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Short Communication

Collaborative Adsorption and Flotation of N-dodecyl Ethylenediamine with Short Chain Alcohol on Quartz

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The laboratory investigation about short chain alcohol effect on flotation performance of quartz using N–dodecyl ethylenediamine (ND) as collector was carried out through flotation tests, zeta-potential measurements, and Fourier transform infrared (FTIR) spectroscopy studies. Experimental results showed that the addition of short chain alcohol could improve flotation performance of ND effectively, resulting in a higher flotation recovery of quartz. Maximum flotation recovery of quartz was obtained when the mass ratio of ND and alcohol was 1:1. More importantly, chain structure of alcohol played an important role in quartz flotation. Longer hydrocarbon chain and more substituents of alcohol usually related to higher flotation recovery. Zeta-potential measurement and FTIR spectroscopy study demonstrated the co-adsorption of diamine and alcohol on quartz surface, of which hydrogen bonding and electrostatic adsorptions between collector and quartz surface were strengthened by the addition of alcohol. Furthermore, higher cross-sectional area of alcohol usually related to stronger hydrogen bonding and electrostatic affinity. Therefore, higher flotation recovery of quartz was obtained.

Keywords: N–dodecyl ethylenediamine; Short chain alcohol; Collaborative adsorption; Quartz; Electrostatic adsorption

1. INTRODUCTION

With the exhausting reserves of high-grade ores in the world, froth flotation that has been considered as the most efficient process in mineral processing to recover valuable minerals from gangue is estimated to conduct over 2×10^9 t ores every year all over the world [1-3].

Collector plays a key role during flotation separation process [4]. And cationic collectors, such as fatty primary alkylamines, ether amines and quaternary ammonium salts [5-8] are usually used in quartz flotation [9,10]. It is known that dodecylamine (DDA), which has strong collecting ability on quartz, is the most common collector to float quartz from other ores in early stage [7,11-13]. Nevertheless, the high viscosity and poor selectivity of most cationic collectors restrict their application, and the prohibitive cost should also be considered [14,15]. Thus, many researchers have been attempted to synthesize a series of high-efficiency but low-cost collectors. Wang et al. [16] developed an economic quaternary ammonium salt (CS–22), which possessed superior collecting ability and selectivity compared with dodecylamine. Another novel quaternary ammonium surfactant (M–302) was also synthesized and used as a collector for flotation of silicates from a magnetite iron ore [3]. It is noteworthy that many synthetic collectors have been successfully utilized in the separation of quartz from iron ores, such as dodecyl ethylenediamine, N-dodecyl-β-amino-propylamide and medium-chain ether-amine acetates [17-19]. Huang et al. [20] utilized one Gemini surfactant in reverse flotation of iron ore, and the flotation performance was compared with dodecylammonium chloride.

Meanwhile, many studies have indicated that the addition of such non-ionic surfactants as fatty alcohols can improve cationic flotation of silicates because it can increase flotation selectivity and recovery compared with individual components, as well as a remarkable decrease in cationic collector consumption [21-23]. Filippov et al. [24,25] demonstrated that the addition of alcohols to DDA or ether diamine could improve the floatability of Fe-bearing mica minerals and quartz, simultaneously, reduce the collector consumption. The mixture of amine and fatty alcohols generates a hydrophobic adsorption layer on the surface of minerals. Liu et al. [26] studied the influence of polyalcohol (PEG) on diamine adsorption on quartz, when amine-alcohol mixture was used. The results showed that the addition of PEG strengthened the electrostatic and hydrogen bond adsorption between quartz and diamine.

However, few works are focus on alcohol structure effect, especially chain length, on quartz flotation along with amine collector, and few studies are available regarding the use of mixtures containing diamine and non-ionic surfactants during the flotation of quartz or other silicates at present [27]. Therefore, the purpose of this work is to reveal the collaborative adsorption of short chain alcohols along with ND on quartz surface, and then discuss the short chain alcohol effect on quartz flotation with ND. Flotation tests, zeta-potential measurements and FTIR studies are carried out in this paper.

