ORIGINAL ARTICLE



Insights into the Optimization of Alkyl Phenol/Alkyl Halide Ratio in Gemini Surfactant Synthesis

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Abstract ¹H NMR and thin layer chromatography (TLC) were applied to analyze the component of two series of synthesized sulfonated Gemini surfactants with different spacer lengths (2, 4, and 6 carbons) and hydrophobic chain lengths (9, 12 carbons). Gemini surfactants were prepared by reacting alkylphenol with alkyl halide followed by sulfonation with chlorosulfonic acid. The influence of the molar ratio of alkyphenol to alkyl halide on the mono- to diether ratio was investigated and the results indicated that the molar ratio is a key factor to minimize impurities in the target material, due to the high reactivity of alkyl halide. In addition, the results showed that alkyl halide with a shorter spacer group length required a higher molar ratio of alkyl halide to alkylphenol. To synthesize the intermediate Gemini product with 80 % diether content, the molar ratios were optimized using n(alkylphenol):n(1,6-dibromohexane) = 1:0.55, n(alkylphenol):n(1,4-dibromobutane) =1:0.7, and n(alkylphenol):n(1,2-dibromoethane) = 1:2.5, respectively.

Keywords Gemini surfactant · Nuclear magnetic resonance · Thin layer chromatography · Reaction ratio

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Introduction

Gemini surfactants, made up of two hydrophobic chains and two polar head groups covalently connected at the head groups or very close to the head groups by a spacer group, have attracted considerable interest in both scientific and industrial applications [1–6]. Most researchers have focused on cationic Gemini surfactants, whereas there are only a few reports about the synthesis of anionic Gemini surfactants, due to difficulties in purification. In the synthesis of anionic Gemini surfactants, it is difficult to get a pure product, since it is easy to generate single-stranded products that have similar physical and chemical characters to the Gemini structure.

According to previous reports [7–9], Gemini surfactants can be purified by solvent extraction and recrystallization and the yield determined by two-phase titration. However, conventional separation and purification methods cannot separate single and double chain products completely. Therefore, the reaction mixture inevitably contains both single-stranded and Gemini surfactants. In this situation, it is difficult to obtain reproducible structure/property relationships for Gemini surfactants. There have been a few literature reports on the separation and purification of single- and double-stranded components [3, 6]. Therefore, it is necessary to establish a method that has potential advantages for simplifying and accelerating the analytical routes for structure identification of constituents in complex reaction mixtures.

Dialkyl diphenyl diether disulfonate is a typical kind of anionic Gemini surfactant. Many researchers have focused on the design and synthesis of this kind of anionic Gemini surfactant, exploring potential surface and interfacial properties and aggregation behavior [3, 10, 11]. In order to get pure Gemini surfactants, it is necessary to separate the monether from the intermediate products. Separation of intermediate products on siliconized chromatoplates can be achieved using organic solvents. Generally, the separation of these substances is influenced by the solvent polarity and molecular weight of the compounds [12]. In this paper, since monether and diether have similar functional groups, the difference in polarity is too small to control for the separation by siliconized chromatoplates. So the molecular weight of each component in the mixture becomes the main factor to control separation during the synthesis process of the Gemini surfactant [12–14].

In recent years, ¹H NMR has been used for quantitative analysis of mixed compounds, such as polyester and cotton plant grass active extract, and the determination of the absolute content of each component in new medicines [12, 15, 16]. There have been no reports on using 1 H NMR for quantitative analysis of single-stranded and double-stranded components in the synthesis of Gemini surfactants. In quantitative analysis of mixed compounds using ¹H NMR spectra [17], the integrated area of the absorption peak is proportional to the number of protons. Therefore, the peak area ratio reflects the relative number of different proton types. A new spectrum analysis method has been used to simplify the process of separation and analysis of complex mixtures, and to identify complex ingredients without complete separation [15-17]. This method shows unique analytical capabilities, especially for trace composition or components with similar polarity which are difficult to separate under conventional separation conditions.

In this paper, a series of Gemini surfactants were synthesized and the single-stranded components and doublestranded products were separated by TLC from the reaction mixture. The relative contents of mono- and diether were determined based on ¹H NMR spectra. Furthermore, the influence of different ratios of raw materials on intermediate products (mixture of diether and monoether) was studied, and an effective method to monitor the synthesis, optimize strandedreaction conditions and examine strandedperformance is provided.

