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Morpholine-based Gemini surfactant: synthesis and its application for reverse froth flotation of carnallite ore in potassium fertilizer production

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Abstract

Potassium fertilizer plays a critical role in increasing the food production. Carnallite is concentrated by reverse froth flotation and used as a raw material to produce potassium fertilizer (KCl) in agriculture. However, all the surfactants used in the carnallite reverse flotation process are conventional monomeric surfactants contain a single similar hydrophobic group in the molecule, which results in a low production efficiency. In this work, a new morpholine-based Gemini surfactant, 1,4-bis (morpholinododecylammonio) butane dibromide (BMBD) was prepared, and originally recommended as a collector for reverse froth flotation separation of halite (NaCl) from carnallite ore. The flotation results indicated BMBD had higher flotation recovery and stronger affinity of halite against carnallite, compared with conventional monomeric surfactant N-(n-Dodecyl) morpholine (DDM). FTIR spectra suggested that BMBD molecules were adsorbed on halite surface rather than the carnallite surface. Additionally, BMBD molecules can strongly reduce the surface tension of NaCl saturated solution. Considering the BMBD's unique properties, such as double reactive centers to mineral surfaces, double hydrophobic groups, and stronger surface tension reducing ability, made it be a superior collector for reverse flotation desalination from carnallite ores than DDM.

Key words: Potassium fertilizer; Morpholine-based Gemini surfactant; Reverse flotation; Halite; Carnallite ore

INTRODUCTION

As food and agriculture are essential to the development of human civilization, modern technology and innovation have been used to address the challenge of the increasing food demand[1]. In modern agriculture, potassium fertilizer is one of the major nutrient to boost the growth of agricultural plants[2, 3]. Carnallite is used as a raw material to produce potassium fertilizer by cold decomposition, with formation of $MgCl_2$ in solution and KCl as a solid phase[4-6]. Reverse froth flotation is widely used in mining industry to produce upgraded carnallite concentrate with low NaCl level[7-9]. Various surfactants are assessed as flotation collectors to float out halite from carnallite ores by reverse froth flotation. In the early stages, fatty acids (R–COOH) have been used for flotation desalination[10]. Later on, N-alkylamides (R–$CONH_2$) have been proved to be the effective collectors in the reverse flotation of carnallite ores[11]. Recently, N-alkylmorpholines (R–$N(CH_2CH_2)_2O$) were used as flotation collectors in industry and possessed significant collecting power for halite and selectivity against carnallite[12,13]. Unfortunately, all the surfactants used in the carnallite reverse flotation process are conventional monomeric surfactants contain a single similar hydrophobic group in the molecule, which results in a low production efficiency.

Gemini molecules are a new type of surfactants that consist of two traditional monomeric amphiphiles that are covalently connected by a spacer unit[14,15]. In contrast to conventional monomeric surfactants, Gemini molecules possess superior properties, such as lower critical micelle concentration, lower Krafft point, higher solubilization power, higher surface activity, improved wetting and foaming properties[16,17]. Therefore, Gemini surfactants are widely applied in different fields such as phase transfer catalysts, drug entrapment/release, body care products, biomedical processes including gene transfection, preparation of high-porosity materials, synthesis of nanomaterials, food industry, oil recovery, polymerizations, antibacterial and antifungal preparations, etc[18-20].

As far as we know, however, Gemini surfactant has not been used as a collector reagent in carnallite flotation desalination process. There is interest in determining whether the Gemini would be more efficient and/or effective in the reverse froth flotation of carnallite ores than conventional monomeric surfactant which contains a single similar hydrophobic group in the molecule. Its unusual amphiphilic properties and the tailored structure, makes it attractive for beneficiation purposes.

In this paper, a novel morpholine-based Gemini surfactant, 1,4-bis (morpholinododecylammonio) butane dibromide (BMBD) was prepared and tested by FTIR, ^{1}H and ^{13}C NMR spectra, and its flotation behaviors to carnallite ore were assessed via micro-flotation and bench-scale flotation experiments. Afterwards, the adsorption mechanism of Gemini collector BMBD to halite and carnallite, and air/NaCl saturated solution interface was evaluated through FTIR and surface tension measurement.

MATERIALS AND METHODS

Materials

Pure halite and carnallite minerals were recieved from Taian and Geermu, respectively. Chemical compositions of the two minerals were shown in Table 1. The crystallinity of these minerals tested by powder XRD was shown in Figure 1. The grinded minerals within a size range of 150–270 μm were chosen for micro-flotation tests. The fine minerals (< 5 μm) were used for FTIR tests. Saturated halite or carnallite solutions for micro-flotation tests and surface tension measurements were separately obtained by dissolving individual halite or carnallite mineral into DI water. Then the obtained saturated solutions were passed through filters to remove mineral residues.

