Electronic Supplementary Information

Highly efficient potassium fertilizer production by using Gemini surfactant

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Experimental Section

Materials. Pure KCl and NaCl minerals were recieved from Haixi and Taian, respectively. Chemical compositions of the two minerals were shown in **Table S1**. The crystallinity of these minerals tested by powder XRD was shown in **Figure S1.** 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 KCl or NaCl solutions for micro-flotation tests and surface tension measurements were separately obtained by dissolving individual KCl or NaCl mineral into DI water. Then the obtained saturated solutions were passed through filters to remove mineral residues.

The potash ore with KCl-NaCl mixture for bench-scale flotation tests were acquired from Qinghai Salt Lake Industry Group Company in China. The samples were mainly composed of 71.32% NaCl, 24.97% KCl, 2.94% clayey-carbonate impurities and 0.77% gypsum by the results of mineralogy analysis. The bench tests were conducted in saturated sylvinite solutions at a temperature of 20°C. Chemical composition of potash ore and saturated sylvinite solutions were shown in **Table S2.**

Gemini surfactant N,N'-bis (octadecyldimethyl)-1,4-butane diammonium dibromide (BOBD), as a collector, was synthesized by our team. N,N-Dimethyl-n-octadecylamine, 1,4-dibromobutane, ethanol and ethyl acetate were acquired from Aladdin Chemistry Co., Ltd., Shanghai, China. 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 BOBD, hydrogen-1 NMR spectra was 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 BOBD 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. 500 g potash ores (crushed to -2 mm before grinding) were added into 0.3 L saturated sylvinite solutions in a closed steel Ø 280×100 mm XMT ball mill, and ground to 95% passing 1 mm. Bench-scale tests were conducted in a 1.5 dm^3 of XFDC cell whose volume for rougher flotation was 1.5 dm^3, and for cleaner flotation was 0.75 dm^3, respectively.

After wet grinding, the effective amounts of saturated sylvinite solutions were added in the cell. Then, the prepared slurry was mixed with a certain amount of BOBD collector for 5 min. After that, a quantitative amount of air was pumped into the centre of the cell and mixed thoroughly with the pulp for 7 min, leading to the exposure of slurry to froth. Finally, KCl-laden bubbles floated out to the top of cell and separated from NaCl mineral. After collecting dry KCl 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 S2.** The XRD of the recovered KCl concentrate and NaCl tailing using Gemini surfactant BOBD was shown in **Figure S3.**

FTIR spectra measurement. Fine mineral (<5 μm, 2g) solid was soaked in 30 mL of saturated KCl or NaCl solutions with or without 1.5×10^{-6} mol/L BOBD 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 KCl solutions in presence of BOBD or OAH 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 BOBD or OAH.

Biodegradation test. The biodegradabilities of the cationic surfactants were evaluated by the biochemical oxygen demand (BOD). The BOD was determined with a BOD Tester (JPSJ-605, Shanghai INESA Scientific Instrument Co. Ltd., China) using the oxygen consumption method according to the Modified MITI Test.[1] Activated sludge was obtained from a municipal sewage plant in Ganzhou City, China. The BOD-biodegradation (BOD/ThOD) was calculated from the BOD values and the theoretical oxygen demand (ThOD).

Synthesis of Gemini surfactant BOBD

The synthesis of Gemini surfactant BOBD was described in **Figure S4.** N,N-Dimethyl-n-octadecylamine (***1***; 35.71 g, 0.12 mol) and 1,4-dibromobutane (***2***; 10.8 g, 0.05 mol) were placed in a 250 mL round bottom flask containing ethanol (60 mL), and the mixture was agitated for two 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 180 mL of ethyl acetate, and then purified by recrystallization from ethyl acetate/ethanol (9/1 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 Gemini surfactant N,N'-bis (octadecyldimethyl)-1,4-butane diammonium dibromide (***3***, 30.01 g, 0.037 mol).

