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## 1. Introduction

Ionic liquids (ILs) are salts with a melting point below 100 °C and are usually composed of organic cations and inorganic or organic anions.<sup>1–4</sup> Common cations in ILs include imidazolium, pyrrolidinium, ammonium, and so forth. The unique physical and chemical properties of ILs,<sup>5,6</sup> such as wide solubility range, low melting point, and thermal stability, have led to their increased utilization in separation, electrochemistry, and catalysts.<sup>3,5,7–10</sup> In addition, the properties of ILs can be changed by selecting different groups of cations and anions, which is why ILs are also called “designer solvents”.<sup>11</sup>

ILs are gradually being used more often in flotation processes due to their excellent solubility and non-volatility. Sahoo *et al.* reported the use of tricaprylmethyl ammonium salicylate (TOMAS),<sup>12</sup> Aliquat-336 (C<sub>25</sub>H<sub>54</sub>ClN),<sup>13</sup> Cetyl pyridinium bromide (CPA)<sup>6</sup> in the flotation of quartz. Azizi *et al.* employed tetrabutylammonium bis(2-ethylhexyl)-phosphate ([N<sub>4444</sub>][DEHP]) for the flotation of monazite and bastnäsite, two minerals that are typical rare earth minerals.<sup>14</sup> Li *et al.* employed tetraethylammonium mono-(2-ethylhexyl)2-ethylhexyl phosphonate ([N<sub>2222</sub>][EHEHP]) for the flotation of bastnäsite and its two common gangue minerals, quartz and

hematite.<sup>5</sup> However, the current application of ILs as collectors in froth flotation is still rare, especially for aluminate minerals or aluminosilicate minerals.

The demand for lithium resources is booming, with the rapid production of lithium-ion batteries for electric vehicles. At the same time, a large number of lithium-ion batteries go retired. As a critical raw material categorized by the European Commission,<sup>15,16</sup> lithium in spent lithium-ion batteries needs to be effectively recycled from an economic and environmental perspective and ensure the security of raw material supply. Currently, pyrometallurgical processing is one of the efficient routes to recycle value metals from spent LIBs.<sup>17,18</sup> Copper, cobalt and nickel can be enriched in an alloy and then recovered after the smelting process but lithium transfers to the slag and is currently not well recovered.<sup>17,19</sup> Lithium can often present as an aluminate mineral phase in many slag types, such as those from the Umicore process and those based on Li<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CaO slags.<sup>19–22</sup>

LiAlO<sub>2</sub> has attracted much attention compared to spodumene, an essential lithium-bearing industrial mineral because it has a higher lithium content and does not require high-temperature roasting for crystal transformation. Improving the separation efficiency between LiAlO<sub>2</sub> and its common gangue mineral melilite solid solution (melilite s.s.)<sup>23</sup> via mineral processing approaches is highly beneficial for the subsequent hydrometallurgical process and is essential for improving the pyrometallurgical recovery path for lithium-ion batteries. Previous research has shown that LiAlO<sub>2</sub> can be floated by certain fatty acids/fatty acid soap such as sodium

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oleate, naphthenic acid, and commercial collector Flotinor FS-2, FS-100, and SM-15 produced by Clariant.<sup>20,23</sup>

Oleic acid and its saponification product, sodium oleate, are widely utilized collectors in industrial flotation practice and in fundamental research.<sup>24</sup> Naphthenic acid is comprised of mixed saturated aliphatic and alicyclic carboxylic acids which contain monocyclic ring, dual ring, or alkyl side chain.<sup>25,26</sup> As a by-product of petroleum refining, it is broadly available, and therefore inexpensive compared to oleic acid. In addition, because of its similar properties to that of fatty acids,<sup>26</sup> naphthenic acid can also be treated as a possible substitute for oleic acid or in combination with oleic acid in flotation. Currently it has been used in many flotation studies, such as scheelite<sup>27</sup> or hematite<sup>28</sup> flotation. Flotinor FS-2 is a commercial collector based on a mixture of saturated and unsaturated carboxylic acids<sup>29,30</sup> and is used in flotation studies of different oxide minerals,<sup>29,31</sup> sulfide minerals,<sup>32</sup> and even industrial wastes.<sup>30</sup>