Experimental

Materials

Nonyl phenol (NP, 97 %) and dodecyl phenol (DP, 98 %) were purchased from Chengdu Chemical Reagent, China, and purified by distillation under reduced pressure at 200 °C prior to use. 1,2-dibromoethane (99 %), 1,4-dibromobutane (98.5 %), chlorosulfonic acid (99 %), methanol (99 %), ethanol (99 %), acetone (99 %),

dichloromethane (99 %) were all purchased from Chengdu Chemical Reagent and used without further purification. 1,6-dibromohexane (99.2 %) was purchased from Beneer Chemistry, USA, and used without further purification. Distilled water was used throughout this study.

Synthesis of Gemini Surfactants

Six Gemini surfactants (GS n-m-n) were synthesized using a two-step reaction as shown in Scheme 1. The synthesis and purification procedures I and II have been reported in the literature [3].

The intermediate product (Mid n-m-n) of diether (DE) and monoether (ME) was obtained as follows. Phase transfer catalyst triethylbenzylammonium chloride (TEBA) and NaOH solution were added to alkylphenol at 70 °C. The solution was heated to 95 °C under stirring, and then alkyl halide was added dropwise into the mixture and allowed to react for 4 h. The target product (GS n-m-n) was acquired by sulfonating DE with chlorosulfonic acid followed by neutralization with sodium hydroxide.

Purification-I

The intermediate product was cooled to ambient condition and dried. The residual solution was washed with 3 wt% glacial acetic acid and distilled water until pH was around at 7, and then the solvent was removed by distilling under reduced pressure at 120 °C to obtain a mixture of DE and ME. The yield of Mid n-m-n was calculated at the end of purification-I.

Purification-II

DE and ME were separated by silica gel thin layer chromatography (TLC) after the preliminary purification I. TLC plates were spotted at 10.0 ng level with the help of graduated capillaries (10.0 µL). Because the polarity difference of the raw materials and Mid-products is relatively small, and polarity difference between diether and monoether is also small, low polarity solvents were used for the separation. Attempts have been made to optimize TLC conditions using different solvents, such as methanol, ethanol, acetone, dichloromethane, cyclohexane and ethyl acetate [17, 18]. The solvent system was optimized by varying the concentration of cyclohexane and dichloromethane. The intermediate product (Mid n-m-n) was purified using a solution of cyclohexane and dichloromethane (5:6, v/v). Pure DE and ME were obtained by stripping each component from the TLC plates. Products obtained by this stripping-method had very high purity and were used as magnetic resonance spectroscopy standards.

Scheme 1 Mid-n-m-n (intermediate product mixture), DE (diether), ME (monoether) and GS n-m-n (target product); n = 9, 12; m = 2, 4, 6



NMR Spectra Area Method

Results and Discussion

According to the literature and chemical shift laws, the biggest difference in hydrogen spectral peaks between dialkyl diphenyl ether sulfonate (diether) [3, 19] and single-alkylphenyl ether sulfonate (monoether) [20] are as follows: the proton chemical shift of hydrogen in aromatic ether linkage of DE is in the range of $\delta 4.0-4.1$. The length of the surrounding carbon chain influenced the chemical shift [12]. Monoether carried both an ether bond and a hydrogen bond with bromine methylene (chemical shift: $\delta 3.4-3.6$) [21].

After preliminary purification of the mixture, the areas of the chemical shifts of both monoether and diether in the NMR spectra can be compared when both monoether and diether exist in the mixture. The proportion of theoretical total hydrogen number Hs' of monoether and diether in the mixture must be equal to Hs, the actual hydrogen number obtained by the spectrum integral value, which ensures that there are no other interfering substances in the mixture. By this method, the content of monoether and diether is determined quantitatively.

The specific formulae used are as follows:

$$4X + 2Y = H_{\delta 3.9 - 4.1} \tag{1}$$

$$2Y = H_{\delta 3.4-3.6}$$

$$Hs = (N_1 X + N_2 Y) / (X + Y) = Hs'$$
(3)

Theoretical hydrogen of X mole diether at the range of $\delta 3.9-4.1 = 4X$; theoretical hydrogen of Y mole monoether at the range of $\delta 3.9-4.1 = 2Y$; theoretical hydrogen of X mole diether = N₁X; theoretical hydrogen of Y mole monoether = N₂Y; Hs' is the theoretical total hydrogen number; Hs is the actual total hydrogen of one mole mixture in the spectra.