N,N'-bis (octadecyldimethyl)-1,4-butane diammonium dibromide (***3***, BOBD), a white powder, yield 74.12%. 400 MHz ^{1}H NMR ($CDCl_3$, TMS, ppm): δ 0.89 (t, 6H, *J*=6.8 Hz, 2 CH_3), 1.24~1.39 (m, 60H, 30 CH_2), 1.78 (m, 4H, 2 CH_2), 2.19 (m, 4H, 2 CH_2), 3.28 (s, 12H, 4 CH_3N^+), 3.41 (t, 4H, *J*=8.6 Hz, 2 CH_2N^+), 4.01 (t, 4H, *J*=6.8 Hz, 2 CH_2N^+).

IR (KBr, cm^{-1}): υ 2910 (υ_{CH3}, υ_{CH2}), 2839 (υ_{CH3}, υ_{CH2}), 1453 (υ_{CH3}, υ_{CH2}), 1394 ($\upsilon_{C—N}$).

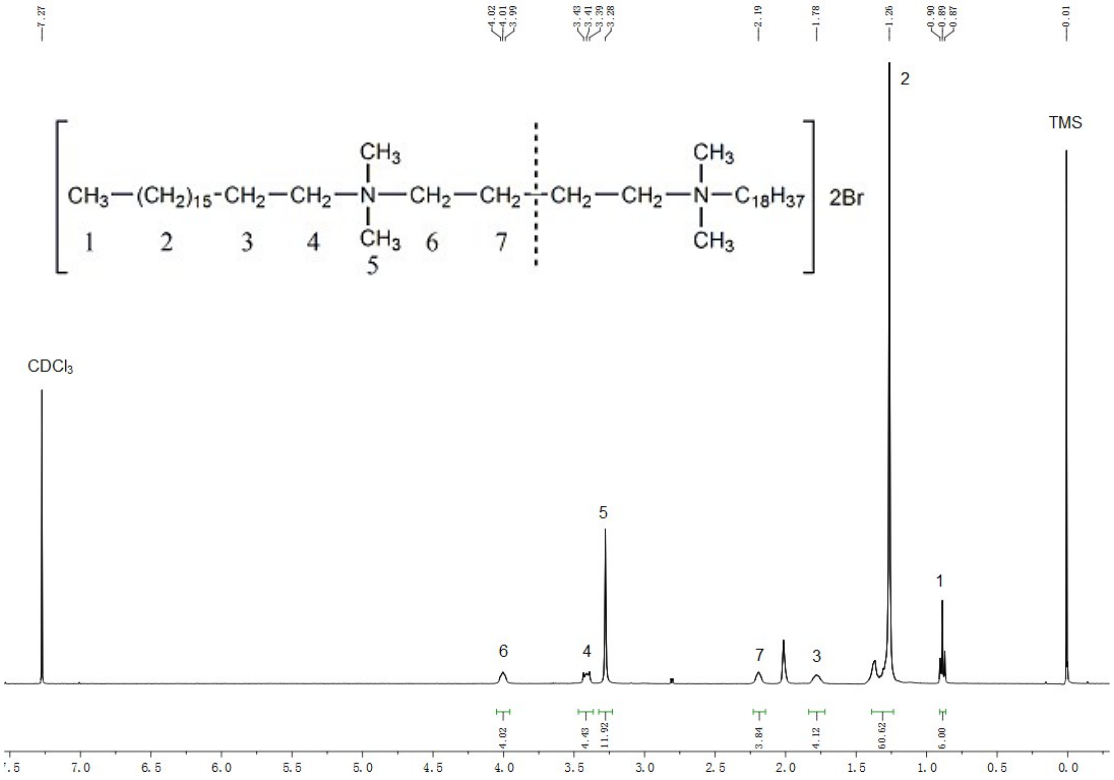


Figure S7. ^{1}H NMR spectra of Gemini surfactant BOBD in $CDCl_3$

Synthesis of Gemini surfactant BOED

The synthesis of Gemini surfactant BOED was described in **Figure S5.** 1-Bromooctadecane (***4***; 36.67 g, 0.11 mol) and N, N, N', N'-Tetramethylethylenediamine (***5***; 5.81 g, 0.05 mol) were placed in a 250 mL round bottom flask containing ethanol (60 mL), and the mixture was agitated for two 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 175 mL of ethyl acetate, and then purified by recrystallization from ethyl acetate/ethanol (9/1 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 Gemini surfactant N,N'-bis (octadecyldimethyl)-1,2- ethane diammonium dibromide (***6***, 29.47 g, 0.0376 mol).

