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Evaluation of a novel morpholine-typed Gemini surfactant as the collector for the reverse flotation separation of halite from carnallite ore

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Abstract

In froth flotation separation process, the collector molecular design has a crucial effect on potash processing to ensure sustainable production of potassium fertilizer (KCl) that is important to secure food supply in human society. Carnallite is an important source of KCl fertilizer production in industry. Reverse flotation has been used to separate halite (NaCl) impurities from carnallite ($KCl·MgCl_2·6H_2O$) for carnallite resources. However, progress in the carnallite resource reverse froth flotation has been constrained by the inherent limitation of traditional collector molecules with a single hydrophilic head and single hydrophobic chain per molecule. Herein, a novel morpholine-based Gemini molecule with double hydrophilic heads and hydrophobic chains, butanediyl-α,

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ω-bis (morpholino tetradecylammonium bromide) (BMTB) was synthesized and applied as the flotation collector in the reverse flotation separation for carnallite mineral. The better flotation performance of Gemini BMTB was achieved, compared to the traditional monomeric surfactant N-(n-Tetradecyl) morpholine (TDM). The bench-scale froth flotation separation results revealed that BMTB exhibited outstanding affinity and selectivity for NaCl crystals from carnallite at natural pH, resulting in less collector dosages – only one third of TDM molecules. In contrast with traditional monomeric surfactant TDM (120 g/t), less amount of Gemini BMTB (40 g/t) – only one third of TDM molecules, was needed to obtain higher KCl recovery (KCl recovery raised by 4.69%). Meanwhile, the grade of NaCl with 40 g/t BMTB collector (2.19 %) was lower than that with 120 g/t TDM collector (3.91 %), and the grade of KCl with BMTB collector (22.59 %) was higher than that with TDM collector (22.12 %). Therefore, this work demonstrated the next-generation of flotation collector for the reverse froth flotation separation of the carnallite resources.

Key words:

Flotation; Morpholine-typed Gemini surfactant; Synthesis; NaCl; Carnallite

1. Introduction

Potassium (K) fertilizer, as one of the most essential fertilizer for the growth of crops in agricultural production [1-4], is critical to secure global food supply [5, 6]. In recent years, world consumption of potassium fertilizer has been continuously increasing due to world population growth and the concurrent need for increased production of food and biofuels. In industry, carnallite ores obtained by evaporation of salt lake solution are the main source for producing potassium fertilizer [7, 8]. Reverse froth flotation is an important method to remove NaCl crystals from carnallite ores to have upgraded carnallite concentrate with NaCl content less than 5% [9-12]. Multifarious surfactants are recommended to be collectors of NaCl flotation. At the inchoate period, aliphatic acid (R–COOH) has been applied in the reverse froth flotation process [13]. Afterwards, fatty acid primary amide (R–$CONH_2$) has been verified to be a efficient flotation collector during the reverse froth flotation for carnallite resources [14]. Currently, alkyl morpholine (R–$N(CH_2CH_2)_2O$) was applied as the reverse froth flotation collector for the carnallite ores in production and showed notable collecting ability to NaCl and selectivity against carnallite [15-17]. However, current surfactant applied on the carnallite reverse froth flotation separation procedure is traditional monomeric surfactant with a single hydrophilic head and single hydrophobic chain per molecule, leading to a low production efficiency.

Gemini surfactant, comprising of two hydrophobic and two hydrophilic groups, has received attention as a new-style surfactant category [18-20]. It is deserving to be studied in synthesis, physical chemistry and apply because of its unique and special properties [21-23]. By comparison to its constituent monomer, Gemini surfactant exhibits superior surfactivity for instance higher water solubility, lower Krafft point, improved wetting and foaming properties, lower CMC (critical micelle concentration), and higher efficiency in decreasing the interfacial tension [24]. Currently, Gemini surfactants have been diffusely used in many realms for instance bactericidal and anti-fungal agents, dyeing detergents, gene delivery, phase transfer catalysts, drug delivery, petroleum collection, fabric softeners, effective corrosion inhibitors, microemulsion stabilization and so on [25-28].

