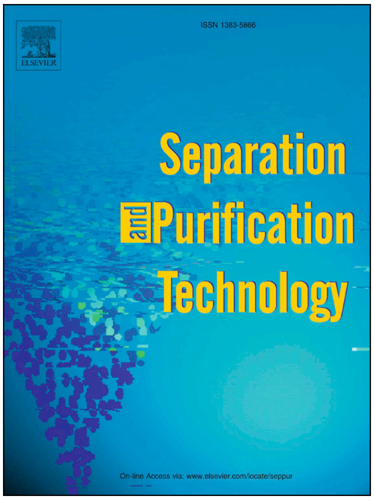

Froth flotation separation of lepidolite ore using a new Gemini surfactant as the flotation collector

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PII: S1383-5866(21)00832-7
DOI: https://doi.org/10.1016/j.seppur.2021.119122
Reference: SEPPUR 119122

To appear in: *Separation and Purification Technology*

Received Date: 30 March 2021
Revised Date: 13 May 2021
Accepted Date: 7 June 2021

Please cite this article as: Z. Huang, S. Shuai, H. Wang, R. Liu, S. Zhang, C. Cheng, Y. Hu, X. Yu, G. He, W. Fu, Froth flotation separation of lepidolite ore using a new Gemini surfactant as the flotation collector, *Separation and Purification Technology* (2021), doi: https://doi.org/10.1016/j.seppur.2021.119122

Froth flotation separation of lepidolite ore using a new Gemini surfactant as the flotation collector

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Abstract

The global lithium supply and demand in this century is accelerated by the energy transition from carbon-based fossil fuels to renewable energy where electrical energy storage and electric vehicles heavily depend on the lithium-ion battery. The lepidolite is one of the main resources for extracting lithium, and it is usually enriched by froth flotation separation technology. However, the traditional lepidolite collector is monomer surfactant with only a single hydrophobic group and hydrophilic group, which usually leads to the low flotation separation efficiency. Therefore, to achieve the flotation separation of lepidolite ore more efficiently, in this work, an amine-based Gemini surfactant, hexanediyl-α, ω-bis (Dimethyldodecylammonium bromide) (HBDB), was synthesized, and compared with the conventional single molecule collector dodecylamine (DA). The experimental results show that the optimum pH value of flotation is 3, and the optimum dosage of HBDB and DA are 150 g/t and 300 g/t respectively. In bench-scale flotation experiments, compared with the conventional

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monomer DA collector (350 g/t), the Gemini HBDB with only 1/2 dosage of DA (175 g/t) increased the recovery of lepidolite by 16.18%. Economic calculation for a lepidolite ore plant, 1500 t/d, demonstrating that using Gemini HBDB can gain more about $ 8.2 million USD per year than using traditional unimolecular DA. Accordingly, this study provides a new and highly efficient collector for the flotation separation of lepidolite ore.

Keywords: Flotation; Gemini surfactant; Clay minerals; Lepidolite

1. Introduction

At present, with the increasing maturity of lithium battery technology, the demand of lithium metal for people is growing rapidly [1-5]. The economic enrichment of lithium has been found in brine, rocks and clays all over the world [6-8]. However, due to the continuous depletion of the lithium mineral and the high cost of extracting lithium from brine, the selective enrichment of lithium-containing clay has become an area of growing concern [9-11]. There are hundreds of lithium-containing minerals in nature, however, there is only a few of which have economic values, such as lepidolite [13-15].

The lepidolite, a clay mineral of the mica group, froth flotation is the most effective physical and chemical separation method to obtain lepidolite concentrate, and the flotation collector is the core factor of the technology [16-20]. Cationic collector is usually used as collector for flotation of lepidolite, among which dodecylamine (DA) is more commonly used [21-24]. Pugh et al. first used dodecylamineas collector to study the effect of pH on mica flotation and correlation with thin aqueous foam film and surface force measurements [25]. Xu studied the adsorption mechanism of dodecylamine surfactant on the surface of muscovite by molecular dynamics simulation [26]. Wei et al. studied the flotation characteristics and action mechanism of mixed collector SOL/DA for lepidolite under the condition that the performance of a single amine collector has certain limitations [27]. Based on the literature review, the collectors commonly used in lepidolite flotation are monomers surfactants, which means the surfactant molecules contain only one hydrophobic/ hydrophilic group [28-30]. As a result, the flotation is not efficient, due to its low selectivity, and large reagent dosage [31]. In addition, when the wastewater containing primary fatty acid amine, quaternary ammonium salt and other surfactants are discharged into the environment in large quantities, it will cause harm to the aquatic ecosystem [32].

Gemini surfactants are a kind of compounds which consisting of two hydrophilic head groups and two hydrophobic tail groups connected by spacers at or near the head group [33-36]. In comparison to the ordinary monomolecular surfactants, Gemini surfactants have outstanding surface properties, such as extremely low critical micelle concentration, better water solubility, excellent wettability, lower Krafft point and foaming properties [37-40]. Its unique properties make it widely used in various industries, such as cosmetics, personal care products, paint additives, pesticides, nanotechnology, petroleum, food industry, biological insecticides, bactericidal and anti-fungal agents, phase transfer catalysts and other fields [41-44].

Nonetheless, few reports on the use of Gemini surfactants as collector for the flotation of clay mineral lepidolite, therefore, it would be worth comparing its flotation performance with the conventional collector with single functional group. In this work, a novel amine-based Gemini surfactant, hexanediyl-α, ω-bis (Dimethyldodecylammonium bromide) (HBDB), was synthesized and characterized by fourier transform infrared spectroscopy (FTIR) and nuclear resonance spectroscopy (NMR). Then, the flotation experiment was conducted under the condition of the optimal pH value and the dosage of reagent to explore the superiority of HBDB as an efficient collector over the traditional single molecule collector DA.