However, when these conventional flotation chemicals are used for flotation, there is a particular risk of polluting the environment. Therefore, the use of new green flotation chemicals is crucial for constructing a circular economy. An alternative process by reducing the needed amount of flotation chemicals *via* a pre-functionalization has been recently reported by our groups.<sup>23</sup>

In this paper, ILs were evaluated for the first time in the flotation of  $\text{LiAlO}_2$  and its gangue mineral melilite s.s. Firstly, reagent screening experiments for single mineral flotation against  $\text{LiAlO}_2$  and melilite s.s. were carried out for seven ILs. From these, IL-1 with an imidazolium cation and a bromide anion and IL-7 with a pyridinium cation and a bromide anion were selected for further flotation experiments (dosage, pH). Flotation experiments were also conducted using naphthenic acid, a conventional fatty acid-based collector, and FS-2, a commercial collector in order to compare the results with the ILs. Moreover, the effects of different counter-anions in the ILs on the flotation were evaluated. Finally, a pre-functionalization was also explored with modified cholesterol derivatives, comparing the effect of cholesteryl sulfate and cholesterylphosphate on the flotation of  $\text{LiAlO}_2$  and melilite s.s. This study is vital for further optimizing lithium recovery from the pyrometallurgical recycling path of lithium-ion batteries and the flotation of primary minerals such as aluminosilicates.

## 2. Materials and methods

### 2.1. Experimental materials

$\text{LiAlO}_2$  (Sigma-Aldrich) and melilite s.s. were employed for flotation experiments. The under 63  $\mu\text{m}$  sieve product of  $\text{LiAlO}_2$ , was used for flotation tests. After grinding, the melilite ore, which came from Vata de Sus, Hunedoara, Romania, was further sieved and the product under 63  $\mu\text{m}$  sieve was sampled and also employed for flotation. The chemical analysis (Table 1) and the X-ray powder diffraction measurement were performed on the sample. According to the XRD analysis (see ESI, p. S1†), besides the main phase melilite s.s., there are also some impurities such as merwinite, wollastonite, and calcite.

Table 1 Chemical composition of melilite s.s.

	Content, %
$\text{Na}_2\text{O}$	0.2
$\text{MgO}$	4.1
$\text{Al}_2\text{O}_3$	15.99
$\text{SiO}_2$	27.49
$\text{P}_2\text{O}_5$	0.02
Cl	0.08
$\text{K}_2\text{O}$	0.02
$\text{CaO}$	31.88
$\text{TiO}_2$	0.409
$\text{MnO}$	0.04
$\text{Fe}_2\text{O}_3$	3.06

The used ILs are listed in Table 2 and are abbreviated as IL-1 to IL-7. These ILs were synthesized according to literature procedures. IL-1,<sup>33</sup> IL-5 and IL-7,<sup>34</sup> IL-3 and IL-4,<sup>35</sup> IL-2 (ref. 36) and IL-6a<sup>37</sup> and IL-6b.<sup>38</sup>

FS-2 (Clariant), naphthenic acid (Fluka) and pine oil (American Cyanamid) were purchased from commercial courses. Naphthenic acid was saponified by adding NaOH to obtain sodium naphthenate.

### 2.2. Methods

**2.2.1. Microflotation.** A modified Hallimond tube (Fig. 1) produced by HI-ALOQUIMICA, Brazil, was used to perform flotation tests. The modified Hallimond tube consists of three parts and it is easy to disassemble them for cleaning. The air can flow into the tube through a piece of porous glass (medium-pore fritted glass) installed in the bottom part. In addition, a small magnetic stirrer bar was placed at the bottom to stir the slurry. The IL screening experiments were conducted at natural pH and ambient temperature and the sample amount for each test was 2 grams. Firstly, the slurry was stirred in a beaker for 1