The carnallite ore for bench-scale flotation tests were acquired from Qinghai Salt Lake Industry Group Company in China. The samples were mainly composed of 77.95% carnallite, 21.01% halite, 0.91% gypsum and 0.13% sylvite by the results of mineralogy analysis. The bench tests were conducted in saturated carnallite solutions at a temperature of 20 °C. Chemical composition of carnallite ore and saturated carnallite solutions were shown in Table 2.

Morpholine-based Gemini surfactant 1,4-bis(morpholinododecylammonio) butane dibromide (BMBD), as a collector, was synthesized by our team. Both the solvent and reagents applied in synthesis process were of analytical grade. They were used as received without further purification. To verify the chemical structure of BMBD, carbon-13 and hydrogen-1 NMR spectra were collected by Bruker Avance 400 spectrometer (Switzerland) in $CDCl_3$ solvent with tetramethylsilane. Fourier-transform infrared spectroscopy (FTIR, Nicolet iS50) was also used to disclose BMBD structure.

Micro-flotation experiments

Micro-flotation experiments were conducted by a 50 mL of flotation equipment (XFG2) at 1500 rpm impeller speed. For each flotation experiment, 3 g of pure mineral particles was put into 30 mL saturated solution in flotation equipment. The slurry was mixed for 4 min in presence of the desired collector. After 7 min of flotation, both the froth products and tailings were separated, filtrated, dried under vacuum condition and finally measured by mass. In each test, the flotation recovery was measured, according to the mass ratio of different solid fractions.

Bench–scale froth flotation

Bench-scale tests were conducted in a 1.5 dm^3 of XFDC cell at l500 rpm impeller speed. 500g carnallite ores were added into 1 L saturated carnallite solutions in the cell. Then, the prepared slurry was mixed with a certain amount of BMBD collector for 6 min. After that, a quantitative amount of air was pumped into the centre of the cell and mixed thoroughly with the pulp for 8 min, leading to the exposure of slurry to froth. Finally, halite-laden bubbles floated out to the top of cell and separated from carnallite mineral. After collecting dry carnallite concentrates and tails separately, the mass of them were measured by the assay for KCl and NaCl, from which the metal recoveries were acquired. Replication were tested three times under each conditions, mean values of which were measured. The flotation flowsheet was shown in Figure 2.

FTIR spectra measurement

Fine mineral (<5 μm, 2g) solid was soaked in 30 mL of saturated halite or carnallite solutions with or without 3×10^{-6} mol/L BMBD at natural pH and 20 °C for 6 h. Then, the residue from the mixed solution was filtrated and dried under vacuum condition. 1mg of dried sample and 150 mg of KBr powder were mixed and pressed into a tablet for FTIR test (700-4000 cm^{-1}) using Nicolet iS50 equipment.

Surface tension measurement

The surface tensions of saturated halite solutions in presence of BMBD or DDM were tested by the Du Noüy ring equipment at 20 °C. Before each test, the platinum Du Noüy ring was treated through a standard cleaning procedure to remove the impurities. In every test, 30 ml of saturated solution was mixed by a certain amount of BMBD or DDM.

RESULTS AND DISCUSSION

Synthesis of morpholine-based Gemini surfactant BMBD

The synthesis of morpholine-based Gemini surfactant BMBD was described in Figure 3. 1-Bromododecane (***1***; 49.85 g, 0.2 mol) was placed in a 250 mL three neck flask with NaOH (12 g, 0.3 mol) and heated to 130 °C. Over 20 minutes, morpholine (***2***; 20.91 g, 0.24 mol) in 25 mL of H_2O was added in dropwise. The mixture was heated for 6 hours further, then cooled to room temperature over 30 minutes, causing 2 layers to form. The top layer of reaction mixture was collected, dried by anhydrous $CaCl_2$, and filtrated to generate the colorless oil of N-(n-Dodecyl) morpholine (***3***; 48.53 g, 0.19 mol), the yield of which was 95%. The resulting compound N-(n-Dodecyl) morpholine (***3***; 30.65 g, 0.12 mol) and 1,4-dibromobutane (***4***; 10.8 g, 0.05 mol) were placed in a 250 mL round bottom flask containing ethanol (50 mL), and the mixture was agitated for three days at the reflux temperature of 90 °C. After removing the ethanol by rotary evaporation, the crude product acquired was subsequently washed three times with 150 mL of ethyl acetate, and then purified by recrystallization from ethyl acetate/ethanol (10/1 v/v) at least three times. The precipitates after removal of ethanol and ethyl acetate through vacuum filtration were dried in vacuum drying oven for 24 h, which gave pure corresponding morpholine-based Gemini surfactant 1,4-bis (morpholinododecylammonio) butane dibromide (***5***, 27.66 g, 0.038 mol).