N,N'-bis (octadecyldimethyl)-1,2-ethane diammonium dibromide (***6***, BOED), a white powder, yield 75.27%. 400 MHz ^{1}H NMR ($CDCl_3$, TMS, ppm): δ 0.84 (t, 6H, *J*=6.8 Hz, 2 CH_3), 1.18~1.33 (m, 60H, 30 CH_2), 1.72 (m, 4H, 2 CH_2), 3.28 (s, 12H, 4 CH_3N^+), 3.41 (t, 4H, *J*=8.6 Hz, 2 CH_2N^+), 3.88 (t, 4H, *J*=6.8 Hz, 2 CH_2N^+).

IR (KBr, cm^{-1}): υ 2924 (υ_{CH3}, υ_{CH2}), 2855 (υ_{CH3}, υ_{CH2}), 1473 (υ_{CH3}, υ_{CH2}), 1122 ($\upsilon_{C—N}$).

Synthesis of Gemini surfactant BCBD

The synthesis of Gemini surfactant BCBD was described in **Figure S6.** N,N-Dimethyl-n-cetylamine (***7***; 32.34 g, 0.12 mol) and 1,4-dibromobutane (***8***; 10.79 g, 0.05 mol) were placed in a 250 mL round bottom flask containing ethanol (75 mL), and the mixture was agitated for two 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 165 mL of ethyl acetate, and then purified by recrystallization from ethyl acetate/ethanol (8/1 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 Gemini surfactant N,N'-bis (cetyldimethyl)-1,4-butane diammonium dibromide (***9***, 31.71 g, 0.042 mol).

N,N'-bis (cetyldimethyl)-1,4-butane diammonium dibromide (***9***, BCBD), a white powder, yield 83.92%. 400 MHz ^{1}H NMR ($CDCl_3$, TMS, ppm): δ 0.89 (t, 6H, *J*=6.8 Hz, 2 CH_3), 1.22~1.42 (m, 52H, 26 CH_2), 1.78 (m, 4H, 2 CH_2), 2.21 (m, 4H, 2 CH_2), 3.27 (s, 12H, 4 CH_3N^+), 3.40 (t, 4H, *J*=8.6 Hz, 2 CH_2N^+), 4.03 (t, 4H, *J*=6.8 Hz, 2 CH_2N^+).

IR (KBr, cm^{-1}): υ 2923 (υ_{CH3}, υ_{CH2}), 2852 (υ_{CH3}, υ_{CH2}), 1469 (υ_{CH3}, υ_{CH2}), 1123 ($\upsilon_{C—N}$).

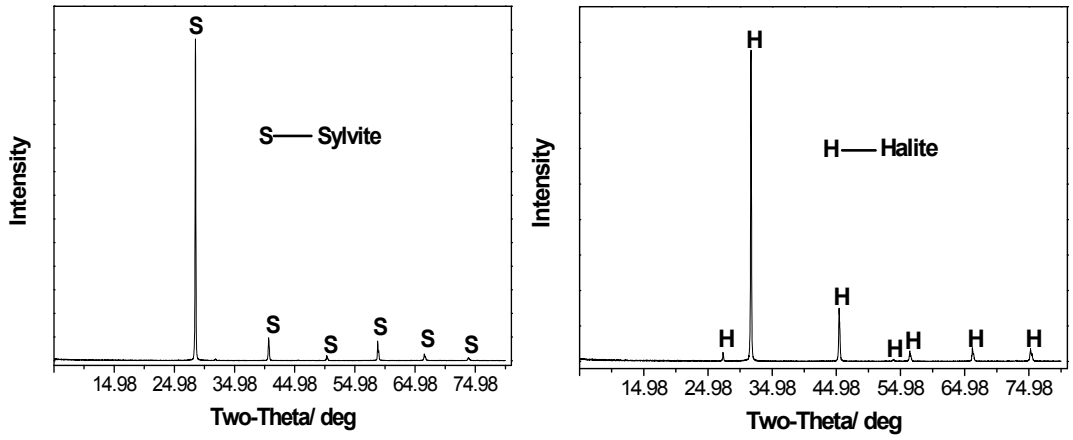


Figure S1. XRD of KCl (sylvite) and NaCl (halite)

