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ORIGINAL ARTICLE

Preparation of a New Oligomeric Surfactant: *N,N,N′,N″,N″*-Pentamethyl Diethyleneamine—*N,N″*-Di-[Tetradecylammonium Bromide] and the Study of its Thermodynamic Properties

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Abstract A new oligomeric surfactant: *N,N,N′,N″,N″*-pentamethyl diethyleneamine—*N,N″*-di-[tetradecylammonium bromide] referred to as 14-2-N(CH_3)-2-14 was synthesized, purified and characterized by Elemental Analysis, ^{1}H and ^{13}C NMR and Electrospray. The micellar properties of this compound were determined by electrical conductivity and surface tension methods. Optical microscopy was also employed to study the behavior of anhydrous surfactant and the binary water/surfactant system as a function of temperature. The critical micellar concentration (cmc), degree of counterion binding and thermodynamic parameters of micellization (standard molar Gibbs energy, enthalpy and entropy of micellization) were determined by electrical conductivity measurements in the temperature range [24–54 °C]. Surface tension measurements also provide information about the dependence of the surface tension at the cmc (γ_{cmc}), pC_{20} (negative logarithm of the surfactant's molar concentration C_{20}, required to reduce the surface tension by 20 mN/m, the surface excess ($\Gamma_{\max}$) at air/solution interface, the minimum area per surfactant molecule at the air/solution interface (Amin), surface pressure at the cmc (Π_{cmc}), critical packing parameter(CPP) and the standard free energies of micellization (ΔG_m^0) and of adsorption ($\Delta G_{\mathrm{ads}}^0$).

Keywords Gemini surfactant · Critical micelle concentration · Micellization · Adsorption · Surface tension · Electrical conductivity · Polarization microscopy

Introduction

Numerous amphiphilic structures with multiple headgroups and hydrophobic chains in different distributions have been reported. They are used as models to study the aggregation of membranes and their disruption caused by the hydrophobic effect, and they are also employed for a wide range of applications [1–4]. Good examples of such compounds are bolaamphiphiles [5, 6] and Gemini surfactants [7–13]. Owing to their extraordinary activity, the Gemini surfactants have excellent properties of solubilization, soil cleanup and oil recovery. The knowledge of the thermodynamic properties of surfactants in solution is necessary to understand their behavior and optimize their use in formulated products as well as in processes.

This paper examines the synthesis of the Gemini surfactant: *N,N,N′,N″,N″*-pentamethyl diethyleneamine—*N,N″*-di-[tetradecylammonium bromide] referred as 14-2-14(CH_3)-2-14. Two techniques have been proposed for the determination of the critical micellar concentration of Gemini surfactants: conductometry and surface tension.

Thermodynamic parameters concerning association behavior were determined by electrical conductivity and surface tension measurements. Polarization microscopy was also employed to study the behavior of the anhydrous surfactant and for the binary water/surfactant system as a function of temperature.

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Experimental

Synthesis

The Gemini N,N,N',N'',N''-pentamethyl diethyleneamine—N,N''-di-[tetradecylammonium bromide] referred to as 14-2-14(CH_3)-2-14 was obtained by the following reaction (Scheme 1).

It is pertinent to mention that the ratio of compound A and B is closely related to the conditions of the reaction (solvent, order of addition of reagent, duration and the intensity of heating…). For instance, an excess of tetradecyl bromide and a solvent with a high boiling point like butanol or propan-2-ol can lead to the synthesis of the trimeric surfactant (compound B). In order to favor the preparation of compound (A), we followed the procedure below.