2. MATERIALS AND METHODS

2.1. Materials

High purity quartz was obtained from Donganshan plant, which located in Liaoning, one province of China. The sample was crushed and then ground in one laboratory porcelain mill orderly to obtain –100 μm samples for flotation studies. Chemical composition analysis showed that SiO_2 content in the sample was 99.5%. The sample also contained trace amounts of aluminum (Al_2O_3, 0.06%), calcium (CaO, 0.09%), and iron impurities (Fe_2O_3, 0.3%). All these results revealed the high purity of the sample. Small part of the sample was further ground to –10 μm in a mortar mill for FTIR and zeta-potential studies.

N–dodecylethylenediamine (ND), which has a molecular weight of 228, was synthesized as the detailed procedure reported by Liu et al. [28]. It was directly acetated and confected as 1% mass concentration acetate solution without any further purification. The analar-grade linear chain alcohols with $C_{2\sim6}$ alkyl chain length were obtained from Sinopharm, China. Alcohols were also prepared as 1% mass percent concentration solutions by dissolving the alcohol in distilled water. A series of ND/alcohol solutions were prepared by mixing ND solution and alcohol solution together in different ratios. Analar-grade NaOH and HCl were diluted with distilled water and used to adjust the pulp pH.

2.2. Flotation tests

Micro–flotation of quartz was conducted in a 30 ml XFG flotation cell with 5 g sample. The flotation cell was impelled at the impeller speed of 1260 r/min. Before flotation reagents addition, the suspension was stirred for 3 min. And then, collector was added into the cell with 3 min conditioning before a flotation period of 5 min. All the flotations were performed at neutral pH of 6–7. Finally, products and tailings were separately weighted and assayed after filtration and drying. And recoveries were calculated on the base of weight and grade.

2.3. Zeta-potential measurements

Zeta-potential measurements of quartz were implemented using a JS94H zeta potential analyzer. 1 g of –10 μm quartz particles were dispersed in 50 mL aqueous solution, containing1×10^{-3} mg L^{-1} KNO_3, as a supporting electrolyte. After the system was adjusted for 12 min at room temperature (25 ℃), a series of pH values were regulated by adding 1% HCl or 1% NaOH solution. And then, zeta potentials of the sample were measured and the average value of five individually measurements was adopted.

2.4. FTIR spectroscopy analysis

Fourier transform infrared spectra were recorded on a Nicolet 740 FTIR spectrometer through KBr disks from 400 cm^{-1} to 4000 cm^{-1}. The samples used for this purpose were ground to less than 10 μm before being conditioned with collector. Fine particles were added into an aqueous solution of 1×10^{-3} mg L^{-1} ND or 1×10^{-3} mg L^{-1} ND/alcohol mixture. After stirring for 20 min, the quartz samples were filtered, washed with distilled water for three times, and dried in a vacuum oven at 20 ℃ for 24h. The pellet in this study was constituted by a mixture of 1 mg pretreated samples and 100 mg KBr.