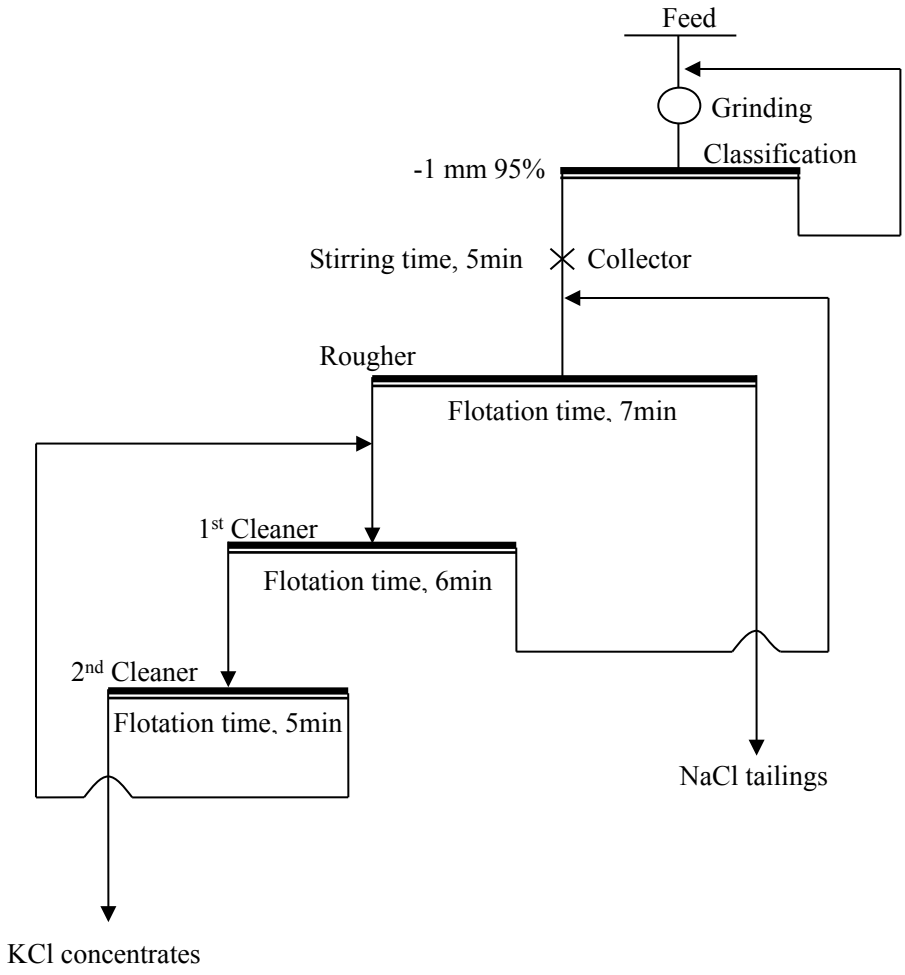


Figure S2. The flowsheet of froth flotation experiments

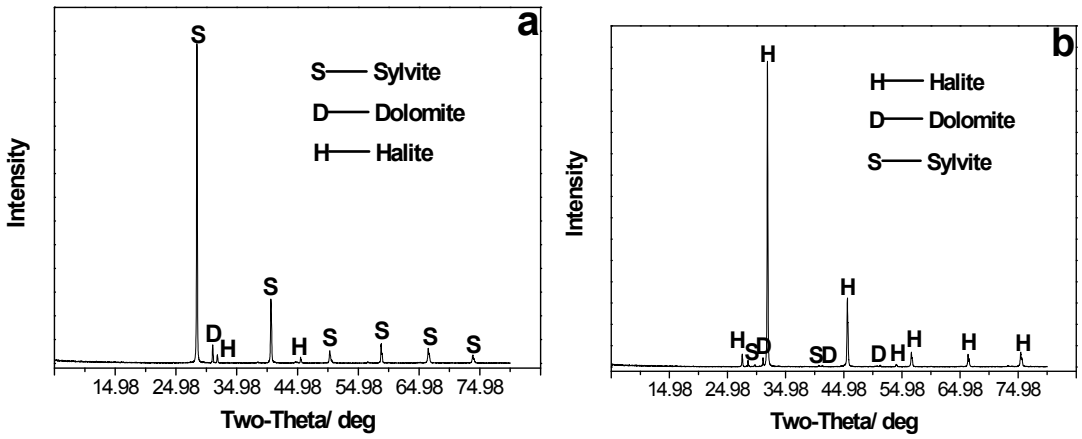
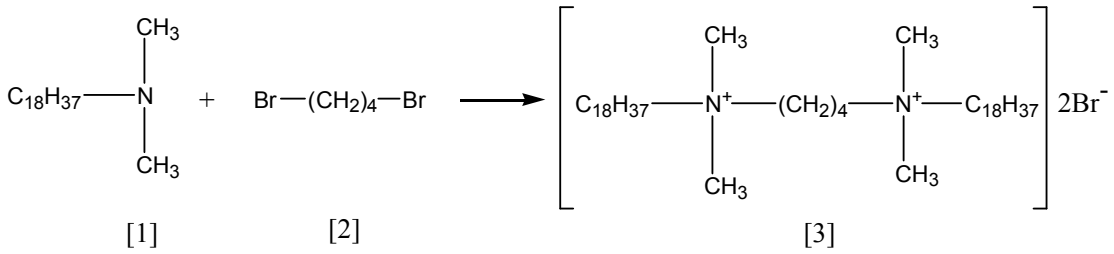