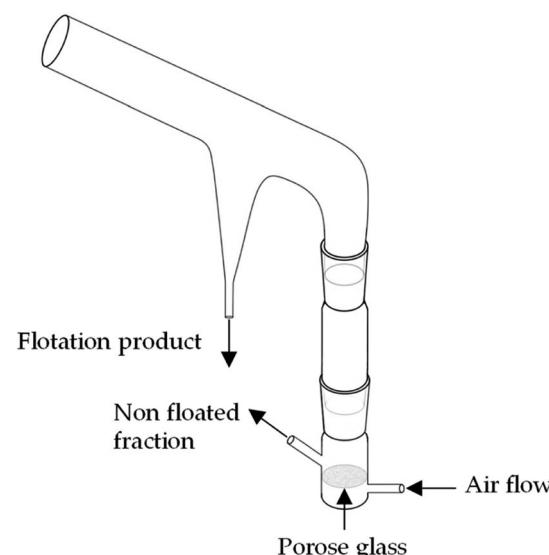


Fig. 1 Sketch of the modified Hallimond tube.<sup>23</sup>



minute, then the conditioning time was also 1 minute after the reagents were added. The slurry was then transferred to a Hallimond tube for flotation. The airflow rate of each test was controlled to be around  $2.1 \pm 0.2 \text{ L h}^{-1}$ , and the rotation speed was controlled to be 500 rpm. The flotation time lasted for 3 min.

In further flotation experiments, IL-1 and IL-7, the two ionic liquids with the highest  $\text{LiAlO}_2$  yields in the screening tests, were selected for flotation tests at three different pHs: natural pH,  $\text{pH } 7 \pm 0.2$ , and  $\text{pH } 9 \pm 0.2$ . The pH was stabilized with a Britton-Robinson buffer consisting of 0.04 M boric acid, 0.04 M phosphoric acid and 0.04 M acetic acid and the desired pH was achieved by adding 0.2 M NaOH.

The collector dosages for  $\text{LiAlO}_2$  flotation were  $0 \text{ g t}^{-1}$ ,  $50 \text{ g t}^{-1}$ ,  $100 \text{ g t}^{-1}$ ,  $150 \text{ g t}^{-1}$ ,  $200 \text{ g t}^{-1}$ ,  $250 \text{ g t}^{-1}$  and  $300 \text{ g t}^{-1}$ . According to our previous research, the yield of  $\text{LiAlO}_2$  is much higher than that of melilite s.s. at the same amount of sodium oleate.<sup>23</sup> Therefore, in this paper, higher dosages of collectors ( $0 \text{ g t}^{-1}$ ,  $300 \text{ g t}^{-1}$ ,  $500 \text{ g t}^{-1}$ ,  $1000 \text{ g t}^{-1}$  and  $2000 \text{ g t}^{-1}$ ) were selected for melilite s.s.

After flotation, the froth product and the pulp product were weighed separately. The flotation effect was compared by the yield of the froth product. The difference in yield of the same collector for different minerals forms the basis for selective flotation separation. The greater the difference, the better the separation efficiency to be expected.

The pre-functionalized samples were not treated with collectors.

**2.2.2. Analytical methods.** ATR-IR-spectra were recorded on an Alpha-T IR (Bruker) with a platinum ATR-unit and diamond crystal. Vibrations are given in  $\text{cm}^{-1}$ .

## 3. Results and discussions

### 3.1. Ionic liquids screening

Through the screening of the seven ILs, it was observed that IL-1, 2, 3, 4, 5, 7 had a significant collecting effect on  $\text{LiAlO}_2$  compared to the flotation tests without the collector. Their collecting ability on melilite s.s. was much weaker than that of

$\text{LiAlO}_2$ . The IL-1, 2, 3 contained an imidazolium cation, while IL-5, 7 contained a pyridinium cation. The anion in IL-1, 5, 7 was bromide, while IL-2, 4 had a methanesulfonate anion. IL-6 was not available for screening tests because it was difficult to dissolve in water.

The principle of micro-flotation reagents screening was that the collection ability of the reagents for  $\text{LiAlO}_2$  and melilite s.s. should be considered at the same time. The flotation yield of the reagent for  $\text{LiAlO}_2$  should be as high as possible, yet its flotation yield for melilite s.s. should be the opposite.

Since IL-1 and IL-7 contributed to a high yield of about 40% for the flotation of  $\text{LiAlO}_2$ , and the difference in yield was reflected in the flotation of melilite s.s., these two reagents were further investigated in subsequent flotation experiments (Fig. 2).

### 3.2. Effects of conventional collectors and ILs on the flotation of $\text{LiAlO}_2$ and melilite s.s.

At natural pH, which is 11, the flotation yields of both conventional fatty acid-based collectors against  $\text{LiAlO}_2$  were better than those of IL-1 and IL-7. The highest yield of 66.9% for  $\text{LiAlO}_2$  flotation was obtained with the collector FS-2 when the dosage was  $250 \text{ g t}^{-1}$ .