2. Materials and methods

2.1. Materials

The lepidolite ore used in flotation separation tests was got from Yichun Tantalum & Niobium Mine in China. The mineralogical analysis of the lepidolite ore shows that the main components of the ore were largely 27.83% lepidolite, 34.59% albite, 17.04% quartz, 7.15% sericite, 5.23% potassium feldspar, 5.06% kaolinite, 1.37% pyrite, 1.04% imonite and 0.69% magnetite. The actual ore flotation test was carried out at 25 °C. The result of chemical study of lepidolite ore is listed in **Table 1**. The pure lepidolite for contact angle measurements and zeta potential measurements was obtained by Donghaijingyuan Crystal Gem Company, Jiangsu Province (China) and its result of X-ray diffraction (XRD) is shown in **Figure 1**.

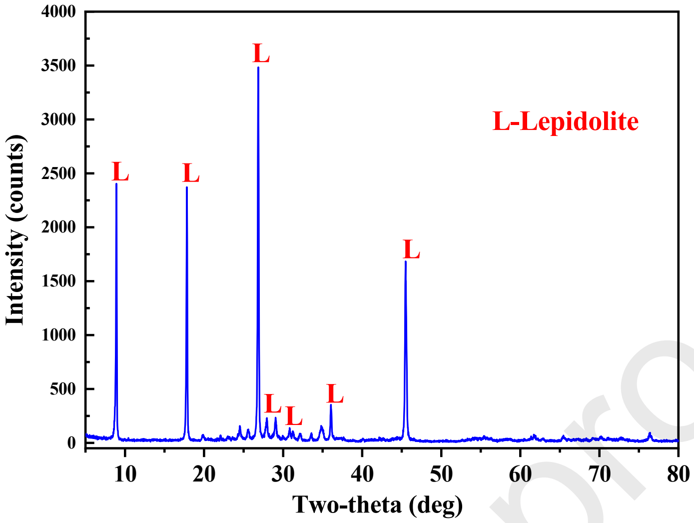


Figure 1 The X-ray diffraction of pure lepidolite

Table 1 The result of chemical study of lepidolite ore (wt%)

Li_2O	SiO_2	Al_2O_3	K_2O	Na_2O	Fe	Mn	L.O.I.
1.18	67.24	19.77	5.03	3.79	0.16	0.15	2.68

Amine-based Gemini surfactant, hexanediyl-α, ω-bis (dimethyldodecylammonium bromide) (HBDB), a collector synthesized by our lab. **Figure 2** illustrates the chemical structures of the amine-based Gemini surfactant HBDB and traditional monomolecular surfactants 1-dodecylamine DA. Since all agents are of analytical grade, they employed in this study do not need further refinement. The Nuclear magnetic resonance (NMR) data were recorded on a 400 MHz Bruker Avance II spectrometer equipped with a 5-mm $^{13}C/^{1}H$ cryoprobe, using a sampleXpress^{TM} automation sample changer. The structure of HBDB was investigated by FTIR analysis using an AVATAR 370 spectrometer (Thermo Nicolet Corporation/USA).

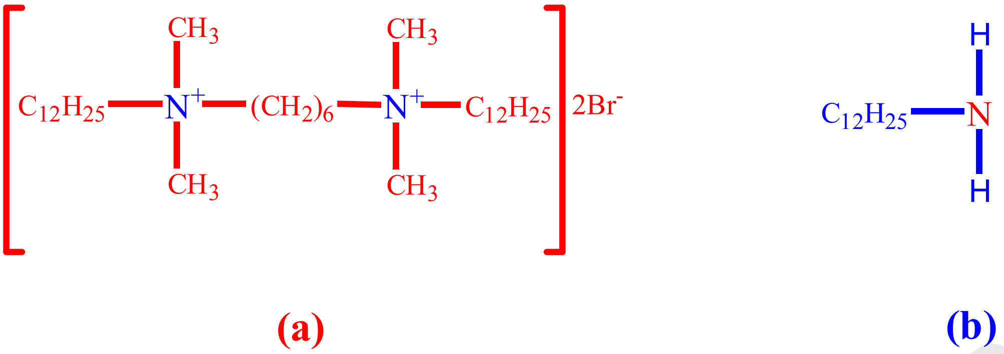


Figure 2 The chemical structures of HBDB (a) and DA (b)

2.2. Bench–scale flotation tests

The flotation separation tests were performed by XFD single cell flotation machine (Changchun Prospecting Machinery, China) with 1500 mL cubage of cell for rougher flotation, and for cleaner flotation was 0.75 dm^3. Froth flotation tests of lepidolite were carried out at temperatures of 25 ℃, using Amine-based Gemini surfactant HBDB and conventional unimolecular surfactant DA as collectors. Adding 500 g lepidolite and 1000 mL tap water to the 1500 mL flotation cell, keep stirring for 3 min to get a uniformly mixed pulp. After that add the collector immediately and stir for 4 min. The operation of air inflation and flotation were carried out for 8 min [27]. In flotation separation test, the froths loaded with lepidolite rose to the pulp surface to separate the lepidolite from the lepidolite ore. Finally, the obtained lepidolite concentrate products were dried, weighed and detected for Li_2O grade. The schematic diagram of flotation process is shown in **Figure 3**.