3. RESULTS AND DISCUSSION

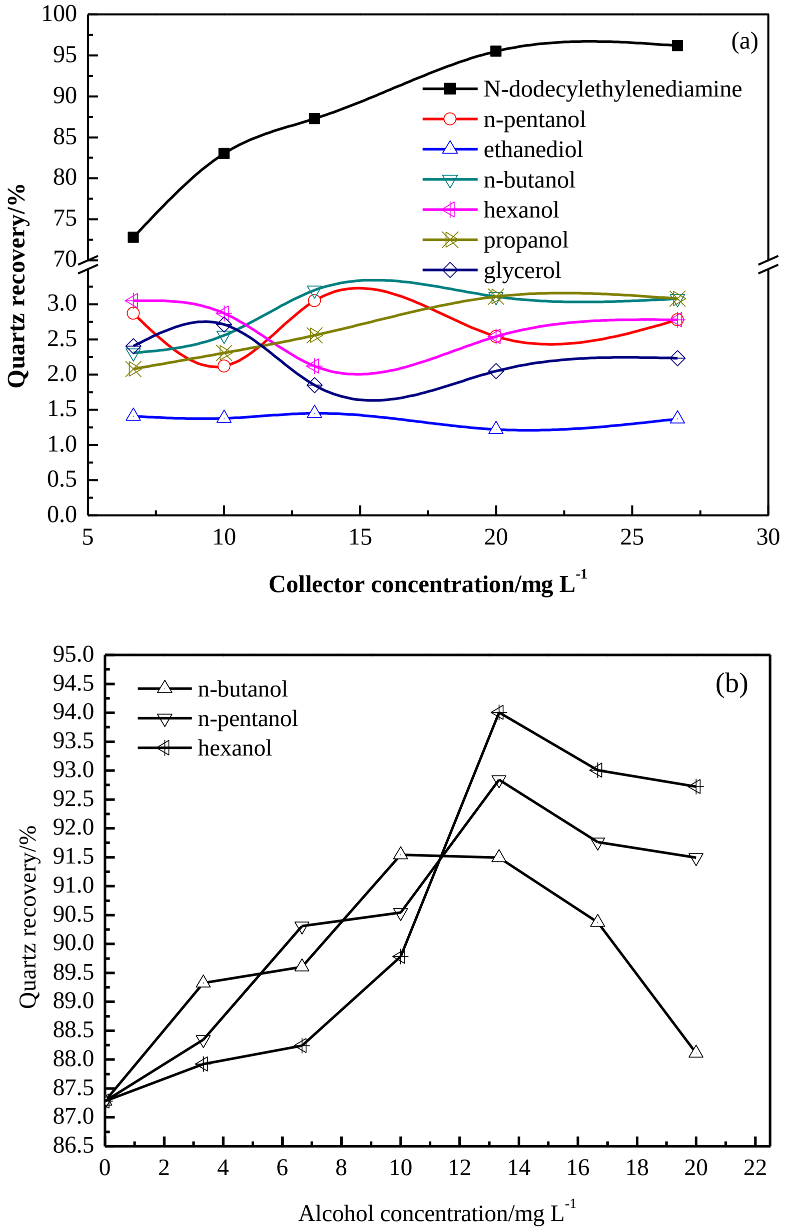
3.1. Froth flotation tests

3.1.1 Effect of alcohol concentration on quartz flotation

The results of collecting performance of ND, alcohols and amine/alcohol mixtures in pure quartz flotation at pH 6-7 was illustrated in Figure 1, in which the collector dosage was increased from

6.67 to 26.67 mg L^{-1}. As shown in Figure 1(a), ND showed strong collecting ability on quartz, and flotation recovery of quartz increased with enhancing collector concentration. Over 95% flotation recovery was achieved when ND concentration was exceeded 20 mg L^{-1}. However, when alcohols were used as collector alone, the recovery of quartz was extremely low, which indicated none collecting ability of alcohols on quartz.

Figure 1(b) and (c) showed the flotation responses of quartz when ND concentration was fixed at 13.33 mg L^{-1} in the presence of different alcohols. It could be concluded that flotation of quartz was increased with alcohol addition. With alcohol concentration increasing, flotation recoveries of quartz sharply increased and then decreased. For most of alcohols, the optimized flotation of quartz was performed when the mass ratio of ND and alcohol was 1:1, namely, the optimal alcohol concentration was 13.33 mg L^{-1}.