The flotation yields of both fatty acid collectors against melilite s.s. were similarly larger than those of IL-1 and IL-7 at natural pH. FS-2 and naphthenic acid flotation yields against melilite s.s. were close to 53% when the collector dosage was  $2000 \text{ g t}^{-1}$ . The lower performance of the ionic liquids may be explained due to their lower hydrophobic character compared to the applied conventional collectors (Fig. 3).

At pH 9 both conventional collectors have higher flotation recovery than IL-1 and IL-7 for  $\text{LiAlO}_2$ . The yields of  $\text{LiAlO}_2$  ranged between 38.8% and 45.1% when FS-2 was used and dropped to 31.3–43.6% when naphthenic acid was employed.

A similar trend was observed in the flotation of melilite s.s. The yields were much lower when using IL-1 and IL-7 than conventional collectors. With FS-2, the yields ranged from 40.8% to 43.5% and when naphthenic acid was used, the yields of melilite s.s. ranged from 39.3% to 46.2% (Fig. 4).

The flotation yields of both conventional collectors against  $\text{LiAlO}_2$  were not satisfactory at pH 7, ranging from 39% to 42.2%. Nevertheless, ILs remained less effective than conventional collectors for  $\text{LiAlO}_2$ . The yields were between 28.4% and 31.5% when IL-2 was used, and the yield of IL-7 was even below 25%.

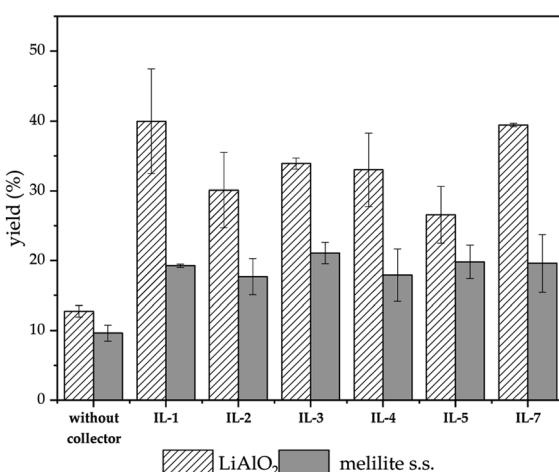


Fig. 2 Screening tests for different ionic liquids.

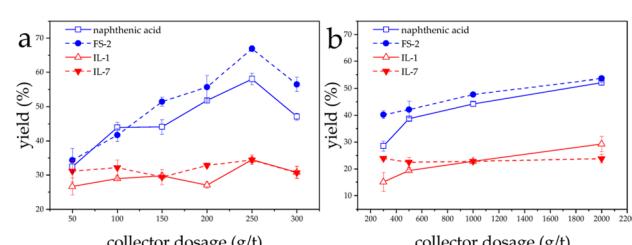


Fig. 3 Effect of collector dosage on flotation of  $\text{LiAlO}_2$  (a) and melilite s.s. (b) using different collectors at natural pH.



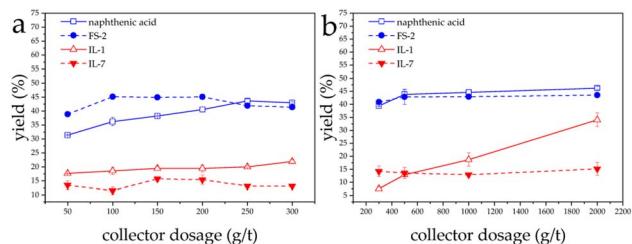


Fig. 4 Effect of collector dosage on flotation of  $\text{LiAlO}_2$  (a) and melilite s.s. (b) using different collectors at pH 9.

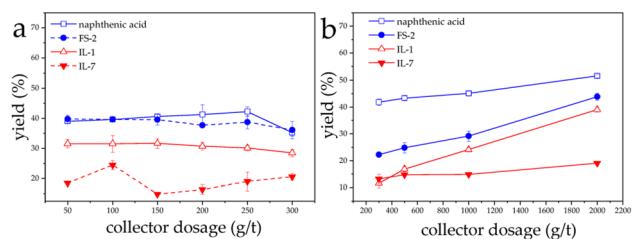


Fig. 5 Effect of collector dosage on flotation of  $\text{LiAlO}_2$  (a) and melilite s.s. (b) using different collectors at pH 7.