To our knowledge, nevertheless, the method of using Gemini surfactant as a collector during the reverse froth flotation separation of NaCl from carnallite ores has not yet been introduced. It is interesting to determine whether Gemini surfactants could be more efficient and/or effective during the reverse flotation separation of NaCl from carnallite resources than traditional unimolecular surfactants which have only a unitary similar hydrophobic group in molecules. Their unique amphipathy and the well-designed molecular structure make them to become charming for flotation separation aims. In this study, we systematically investigated the effect of Gemini molecule as the flotation collector in the reverse flotation separation of the carnallite minerals.

2. Materials and methods

2.1. Materials

The carnallite mineral for flotation separation tests was obtained from Qarhan Salt Lake (Qinghai Province, China). The ingredient of carnallite ores by mineralogy analysis were largely 78.27% carnallite ($KCl·MgCl_2·6H_2O$), 19.94% halite ($NaCl$), 1.02% gypsum ($CaSO_4·2H_2O$) and 0.77% sylvite (KCl). The bench-scale flotation separation tests were performed in saturated carnallite solutions at room temperature (25 °C). The chemical composition of carnallite mineral and saturated carnallite solutions are listed in **Table 1**.

Table 1 Chemical composition of carnallite minerals and saturated carnallite solutions (wt%)

Specimen	KCl	NaCl	$MgCl_2$	$CaSO_4$	H_2O
Carnallite minerals	17.14	18.55	28.62	1.41	34.28
Saturated carnallite solutions	0.49	0.11	33.85	0.07	65.48

Morpholine-typed Gemini surfactant butanediyl-α, ω-bis (morpholino tetradecylammonium bromide) (BMTB), synthesized by ourselves, was introduced to be a collector. The molecular structures of the morpholine-typed Gemini collector BMTB and conventional unimolecular collector N-(n-Tetradecyl) morpholine TDM are illustrated in **Figure 1**. All of the chemical reagents used in the experiment were analytical grade and had not been further refinement. Carbon-13 and hydrogen-1 NMR spectrum were acquired by BRUKER AVANCE III HD 400 MHz spectrometer (Switzerland) in $CDCl_3$ solvent with tetramethylsilane to check on the molecular structure of BMTB. Fourier-transform infrared spectroscopy (AVATAR 370 FT-IR, Thermo Nicolet Corporation, USA) was also used to disclose the BMTB structure.

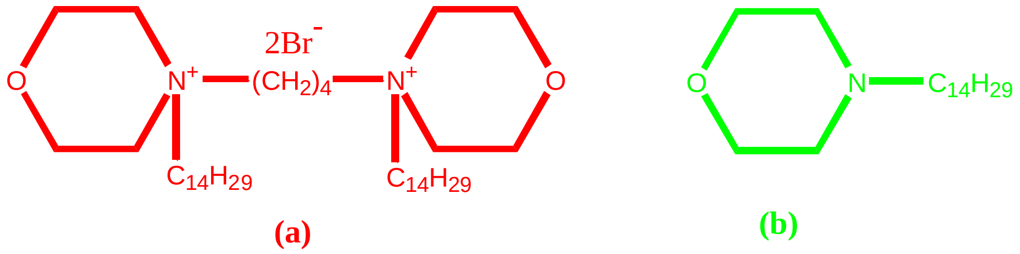


Figure 1 Molecular structures of BMTB (a) and TDM (b)

2.2. Bench–scale flotation tests

Bench–scale flotation separation tests were implemented using XFD single-cell flotation machine (self aeration, Jilin Prospecting Machinery, China) with 750 mL cubage of cell. In the carnallite ore flotation separation tests, the pulp was prepared by adding 225 g carnallite ore to 750 mL saturated carnallite solutions. Morpholine-typed Gemini surfactant BMTB and traditional monomeric surfactant TDM were used as a collector for these tests at 25 °C. The suspension was stirred for 2 min to homogeneous, then add collector and stirred for 3 min, continue to float for 7 min. These processing parameters were selected according to the previous flotation study of carnallite ores [29, 30]. In the flotation process, halite (NaCl) - loaded foams rose to the surface of the pulp and made NaCl to be separated from carnallite ore. The carnallite concentrate was collected, filtered, dried, weighed and measured the contents of NaCl and KCl in it. The diagrammatic sketch of flotation behavior with using BMTB or TDM as the collector is depicted in **Figure 2**.