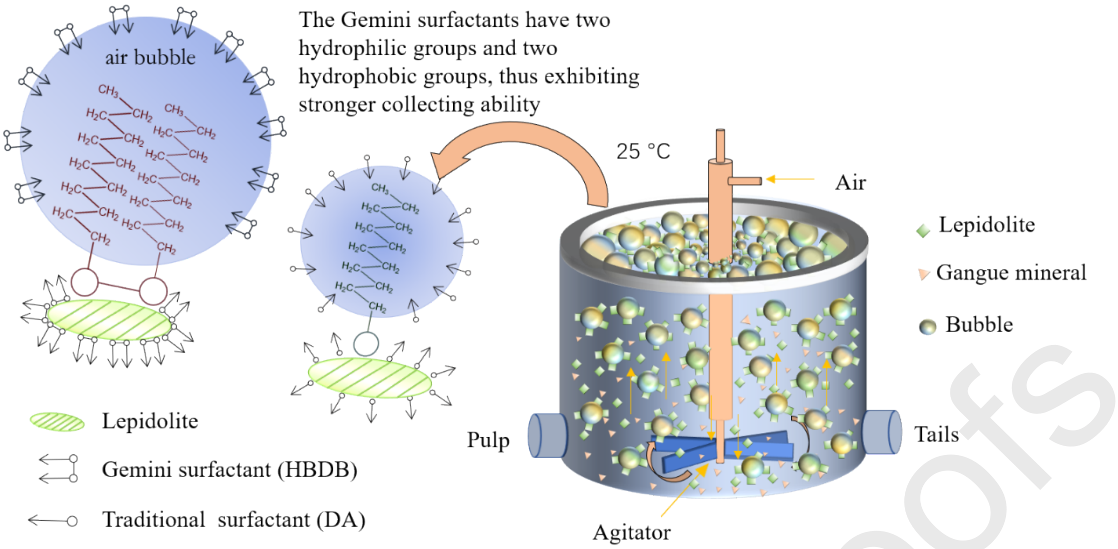


Figure 3 The schematic diagram of flotation behavior

2.3. Contact angle measurements

Under the condition of pH=7, the Kruss DSA 100 instrument (Germany), which was used to measure the contact angles of lepidolite surfaces treated by different concentration of HBDB and DA respectively. For each measurement, a freshly isolated lepidolite flake should be immersed in 30 mL designed concentration of collector solution for a span of 20 min. Whereafter, take it out, dry, and prepare for the measurement of contact angle.

2.4. Zeta potential measurements

Zeta-potentials of minerals were measured using a Brookhaven Zetaplus zeta potential analyzer (USA). Adding a sample of 50 mg of the lepidolite below 5 μm to 30 mL aqueous solution with or without 2.0×10^{-4} mol/L HBDB/DA, stirred for 5 min, adjusted pH and measured in proper sequence. The prerequisite for all the measurements were conducted in a 0.1 mol/L background electrolyte solution of KNO_3. The agitated suspension was sampled to record the zeta-potential. The results presented were the average of three independent measurements with a typical variation of ±2 mV.

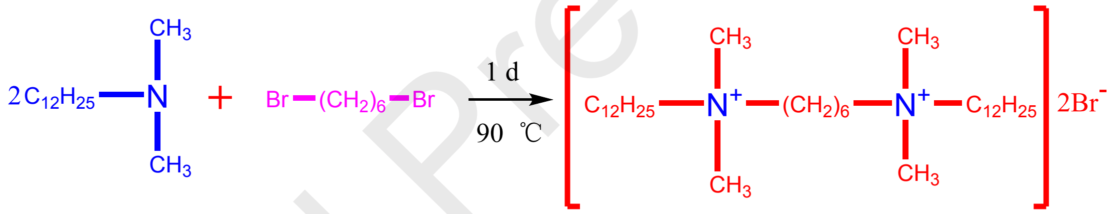
2.5. Economic calculation

Economic calculation was carried out on a medium-scale lepidolite ore processing plant. According to the feed of 1500 t/d and the actual production days per year of 330, the cost of traditional reagent and new reagent and the increased profit of the product were calculated.

3. Results and discussion

3.1. Synthesis of HBDB

Figure 4 shows the synthesis of amine-based Gemini collector HBDB. A mixture of lauryldimethylamine (***1***; 51.22 g, 0.24 mol) and 1, 6-dibromo-hexan (***2***; 24.40 g, 0.1 mol) was placed in the three-necked flask containing ethanol (130 mL), then reacted under reflux for 1 day. In order to obtain pure hexanediyl-α, ω-bis (dimethyldodecylammonium bromide) (***3***, 58.74 g, 0.087 mol), the product was distilled under reduced pressure, washed with 30 mL ethyl acetate, recrystallized by 150 mL acetic acid ethyl ester/15 mL ethanol, and finally dried in vacuum.



[1] [2] [3]

Figure 4 Synthesis equation of HBDB

Hexanediyl-α, ω-bis (dimethyldodecylammonium bromide) (***3***, HBDB), a white powder, yield was 87.58%. The result of NMR analysis is showed in **Figure 5**. 400 MHz ^{1}H NMR (chloroform-d, TMS, ppm): δ 0.84 (t, 6H, J=6.8 Hz, 2 CH_3), 1.18~1.33 (m, 36H, 18 CH_2), 1.53 (m, 4H, 2 CH_2), 1.67 (m, 4H, 2 CH_2), 1.95 (m, 4H, 2 CH_2), 3.34 (s, 12H, 4 CH_3N^+), 3.45 (t, 4H, J=8.6 Hz, 2 CH_2N^+), 3.66 (t, 4H, J=6.8 Hz, 2 CH_2N^+). 100 MHz ^{13}C NMR (chloroform-d, ppm): δ 14.14 (aCH_3), 21.71 (bCH_2), 22.69 (oCH_2) , 22.90 (cCH_2), 24.56 (pCH_2), 26.34 (dCH_2), 29.30 (eCH_2), 29.33 (fCH_2), 29.43 (gCH_2), 29.49 (hCH_2), 29.60 (iCH_2), 29.65 (jCH_2), 31.90 (kCH_2), 51.05 (mCH_3N^+), 64.13 (nCH_2N^+), 64.69 (lCH_2N^+).