1,4-Bis (morpholinododecylammonio) butane dibromide (***5***, BMBD), a white powder, yield 76.19%. 400 MHz ^{1}H NMR ($CDCl_3$, TMS): δ 0.87 (t, 6H), 1.16~1.45 (m, 40H), 1.93 (m, 8H), 2.98 (m, 4H), 3.47 (m, 4H), 3.97 (m, 8H), 4.37 (m, 4H). 100 MHz ^{13}C NMR ($CDCl_3$): δ 13.98, 22.50, 23.13, 26.56, 28.90, 29.41, 31.71, 51.61, 57.65, 63.34. IR (KBr): 2923, 2853, 1468, 1112, 1066 cm^{-1}.

Micro-flotation of pure minerals

As shown in Fig. 4(a), the relationship between halite recovery and the concentration of BMBD or DDM collectors suggested that halite recoveries grew fast with the increase of collector concentrations, reaching the high recoveries (>99%) at 1×10^{-5} mol/L of BMBD and 1×10^{-4} mol/L of DDM, respectively. The result clearly illustrated that BMBD was more potent collector for halite than DDM, since the BMBD concentration required for high halite recovery was one order of magnitude less than that of DDM concentration at neutral pH.

Fig. 4(b) presented the effect of collector concentration on the carnallite recovery, indicating that both BMBD and DDM had extremely low affinity for carnallite mineral surface due to the low carnallite recoveries (<6%) in the whole range concentration of collectors. In particular, the optimum concentration of BMBD collector was 1×10^{-5} mol/L owing to the high halite recovery (98%) and low carnallite recovery (<4%).

Bench froth test of carnallite ore

The flotation flowsheet of bench tests was shown in Figure 2. The test conditions and results in Table 3 indicated that the carnallite concentrates containing 22.44 % KCl and 2.45 % NaCl was produced via adding 40 g/t BMBD collector at pH of 6.83, and the KCl recovery was 98.17%. This indicated Gemini surfactant had powerfully collecting power for halite and excellent selectivity against carnallite at natural pH. While for 120 g/t DDM, the grade of its carnallite concentrates were 22.07 % KCl and 4.04 % NaCl, and the flotation recovery of KCl was 93.93 %. Therefore, achieving the comparative flotation performance (KCl recovery >90%), the dosage of Gemini type BMBD collector (40 g/t) is three times less than that of monomeric DDM collector (120 g/t). The results also suggest the tailing produced by 40 g/t BMBD contains slightly higher amount of KCl and lower NaCl content than the tailing generated by 120 g/t DDM. Therefore, compared with DDM, Gemini BMBD has been demonstrated as a better collector of carnallite ore for potassium fertilizer production.

FTIR spectra

Figure 5 presented the FTIR spectra of BMBD, halite and carnallite particles with or without BMBD treatment. As shown in Fig. 5(a), the IR spectra of BMBD indicated that the absorption bands at 2923, 2853 and 1468 cm^{-1} were attributed to stretching of C–H[21-25]. The C–N vibrations occurred on 1112 cm^{-1} [26-29]. The band at 1066 cm^{-1} was attributed to C–O stretching vibration[30-32]. Fig. 5(a) also showed that the C–H stretching peaks at 2923, 2853 and 1468 cm^{-1} appeared at halite surface in presence of BMBD, and the stretching vibrations of C–N bonds originated from BMBD appeared at 1112 cm^{-1} on halite, indicating the adsorption of BMBD on halite surfaces. But for carnallite treated with BMBD shown in Fig 5(b), the absence of FTIR bands of BMBD molecules suggested the negligible interaction between BMBD and carnallite[33-36].

Surface tension results

The surface tension (γ) measurements of BMBD and DDM in a NaCl-saturated solution at natural pH were shown in Fig. 6. The CMC values (critical micellization concentration) and the γ_{CMC} values were shown in Table 4.

Surface tension in Fig. 6 declined fastly with the rise of surfactant concentration, then reached a platform at CMC concentration. The results also suggested that Gemini surfactant BMBD was a stronger collector than the conventional monomeric surfactant DDM at decreasing the air–NaCl surface tension. At 3×10^{-6} mol/L, BMBD reduced the solution surface tension to 28.6 mN/m, whilist the surface tension in presence of DDM was 60.7 mN/m. Table 4 showed that the CMC values of BMBD and DDM were 3×10^{-6} mol/L and 2.5×10^{-5} mol/L respectively, wherein CMC value of BMBD was nearly one order of magnitude less than that of DDM, which was consistent with prior studies[37-39].

