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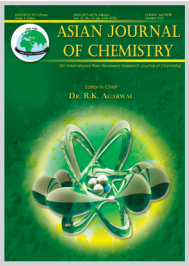

Synthesis and Quantitative Determination of Gemini Surfactants

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The intermediate 1-bromo-2-(2-bromoethoxy)ethane was synthesized from diglycol and phosphorus tribromide. Cationic Gemini surfactants, diethyl ether-*bis*-(dimethyl alkylammonium bromide) were synthesized from the intermediate and tertiary amines with different alkyl chains by using isopropanol as solvent. The reactants were recystallized in the ethyl acetate-ethanol solvent mixture (volume ratio is 2:1), the yields were all up to 70 %. The Gemini surfactants were characterized by infrared and ^{1}H NMR analysis and were also quantitatively determined by the two phase chemical titration using bromophenol blue as the indicator and chloroform as the phase dispersing agent. The results showed that the purity of the six Gemini surfactants synthesized are greater than 96 % in weight.

Key Words: Diglycol, Phosphorus tribromide, *N,N*-dimethyl alkyl tertiary amine, Bromination, Titration analysis.

INTRODUCTION

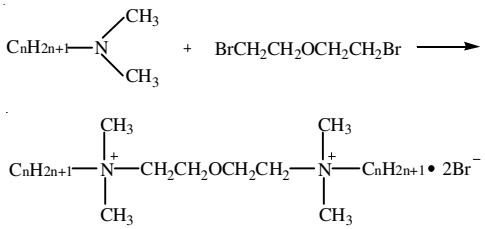
Gemini surfactants are novel surfactants with two hydrophobic chains and two hydrophilic head groups connected by a linkage adjacent to the hydrophilic head groups in a molecular[1-3]. Because of this unique structure, Gemini surfactants exhibit superior surface activity and application performance, so they have been pained great attention in many application fields, such as oil exploitation[4], preparation of novel materials, synthetic fiber industry and personal care products[5]. Gemini surfactants are current hot research focus of surfactant.

EXPERIMENTAL

Synthesis of the intermediate 1-bromo-2-(2-bromoethoxy)ethane[6]: The dibromo precursor was synthesized by the addition of phosphorus tribromide to diethylene glycol in a dropwise manner over a period of 1 h at 0 ºC[7,8]. Then the mixtures were stirred with concomitant heating at 50-60 ºC for 12 h. The reaction mixture was then cooled to ambient temperature and dissolved in chloroform (25 mL). Water was added slowly and the mixture was transferred into a separatory funnel. The organic layer was separated out after washing with water, sodium bicarbonate and again with water and finally passed through a bed of anhydrous sodium sulfate. The resulting chloroform solution was concentrated and loaded on a silica gel column (60-120 mesh) and was eluted with hexane to give a colourless liquid.

Synthesis of the Gemini surfactants[9-11]: All the surfactants were obtained by refluxing the dibromo precursor with *N,N*-dimethyl alkyl tertiary amine in dry ethanol at 80 ºC for 72-96 h. At the end of this period, solvent was removed under vacuum from the reaction mixture and the solid thus obtained was recrystallized several times from 10 mL of ethyl acetate containing 5 mL of ethanol to obtain solid surfactants as pure product as determined from ^{1}H NMR spectra and elemental analysis. The overall yields of the surfactants ranged from 70 to 75 %.

The reaction is as follows:



n = 8, 10, 12, 14, 16, 18

For convenience, the surfactants are abbreviated as Gemini 8-Y-8, Gemini 10-Y-10 Gemini 12-Y-12, Gemini 14-Y-14, Gemini 16-Y-16, Gemini 18-Y-18, respectively.

RESULTS AND DISCUSSION

It can be seen from the infrared spectrum of Gemini 8-Y-8 (Fig. 1) that the stretching vibration absorption bands of

TABLE-1
CHEMICAL SHIFTS OF ^{1}HNMR FOR GEMINI SURFACTANTS SYNTHESIZED

Surfactant	Chemical shift						
	Alkyl chain				NCH_3	Spacer group	
	CH_3	CH_2	$NCCH_2$	NCH_2		$NCCH_2$	NCH_2
8-Y-8	0.82(6H)	1.25(20H)	1.68(4H)	3.61(4H)	3.41(12H)	3.99(4H)	4.30(4H)
10-Y-10	0.86(6H)	1.28(28H)	1.70(4H)	3.62(4H)	3.44(12H)	4.03(4H)	4.34(4H)
12-Y-12	0.86(6H)	1.29(36H)	1.71(4H)	3.63(4H)	3.45(12H)	4.04(4H)	4.35(4H)
14-Y-14	0.88(6H)	1.30(44H)	1.73(4H)	3.65(4H)	3.46(12H)	4.06(4H)	4.37(4H)
16-Y-16	0.86(6H)	1.28(52H)	1.69(4H)	3.62(4H)	3.45(12H)	4.03(4H)	4.36(4H)
18-Y-18	0.87(6H)	1.31(60H)	1.70(4H)	3.62(4H)	3.45(12H)	4.04(4H)	4.36(4H)

CH_3-, -CH_2- ranges from 3000 to 2850 cm^{-1}, with its bending vibration absorption bands at 1470-1450 cm^{-1} and 725-720 cm^{-1}. The stretching vibration of C-N is at 1230-1030 cm^{-1} range while the stretching vibration of -C-O-C- is near 1140 cm^{-1}. The absorption bands, which is in the range of 1680-1620 cm^{-1} or 3540-3410 cm^{-1} indicates that there is water in the samples, which might be attributed to the fact that the oxygen atoms in -C-O-C-bond can easily combine with the hydrogen atoms in the H_2O molecule to form hydrogen bonds.