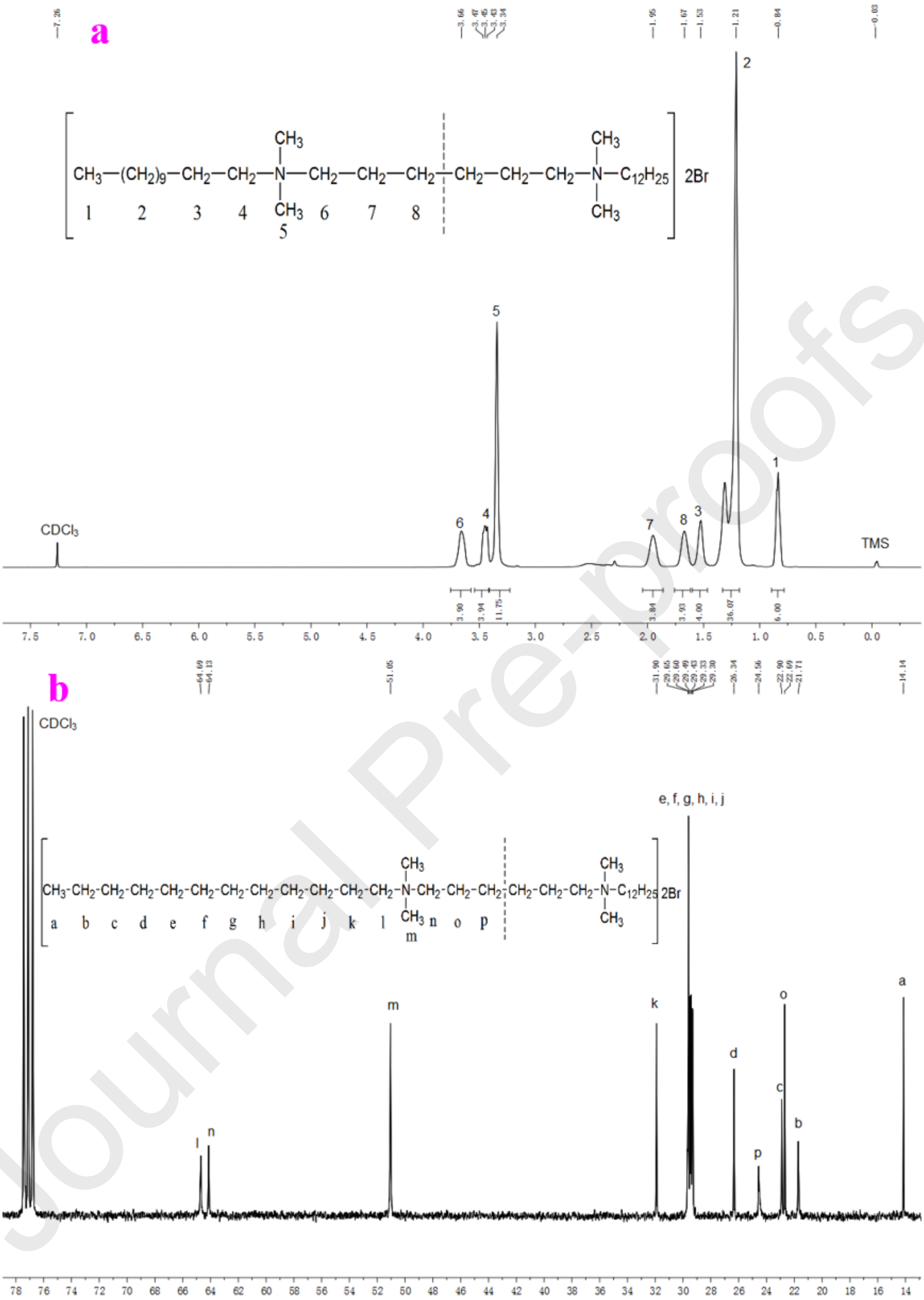


Figure 5 ^{1}H (a) and ^{13}C (b) NMR spectrum of HBDB in $CDCl_3$

The FTIR spectrum of HBDB is presented in **Figure 6.** IR (KBr), ν (cm^{-1}): 2917 (C-H), 2846 (C-H), 1461 (C-H), 1119 (C-N) [45].

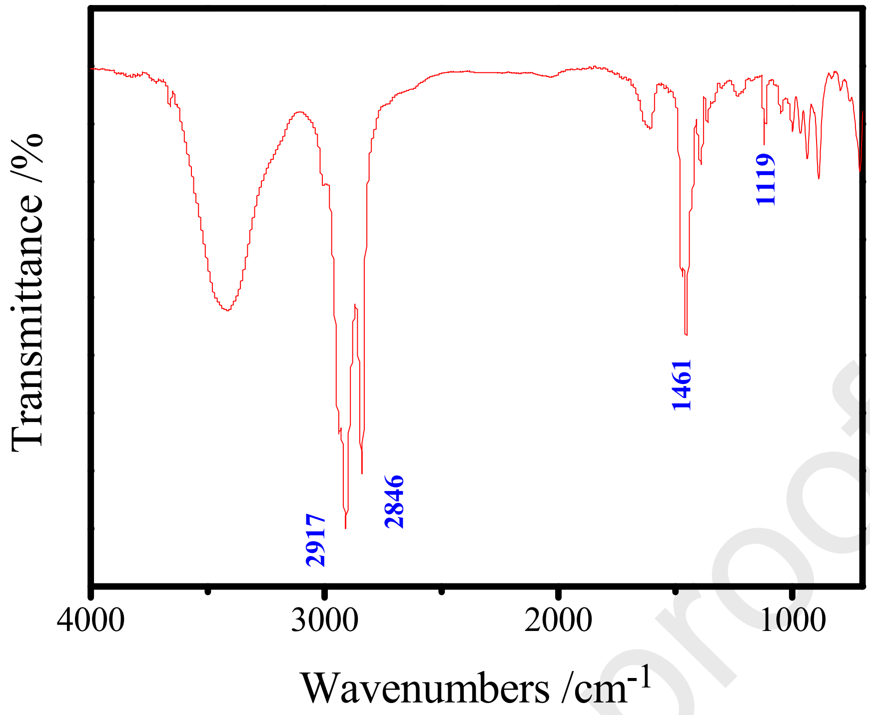


Figure 6 The FTIR spectrum of HBDB

3.2. Bench-scale flotation tests of lepidolite ore

3.2.1. Effect of pulp pH

To optimize the pulp pH of lepidolite ore using collector HBDB or DA in test, bench-scale flotation tests were conducted based on the flowsheet in **Figure 7**. **Figure 8** illustrated the influence of pulp pH to the Li_2O recovery and grade in lepidolite concentrate by using HBDB (100 g/t) or DA (200 g/t). From **Figure 8,** we can see that Li_2O recovery in lepidolite concentrate raised when increasing the pulp pH, while the corresponding Li_2O grade decreased. It showed that the optimal pulp pH range for lepidolite ore flotation separation using DA as the collector was pH 2–3 in this work, where the Li_2O grade of lepidolite concentrate was maximized. The lepidolite concentrates with 3.52 % Li_2O was observed by using 200 g/t DA collector at pH of 3, and its corresponding Li_2O recovery was 46.68 %. However, when using HBDB as the collector, high Li_2O grade and better lepidolite recovery was achieved over most of the pH range. **Figure 8** also showed that the lepidolite concentrate grade of 4.04 % Li_2O with 63.09% recovery was achieved at pH 3 by using 100 g/t HBDB. Thus, it was inferred that Gemini surfactant BDBD not only shows favorable collecting effect on lepidolite, but also has an extraordinary selectivity for gangue minerals when pH value is 3, and was more efficient during the flotation separation of lepidolite ore than conventional monomeric surfactants DA which contains only a single homologous hydrophobic group in its molecule.