Figure S3. XRD of the recovered KCl concentrate (a) and NaCl tailing (b) using Gemini surfactant BOBD



[1] [2] [3]

Figure S4. Synthetic route for Gemini surfactant BOBD

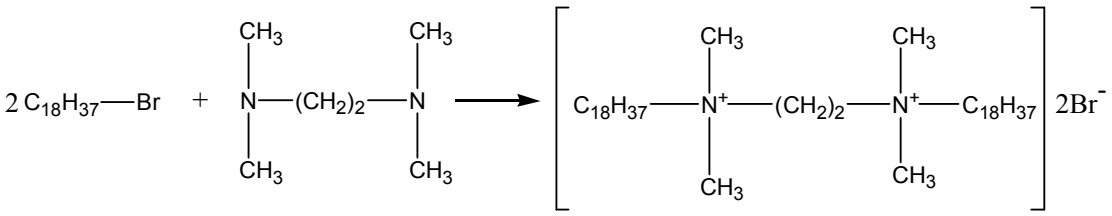
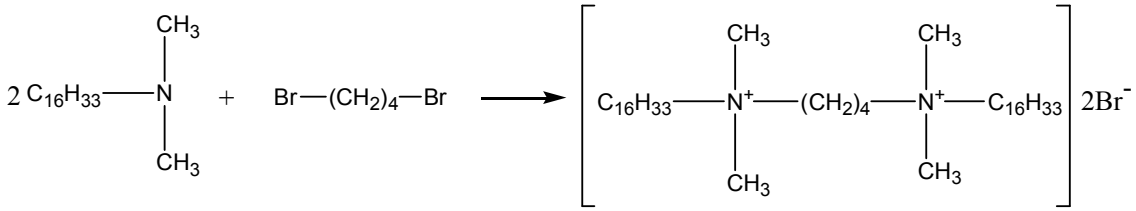


Figure S5. Synthetic route for Gemini surfactant BOED



[7] [8] [9]

Figure S6. Synthetic route for Gemini surfactant BCBD

Table S1. Chemical composition of the pure minerals (wt%)

Sample	KCl	NaCl	$MgCl_2$	$CaSO_4$	H_2O
Sylvite	99.70	—	—	—	0.30
Halite	—	99.50	—	—	0.50

Table S2. Chemical composition of potash ore and saturated sylvinite solutions (wt%)

Sample	KCl	NaCl	$CaSO_4$	H_2O	Clayey-carbonate impurities
Potash ore	25.63	70.18	0.55	1.37	2.27
Saturated sylvinite solutions	8.95	21.63	0.13	69.29	—

Table S3. Values of the CMC and γ_{CMC} for BOBD and OAH

Surfactant	CMC (g/L)	γ_{CMC} (mN/m)
BOBD	8.1×10^{-4}	31.3
OAH	2.5×10^{-3}	33.2

References

1. Organization for Economic Cooperation, Development (OECD) (1981) OECD guidelines for testing of chemicals, 301C modified MITI test. OECD, Paris