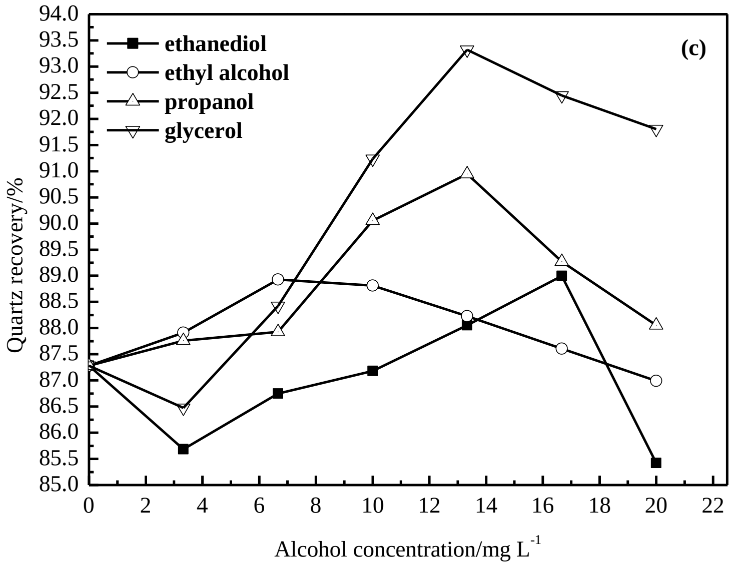


Figure 1. Flotation of quartz as a function of ND, alcohol (a) and amine/alcohol mixture (b and c) concentration.

The flotation recoveries of quartz were improved from 87.28% to 94.01%, 92.84% and 91.50%, respectively, when hexanol, n-pentanol and n-butanol were added. Nevertheless, only a little improvement for quartz flotation recovery was achieved when ethanediol and ethyl alcohol were added. And the maximum flotation recoveries of quartz were 88.93 % for ethyl alcohol and 89.00 % for ethanediol, respectively, when the mass ratios of ND and alcohol were 2:1 and 4:5, respectively.

3.1.2 Effect of alcohol structure on quartz flotation

Molecular structures of collectors are very important in flotation, not only the polar head group but also the hydrocarbon chain [29-31]. Thus, the addition of various alcohols which have different molecular structures may cause different flotation response of quartz. Figure 2 showed the effect of alcohol chain length and number of hydroxyl groups in alcohol on quartz flotation when the collector concentration of amine/alcohol mixture was 26.67 mg L^{-1} and the mass ratio of ND/alcohol was 1:1.

Effect of alcohol chain length on quartz flotation recoveries were shown in Figure 2(a) when amine and alcohol were used at a particular concentration. The results indicated that better quartz flotation recovery was obtained with longer alkyl chain alcohol. With alcohol chain length increasing, flotation recoveries of quartz were enhanced significantly. When hexanol was added into the amine flotation system, flotation recoveries of quartz varied from 87.28% to 94.01%. Hydroxyl groups in alcohol may make negative effect on mineral floatability for a large number of hydrophilic groups (often hydroxyls) are frequently distributed through the depressant molecule [32]. So the effect of the hydroxyl group in alcohol on quartz flotation recovery was also investigated and the corresponding results were shown in Figure 2(b). However, the results revealed that the number of hydroxyl groups in alcohol had little impact on mineral flotation. When glycerol with three hydroxyl groups was added, a better quartz flotation recovery of 93.32% was obtained.