Discussion

The micro-flotation and bench-scale flotation results suggested that Gemini surfactant BMBD had better flotation ability of carnallite ore than the conventional monomeric surfactant DDM, as well as excellent collecting power for halite and significant selectivity against carnallite. FTIR spectra results showed that the characteristic absorption peaks of C–H and C–N stretching vibrations in BMBD moleucles appeared on halite surfaces, indicating the adsorption of BMBD on halite. No adsorption band of BMBD was found on the surface of carnallite, suggesting that the BMBD had a negligible effect on the carnallite surface. Therefore, BMBD presented excellent collecting power for halite and significant selectivity against carnallite in accrodance with the micro-flotation and bench-scale flotation findings, which was consistent in prior studies [40,41].

Surface tension measurements results suggested BMBD molecule was much stronger than the conventional monomeric surfactant DDM in reducing the air-NaCl saturated solution interfacial tension. BMBD was able to decrease the air-NaCl saturated solution interfacial tension to 28.6 mN/m, compared with the corresponding value (60.7 mN/m) for DDM at the same concentration 3×10^{-6} mol/L (Fig.6). A low surface tension could be beneficial to the formation of stable and small bubbles in the flotation process[42,43]. Besides, in consequence of the addition of collector BMBD or DDM, the air bubbles generated below the surface of NaCl-saturated solution were partly lined with a monomolecular sheath of BMBD or DDM molecules that decreased the air-NaCl saturated solution interfacial tension[44]. This enabled each bubble with its lining to approach other bubbles without coalescing. Since BMBD was much stronger than DDM in reducing the air-NaCl saturated solution interfacial tension, the obstruction of bubble coalescence and the stability of froth generated by BMBD were greater than that by DDM, which was consistent in prior studies [45,46].

As BMBD or DDM was put to the pulp, they might adsorb on the mineral particles with their non-polar ends orientated towards the bulk solution, thus transforming the surfaces of minerals from a hydrophilic condition to a hydrophobic condition, which created the required condition for attachment to air bubbles[47]. BMBD had two hydrophobic chains per molecule, and this might raise the collision probability between the hydrophobic minerals and bubbles. Whilst, the hydrophobic minerals attached to bubbles via collector's non-polar groups orientated towards the air[48], and the interfacial tension of BMBD at air-NaCl saturated solution interface was lower than that of DDM, hence the attachment between minerals and froth might be more stable by using BMBD as a collector. Therefore, BMBD presented better flotation ability of carnallite ore than DDM for potassium fertilizer production. The potential flotation mechanism of BMBD or DDM for carnallite ore was illustrated in Fig. 7.

In conclusion, a novel morpholine-based Gemini collector 1,4-bis (morpholinododecylammonio) butane dibromide (BMBD) was synthesized and characterized in this paper. The flotation performance of BMBD was compared with conventional monomeric collector N-(n-Dodecyl) morpholine (DDM) in reverse froth flotation of carnallite ore. The micro-flotation and bench-scale flotation results indicated that Gemini surfactant exhibited higher collector capacity and selectivity for halite than the conventional monomeric surfactants. Compared with conventional monomeric collector DDM (120g/t), less amount of BMBD (40 g/t) is needed to achieve better KCl recovery and lower NaCl content in the final tailing. FTIR spectra recommended that BMBD could preferentially bind to the surface of halite mineral rather than the carnallite surface. Surface tension measurements demonstrated that BMBD was more efficient than DDM at decreasing the air-NaCl saturated solution interfacial tension. Therefore, Gemini-type BMBD surfactant with both strong hydrophobic and hydrophilic groups is an excellent collector candidate to separate halite from carnallite ore in potassium fertilizer industry.

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Notes

The authors declare no conflict of interest.

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Tables

Table 1. Chemical composition of the pure minerals (wt%)

Table 2. Chemical composition of carnallite ore and saturated carnallite solutions (wt%)

Table 3. Reverse flotation results of carnallite ore with 40 g/t BMBD or 120 g/t DDM as a collector at natural pH 6.83

Table 4. Values of the CMC and γ_{CMC} for BMBD and DDM

Table 1. Chemical composition of the pure minerals (wt%)

Sample	KCl	NaCl	$MgCl_2$	$CaSO_4$	H_2O
Halite	—	99.50	—	—	0.50
Carnallite	26.33	0.66	33.62	1.05	38.34

Table 2. Chemical composition of carnallite ore and saturated carnallite solutions (wt%)

Sample	KCl	NaCl	$MgCl_2$	$CaSO_4$	H_2O
Carnallite ore	18.13	19.95	27.78	1.29	32.85
Saturated carnallite solutions	0.88	0.17	32.34	0.09	66.52

