ORIGINAL ARTICLE

Gemini Cationic Surfactants: Synthesis and Influence of Chemical Structure on the Surface Activity

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Abstract Three cationic gemini surfactants were synthesized and characterized using different methods. Their surface activities were measured using surface and interfacial tension measurements. The effect of the spacer chain length on the surface activity, emulsification power and interfacial tension was studied. The thermodynamic parameters showed the tendency towards micellization and adsorption. The results showed that longer spacers increased the micellization tendencies of the surfactants, while shorter spacers increased the adsorption tendency at the air–water interface.

Keywords Gemini surfactants · Spacer group · Surface activity · Thermodynamics

Introduction

Gemini surfactants are a novel type of surfactant synthesized in recent years. Their advent has greatly broadened the perspective of interfacial science [1-3]. Compared with conventional surfactants, gemini surfactants are more efficient at lowering surface tension and have much lower critical micelle concentration values (CMC). Despite their

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J. M. Marquis Cooperation Petroleum, Cairo, Egypt recent development, gemini surfactants are already a hot topic in colloids and surface science and are considered to be a type of surfactant that will be most widely used in the 21st century [4–6]. Gemini cationic surfactants have been extensively studied due to their easy preparation. This has also made them particularly interesting from an industrial point of view, and much of the published information concerning the solution properties of gemini surfactants is based on cationic species [7–10].

Experimental

Synthesis of Aminopyridine Schiff Base (SB)

A mixture of benzaldehyde (0.15 mol, 15.75 g), *p*-aminopyridine (0.15 mol, 14.1 g) and xylene (150 mL) was added to a round flask and heated with continuous removal of water of the reaction [11]. The reaction was stopped after removal of 2.7 mL of water. The obtained Schiff base was viscous brown color, $C_{12}H_{10}N_2O$, elemental analysis % (calc/found): C = 77.6/77.1, H = 5.9/5.8, N = 16.5/16.3.

Synthesis of Cationic Gemini Surfactants

A mixture of the prepared Schiff base (SB) (0.05 mol, 8.51 g), 0.025 mol of dibromoalkanes namely: 1,2-dibromoethane, 1,6-dibromohexane and 1,12-dibromododecane (4.7 g, 6.1 g and 8.2 g, individually) and 100 mL of acetone was put into a round flask and refluxed for 12 h. The reaction mixture was allowed to cool overnight, and then the reaction products were filtered off and washed twice by diethyl ether and dried under vacuum [12]. The obtained products were designated as: SB-2, SB-6 and SB-12, in

Scheme 1 Synthesis of the gemini cationic surfactants



Scheme 1. The molecular weights and the elemental analysis of the obtained surfactants were listed in Table 1.

Measurements

FTIR spectra using an ATITM Mattsonm Infinity series, Bench top 961 instrument controlled by Win FirstTM V2.01 software. H¹H-NMR spectra were measured in DMSO-d₆ by Spect. Varian, Gemini 200 (¹H 200 MHz).

Surface and Interfacial Tension Measurements

Surface and interfacial tension measurements were performed using a Krüss K6 tensiometer by the platinum ring detachment method (± 0.5 mN/m). Freshly prepared aqueous solutions of the synthesized gemini surfactants were used with a concentration range of 0.01–0.00001 M/L at 25 °C. The solutions were poured into a clean Teflon cup with a mean diameter of 28 mm (Teflon cup was used to prevent the adhesion of the surfactant to the glass cup walls). The solutions were left for 2 h to allow the stabilization and complete adsorption at the solution surface, then the apparent surface tension values were measured a minimum of three times and the recorded values were taken as the average of these values [13]. The platinum ring was then removed, washed with a diluted HCl solution followed by distilled water.

The interfacial tension measurements were obtained between aqueous solutions of the synthesized gemini cationic surfactants at a concentration of 0.1 % by weight and

light paraffin oil at 25 °C using the same procedures of the surface tension measurements [14].

Emulsion Stability

Emulsion stability was measured by vigorously stirring a mixture of 10 mL (0.5 %) of the synthesized cationic surfactant solutions and 10 mL of paraffin oil at 25 °C [15]. The emulsion was formed by hand shaking of the cylinder containing the oil and the surfactant solution for 10 min. Emulsifying power (emulsion stability) of the surfactant solutions was expressed as the time required for the separation of 9 mL of pure surfactant solution.