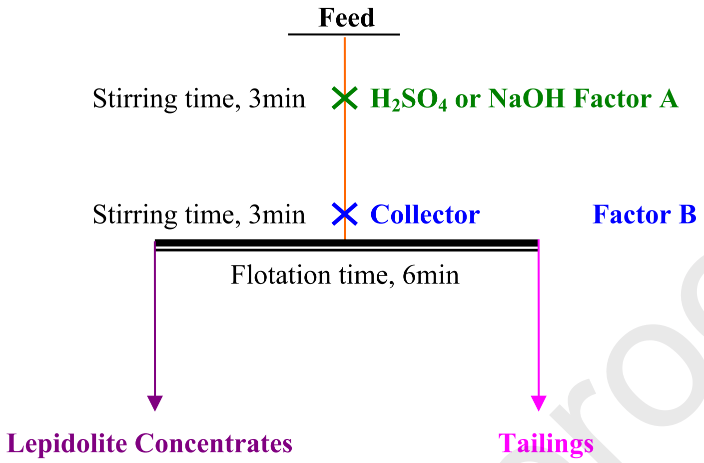


Figure 7

The flowsheet of condition flotation tests

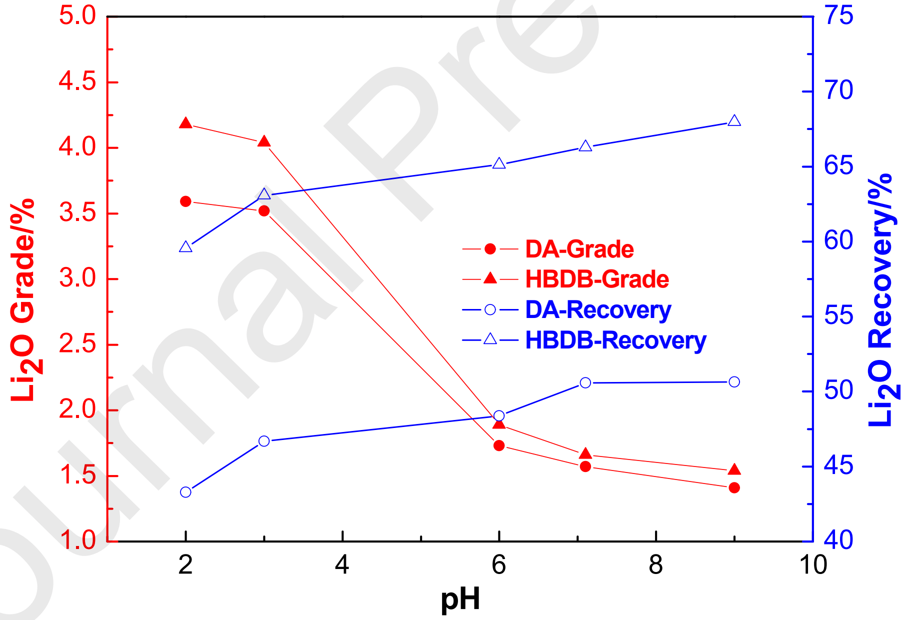


Figure 8 The content of Li_2O in lepidolite concentrate using 200 g/t DA or 100 g/t Gemini HBDB as the collector

3.2.2. Effect of collector dosage

The flotation effects of HBDB and DA collector at different dosage were compared at pH 3 according to **Figure 9**. Under the optimal pH 3, the effect of the dosage of HBDB or DA on Li_2O recovery and lepidolite grade in final concentrate were studied, as shown in Figure 8, which shows the more flotation collector dosage added, the lower grade of Li_2O in lepidolite concentrate will be got ， while the corresponding recovery is on the contrary. The optimal dosage of HBDB is 150 g/t, which could obtain a lepidolite concentrate with 3.79% of Li_2O grade and 67.12% of Li_2O recovery at pH 3. However, the optimal dosage of DA is 300 g/t, which could obtain a lepidolite concentrate with only 3.26% of Li_2O grade and 51.37% of Li_2O recovery. It indicates that the HBDB has excellent collecting performance to lepidolite and significant selectivity for gangue minerals at pH 3 in actual production. Compared with the conventional unimolecular collector DA (300 g/t), Gemini HBDB used less (150 g/t), which was only half of the amount of DA molecule, and could achieve a higher Li_2O grade and recovery (Li_2O grade and recovery increased by 0.53% 15.75%, respectively). It is obviously indicated that Gemini surfactant HBDB was a stronger collector for lepidolite ore when it compared to conventional monomeric surfactant DA. Furthermore, as the function of long and double hydrophobic groups, the mineral has better hydrophobization and better flotation performance [46].