To 20 mmol (3,466 g) of N,N,N',N'',N''-pentamethyldiethylenetriamine from Fluka (reference 26828) dissolved in dry acetone (35 mL) was added 50 mmol (13,865 g) of tetradecyl bromide from Fluka (reference 18390) dropwise with continuous stirring under reflux for 48 h. The reaction was carried out at 56 °C. The reaction was followed by thin layer chromatography (Silica gel plate 60 F254) eluted with a mixture of butanol/pyridine/glacial acetic acid/water (60:20:6:24) in volume or acetone/methanol (90/10); the layer chromatography plates were sprayed with the Dragendorff or Ninhydrine reagents. After completion of the reaction, the solvent was removed by rotary evaporation at 30 °C under reduced pressure, leaving a waxy product. The resulting product was dissolved in the minimum volume of absolute ethanol and successive extractions were carried out with ether and hexane in the order to eliminate the excess of alkyl bromide. The obtained product was treated with a large excess of diethyl ether until precipitation took place. A white product was finally obtained by filtration under vacuum. The product was dried and stored in a desiccator. In general, the yield of reaction was less than 30%. It must be noted that it is likely that the reaction above can give rise, in addition to 1,3-dialkyled ammonium dibromide product, to 1,2 and 2,3-dialkyled ammonium dibromides which are in fact indistinguishable from each other. Although the analytical conditions in thin layer chromatography have been well examined, we have always observed a single spot. Also the result of NMR spectroscopy is close to 1,3-dialkylammonium bromide therefore we retained the product A: (N,N,N',N'',N''-pentamethyl diethyleneamine—N,N''-di-[tetradecylammonium bromide] referred as 14-2-14(CH_3)-2-14) to conduct this study.

Analytical Methods

^1H and ^{13}C NMR. Depth and correlation with ^1H and ^{13}C as well as Electrospray (ES^+) and microanalysis were carried out in the laboratories of the Consejo Superior of Investigation of Barcelona Spain. ^1H and ^{13}C NMR analyses were realized with a Varian 300 MHz spectrometer; the chemical shifts are reported in parts per million (δ, in ppm) downfield from tetramethylsilane (TMS).

H^1 -NMR (300 MHz, δ, $CDCl_3$/TMS): (Scheme 2)

(a) $\delta = 0{,}86$ (t,3H); (b) $\delta = 1{,}26$ (44H,m); (c) $\delta = 1{,}8$ (4H,m), (d) $\delta = 2{,}03$ (4H,t); (e) $\delta = 3{,}33$ (12H,s); (f) $\delta = 3{,}99$ (4H,s); (g) $\delta = 3{,}55$(4H,t); (h) $\delta = 1{,}43$ (3H,s)

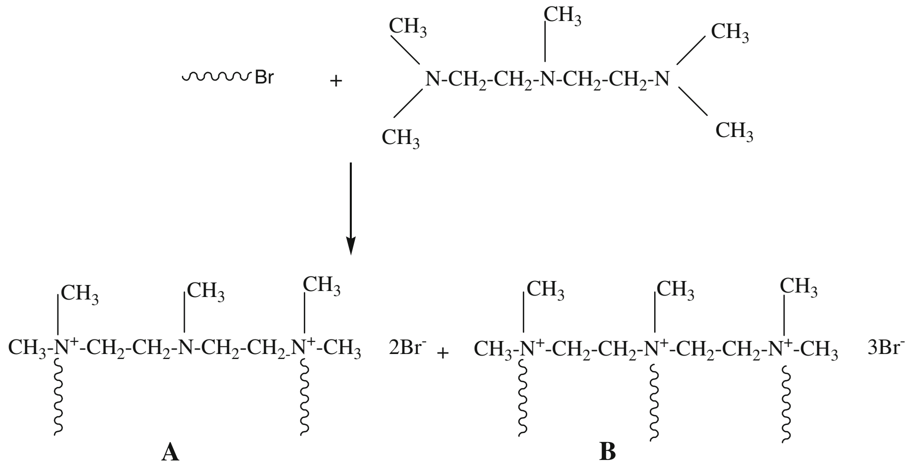
^{13}C NMR (300 MHz, δ, $CDCl_3$/TMS):

