of the gemini surfactant were better in terms of SiO₂ content than those obtained with four times higher dosages of the conventional collectors.

1. Introduction

Reverse froth flotation using primary ammonium collector, dodecylamine (DA) has been proven to be efficient beneficiation method to obtain high grade magnesite concentrate (low SiO₂ content) (Yao et al., 2016). DA is one of the most used collectors in the reverse froth flotation of silicates from bauxite (Liu et al., 2015) and is also suitable for the reverse cationic flotation of high silica iron ore (Fillipov et al., 2014). Dodecyl tertiary amines (Liu et al., 2009) and quaternary amines (Wang et al., 2004; Jiang et al., 2014) can also be used as collectors of silicate minerals with good results.

Recent findings have however proven, that cationic gemini surfactants have stronger collecting power than their monomeric equivalents (Xia et al., 2009). Dimeric or gemini surfactants are compounds with two hydrophobic chains and two hydrophilic head groups, covalently connected through a spacer chain. Gemini surfactants, when compared to their monomeric equivalents are more efficient at lowering the surface tension of water and have lower critical micellization concentrations, resulting in better hydrophobization of minerals and better flotation performance (Xia et al., 2009). Gemini surfactants have also been proven to be more efficient in studies of the reverse froth flotation of iron ore (Huang et al., 2014) and bauxite (Xia et al., 2010).

To our knowledge, however, the use of quaternary ammonium gemini surfactants in the reverse froth flotation of magnesite ore has not yet been described. Therefore, our interest is to verify whether the gemini surfactants can be efficiently used in the reverse flotation of magnesite ore by a direct comparison of results of laboratory froth flotation using dimeric ammonium based gemini surfactant and similar conventional surfactants which contain one hydrophobic group in the molecules.

2. Experimental

2.1. Minerals and reagents

Ground magnesite ore (95% passing 265 µm) and hand-picked samples of magnesite and quartz were acquired from the company Gemerská nerudná spoločnost, Hnúšťa-Mútnik, Slovakia. Phase composition characterization of finely powdered ore was done using X-ray diffraction (XRD) analysis on D8 Bruker 20 diffractometer using CuKα radiation. JCPDS PDF 2 database was used for interpretation of the measured spectra.

The 12-4-12 gemini quaternary ammonium salt 1,4-bis(dodecyl-N,N-dimethylammoniumbromide)butane (BDDAB) surfactant was synthesized by refluxing 0.1 mol of 1,4-Dibromobutane (99%, ACROS Organics, Belgium) with 0.21 mol of N,N-Dimethyldodecylamine (95 %, ACROS Organics, Belgium) in dry acetone (99.5%, mikroCHEM, Slovakia) for 20 h. The solvent and the reagents were used as received without further purification. Solid, that precipitated upon cooling was then filtered, washed with dry acetone and recrys-
tallized from dry acetone to obtain the desired gemini cationic surfactant in form of a pure white powder. The yield of the reaction was 88.4% of the theoretical amount.

$^1$H and $^{13}$C NMR spectra were recorded in DMSO-$d_6$ on a Varian VNMR spectrometer operating at 599.87 MHz ($^1$H) and 150.84 MHz ($^{13}$C) at room temperature, using an internal standard tetramethylsilane (0.00 ppm). The spectra, which are included as a supplementary material, confirmed a high purity of the sample which was better than 99%. The methyl and methylene proton signals showed expected chemical shifts and integral intensities. The HSQC experiment allowed assignment of the $^{13}$C NMR signals. Signals of the methyl and methylene protons and carbons attached to protonated nitrogens were deshielded and adequately shifted downfield.

$^1$H NMR spectrum (ppm): $\delta_H = 0.86$ (6H, t, $J = 7.2$ Hz, 2 CH$_3$), 1.22–1.35 (36H, m, 18 CH$_2$), 1.63–1.70 (8H, m, 4 CH$_2$), 3.01 (12H, s, 4 CH$_3$N($\pm$)), 3.22–3.27 (4H, m, 2 CH$_2$N($\pm$)), 3.28–3.33 (4H, m, 2 CH$_2$N($\pm$)).