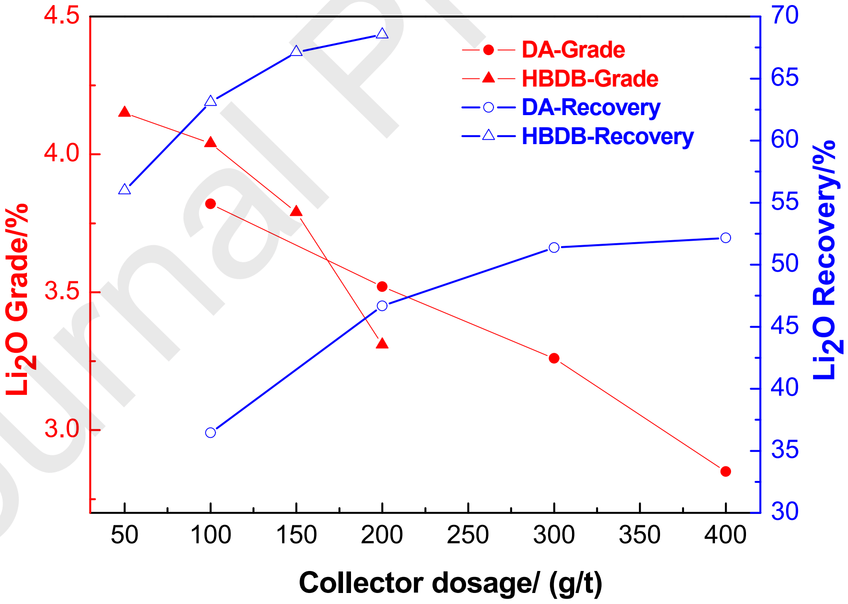


Figure 9 The content of Li_2O in lepidolite concentrate by HBDB or DA at pH 3

3.2.3. Froth flotation test of lepidolite ore

Based on the optimized flotation conditions mentioned above, the froth flotation test of lepidolite ore was conducted. The flotation flowsheet of bench tests was revealed in **Figure 10**. **Figure 11** indicates the locked-cycle flotation results of bench-scale flotation tests by using 350 g/t DA or 175 g/t Gemini HBDB at pH 3. It is concluded that under the condition of pH=3, 175 g/t HBDB collector could obtain a lepidolite concentrate with 4.12% of Li_2O grade and 71.15% of Li_2O recovery. This result suggests HBDB has excellent collecting performance to lepidolite and significant selectivity over gangue minerals. However, when the amount of DA was 300 g/t, the lepidolite concentrate with 4.05% of Li_2O grade and 54.97% of Li_2O recovery was obtained. Compared with the conventional unimolecular collector DA (350 g/t), Gemini HBDB used less (175 g/t), which was only half of the amount of DA molecule, and could achieve a higher Li_2O grade and recovery (Li_2O grade and recovery increased by 0.07% and 16.18%, respectively). Therefore, we have concluded that Gemini surfactant HBDB is a highly effective collector for flotation of lepidolite, and showed excellent selectivity to gangue minerals at pH 3. It is a more promising collector for the froth flotation of lepidolite ore than conventional monomeric surfactant.

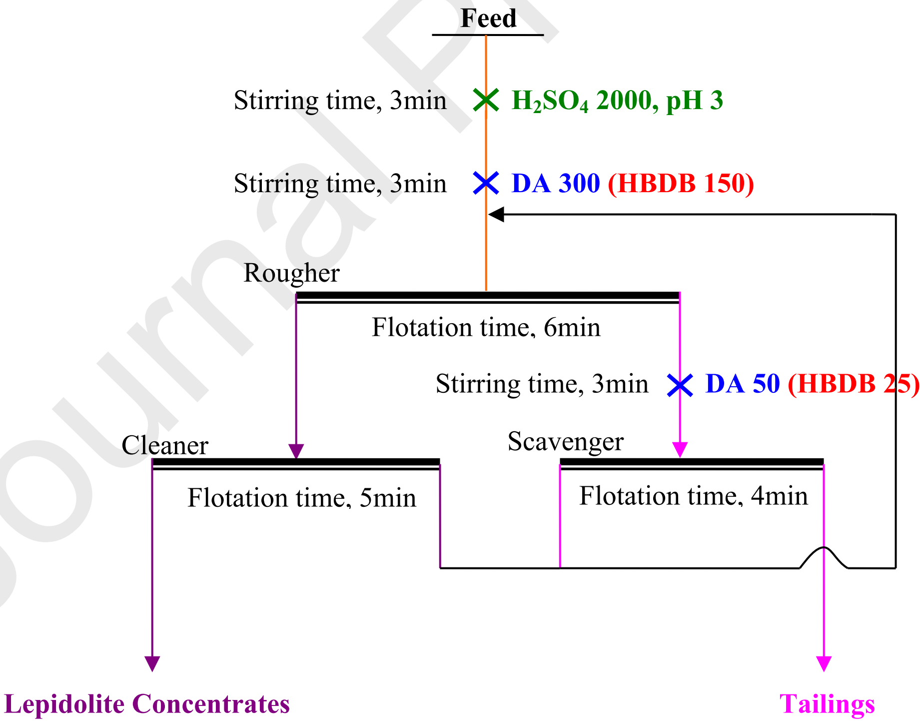


Figure 10 The flowsheet of locked cycle flotation tests for lepidolite ore using DA or Gemini HBDB as the collector

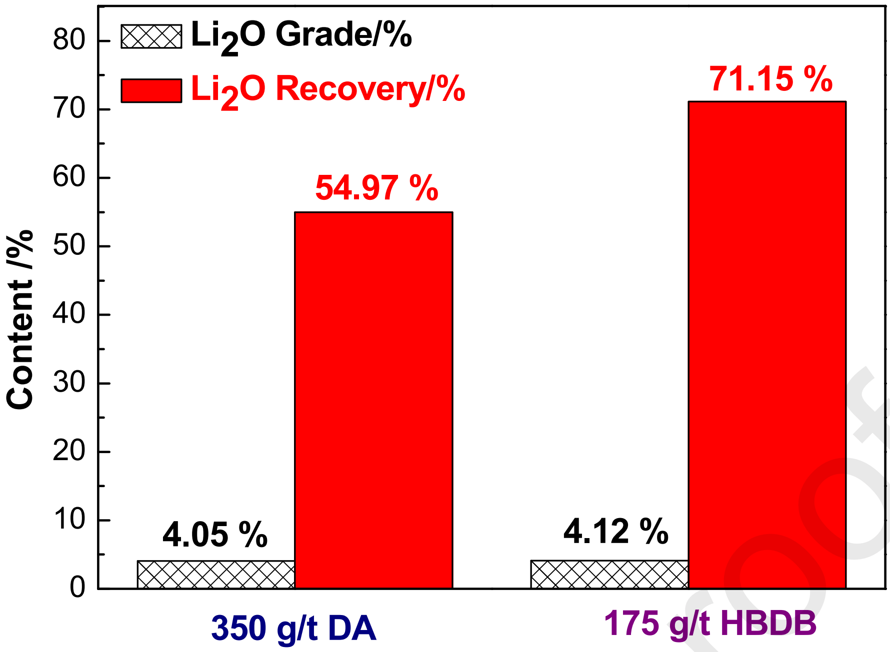


Figure 11 Froth flotation results of lepidolite ore with HBDB or DA as a collector