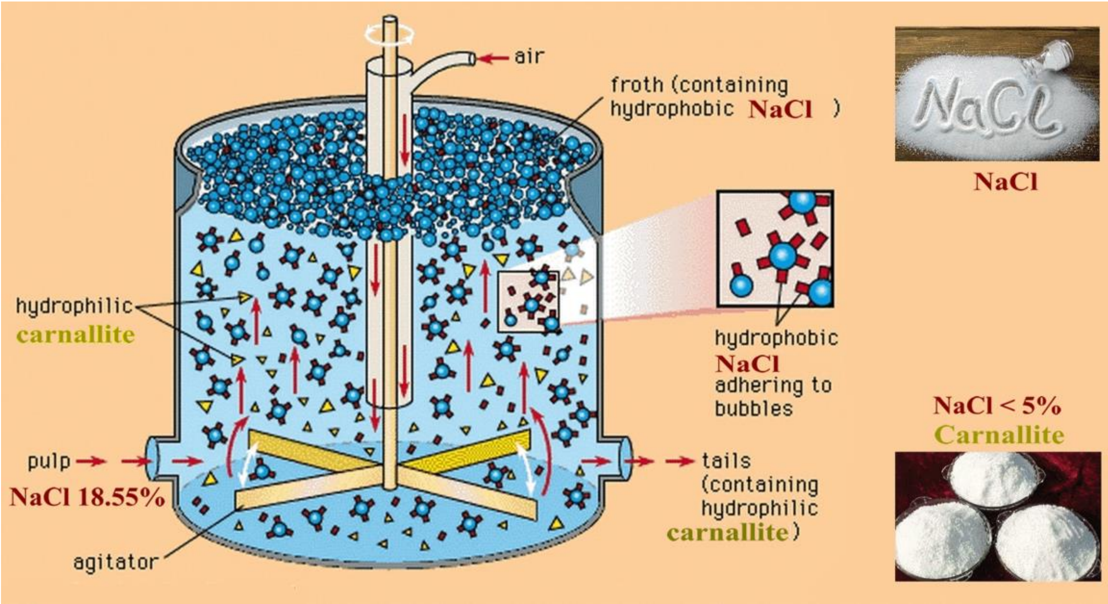


Figure 2 The diagrammatic sketch of flotation separation behavior

3. Results and discussion

3.1. Synthesis of BMTB

The preparation of morpholine-typed Gemini surfactant BMTB is shown in **Figure 3**. 1-Bromotetradecane (***1***; 27.73 g, 0.1 mol) was mixed in a reactor with NaOH (4.8 g, 0.12 mol) at 130 °C for 30 mins. Then, an aqueous solution of morpholine (**2**; 10.455 g, 0.12 mol) was injected slowly. The reaction time is 7 hours. Then, cooling down the mixture to 20 °C leaded to two liquid phase separation. The top phase contained the product, dried to remove water and produced the achromatous oil which was N-(n- Tetradecyl) morpholine (***3***; 26.32 g, 0.093 mol, 93% yield). The obtained N-(n-Tetradecyl) morpholine (***3***; 16.98 g, 0.06 mol) and 1,4-dibromobutane (***4***; 5.40 g, 0.025 mol) were mixed and set into a reactor containing ethanol (50 mL), and refluxed for 3 days. The obtained product butanediyl-α, ω-bis (morpholino tetradecylammonium bromide) (***5***, 14.645 g, 0.0185 mol) was purified through solvent evaporation, washing four times by 200 mL of ethyl acetate, recrystallization in mixed solvent (9/1 v/v ethyl acetate/ ethanol) and vacuum drying.