Effect of the Molar Ratio (W_m) Between Alkylphenol and Alkyl Halide

After purification-I, the intermediate product will be a mixture of unreacted alkyphenol, diether and side product monoether. To reduce the unreacted alkyphenol and produce more diether, it is necessary to adjust the molar ratio (W_m) between alkylphenol and alkylhalide (W_m is defined as the molar ratio of alkylphenol/alkyhalide). Consequently, the molar ratio plays a key role in the synthesis of the Gemini surfactant with less single-stranded surfactant produced [22–24].

Results by TLC

(2)

Figure 1 shows the TLC identification of the raw material and Mid n-m-n (Mid 9-2-9 and Mid 12-6-12) with $W_m = 1:0.5-1:2.5$. According to our previous study, the molecular weight is the main factor that affects the speed of separation and the retention factor (R_f) of each substance. That is because there was a slight polarity difference between monoether and diether while great difference existed in the molecular weight. The point "a" in Fig. 1 is the starting raw material with stronger polarity, point "b" is diether and "c" is the monoether.

Figure 1 (left) shows that Mid 9-2-9 consists mainly of unreacted nonylphenol, diether and monoether when W_m values were 1:0.7 and 1:1. The conversion of the raw material nonylphenol was increased with the increment of the W_m value. As the W_m value is 1:2.5, the raw material spot disappeared and two obvious spots of diether and monoether were found on the TLC plates. Therefore, the



Fig. 1 TLC identification of Mid n-m-n at different reaction ratios after 4 h. *Left 1* Nonylphenol, 2 Mid 9-2-9 ($W_m = 1:0.7$), 3 Mid 9-2-9 ($W_m = 1:1$), 4 Mid 9-2-9 ($W_m = 1:2$), 5 Mid 9-2-9 ($W_m = 1:2.5$). *Right 1* Dodecyl phenol, 2 Mid 12-6-12 ($W_m = 1:0.5$), 3 Mid 12-6-12 ($W_m = 1:0.5$), 4 Mid 12-6-12 ($W_m = 1:0.7$), 5 Mid 12-6-12 ($W_m = 1:1.5$)

optimal molar ratio for the synthesis of Mid 9-2-9 was taken to be 1:2.5.

Figure 1 (right) shows the synthesis results of the reaction between dodecylphenol and 1, 6-dibromohexane with different molar ratios from 1:0.5 to 1:1.5. When the value of $W_{\rm m}$ was 1:0.5, there was unreacted dodecylphenol in Mid 12-6-12. However, increasing the $W_{\rm m}$ value to 1:0.55, dedocylphenol can be reacted completely with 1, 6-dibromohexane, which indicated that 1, 6-dibromohexane has higher reactivity than 1, 2-dibromoethane. As the $W_{\rm m}$ value was increased in the range of 1:0.55 to 1:1, the distribution of diether and monoether was changed regularly. However, quantitative conclusions were hard to draw using the TLC method [24–26].

The Content of Diether and Monoether in the Intermediate Products

The TLC method is a simple method for qualitative research, while the ¹H NMR spectra area method is good for quantitative research. The content of diether and monoether in the intermediate product after purification-I was analyzed using the ¹H NMR spectra area method. Figure 2 shows the ¹H NMR spectra of DE 12-6-12 and Mid 12-6-12 obtained at different reaction ratios $W_{\rm m} = 1:0.5-1:1$. Based on the results in Fig. 2, the characteristic groups of dodecylphenol, diether and monoether were at chemical shifts, $\delta \approx 5.1$; $\delta \approx 4$; $\delta \approx 3.47$, respectively. When the $W_{\rm m}$ value was 1:0.5, peaks at $\delta \approx 5.1$ and $\delta \approx 4$ were observed, which indicates

unreacted 1, 6-dibromohexane and target product diether in the mixture of Mid 12-6-12. When the molar ratios were changed to 1:0.55, 1:0.7 and 1:1, the area ratio of $S(\delta 4.02)$: $S(\delta 3.47)$ was 4:0.44, 4:1.14 and 4:1.9, respectively. According to the formula in the experimental section, the exact content of diether and monoether was calculated, and listed in Table 1. When the molar ratio was changed to 1:0.55, 1:0.7 and 1:1, the ratio between diether and monoether in the Mid 12-6-12 was 80.9:19.1 %, 55.8:44.2 %, and 34.5:65.5 %, respectively. The results show that the molar ratios between dodecylphenol to 1, 6-dibromohexane are responsible for the distribution of diether, monoether and unreacted dodecylphenol in the crude product Mid 12-6-12.