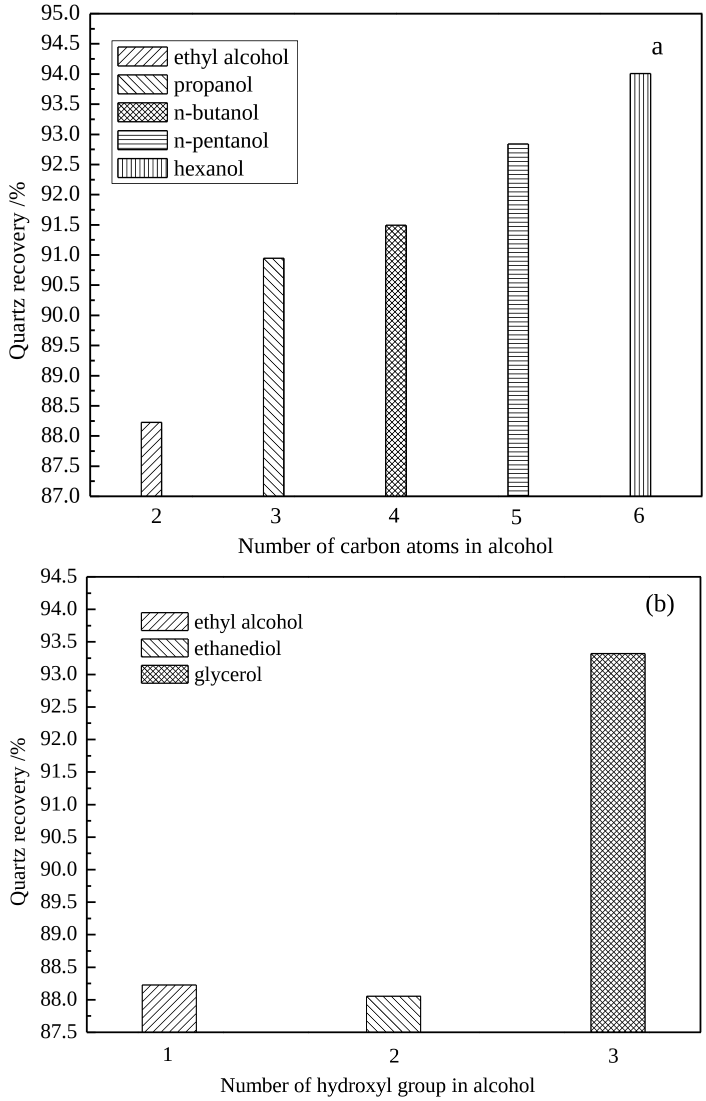


Figure 2. Effect of alkyl chain length (a) and number of hydroxyl group (b) of alcohol on quartz flotation.

Concluded from the results, co-adsorption of alcohols accompanied with amine has taken place to enhance quartz flotation, which has been previously suggested by Vidyadhar et al. [23]. Additionally, the structural variations of alcohol had a significant influence on flotation kinetics and mineral recovery. With enlarging cross sectional area of alcohol, flotation recovery of quartz was increased. With the increase of carbon atom number, the hydrocarbon chain of alcohols became longer and their cross sectional areas were larger [33], thus, quartz flotation recovery got improvement with the increase of alcohol hydrocarbon chain. The cross sectional area of glycerol was 3.06×10^{-19} m^2, which was much larger than that of ethanediol (2.25×10^{-19} m^2) [34] and ethyl alcohol (2.16×10^{-19} m^2). Therefore, much higher flotation recovery of quartz was obtained when glycerol was added.

In general, surface hydrophobicity of the minerals was an important factor to mineral flotation. And the blockage of surface hydroxyl groups by surfactant molecules was an essential factor to affect surface hydrophobicity of the minerals [35]. When ND co-adsorbed with alcohols with larger cross sectional area on quartz surface, they could pack closely on quartz surface and block more surface hydroxyl groups, and thus made the surface more hydrophobic. Therefore, higher quartz flotation recovery was achieved with the increase of alcohol cross sectional area.

3.2. Synergistic adsorption mechanism

3.2.1 Zeta-potential measurements

Zeta potential variations of quartz before and after being conditioned with ND and ND/alcohol mixtures were contrasted and illustrated in Figure 4. In the experiment, both ND and ND/alcohol (1:1, mass ratio) mixture were added at a concentration of 26.67 mg L^{-1}.

Generally, quartz that make up of continuous framework of silicon-oxygen tetrahedron (SiO_4) is a trigonal crystal mineral. When it is ground or crushed, amount of Si-O bounds are broken, resulting in $–Si–O^-$ or Si^+ sites generation on particle surface. Then, quartz surface is hydroxylated with the existence of water in crushing and grinding process for the generation of silanol groups [36]. After that, ionizations become dominant by the pH of the pulp. Adsorption or dissociation of H^+ and OH^- are the controlling factor in the charge mechanism of quartz surface. Thus, quartz surface is usually electronegative. This process could be described as in Figure 3.

