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Intensify dodecylamine adsorption on magnesite and dolomite surfaces by monohydric alcohols



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Hao Zhang^a, Wengang Liu^{a,b,*}, Cong Han^{a,*}, Dezhou Wei^a

^a School of Resources & Civil Engineering, Northeastern University, Shenyang 110819, China ^b State Key Laboratory of Mineral Processing, Beijing General Research Institute of Mining & Metallurgy, Beijing 100160, China

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1. Introduction

Surfactants were widely used in many fields, such as the synthesis of medicament [1], emulsion polymerization [2,3], petroleum processing [4]. Furthermore, surfactant was an important factor in flotation, which was often used as collector and frother [5]. In general, the mixture of dissimilar surfactants was applied as collectors rather than pure unitary surfactants, because the former was more effective to adsorb on mineral surfaces with the advantage of the larger potential in performance over the single surfactant. Hence then, utilization of blended surfactants in mineral flotation process had gained wide attention from researchers [6–11].

Magnesite (MgCO₃) and dolomite (MgCa(CO₃)₂) were the most important magnesium-bearing carbonate minerals, which were widely utilized in many fields such as aerospace, building and electronic industry, for the manufacturing of basic refractories [12–14]. Flotation was an effective method for separating and purifying of magnesite and dolomite. As the key factor of flotation, collectors cost too much in the two mineral processing [15–17]. In addition, alcohols were cheaper and common auxiliary reagents, which have been applied in the flotation of minerals with other collectors.

ABSTRACT

The flotation of magnesite and dolomite were investigated with the presence of single dodecylamine (DDA) and combined mixtures of DDA and monohydric alcohols, respectively. The adsorption behavior of DDA, butanol, hexanol and octanol on the surface of the two minerals were shown by molecular dynamics simulation, and the results were corresponding with the analysis of zeta potential, measurements of the contact angle and adsorption. Flotation results indicated that part of DDA could be replaced by the three alcohols (butanol, hexanol, octanol) to get better flotation results. Molecular dynamics simulation and the results of zeta potential and contact angle measurements indicated that adsorption of DDA on mineral surfaces could be strengthened by monohydric alcohols.

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Monte [18] had illustrated that sylvite could be selectively floated from halite with the use of cationic collectors DDA along with long chain alcohols. Vidyadhar [19] had shown that better flotation results of silicates (albite and quartz) could be achieved by longchain alcohols along with amine cations compared to the amine alone at the same concentration. Although the effect of alcohols on the flotation of different minerals was studied, their coadsorption mechanism and aggregation behaviors on mineral surfaces were still needed further research. Nowadays, with the development of numerical simulation technology, using the molecular dynamics simulations to study the adsorption behavior was feasible.

Molecular dynamics (MD) simulations had been widely applied to discuss the adsorption behavior and interaction energy of surfactants at the liquid/gas and liquid/solid interfaces [20–24]. Hao et al. [25] researched the adsorption models of sodium oleate on siderite, hematite and quartz by molecular dynamic simulation, respectively. Based on the molecular simulation in solution with water as medium, adsorption quantity and interaction capability of oleate ions on the three minerals indicated that siderite could be collected efficiently by sodium oleate at neutral pH. The simulation results showed a better match with experimental results. Beena Rai et al. [26] used molecular dynamics simulations to investigate the interaction of oleate and dodecylammonium chloride surfactants with aluminosilicate minerals and the surface energies were computed for the cleavage planes of these minerals. Simulation results showed the adsorption mechanisms of anionic



^{*} Corresponding authors at: No. 3-11, Wenhua Road, Heping District, Shenyang 110819, China (W. Liu).

E-mail addresses: liuwengang@mail.neu.edu.cn (W. Liu), hancong@mail.neu.edu. cn (C. Han).

chemisorbing type oleate and cationic physisorbing type dodecylammonium chloride molecules were on two different crystal planes of spodumene and jadeite and that were $(1\ 1\ 0)$ and $(0\ 0\ 1)$ which coincided with the experiment results. de Leeuw et al. [27] calculated the electronic structure of fluorite (CaF₂) and the energies of adsorption of water at the main $(1\ 1\ 1)$ cleavage plane and studied the competitive adsorption of water and methanoic acid at the planar and stepped $(1\ 1\ 1), (0\ 1\ 1)$ and $(3\ 1\ 0)$ surfaces. Also, they indicated that lots of calculations of the co-adsorption of water and methanoic acid that the presence of solvent made a significant contribution to the final adsorption energies and that the explicit inclusion of the solvent in calculations was necessary to correctly predict relative reactivities of different surface sites.

In present work, in order to study the surfactant adsorption behaviors and the intensify DDA adsorption by monohydric alcohols, parts of DDA were substituted by different kinds of monohydric alcohols for the flotation of magnesite and dolomite. The intensified adsorption of DDA on magnesite and dolomite surface was discussed by molecular dynamics simulations with the addition of zeta potential, contact angle measurements and adsorption measurement.

2. Materials and methods

2.1. Materials

Magnesite and dolomite used for this work were obtained from Haicheng of Liaoning Province, China. Both single mineral samples were hand-sorted and ground to -0.074 + 0.015 mm by porcelain ball mill. The chemical compositions of magnesite included 48.53% MgO, 0.44% CaO, 0.15% SiO₂, 0.09% Al₂O₃, 0.12% Fe₂O₃ and the dolomite contained 21.28% MgO, 30.66% CaO, 0.39% SiO₂, 0.07% Al₂O₃, and 0.06% Fe₂O₃. Based on the X-ray diffraction showed in Fig. 1, no other impurities were detected in both samples. All the surfactants including DDA, butanol, hexanol and octanol used in this work were purchased from China National Pharmaceutical with analytical pure.

2.2. Micro-flotation experiments

Flotation experiments were carried out in a 30 mL flotation cell by adding into 2.0 g minerals samples and 30 ml deionized water. Flotation cell was suspended on laboratory XFG self-aeration flotation machine (Jilin Exploration Machinery Plant, China) operating at 1620 r/min. NaOH and HCl were prepared for adjusting the slurry pH. Then surfactant DDA and combined collectors of DDA and different monohydric alcohols were used as the collectors in flotation, respectively. Finally, the concentrates and the tailings were filtered, dried, weighed and analyzed. Each experiment was performed at least three times for getting the average result and the standard deviations were also presented. It was reminded that the pH values, surfactant concentration and type for different experiments were changed, but other parameters, including impeller speed, test temperature, and air flow rate were kept constant during the experiments. The flotation flow sheet was shown in Fig. 2.

2.3. Zeta-potential measurements

Zeta potential measurements were carried out using a Nano-ZS90 zeta potential analyzer (Malvern Instruments Ltd, Britain). 0.5 g mineral samples were suspended in 50 ml KCl solution which was used as background electrolyte ($0.001 \text{ mol}\cdot\text{L}^{-1}$). Suspensions were stirred for 20 min after surfactants addition by a magnetic stirrer and were allowed to equilibrate for 10 min at each pH value prior to taking a measurement. The test results were the average of at least five individual repeated experiments with standard deviations being presented. NaOH and HCl were used for adjusting the pH of dispersed suspensions. The temperature was kept constant at 25.0 °C.



Fig. 2. The flotation flow sheet of magnesite and dolomite.



Fig. 1. XRD patterns of (a) magnesite and (b) dolomite.

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