For melilite s.s. flotation, both conventional collectors also showed higher yields at pH 7 than IL-1 and IL-7. Yields of melilite ranged between 22.2% and 43.8% when FS-2 was applied. With naphthenic acid melilite s.s. was isolated between 41.8% and 51.5% (Fig. 5). Obviously, the natural pH of  $\text{LiAlO}_2$  at 11 is needed to have a sufficient amount of deprotonated carboxylic acids present in the system. This explains the strong influence of the pH values on the carboxylic acid collector. The presence of carboxylate leads to a stronger interaction with these collectors with the surface of the mineral.

After being treated with different collectors, the IR-spectra of  $\text{LiAlO}_2$  displayed a new band at  $1360\text{--}1380\text{ cm}^{-1}$ . The appearance of this new band might be due to chemisorption according to our previous research (Fig. 6).<sup>23</sup>

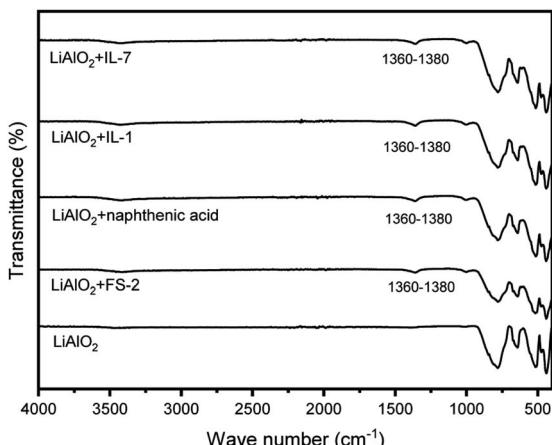


Fig. 6 FT-IR measurement of  $\text{LiAlO}_2$  treated with different collectors at natural pH.

### 3.3. Comparation of bromide and chloride

Different anions in ILs can influence their viscosity<sup>39</sup> which thus can affect the flotation yield. Therefore, it was decided to perform flotation experiments with two different anions,  $\text{Br}^-$  and  $\text{Cl}^-$ , to compare their effects on the flotation yield. As shown in Fig. 7, when the cation in the IL was 1-ethyl-3-methylimidazolium (EMIM), the two anions did not have a great influence on the flotation yield and the yield of  $\text{LiAlO}_2$  was very close. However, when the cation in the ionic liquid was 1-methyl-3-octylimidazolium (OMIM), the anion  $\text{Cl}^-$  had a higher yield of  $\text{LiAlO}_2$  than  $\text{Br}^-$ . This is interesting since that harder anion leads to a better result. It would have been reasonable to assume that the softer anion is superior, because the overall IL would be more hydrophobic. It could be that the harder chloride anions could form more easily a layer over the  $\text{LiAlO}_2$  surface due to the better interaction with the hard Li and Al ions present on the surface of the mineral compared to the softer bromide anion. The anion layer could then bind the lipophilic OMIM cation easier on the surface layer.

### 3.4. Mixture of ILs and conventional collector

When specific flotation reagents are mixed in certain proportions, a synergistic effect can occur with the flotation effect better than that of a single reagent.<sup>40</sup> For example, Xu *et al.* reported a mixed anionic and cationic collector for the flotation of spodumene, where the anionic collector was sodium oleate, and the cationic collector was dodecyl trimethyl ammonium chloride (DTAC). After adding the mixed collector in the artificially

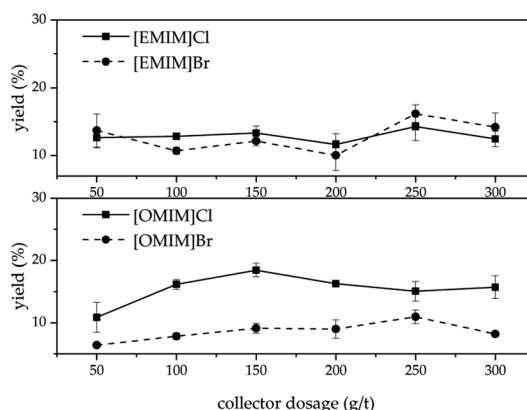


Fig. 7 Effect of  $\text{Br}^-$  and  $\text{Cl}^-$  in ionic liquids on flotation yield.