Table 3. Reverse flotation results of carnallite ore with 40 g/t BMBD or 120 g/t DDM as a collector at natural pH 6.83

Collector	Entry	Product	Weight/%	Grade/%		Recovery/%	
				KCl	NaCl	KCl	NaCl
	1	Tailings	80.19	22.46	2.25	97.93	8.92
		Concentrates	19.81	1.92	92.98	2.07	91.08
		Feed	100.00	18.39	20.22	100.00	100.00
	2	Tailings	80.51	22.33	2.48	98.18	9.91
BMBD 40 g/t		Concentrates	19.49	1.71	93.15	1.82	90.09
		Feed	100.00	18.31	20.15	100.00	100.00
	3	Tailings	81.08	22.52	2.61	98.39	10.85
		Concentrates	18.92	1.58	91.87	1.61	89.15
		Feed	100.00	18.56	19.50	100.00	100.00
	Average	***Tailings***		***22.44***	***2.45***	***98.17***	***9.89***
	RSD			0.43	7.45	0.23	9.76
	4	Tailings	78.21	22.08	3.89	93.33	14.38
		Concentrates	21.79	5.66	83.13	6.67	85.62
		Feed	100.00	18.50	21.16	100.00	100.00
	5	Tailings	79.07	22.01	4.17	94.39	15.57
DDM 120 g/t		Concentrates	20.93	4.94	85.42	5.61	84.43
		Feed	100.00	18.44	21.17	100.00	100.00
	6	Tailings	78.60	22.12	4.06	94.06	15.29
		Concentrates	21.40	5.13	82.64	5.94	84.71
		Feed	100.00	18.48	20.88	100.00	100.00
	Average	***Tailings***		***22.07***	***4.04***	***93.93***	***15.08***
	RSD			0.25	3.49	0.58	4.13

Table 4. Values of the CMC and γ_{CMC} for BMBD and DDM

Surfactant	CMC (mol/L)	γ_{CMC} (mN/m)
BMBD	3×10^{-6}	28.4
DDM	2.5×10^{-5}	31.1

Figures

Figure. 1. XRD of halite and carnallite

Figure. 2. The flowsheet of reverse froth flotation experiments

Figure. 3. Synthetic route for morpholine-based Gemini surfactant BMBD

Figure. 4. Flotation recovery of halite (a) and carnallite (b) as a function of collector concentration at natural pH

Figure. 5. FTIR spectra of BMBD, halite (a) and carnallite (b) before and after interaction with BMBD

Figure. 6. The surface tension for BMBD and DDM in a NaCl-saturated solution

Figure. 7. BMBD or DDM as a collector for reverse froth flotation separation of halite from carnallite ore for potassium fertilizer production

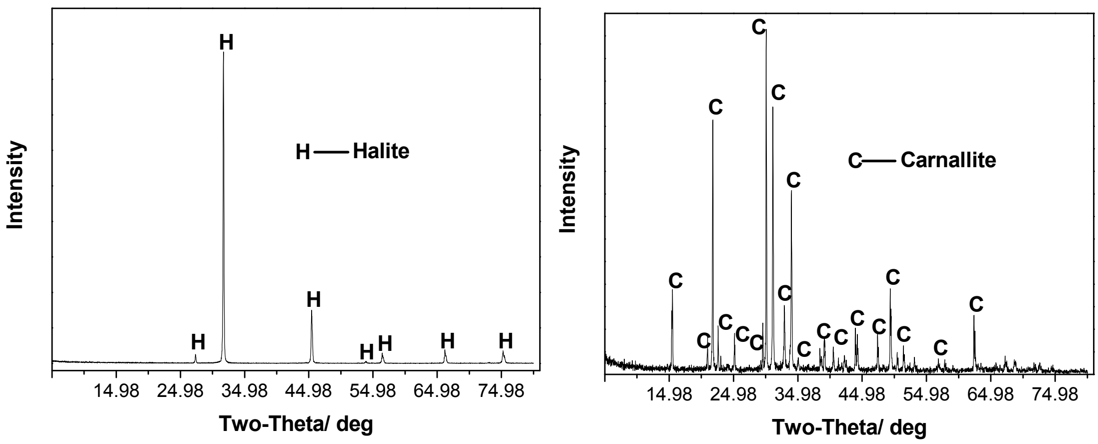
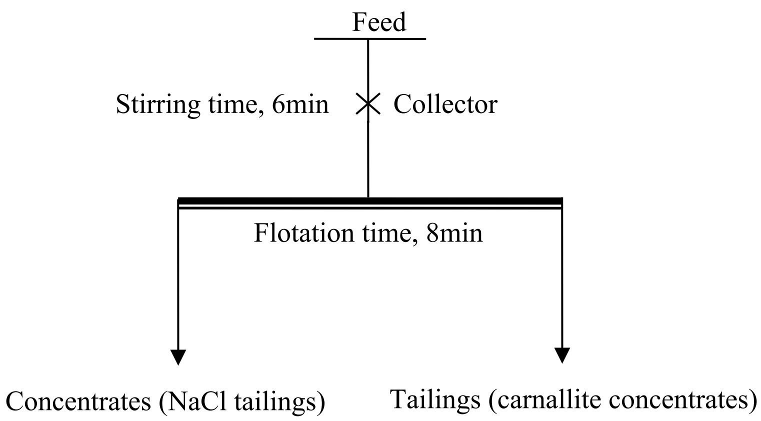