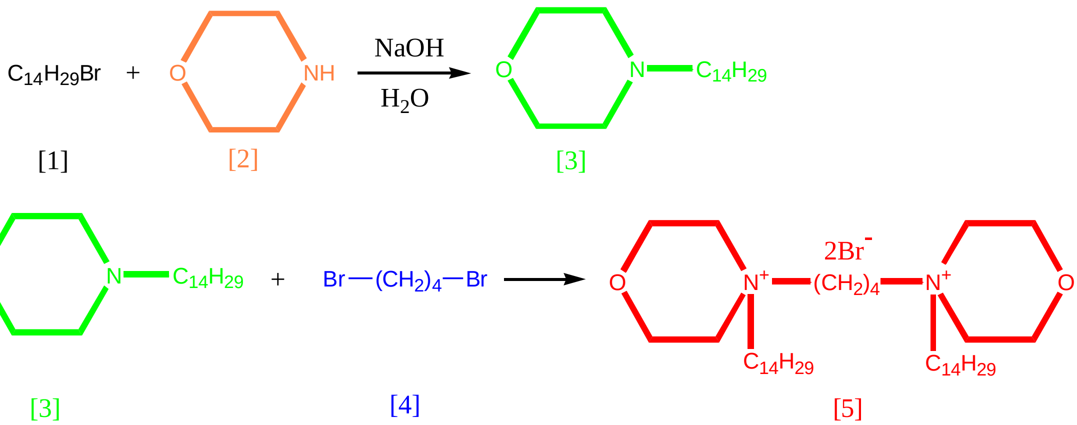
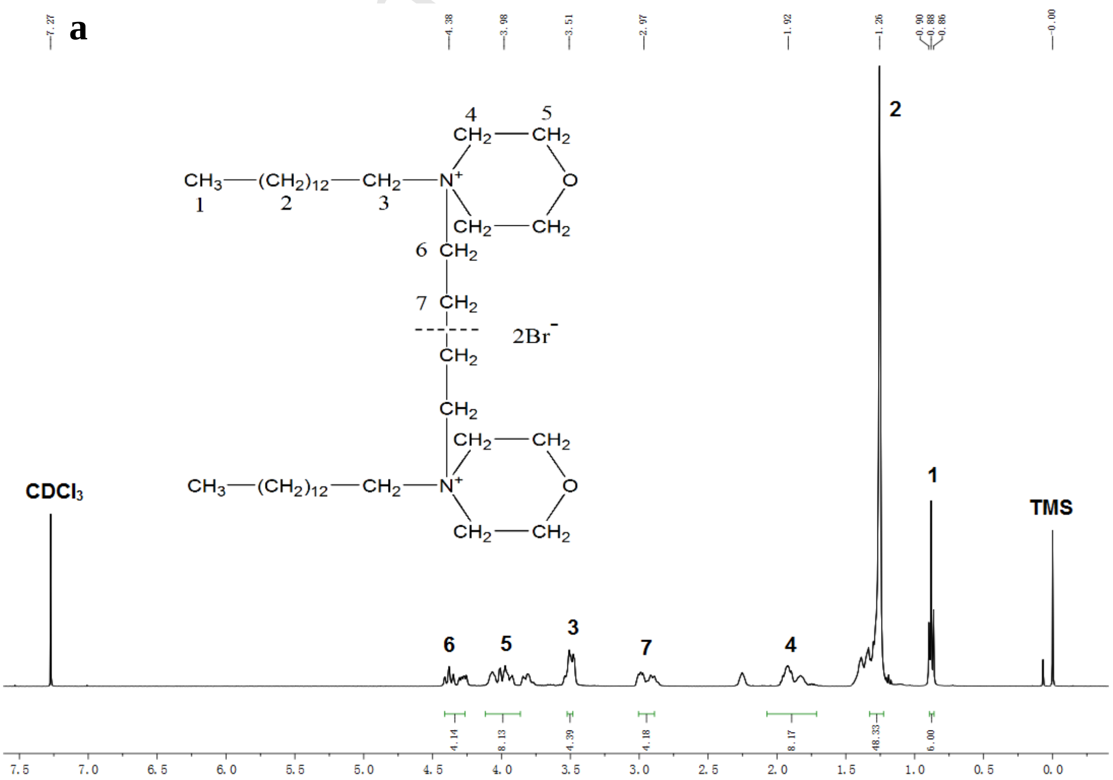