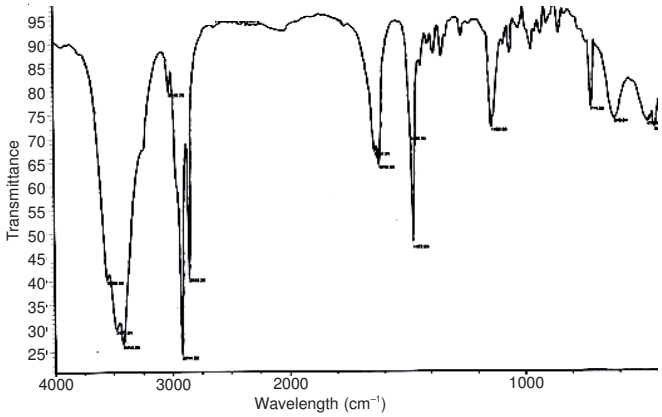


Fig. 1. Infrared spectra of Gemini 8-Y-8

Fig. 2 shows the ^{1}H NMR spectrum of synthetic Gemini 8-Y-8 surfactant. From the figure the H chemical shifts δ of the various groups are: long-chain alkyl CH_3-δ 0.82(6H), -CH_2- δ 1.25(20H), -N-C-CH_2- δ 1.68(4H), -N-CH_2- δ 3.61(4H); -N-CH_3 3.41(12H); connected group -N-C-CH_2- δ 3.99 (4H), -N-CH_2- δ 4.30 (4H); the peak of impurity δ 2.61. All the chemical shifts of ^{1}H NMR for surfactants synthesized are listed at Table-1.

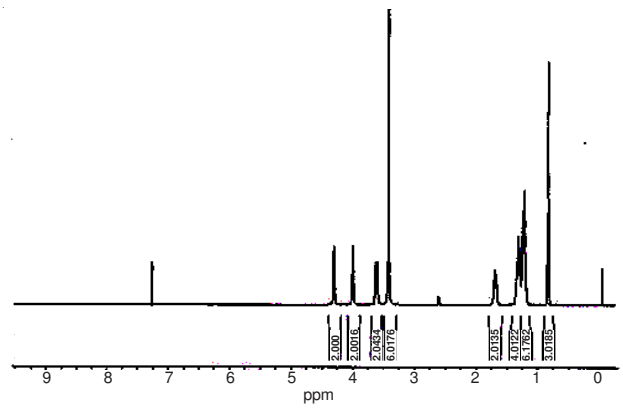


Fig. 2. Chemical shifts of nuclear magnetic resonance for Gemini 8-Y-8

Quantitative determination of Gemini surfactants: A quantitative known concentration of KCl solution, in which excess quantitative of sodium tetraphenylborate standard solution was added[12]. The residual sodium tetraphenylborate was then titrated by double quaternary ammonium salt. The formation of bromophenol blue and slightly quantitative of double quaternary ammonium salt at the titration end-point gave a chlorinated organic solvent soluble salt, which gave a visible colour of blue in this solvent. Repeat the above procedure as a blank test without adding KCl.

The reactions are as follows:

$NaB(C_6H_5)_4 + KCl \rightarrow KB(C_6H_5)_4 \downarrow + NaCl$

$2NaB(C_6H_5)_4 + RN^+ (CH_3)_2CH_2CH_2OCH_2CH_2(CH_3)_2N^+ R\text{-}2Br^- \rightarrow RN^+(CH_3)_2CH_2CH_2OCH_2CH_2(CH_3)_2N^+R\text{-}2^-B(C_6H_5)_4 + 2NaCl$

The content of the Gemini surfactant solution could be calculated by the following formula:

$$\frac{0.08\times V_0\times M}{(V_2-V_1)\times m\times 1000}\times 100\%$$

where, V_0 (mL) is the volume of the Gemini surfactant solution; V_1 (mL) is the volume of the Gemini surfactant solution which titrate residual sodium tetraphenylborate; V_2 (mL) is the volume of the Gemini surfactant solution which titrate residual sodium tetraphenylborate at blank test without adding KCl; m(g): sampling amount of the Gemini surfactant; M(g/mol): Mole weight of the Gemini surfactant.

The content of the Gemini surfactants synthesized are listed at Table-2.

TABLE-2
CONTENT OF CATIONIC GEMINI SURFACTANTS SYNTHESIZED

Surfactant	V_2 (mL)	V_1 (mL)	Sampling amount (g)	Content (%)
8-Y-8	33.34	20.05	0.3392	96.8
10-Y-10	28.90	17.34	0.4338	96.0
12-Y-12	30.84	18.53	0.4417	96.9
14-Y-14	40.09	24.07	0.3725	95.8
16-Y-16	26.66	16.06	0.5934	97.8
18-Y-18	25.03	15.01	0.6790	97.1

Conclusion

The Gemini cationic surfactant was composed from the bromination and quaternization of the raw solution, which was obtained by dissolving diethylene glycol, phosphorus tribromide and tertiary amine in isopropanol solvent. Structure characterization of the reaction product, recrystallized from

ethanol-ethyl acetate mixture, was carried out through IR and ^{1}H NMR. The content was determined to be more than 95 % by means of diphasictitration with bromophenol blue as the indicator and chloroform as the dispersed phase, which is a more trouble-saving method than those demanding demarcation of anionic surfactent standard solution in references and also, more efficient and accurate. The as-composed high-purity Gemini cationic surfactant guarantees the reliability of subsequent theoretical research of solubilization and phase behaviour.

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