Figure. 1. XRD of halite and carnallite



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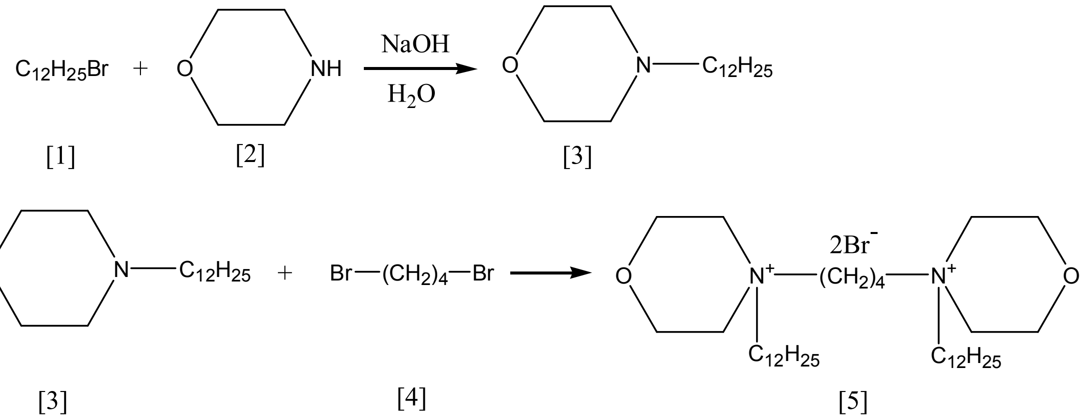
407 **Figure. 2.** The flowsheet of reverse froth flotation experiments



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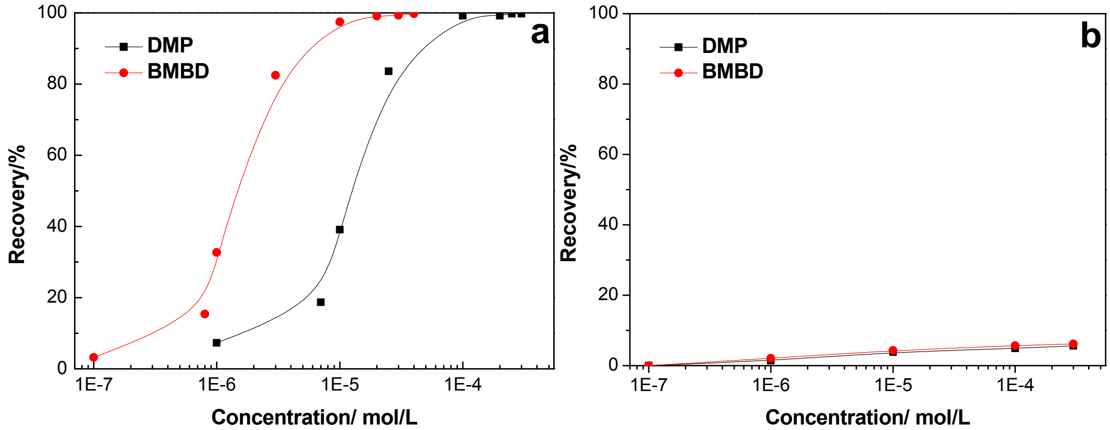
413 

414 **Figure. 4.** Flotation recovery of halite (a) and carnallite (b) as a function of collector concentration