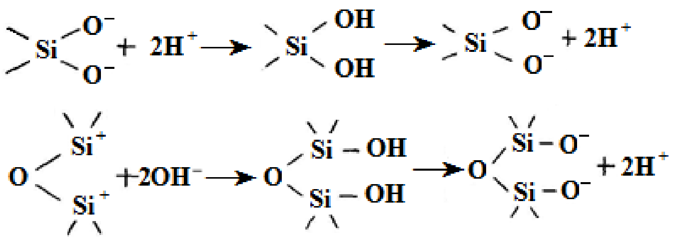


Figure 3. The charging mechanism of quartz surface.

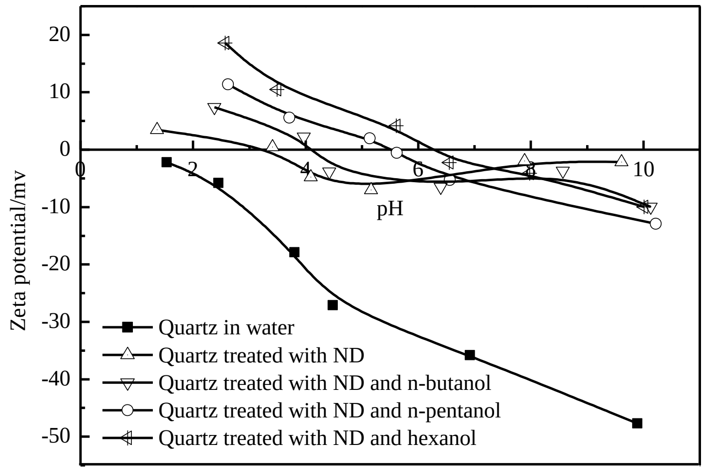


Figure 4. Zeta potentials of quartz before and after being conditioned with ND and alcohols.

Experimental results indicated that zeta potentials of pure quartz, which were found to be negative in the whole experimental range of pH values, were dependent of slurry pH, and its isoelectric point (IEP) was less than 2.00. However, quartz zeta potentials were altered dramatically by the addition of ND, and IEP of quartz was significantly increased to 3.26. The marked shift towards more positive charges of quartz was taken place after ND adsorption, revealing the electrostatic affinity, which was existed between cationic ND molecules and quartz surface, was the chief adsorption force [37]. Furthermore, more positive zeta-potentials of quartz were obtained with the existence of ND/alcohol mixture, indicating the existence of even stronger electrostatic adsorption between amine/alcohol mixture and quartz. Additionally, with the extension of hydrocarbon chain, the IEP of quartz was obtained at a higher pH. And the IEPs of quartz were enhanced to 4.09, 5.50 and 6.27, separately, with ND/n-butanol, ND/n-pentanol and ND/hexanol addition. Thus, even stronger electrostatic adsorption was obtained when longer hydrocarbon chain alcohols were added. Therefore, greater hydrophobicity surface of quartz was obtained with longer hydrocarbon chain, resulting in higher flotation recovery.

Several studies have indicated that hydrocarbon chain length of the surfactant plays a key role in adsorption process due to chain-chain interactions in the Stern plane [38]. Thus, effect of alcohol chain length on △-IEP (the difference value of quartz IEP adsorbing ND with and without alcohol) and flotation recovery of quartz were investigated and shown in Figure 5. From the figure, it could be concluded that the △-IEP and flotation recovery of quartz were dependent on carbon atom number of alcohol. With the increase of alcohol hydrocarbon chain length, higher △-IEP was obtained, indicating higher adsorption affinity between quartz and collector, also related to a systematic decrease in collector hemimicelle concentration [38]. Therefore, flotation recovery of quartz was enhanced with the increasing of alcohol hydrocarbon chain length.