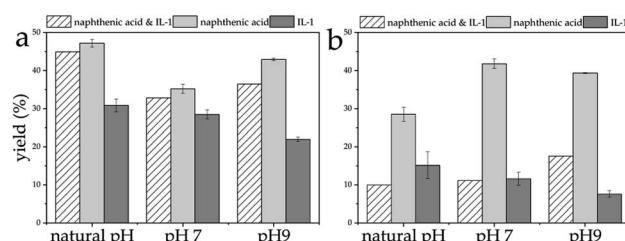


Fig. 8 Flotation yield of  $\text{LiAlO}_2$  (a) and melilite s.s. (b) by mixed collector - naphthenic acid and IL-1 at different pH.



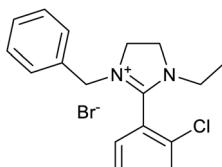
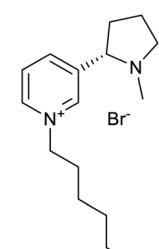
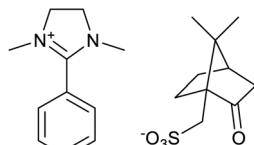
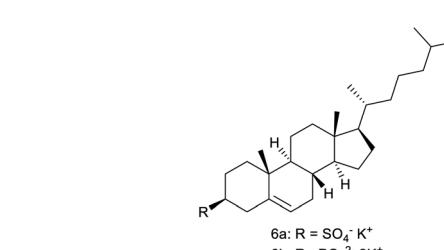
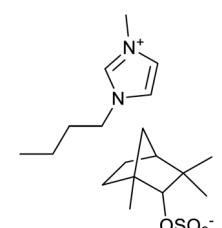
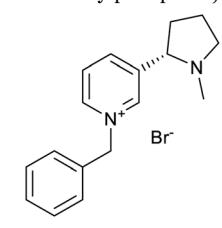
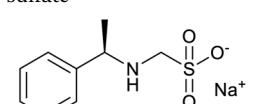
mixed mineral system, the  $\text{Li}_2\text{O}$  grade increased to 5.57%. If only sodium oleate was used, the  $\text{Li}_2\text{O}$  grade decreased to 4.13%.<sup>40</sup> Bayat *et al.* tried a mixture of three cationic collectors,

AERO 3030C, AERO 801 and AERO 825, for the feldspar flotation and the mixed collector exhibits better selectivity than the single one. The trace elements of the main impurity, Ti and Fe-content in the concentrates, are lower than that with the single collector.<sup>41</sup> Xu *et al.* reported a mixed anionic and non-ionic collector for the separation of spodumene and feldspar in an artificial mixed mineral micro-flotation, where the anionic collector was sodium oleate, and the non-ionic collector was dodecyl succinimide. The mixed collectors achieve a Li recovery of 82.67%, which is higher than the single collector used (68.11% recovery).<sup>42</sup>

The flotation yields were not satisfactory when a single IL as a collector was used. It may be because the carbon chain length of the ionic liquid was not long enough. ILs are generally not surface active, but when the number of hydrophobic alkyl

Fig. 9 Flotation yield of  $\text{LiAlO}_2$  (a) and melilite s.s. (b) by mixed collector – FS-2 and IL-1 at different pH.

Table 2 Applied ionic liquids

IL Structure and name	IL Structure and name
	
1 3-Benzyl-2-(2-chlorophenyl)-1-ethyl-4,5-dihydro-1 <i>H</i> -imidazol-3-ium bromide	
	
2 1,3-Bimethyl-2-phenyl-4,5-dihydro-1 <i>H</i> -imidazol-3-ium-(7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonate	6a: potassium-(3 <i>S</i> ,8 <i>S</i> ,9 <i>S</i> ,10 <i>R</i> ,13 <i>R</i> ,14 <i>S</i> ,17 <i>R</i> )-10,13-dimethyl-17-(( <i>R</i> )-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1 <i>H</i> -cyclopenta[ <i>a</i> ]phenanthren-3-yl sulfate(potassium cholestrylsulfate) 6b: phosphate(potassium cholestryolphosphate)
	
3 1-Butyl-3-methyl-1 <i>H</i> -imidazole-3-ium-1,3,3-trimethylbicyclo[2.2.1]heptan-2-yl sulfate	
	
4 Sodium-( <i>R</i> )-((1-phenylethyl)amino)methanesulfonate	



carbon chain atoms on the IL exceeds 8, the ionic liquid can be more surface-active.<sup>43</sup> Therefore, the next was to mix the IL with a fatty acid-based collector.