Results and Discussion

Structure

The chemical structures of the synthesized gemini surfactants were confirmed using elemental analysis, IR and NMR spectra. Table 1 represents the calculated and obtained ratios of the different elements in the chemical structures of the different surfactants, which proves their purity. FTIR spectra showed absorption bands at 3,035, 2,920, 2,830, 1,635, 780–920 cm⁻¹. NMR spectra showed signals at: δ (ppm) = 1.3 (CH₂, *m*, nH), 4.5 (CH = N, *s*, 2H), 7.3 (phenyl, *m*, 18H). These data proved the expected chemical structures of the synthesized surfactants as represented in Scheme 1.

Table 1 Characterization of the synthesized gemini surfactants

Compound	Molecular weight M.Wt. (g/mol)	Carbon %		Hydrogen %		Nitrogen %		Bromine %	
		Calc	Found	Calc	Found	Calc	Found	Calc	Found
SB-2	554.32	56.34	54.32	4.73	4.90	10.11	9.97	28.83	28.62
SB-6	608.41	59.22	58.93	5.30	5.32	9.12	9.30	26.27	27.01
SB-12	691.57	62.52	63.05	6.28	6.43	8.12	8.18	23.11	23.15



Fig. 1 Surface tension versus concentration of the synthesized gemini cationic surfactants (*square* SB-2, *triangle* SB-6, *circle* SB-12) at 25 $^{\circ}$ C

Surface Activity

The surface tension versus –log concentration profiles of the aqueous solutions of the synthesized gemini surfactants SB-2, SB-6 and SB-12 were obtained at 25 °C. The profiles showed no minimum, which indicate the purity of the surfactants. The minimum is appeared mainly in an impure or contaminated surfactant solutions due to the residual compounds have high surface activities than the surfactants under investigation, and appeared in lower concentration regions.

The obtained surface tension values are decreased with the increasing of concentration at the lower ranges (premicellar region), until reached almost constant values at higher concentrations (post micellar region), Fig. 1. The break points of these two regions are determined the critical micelle concentrations (CMC) of the surfactants, Table 2.

The adsorption of the surfactant molecules at the air– water interface can be interpreted by studying two parameters: the surface pressure and the maximum surface excess (Γ_{max}). The surface pressure $(\partial \gamma / \partial \log C)$ indicates the pumping of surfactant molecules to the interface of their solutions. Increasing this term revealed that the surfactant molecules are adsorbed at the air–water interface more preferably [16]. It is clear from the data in Table 2 that the increase in spacer chain length decreases the surface pressure of the surfactant towards the interface.

The maximum surface excess is defined as the maximum concentration of surfactant molecules at the interface of their solutions in the saturation case. The maximum surface excesses of the synthesized gemini surfactants were calculated using the slopes of the pre-micellar part ($\partial\gamma/\partial\log C$) in Fig. 2, according to the Gibbs' adsorption equation as follows:

$\Gamma_{\rm max} = (\partial \gamma / \partial \log C) / 2.303 {\rm nRT}$

where, Γ_{max} is the maximum surface excess under saturation conditions, n is the number of active species in the surfactant solution and equal to 3 in the case of gemini surfactants, R is the universal gas constant and T is the absolute temperature, the results were listed in Table 2. It is clear from data in Table 2 that the gradual increase in the spacer chain length decreases the concentration of the surfactant molecules at the interface.

On the other hand, the average area occupied by each surfactant molecule at the solution interface can be calculated using Γ_{max} values according to the following equation:

$$A_{\min}=1/(N_{av}.\Gamma_{\max})$$

where, $N_{\rm av}$ is Avogadro's number.