Based on the investigation of optimizing reaction conditions, we found that different alkyl halides should require different optimal reaction ratios of n(alkyl phenol):n(alkyl halide). Under different reaction ratios, a series of intermediate products with different spacer lengths (2, 4, and 6) and hydrophobic chain lengths (9, 12) were synthesized. ¹H NMR spectra of Mid 9-4-9, Mid 12-4-12 and Mid 12-2-12 obtained at different molar ratios of n(alkylphenol):n(alkyl halide) are shown in Fig. 3. The calculated species distribution from the ¹H NMR analytical results are given in Table 2.

The alkyl halide with the shorter spacer group required a higher optimal molar ratio. When the molar ratio was 1:0.5 for Mid 9-6-9 and Mid 12-6-12, there was unreacted alkyl phenol. When the reaction molar ratios were changed to 1:0.55, 1:0.7 and 1:1, the ratios between diether and monoether in the Mid 9-6-9 were 79.3:21.7 %, 53.4:46.6 % and 32.8:66.2 %, respectively. This was consistent with the regularity of Mid 12-6-12, which proved that the alkyl phenol had little influence on the optimal reaction ratio. When the reaction molar ratios were 1:0.5 and 1:0.55, there was unreacted alkyl phenol in the product of Mid 9-4-9 and Mid 12-4-12. When the reaction ratio was increased to 1:0.7, the alkyl phenol reacted completely with the alkyl halide. When the molar ratios were changed to be 1:0.7, 1:1 and 1:2.5, the ratio between diether and monoether in the Mid 12-4-12 were 80.7:19.3 %, 64.6:35.4 % and 37.8:63.2 %, respectively, where in Mid 9-4-9 the corresponding ratios were 79:21 %, 62.9:38.1 and 31.5:69.5 %. When the molar ratio varied from 1:0.5 to 1:1, there were still some unreacted alkyl phenol left in the product of Mid 9-2-9 and Mid 12-2-12. Therefore, in order to obtain the product of around 85 % diether and 15 % monoether, the optimal molar was taken as 1:2.5.

Based on this study, the reactivity and steric effect of the alkyl halide had a strong influence on the required amount of the corresponding alkyl phenol. According to the chemical reaction equation, the molar ratio between alkyl phenol and alkyl halide should ideally be 1:0.5 to generate

Fig. 2 ¹H NMR spectra of Mid12-6-12 under different ratios of n(alkylphenol):n(alkyl halide). (1:0.5), (1:0.55), (1:0.7) and (1:1) represent the different ratios of n(dodecylphenol):n(alkyl halide)



Table 1Effect ofn(dodecylphenol):n(alkylhalide) on the synthesis of Mid12-6-12

n(dodecylphenol):n(alkyl halide)	1:0.5	1:0.55	1:0.7	1:1
S(84.02):S(83.47)	4:0	4:0.44	4:1.14	4:1.9
n(DE):n(ME) = X %: Y %	100:0	80.2:19.8	55.8:44.2	34.5:65.5
Hs' = (70X + 41Y)/(X + Y)	70	64.8	57.8	51
Hs	69.3	64.1	57.2	49.8
Total yield (DE + ME) %	65.7	81.6	86.5	83.2



Fig. 3 ¹H NMR spectra of Mid n-m-n under different ratios of n(alkylphenol):n(alkyl halide). *1:0.7* and *1:2.5* represent the different ratios of n(alkylphenol):n(alkyl halide)

1 mol of diether. However, differences existed in the real reaction because the alkyl halides with different spacer lengths have different reactivity and varied steric effects. The results show that 1,6-dibromohexane has a better activity than the others. Therefore, the reactions for different alkyl halides required different optimal reaction ratios of alkyl phenol and alkyl halide. In addition, compared with the alkyl halide, the results indicated that alkylphenol had only slight effects on the reaction condition.