Figure 3 Synthesis equation of BMTB

Butanediyl-α, ω-bis (morpholino tetradecylammonium bromide) (***5***, BMTB), a white powder, yield 74.93%. The result of nuclear magnetic resonance spectrum analysis is showed in **Figure 4**. 400 MHz ^{1}H NMR ($CDCl_3$, TMS, ppm): δ 0.88 (t, 6H, 2 CH_3), 1.15~1.48 (m, 48H, 24 CH_2), 1.92 (m, 8H, 2 $CH_2N^+CH_2$), 2.97 (m, 4H, 2 CH_2), 3.51 (m, 4H, 2 CH_2N^+), 3.98 (m, 8H, 2 CH_2OCH_2), 4.38 (m, 4H, 2 CH_2N^+). 100 MHz ^{13}C NMR ($CDCl_3$, ppm): δ 14.04, 22.59, 23.15, 26.64, 28.97, 29.55, 31.82, 51.70, 57.77, 63.44.



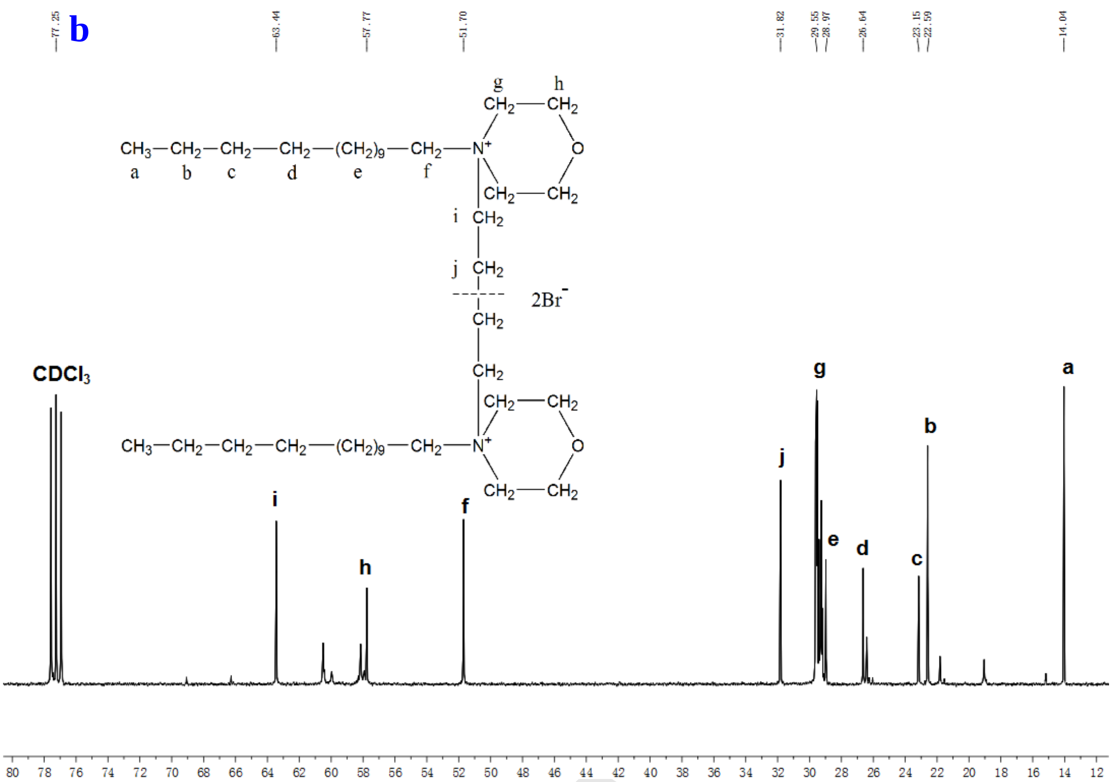


Figure 4 ^{1}H (a) and ^{13}C (b) NMR spectrum of BMTB in $CDCl_3$

The fourier-transform infrared spectroscopy of BMTB is shown in **Figure 5.** IR (KBr, cm^{-1}): υ 2921 (υ_{CH3}, υ_{CH2}), 2852 (υ_{CH3}, υ_{CH2}), 1467 (υ_{CH3}, υ_{CH2}), 1113 ($\upsilon_{C—N}$), 1069 ($\upsilon_{C—O}$).