The average area at the interface available for each surfactant molecule is increased by increasing the spacer chain length. The maximum area occupied at the interface was 67.4 nm² which obtained for the SB-12 surfactant, while the lowest area was 44.6 nm² for SB-2 surfactant. The values of A_{min} were larger than the published values for the saturated gemini surfactant [17]. That can be attributed to the geometry of gemini surfactant molecules at the interface. Analyzing the A_{min} data in Table 2 showed that the increase in A_{min} was

Table 2 Surface activities of the gemini surfactants at 25 °C

Compound	CMC (mM)	$\gamma_{\rm CMC}$ (mNm ⁻¹)	Interfacial tension (mNm ⁻¹)	$\frac{\pi_{\rm CMC}}{({\rm mNm}^{-1})}$	С ₂₀ , ×10 ⁶ М	∂γ/ ∂logC	$\begin{array}{c} \Gamma_{max} \\ (\times 10^{11}) \end{array}$	CMC/ C ₂₀	$\begin{array}{c} A_{min} \\ (nm^2) \end{array}$	Emulsification (Sec)	$\frac{\Delta G_{\rm mic}}{(\rm kJmol^{-1})}$	ΔG_{ads} (kJmol ⁻¹)
SB-2	1.33	50	15	21.8	316	-6.37	3.72	4.21	44.6	120	-16.4	-22.3
SB-6	0.61	47	13	24.8	66.8	-5.03	2.94	9.13	56.5	300	-18.3	-26.8
SB-12	0.28	41	6	30.8	3.87	-4.22	2.47	72.35	67.4	Stable	-20.3	-32.7

CMC critical micelle concentration in mM, γ_{CMC} surface tension at CMC, π_{CMC} effectiveness, C_{20} efficiency, Γ_{max} maximum surface excess, $\partial\gamma/\partial logC$ slope of surface tension vs concentration profile, *CMC/C*₂ ratio between CMC and efficiency, A_{min} minimum surface area, ΔG_{mic} micellization free energy, ΔG_{ads} adsorption free energy

22.8 nm² by increasing the spacer chain length from 2 to 12 methylene groups. Hence, the average A_{min} of the methylene group at the interface is 2.28 nm², which is in a good agreement with our previously published data (2.2 nm²) [9].

The chemical structures of the gemini surfactants play an important role in their surface activity, and mainly regarding the CMC values. In the case of saturated gemini surfactants, the terminal alkyl chains have a high tendency towards geometrical conformation at the interface [18], which decreases the area occupied by each molecule at that interface. As a result, the surface concentration is increased gradually by increasing the terminal alkyl chain length, and also by the gradual increase in the spacer chain length. The increase in surface concentration increases the concentration of surfactant molecules at the interface, which consequently increases the CMC values. Gemini surfactant molecules adopt different conformations depending on the spacer length. Before micellization 12-2-12 monomers are in the trans-conformation. While in case of 12-4-12 and 12–6–12, they are in the *cis*- conformation [19]. In the case of the trans-conformation, the free energy of transfer for the surfactant monomer from the aqueous phase to the pseudo micellar phase is relatively lower as compared to the cis-conformation case. Hence, micellization is relatively more easily facilitated for 12-2-12 (lower CMC) and vice versa for 12-4-12 and 12-6-12. In the case of the unsaturated or conjugated terminal hydrophobic groups, the geometry of these groups restricts their conformation and consequently they are forced to be planar at the interface. Hence, increasing the spacer chain length increases the area occupied by each molecule at the interface. That decreases the surface concentration of these molecules at the interface, which forces the molecules to micellize at a lower concentration than the saturated molecules do.

In the case of the synthesized gemini cationic Schiff bases, the terminal groups are two phenyl groups linked to each other by a double bond (azomethine group), while the spacer groups vary from 2 to 12 methylene groups, as seen in Scheme 1. The geometry of these molecules is forced to be planar at the interface due to lack of flexibility. The rigidity of the targeted surfactant molecules increases their area at the interface, which consequently decreases the surface concentration. The decrease in surface concentration indicates that the interface is completely covered by adsorbed surfactant molecules. Hence, the molecules in the bulk of their solution form micelles. The critical micelle concentrations of the synthesized surfactants were decreased gradually by increasing the spacer chain length from 2 to 12 methylene groups as shown in Fig. 2.