3.3. Contact angle measurements

The results of contact angle measurements are displayed in **Figure 12**. The experimental results argues that the contact angle with 2×10^{-4} mol/L HBDB could reach up to 85.2°, whereas that with DA was only 62.6°. Thus, it had a great improvement on contact angle of lepidolite by using HBDB collector, which indicated that HBDB had a strong adsorption effect on the lepidolite surface, therefore, showing a giant leap in lepidolite hydrophobicity. Hence, the HBDB collector can increase the flotation recovery of lepidolite.

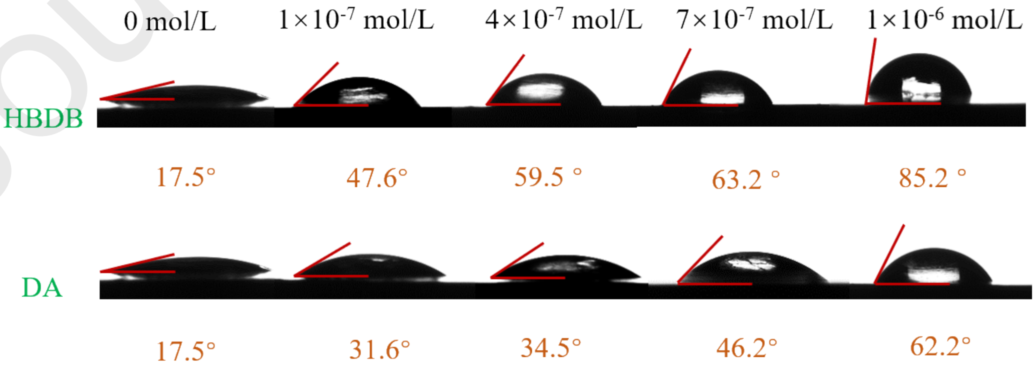


Figure 12 The results of contact angle measurement

3.4. Zeta potential measurement results

Zeta-potential changes on the lepidolite surface under the influence of HBDB and DA, respectively, are shown in **Figure 13**. The measured results show that the zero electric point on the pure lepidolite surface is about 3, which is in accordance with the literature record [47]. The adsorption of HBDB and DA on the lepidolite surface shifts its zeta potential significantly toward the positive one, indicating that both two collectors are adsorbed on the lepidolite surface by electrostatic attraction. Meanwhile, the positive potential increment of Gemini collector HBDB on lepidolite is far higher than that of conventional monomeric collector DA, which indicates that HBDB has better flotation effect on lepidolite. Therefore, Gemini collector HBDB is physically adsorbed on the lepidolite surface by stronger electrostatic attraction between the $HBDB^+$ and the negative charge on lepidolite surface, which enables a better flotation separation of lepidolite.

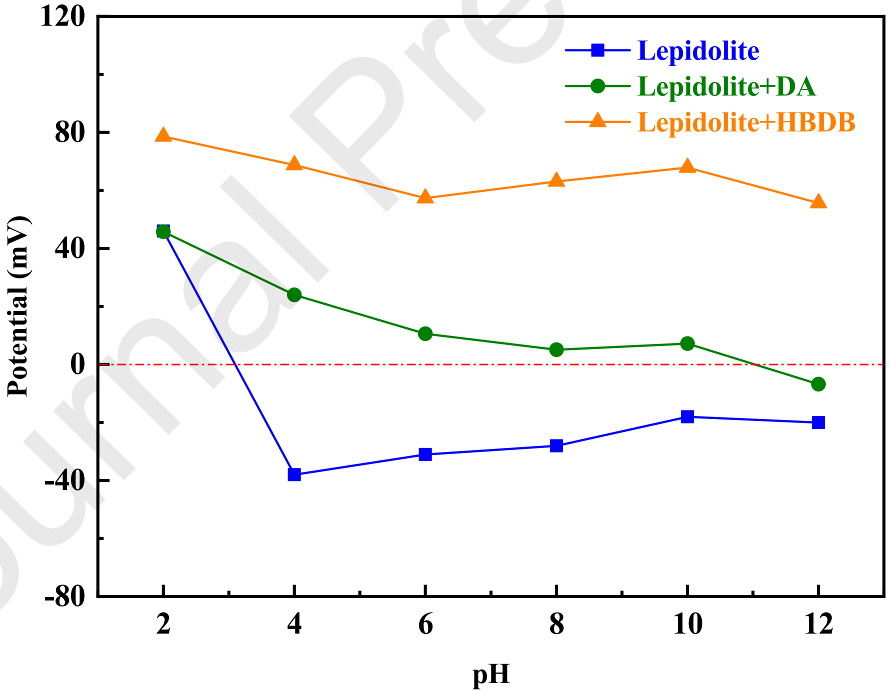


Figure 13 Zeta potential of lepidolite as a function of pH

3.5. Economic calculation

Table 2 shows the relative molecular mass and market prices of the main reagents. The synthetic yield of HBDB was 87.58%, and the raw materials takes about 80% cost when it refers to the total product cost of chemical companies.