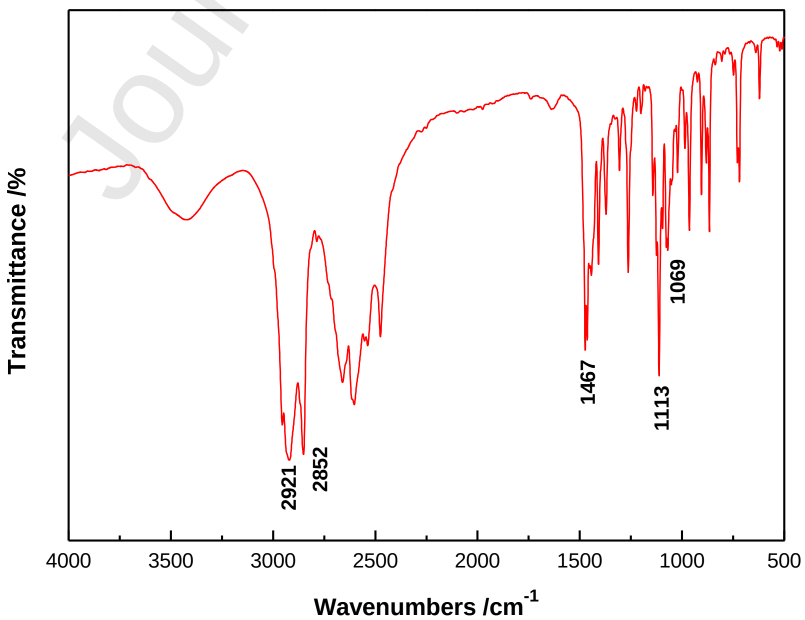


Figure 5 Fourier-transform infrared spectroscopy of BMTB

3.2. Bench-scale flotation tests of carnallite ore

To optimize the amount of collector BMTB or TDM in flotation, bench experiments were carried out based on **Figure 6**. Under the flotation condition of pulp natural pH 6.83, the influence of BMTB or TDM addition to the NaCl recovery and grade in carnallite concentrate at natural pH 6.83 was illustrated in **Figure 7**. It can be seen from **Figure 7** that both NaCl grade and NaCl recovery in carnallite concentrates reduced with a rise of flotation collector amount. **Figure 8** shows the KCl grade and recovery in carnallite concentrate by using TDM or Gemini BMTB at pH 6.83. From **Figure 8,** we can see that KCl grade in carnallite concentrate raised when adding more collectors, while the corresponding KCl recovery decreased. The optimal collector amounts of BMTB and TDM are 40 g/t and 120 g/t, respectively. Under this condition, the carnallite concentrate containing 22.59 % KCl and 2.19 % NaCl was attained by adding 40 g/t BMTB at natural pH=6.83, and the KCl recovery was 97.98 %. It means that the BMTB has outstanding collecting property to NaCl and great selectivity for carnallite in actual production. When the dosage of TDM was 120 g/t, the concentrate with TDM collector with 22.12 % KCl and 3.91 % NaCl was produced, and the KCl recovery was 93.29 %. In contrast with traditional monomeric surfactant TDM (120 g/t), less amount of Gemini BMTB (40 g/t) – only one third of TDM molecules, was needed to obtain higher KCl recovery (KCl recovery raised by 4.69%). Meanwhile, the grade of NaCl with 40 g/t BMTB collector (2.19 %) was lower than that with 120 g/t TDM collector (3.91 %), and the grade of KCl with BMTB collector (22.59 %) was higher than that with TDM collector (22.12 %). So, we can know through this study that Gemini surfactant BMTB is a sort of high-performance collector for reverse flotation of NaCl and has surpassing selectivity for carnallite. It has the ability to become a more admirable collector in carnallite ore flotation separation than traditional unimolecular collector.