The diether reaction is a classic nucleophilic bimolecular substitution (SN_2) . The functional group in the alkyl halides is a carbon-halogen bond, the common halogens being fluorine, chlorine, bromine and iodine. With the exception of iodine, these halogens have electronegativities significantly greater than carbon. During the reaction, more

Table 2 Effect of n(alkyl					
phenol):n(alkyl halide) on the					
systhesis of Mid m-n-m					

n(alkyl phenol)):n(alkyl halide)	1:0.5	1 %:0.55 %	1 %:0.7 %	1 %:1 %	1 %:2.5 %
Mid12-6-12	n(DE):n(ME)	-	80.9:19.1	55.8:44.2	34.5:65.5	-
Mid9-6-9	n(DE):n(ME)	_	79.3:21.7	53.4:46.6	32.8:66.2	-
Mid12-4-12	n(DE):n(ME)	_	_	80.7:19.3	64.6:35.4	37.8:63.2
Mid9-4-9	n(DE):n(ME)	_	_	79:21	62.9:38.1	31.5:69.5
Mid12-2-12	n(DE):n(ME)	_	_	_	-	85.2:14.8
Mid9-2-9	n(DE):n(ME)	-	-	-	-	84.6:15.4

reactive species dibromoalkane (Br-C-C-Br) was used, and RArO- was used as a nucleophile. Consequently, the functional group in the alkyl halide is polarized so that the carbon is electrophilic and the halogen is nucleophilic. Alkyl halides undergo two basic types of reactions in organic chemistry: substitutions and eliminations. Some of the most important information concerning nucleophilic substitution and elimination reactions of alkyl halides has come from studies in which the structure of the alkyl group has been varied. There are a few factors that affect substitution and elimination reactions: nucleophilicity, leaving group, steric effect, solvent effect, alkyl moiety, and molecularity. With primary alkyl halides, the SN₂ mechanism almost always predominates. However, the strong steric effect in dibromoalkane may cause elimination (E_2) to occur accompanied by SN2 substitution. The transition state is too crowded to go through the inversion process.

The rate of the SN₂ reaction is directly linked to the concentration of the two species, the nucleophile (Nuc) and the alkyl halide (RX) undergoing substitution. Changing the concentration means changing the number of possible collisions. When it came to 1,2-dibromoethane, because of a stronger steric effect during the substituent process, it was easy for the elimination reaction or SN2 on one side of the dibromoetheane which resulted in an excess of 1,2-dibromoethane being required to generate the target product diether. As n(alkylphenol):n(1, 2-dibromoethane) was below 1:2.5, most of the 1,2-dibromoethane was sacrificed in the elimination reaction and only a small part reacted with alkylphenol to produce diether or monoether. Consequently, the conversion of alkyl phenol was very low. As for 1,4-dibromoethane and 1,6-dibromohexane, the distance between the two halogen atoms was greater so the steric effect was not as strong as that in 1,2-dibromoethane. It was more active for them to generate SN₂ substitution with alkylphenol. At the condition of n(alkylphenol):n(alkyl halide) = 1:0.55-1:0.7, more than 80 % of the products was diether. When the amount of the alkyl halide increased, the surplus C-Br made more monoether.

The appropriate ratio is the key factor to control the content of diether and monoether. The conclusion drawn from the ¹H NMR spectra area method is in agreement with the results from TLC analysis as follows: alkyl halides with

a shorter spacer group required a higher optimal molar ratio, and by increasing the molar ratio of alkyl phenol to alkyl halide, more monoether was generated in the intermediate product. Few literature reports mention the effect of chain length on the reactivity of alkyl halides and how they influence the synthesis procedure of Gemini surfactants.

Conclusions

In this paper, two series of sulfonated Gemini surfactants GS m-n-m (m = 9, 12; n = 2, 4, 6) with different spacer lengths and hydrophobic chain lengths were synthesized and characterized. The relationship between spacer length, hydrophobic chain length, and the molar ratio of alkyl phenol to alkyl halide were determined by TLC and NMR. At a constant n(alkyl phenol):n(NaOH) rato of 1:5.4, the reaction ratio of n(alkyl phenol):n(alkyl halide) can be adjusted to improve the yield of diether, and the difficulty of the purification was reduced. A series of proportional and controllable mixtures of diether and monoether were obtained. The results drawn by NMR area and TLC methods were consistent as follows: alkyl halides with shorter spacer group lengths required higher optimal molar ratios, and by increasing the molar ratio of alkyl phenol to alkyl halide, more monoether was generated in the intermediate product.

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