$^{13}$C NMR spectrum (ppm): $\delta_C = 13.93$ (2 CH$_3$), 18.99, 21.71, 22.06, 25.81, 28.53, 28.68, 28.84, 28.94, 29.00, 29.00, 31.26 (11 × 2 CH$_3$), 50.02 (4 CH$_3$N($\pm$), 62.00 (2 CH$_2$N($\pm$)), 63.18 (2 CH$_2$N($\pm$)).

Synthesis route and resulting structure of the BDDAB surfactant is shown in Fig. 1.

2.2. Zeta potential analysis

Zeta ($\zeta$) potential was determined using SurPASS (Anton-Paar, Austria) electrokinetic analyzer equipped with an automatic titration unit and calculated by Attract software from streaming potential measurements using the Fairbrother - Mastin equation.

2.3. Laboratory froth flotation

Froth flotation tests were done in a 3-litre flotation cell. After the slurry (density of 300 g L$^{-1}$) was transferred to the agitated flotation cell (1600 rpm) and agitated for 3 min, pH was adjusted to 6.5 using an HCl solution. The surfactant solution was then added and the slurry was agitated for 15 min. After the conditioning period, 65 g t L$^{-1}$ of Methyl Isobutyl Carbinol (MIBC) frother was added and agitated for another 1 min. The air was then introduced with 4 L·min$^{-1}$ volumetric flowrate and 10 min flotation period was conducted. Three tests were run at each condition and average values are reported.

3. Results and discussion

3.1. Ore analysis

The XRD measurement confirmed the presence of magnesite as a valuable mineral, which is accompanied with talc, chlorite, quartz and dolomite in intergranular layers. The chemical composition of the ore used in flotation tests was 47.8% LOI, 43.1% MgO, 4.0% SiO$_2$, 2.4% Fe$_2$O$_3$ and 0.4% CaO, characterized by the d$_{50}$ value of 190 µm and only 5.0 wt.% of fine particles below 45 µm.

3.2. Investigation of collector properties

Both conventional (Liu et al., 2015, 2009; Fillipov et al., 2014; Jiang et al., 2014) and gemini (Xia et al., 2009; Huang et al., 2014) cationic collectors are physically adsorbed on the surface of minerals by an electrostatic attraction. Adsorption of these collectors on individual minerals can be controlled by the adjustment of pH of the system. The point of zero charge (PZC) of the minerals is thus the most important property (Fuerstenau and Pradip, 2005).

The PZC of present silicate minerals, talc (Fuerstenau and Pradip, 2005) and chlorite (Tan et al., 2013), and that of quartz (Yao et al., 2016; Huang et al., 2014; Fuerstenau and Pradip, 2005) lies in the acidic range, below pH 3.0. The PZC values of magnesite and dolomite were measured at pH 6.7 and 6.2, respectively (Yao et al., 2016).

At pH 6.5, chosen for the batch flotation tests, the surface charge of magnesite should be positive, while that of the silicate minerals and quartz should be negative. Neutral, up to slightly acidic pH was also found to provide the best flotation recovery for silicate minerals using dodecylamine (Guo, 2010), dodecyl tertiary amines (Liu et al., 2009), quaternary amines (Wang et al., 2004; Jiang et al., 2014) and also ammonium gemini surfactant (Xia et al., 2009).

Decreasing collecting abilities of amine collectors in alkaline pulps can be attributed to the formation of their basic amine forms and the simultaneous decrease (especially at pH > 8) of their presence in protonated ammonium forms. pKa values found in specifications of chemical properties of the surfactants are 10.63 and 9.97 for DA and DDA, respectively. In protonated forms, the nitrogen cations of the collectors are electrostatically attracted to the negatively charged surfaces of minerals. The nitrogen atom of a neutral amine present in alkaline pulp environments does not interact with negatively charged surfaces and there is, therefore, a drop in the achieved recoveries. The gemini collector does not have protonation states, because the addition of a fourth alkyl substituent to nitrogen results in a permanent cationic

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**Fig. 1.** Synthesis route of the gemini surfactant BDDAB.