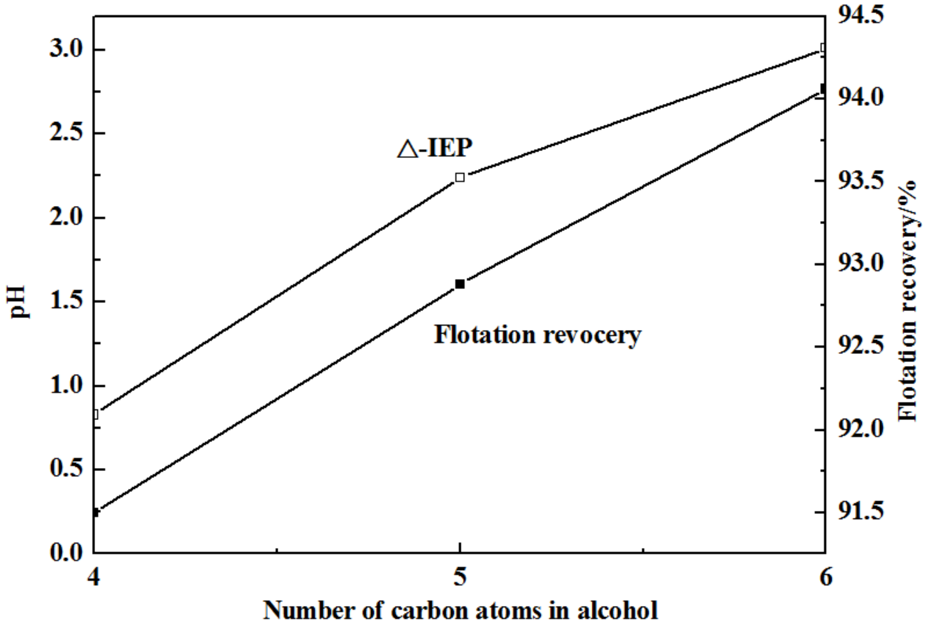


Figure 5. Effect of alcohol chain length on IEP and flotation recovery of quartz.

3.2.2 FTIR studies

FTIR spectra of untreated quartz and these treated with ND (1×10^{-3} mg L^{-1}) and ND/hexanol (1:1, mass ratio) mixture (1×10^{-3} mg L^{-1}) at pH 6–7 were shown in Figure 8.