415 at natural pH

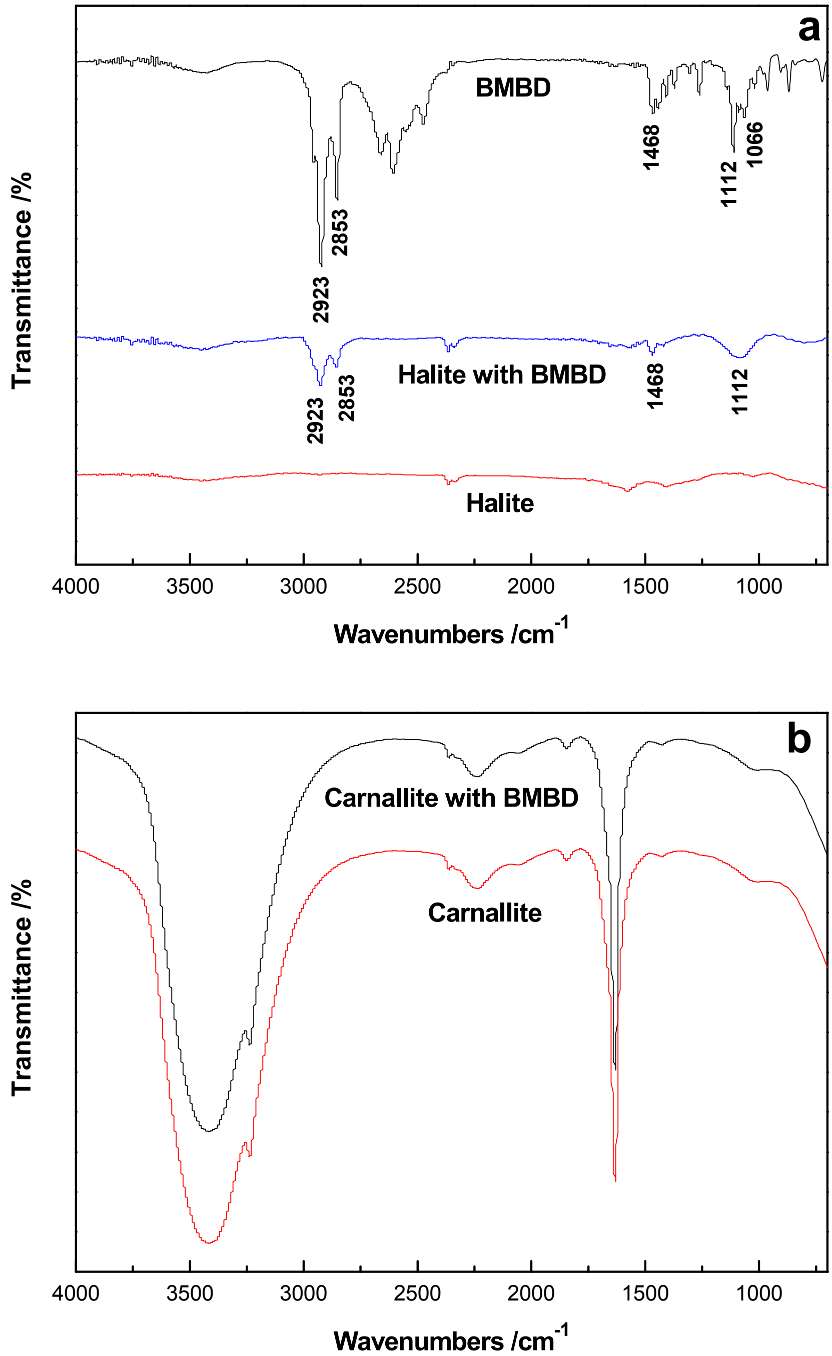


Figure. 5. FTIR spectra of BMBD, halite (a) and carnallite (b) before and after interaction with BMBD