Table 2 The market prices of agents

Agent	Molecular mass (g/mol)	Price (USD per t)
Dodecyl dimethyl amine	213.41	2803
Hexane,1,6-dibromo	243.97	5942
DA	185.35	3316
HBDB	670.7	-

Price of HBDB

$$= [(1/670.7\times2)/87.58\% \times213.41 \times2803 + (1/670.7)/87.58\% \times243.97 \times5942]/80\%$$

$$= \$\ 5630.85 \text{ USD per t} \tag{1}$$

Cost of HBDB

$$= 175 \text{ g/t} \times1500 \text{ t/d} \times330\text{d} \times5630.85 \text{ USD per t}$$

$$= \$\ 487772.38 \text{ USD} \tag{2}$$

Cost of DA

$$= 350 \text{ g/t} \times1500 \text{ t/d} \times330\text{d} \times3316 \text{ USD per t}$$

$$= \$\ 574497 \text{ USD} \tag{3}$$

In the actual ore flotation tests, the Li_2O recoveries using Gemini HBDB were enhanced by 16.18% compared with DA. The price of lepidolite concentrate (grade 4%) on the current market is approximately 355 USD per t. It is finally calculated that the replacement of DA collector by HBDB collector can increase net profit by about 8229957.61 USD per year. The massive application of HBDB collector for lepidolite ores around the world can considerably increase economic benefits in lepidolite mining industry.

Profit of Li_2O

$$= [(1500 \text{ t/d} \times330 \text{ d} \times1.18\% \times16.18\%)/4.12\%] \times 355 \text{ USD per t}$$

$$= \$\ 8143232.99 \text{ USD} \tag{4}$$

Net profit

$$= \$\ 8143232.99 \text{ USD} + (\$\ 574497 \text{ USD} - \$\ 487772.38 \text{ USD})$$

$$= \$\ 8229957.61 \text{ USD}$$

4. Conclusions

The novel Gemini-typed molecule hexanediyl-α, ω-bis (dimethyldodecylammonium bromide) (HBDB) was synthesized and applied as a lepidolite collector. Bench-scale flotation tests indicated that in contrast with conventional unimolecular DA collector (350 g/t), only one half of HBDB amount (175 g/t) showed outstanding collecting property for preferable lepidolite recovery at pH 3, producing high-quality lepidolite concentrate. According to the contact angle test, it indicates that HBDB is more effective than the conventional monomolecular collector DA in improving the wettability of lepidolite surface. The zeta potential proved that the collector HBDB is adsorbed on the lepidolite surface by electrostatic force, and the electrostatic attraction is stronger. Therefore, it can be seen that Gemini surfactant HBDB is better for flotation separation of lepidolite. Economic accounting for a lepidolite ore plant of 1500 t/d will save cost about $ 8.2million USD per year by using Gemini HBDB compared with traditional unimolecular DA. Therefore, the molecular design of Gemini surfactant has opened up a new way for the field of flotation collector, which can meet the urgent requirements for performance improvement and chemical consumption reduction in industrial applications.

Acknowledgements

The authors express their appreciation for the support of the Natural Science Foundation of Jiangxi, China (Grant No. 20202ACBL213008, 20202ZDB01005 and 20171BCB18002), Natural Science Foundation for Distinguished Young Scholars of Jiangxi province (Grant No. 20192BCB23016), Jiangxi Double Thousand Plan (Grant No. JXSQ2019201114), the National Natural Science Foundation of China (Grant No. U1607108 and 51774152), Program of Qingjiang Excellent Young Talents, Jiangxi University of Science and Technology.

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Research highlights

► A novel amine-based Gemini surfactant HBDB was synthesized in our lab.

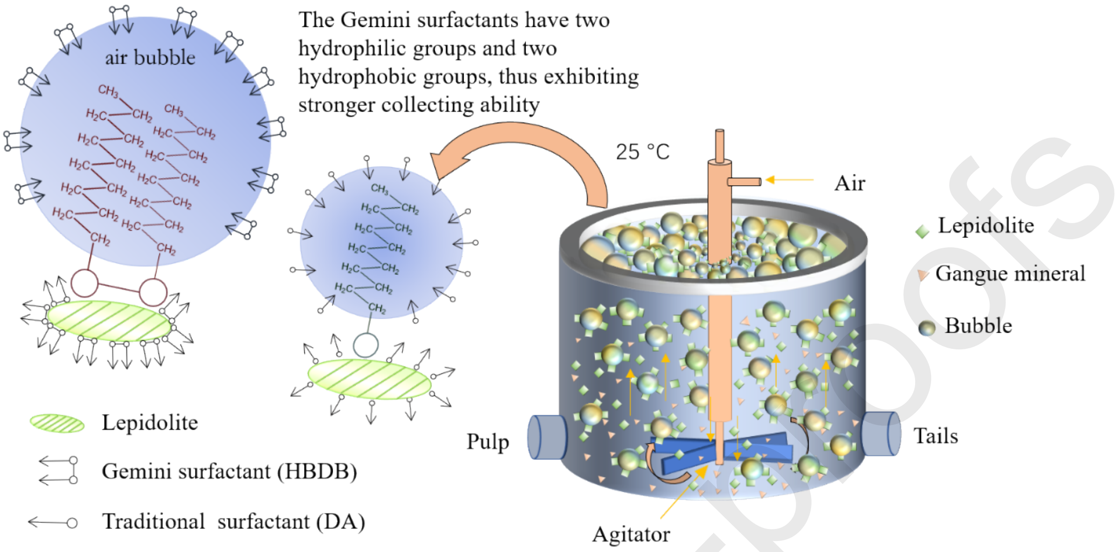
► HBDB was introduced as an efficient collector of lepidolite flotation.

► HBDB has better collecting ability and selectivity than traditional collector DA.

► Using less dosage HBDB obtained a higher quality lepidolite concentrate.

Graphical abstract

Comparison diagram of flotation behavior of lepidolite by new Gemini collector HBDB and traditional monomolecular collector DA.



The Gemini surfactants have two hydrophilic groups and two hydrophobic groups, thus exhibiting stronger collecting ability

Author Statement

Shuyi Shuai: Methodology. **Zhiqiang Huang:** Funding acquisition. **Hongling Wang:** Writing - review & editing. **Rukuan Liu:** Investigation. **Shiyong Zhang：** Data curation. **Chen Cheng:** Formal analysis. **Yajing Hu:** Investigation. **Xinyang Yu:** Data curation. **Guichun He:** Project administration. **Weng Fu:** Formal analysis.