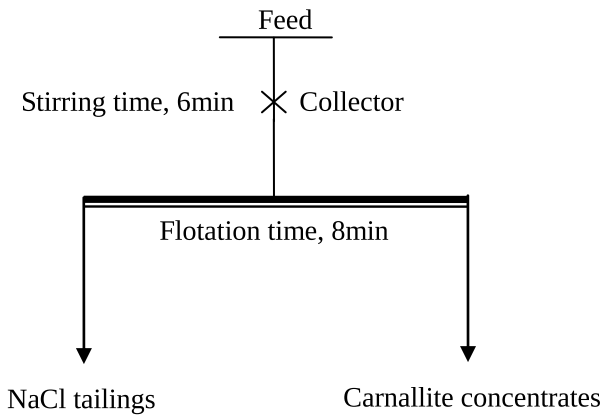


Figure 6 The flowsheet of condition flotation tests for reverse flotation of carnallite minerals

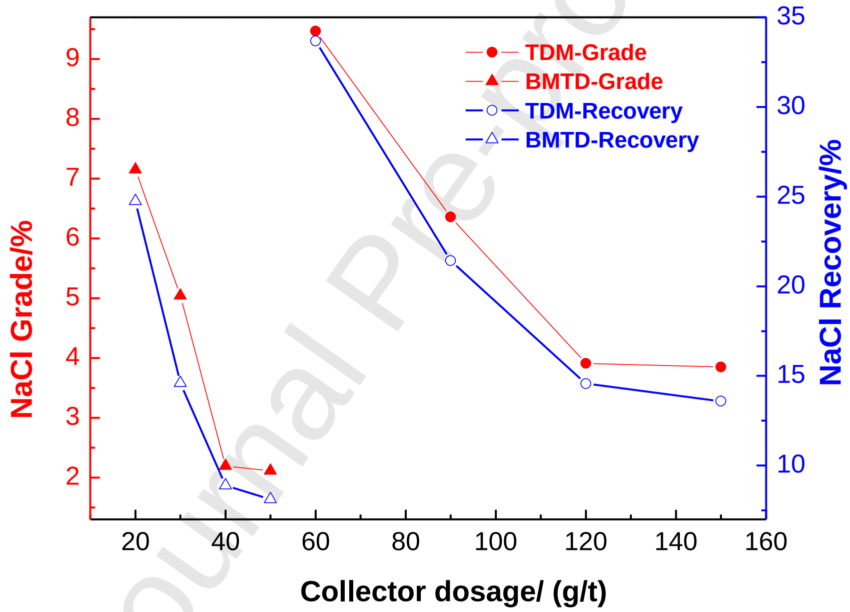


Figure 7 Grade and recovery of NaCl in carnallite concentrate by using TDM or BMTB at natural pH 6.83

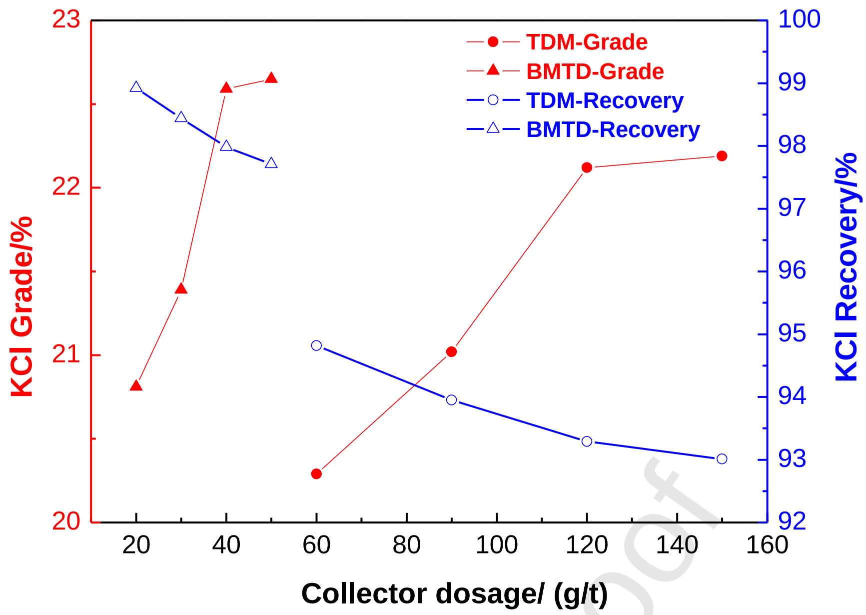


Figure 8 Grade and recovery of KCl in carnallite concentrate by using TDM or BMTB at natural pH 6.83