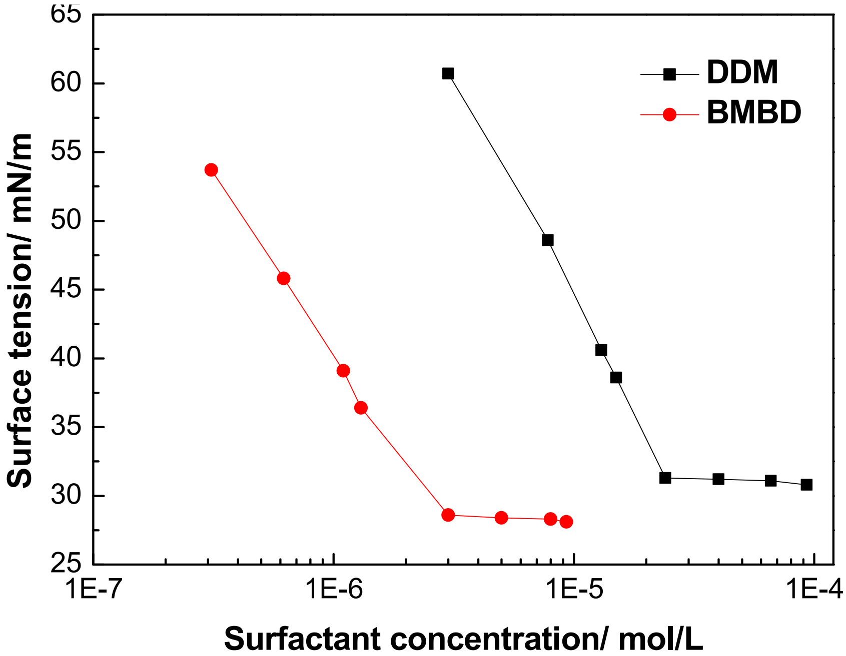
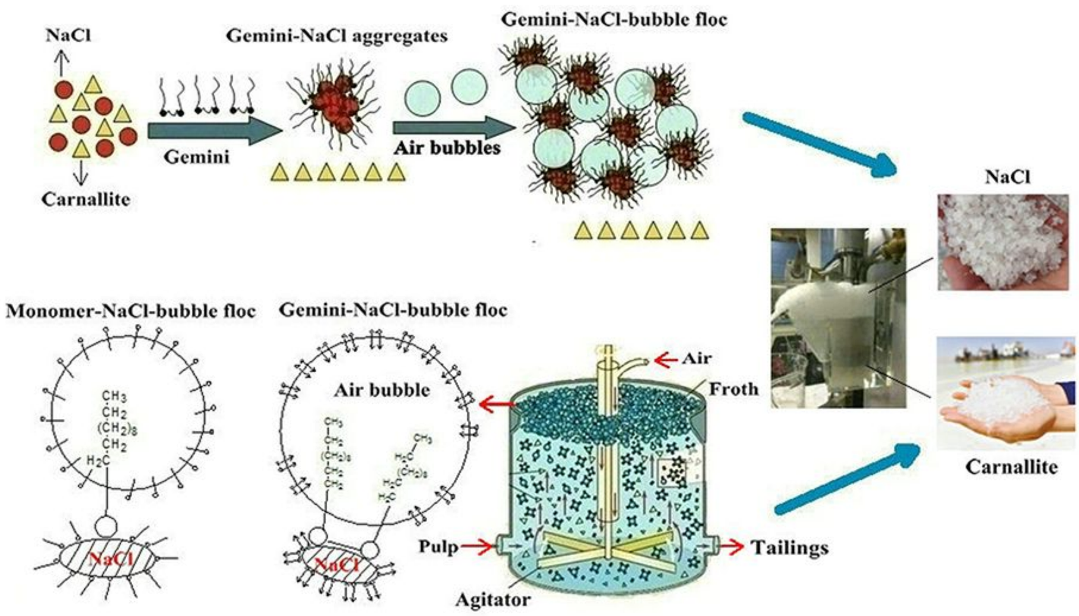
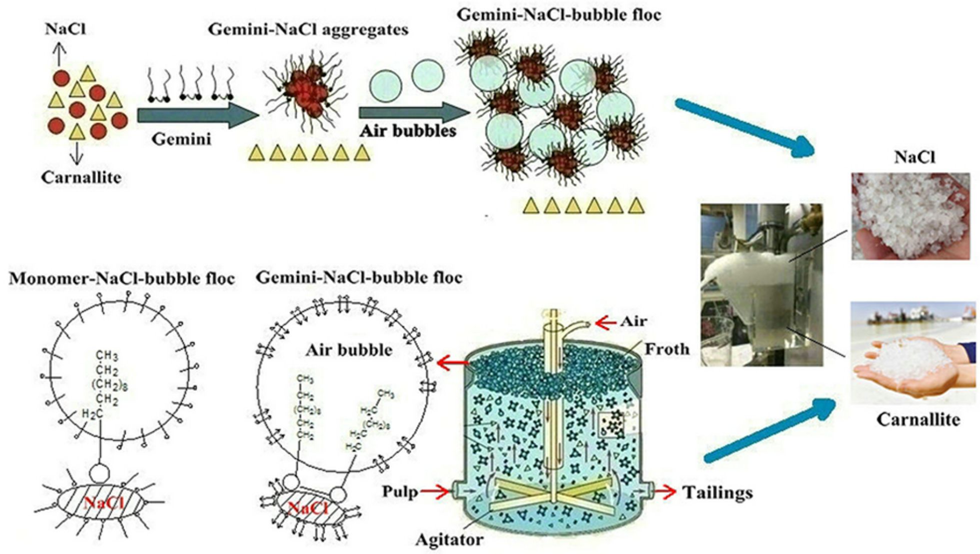


Figure. 6. The surface tension for BMBD and DDM in a NaCl-saturated solution



424 **Figure. 7.** BMBD or DDM as a collector for reverse froth flotation separation of halite from
425 carnallite ore for potassium fertilizer production



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