Fig. 2 Effect of spacer chain length on the critical micelle concentration of the synthesized gemini surfactants at 25 $^{\circ}C$

Surface Tension Reduction, Effectiveness and Efficiency (γ_{CMC} , π_{CMC} , Pc₂₀)

The surface tension reduction at the critical micelle concentration of the synthesized surfactants ranges between 50 and 41 mN/m (Table 2). That indicates a lower surface activity of these surfactants compared to saturated cationic gemini surfactants [19]. This can be attributed to the lower surface concentration of the surfactants at the interface and also to the highly hydrophobic character of the surfactant molecules [10]. The higher surface tension reduction accompanied by longer hydrophobic spacer chain length is attributed to the fast interface saturation. That describes the fast adsorption of surfactant molecules on the interface. The SB-2 surfactant has the highest surface tension reduction at the CMC, which indicates its lower adsorption tendency than SB-6 and SB-12 surfactants.

The effectiveness values (π_{CMC}) of the prepared surfactants are listed in Table 2, where the efficiency values are slightly increased from 21 to 30 mN/m by increasing the number of methylene groups in the spacer chains from 2 to 12. The efficiency of adsorption at interfaces increases linearly by increasing the number of methylene groups in the hydrophobic groups [20, 21]. While, the efficiency values (Pc₂₀) were decreased gradually by increasing the hydrophobic chain length. The efficiency parameter indicates the adsorption behavior of surfactant molecules at the interface. Higher efficiency values revealed a lower adsorption tendency.

The ratio between CMC and the efficiency determines the tendency of surfactant molecules towards micellization and adsorption in their solutions. Increasing this ratio indicates the higher tendency of surfactant molecules towards adsorption at the air-solution interface than micellization in the bulk, and vice versa. It is clear from CMC/ C_{20} values listed in Table 2 that the surfactants have a tendency towards adsorption. SB-2 has a 4-fold lower tendency towards adsorption at the air-water interface than micellization. SB-12 has a higher adsorption tendency than micellization by 67-folds.

Emulsification Power and Interfacial Tension

The emulsification power of the synthesized gemini cationic surfactants is determined as the time required for breakdown of the emulsion formed between surfactant solution and paraffin oil. Emulsification is one of the most important surface properties of the surfactants at the interface. The emulsification tendency in some cases is an important property which is needed in surfactants to form stable emulsions, as in the case of solubilization, emulsification processes, cosmetics and drug formulations. Contrarily, some applications do not favor this, especially in the case of petroleum applications including demulsification and corrosion inhibition. Table 2 lists the emulsification tendency of the different synthesized surfactants in the presence of light paraffin oil. It is clear that the emulsification power of the surfactants is completely dependent on the spacer chain length. Short spacer chain which contains two methylene groups (SB-2) has the lowest emulsification tendency at 120 s, while increasing the spacer chain length to six methylene groups considerably increases the emulsification power of SB-6 to 300 s.

The longest spacer chain of twelve methylene groups (SB-12) produces a stable oil/solution emulsion for 30 days. The results can be easily related to the depression in the surface tension and the saturation concentration of the different surfactants at the air-solution interface.

On the other hand, the interfacial tension values of SB-2, SB-6 and SB-12 surfactants are related to the saturation of the surfactant molecules at the air–water interface. Data listed in Table 2 revealed that, the interfacial tension values of the surfactants under consideration were decreased by increasing the spacer chain length. The lowest interfacial tension was obtained in the presence of the longest spacer chain in the studied series.

Thermodynamics of Adsorption and Micellization

The thermodynamic data of adsorption and micellization of the synthesized surfactants in their solution were calculated using the following equations, where n is equal to the number of the ionic species in the solution = 3 [22]:

$$\Delta G_{\rm mic} = 2.303 \rm nRT(\log \ CMC)$$

 $\Delta G_{\rm ads} = \Delta G_{\rm mic} - (0.6 x \pi_{\rm CMC} x A_{\rm min})$

The listed values in Table 2 revealed that the adsorption and micellization processes occur spontaneously with a higher preference towards adsorption than micellization. That was indicated by the more negative values of the adsorption free energy than the micellization. Furthermore, SB-12 showed a large difference between the adsorption and micellization free energies, with more negativity in the adsorption free energy. This showed the stability of the adsorbed monolayer of SB-12 at the air–water interface rather than the aggregated molecules in the bulk of the solution.

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