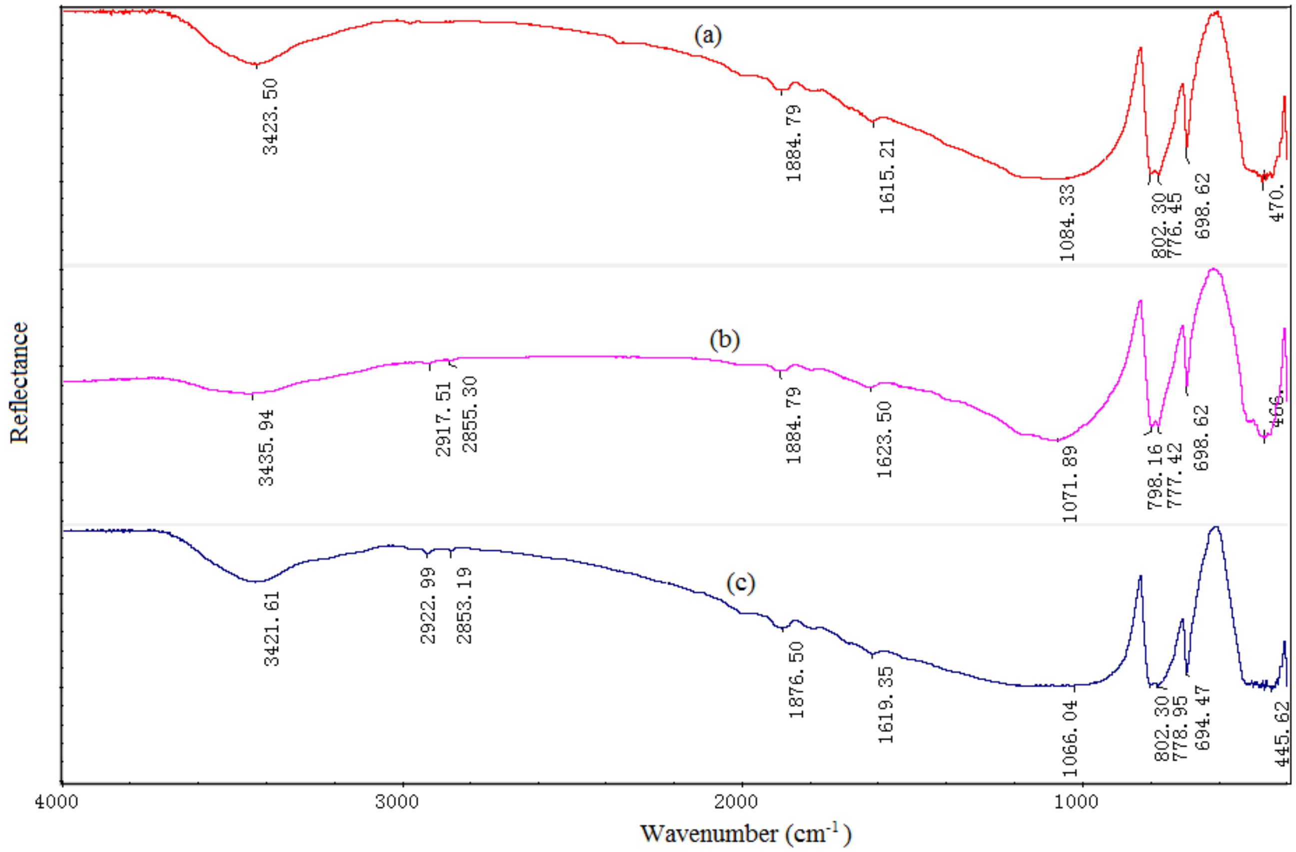


Figure 6. FTIR spectra of quartz before and after being treated with ND and alcohol at pH 6–7. (a) quartz; (b) quartz treated with ND; (c) quartz treated with ND/n–pentanol.

As shown in Figure 8(a), in the spectrum of untreated quartz, the characteristic sharp bands at 1084.33 cm^{-1} and 776.45 cm^{-1} were belong to the asymmetric and symmetric stretching vibration of Si–O, respectively. And band at 470 cm^{-1} were due to the blending vibration of Si–O. The adsorption peak of the hydroxyl group at 3423.50 cm^{-1} was also visible in the figure, indicating crystal water existence in quartz. [39]. Spectrum of quartz treated with ND presented characteristic peaks of –CH stretching, which existed at 2917.15 cm^{-1} and 2855.30 cm^{-1} (Figure 6(b)). This indicated the ND adsorption on quartz surface. However, no diagnostic peaks changed clearly except a red-shift, vibration of Si–O in quartz shifted from 1084.33 cm^{-1} to 1071.89 cm^{-1}, indicating the adsorption of ND on quartz was dominated by physical adsorption [40]. For the spectrum of quartz treated with ND/n–pentanol mixture, there was still no novel characteristic peak generated on quartz surface, but the adsorption peaks shifted to lower wave numbers. This demonstrated that the hydrogen binding adsorption between quartz and ND was strengthened by the addition of alcohol.

4. CONCLUSION

Froth flotation tests indicated that quartz flotation recovery could be enhanced by short chain alcohol addition for synergistic adsorption of ND and alcohol on quartz surface. For most of alcohols, best flotation recovery of quartz was achieved when the mass ratio of ND and alcohol was 1:1. Meanwhile, the structural variations of alcohols had significant influence on flotation kinetics and mineral recovery. The longer of alcohol hydrocarbon chain, the higher flotation recovery was obtained. Zeta-potential measurements indicated that zeta potentials of quartz were more positive in the presence of amine/alcohol mixture than that in the presence of ND alone. Thus, alcohols strengthened the electrostatic adsorption of ND on quartz. Furthermore, longer hydrocarbon chain of alcohols usually resulted in stronger electrostatic affinity. The fact that alcohols enhanced hydrogen binding adsorption between collector and quartz was proved to be true by FTIR measurement because the absorption peaks shifted to much lower wavenumbers in the presence of alcohols.

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