By mixing conventional collectors with ILs for flotation, the yield of the combination of naphthenic acid and IL-1 for  $\text{LiAlO}_2$  at natural pH was higher than that of IL-1 alone but slightly lower than that of naphthenic acid. The yield of the combination of naphthenic acid and IL-1 for melilite s.s. at natural pH was much lower than that of the single collector naphthenic acid and also lower than that of IL-1. The yield difference between  $\text{LiAlO}_2$  and melilite s.s. reached about 35% for this collector mixture. The flotation yield difference between  $\text{LiAlO}_2$  and melilite s.s. at natural pH with naphthenic acid was only about 18%. At pH 7, the yield difference between  $\text{LiAlO}_2$  and melilite s.s. reached 21% with the mixed collectors. The difference in flotation yield between  $\text{LiAlO}_2$  and melilite s.s. at pH 7 using naphthenic acid was about 6%. At pH 9, the yield difference between  $\text{LiAlO}_2$  and melilite s.s. reached about 19% with the mixed collectors. The flotation yield difference between  $\text{LiAlO}_2$  and melilite s.s. at pH 9 using naphthenic acid was about 3.5% (Fig. 8).

Another collector combination, FS-2 and IL-1 showed a similar trend. The yield of the combination of FS-2 and IL-1 collector for  $\text{LiAlO}_2$  at natural pH was higher than that of the IL-1, but lower than that of naphthenic acid. The yield difference between  $\text{LiAlO}_2$  and melilite s.s. reached about 31% for this mixed collector. The difference in flotation yield between  $\text{LiAlO}_2$  and melilite s.s. at natural pH with FS-2 was about 17%. At pH 7, the yield difference between  $\text{LiAlO}_2$  and melilite s.s. reached about 35% with the mixed collectors. The difference in flotation yield between  $\text{LiAlO}_2$  and melilite s.s. pH 7 was about 14% using FS-2. At pH 9, the yield difference between  $\text{LiAlO}_2$  and melilite s.s. reached about 7% with these mixed collectors. The difference in flotation yield between  $\text{LiAlO}_2$  and melilite s.s. at pH 9 using FS-2 was about 19% (Fig. 9).

### 3.5. Pre-functionalized cholesterol

Since IL-6 was insoluble in water,  $\text{LiAlO}_2$  and melilite s.s. were pre-functionalized with cholesterylsulfate and cholesterylphosphate in advance. The advantage of this method is that the materials can be pre-treated in advance, making it unnecessary to continue adding the collector in the subsequent flotation.<sup>23</sup>

Through flotation experiments, a difference in the flotation yield of  $\text{LiAlO}_2$  and melilite s.s. after the pretreatment effect of cholesterylsulfate, about 25%, as shown in Table 3.  $\text{LiAlO}_2$  and melilite s.s. after cholesterylphosphate pretreatment showed their strong hydrophobicity (Table 3).

**Table 3** Flotation yield of cholesterylsulfate pre-functionalized  $\text{LiAlO}_2$  (a) and melilite s.s. (b)

Pre-functionalized samples		Yield, %
$\text{LiAlO}_2$	Chol. + $\text{SO}_4$	53.51
Melilite s.s.	Chol. + $\text{SO}_4$	28.49

## 4. Conclusions

Different ILs were investigated for the first time in the flotation of  $\text{LiAlO}_2$  and its gangue mineral melilite s.s. A significant influence of the hardness of the counter anions chloride and bromide of the ILs in the flotation process was observed. Furthermore, it was possible to apply ILs as additives with known collectors in order to increase the selectivity of the flotation process significantly. This study is vital for the further optimization of lithium recovery from the pyrometallurgical recycling path of lithium-ion batteries and the flotation of primary minerals such as aluminosilicates.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

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