4. Conclusions

A new Gemini-typed molecule butanediyl-α, ω-bis (morpholino tetradecylammonium bromide) (BMTB) was prepared and utilized as flotation collector surfactant. Compared to traditional monomeric TDM collector (120 g/t), only one third of BMTB dosage (40g/t) presented a better flotation performance for better KCl recovery and higher NaCl rejection, producing high-quality carnallite concentrate. Thus, the molecular-level designed Gemini collector meets the urgent requirements for the next generation of reverse flotation reagents with improved performance and less chemical usage in industrial application.

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Author Statement

Zhiqiang Huang: Methodology. Shiyong Zhang, Feng Zhang, Hongling Wang and Jianrong Zhou: Investigation. Xinyang Yu: Funding acquisition. Rukuan Liu, Chen Cheng and Zuwen Liu: Formal analysis. Zhiqun Guo and Guichun He: Data curation, Formal analysis. Guanghua Ai: Investigation. Weng Fu: Writing - review & editing.

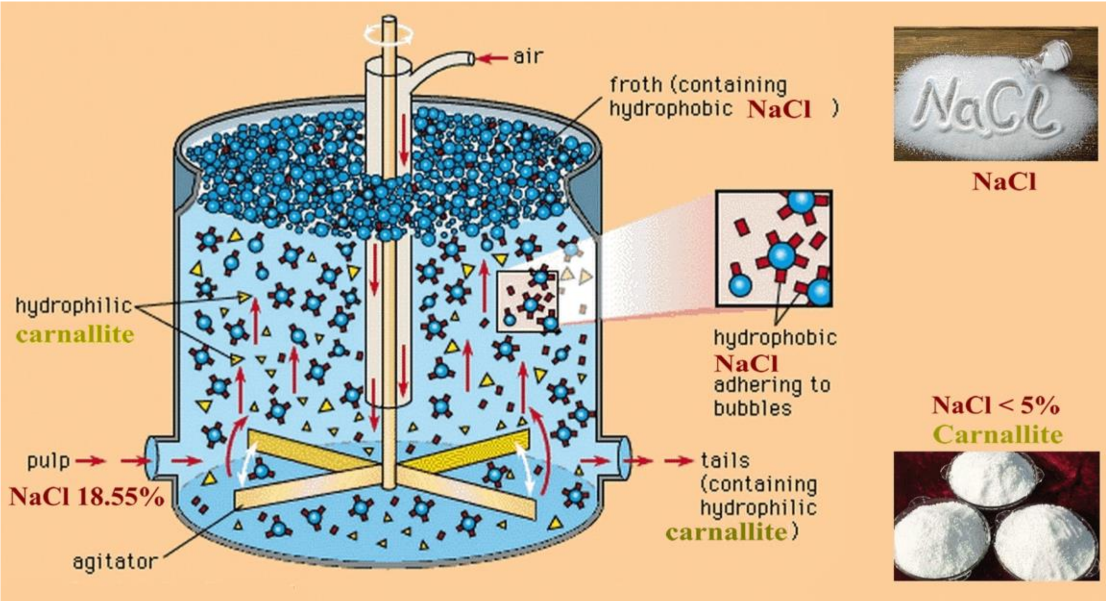
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract

Gemini surfactant as a collector for reverse froth flotation separation of halite from carnallite ore for potassium fertilizer production



Research highlights

► Halite was separated by reverse flotation using a Gemini surfactant BMTB.

► BMTB exhibited superior selectivity for halite against carnallite.

► BMTB displayed superior flotation performances than conventional surfactant TDM.

► Gemini surfactant is hopeful to the reverse flotation separation of carnallite ore.