(a) $\delta = 14{,}1$; (b) $\delta = 22{,}7–29{,}54$; (c) $\delta = 31{,}46$; (d) $\delta = 43{,}04$; (h) $\delta = 65{,}33$

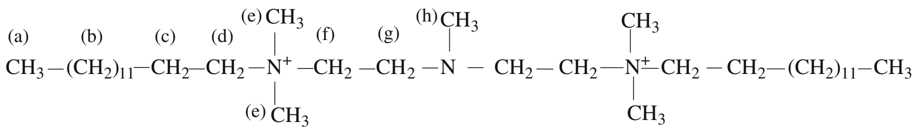
Electrospray ES(+): 729

Thailed pic P, P+2 corresponding to 646,56 and 648,56 $[CH_3\text{-}(CH_2)\text{-}C_2\text{-}N(CH_3)_2\text{-}CH_2\text{-}CH)_2, Br^+$

Scheme 1 Synthetic routes to dimeric (**a**) and trimeric (**b**) surfactants



Scheme 2 NMR characteristics of Gemini surfactant studied



$$\overset{(a)}{\mathrm{CH_3}}-\overset{(b)}{(\mathrm{CH_2})_{11}}-\overset{(c)}{\mathrm{CH_2}}-\overset{(d)}{\mathrm{CH_2}}-\overset{(e)\,\mathrm{CH_3}}{\underset{(e)\,\mathrm{CH_3}}{\overset{|}{\underset{|}{\mathrm{N^+}}}}}-\overset{(f)}{\mathrm{CH_2}}-\overset{(g)}{\mathrm{CH_2}}-\overset{(h)\,\mathrm{CH_3}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\overset{|}{\underset{|}{\mathrm{N^+}}}}}-\mathrm{CH_2}-\mathrm{CH_2}-(\mathrm{CH_2})_{11}-\mathrm{CH_3}$$

Elemental analysis

	C%	H%	N%
Calculated	61.24	11.17	5.79
Found	61.14	11.23	5.84

Electrical Conductivity Measurements

Electrical conductivity measurements were performed for different concentrations of surfactant solutions in the temperature range 24–54 °C, using a WTWLF 90 conductimeter with a WTW KL E1 cell. The solutions were continuously stirred and thermostated at ± 1 °C. The measured conductivity was plotted as a function of the surfactant concentration, and the critical micelle concentration (cmc) was taken at the intersection of the two linear parts of the conductivity curve by the least-squares method.

Surface Tension Measurements

Surface tension measurements were carried out at 25 °C with a Lauda tensiometer. All sample solutions were aged (at least 10 min prior to measurement) before taking a measurement. Double distilled water was used for preparing the solutions. The cmc value was determined as usual from the break point of the plot of surface tension versus the logarithm of the concentration.

Qualitative Phase Behavior

Optical microscopy was employed to study the behavior of anhydrous surfactant and for binary water/surfactant systems as function of temperature. For the water mixture system, the optical observations were performed according to the "flooding" penetration method of Lawrence [14]. A Reichert Polyvar R Leica polarizing microscope equipped with a hot stage was employed. A camcorder and PC with Leica IM500 software were used to capture images. In a flooding experiment, water was allowed to diffuse in the anhydrous surfactant placed between a slide and a cover slip. After a short time, gradient in composition were produced and different separated mesophases developed around the crystalline surfactant.

Results

Conductometric Measurements

Typical plots of conductivity χ versus concentration for the Gemini surfactant (14-2-N(CH_3)-2-14) at various temperatures (22–54 °C) are shown in Fig. 1; conductivity increases with increasing temperature and concentration of surfactant. Calculated values for the cmc are listed in Table 1. It may be seen from the table that the cmc increases slightly with increasing temperature.

The ionization degree α was calculated from the slopes of the two linear parts of the conductivity curves from the relation (1) [15–19]:

$$\alpha = \frac{S_2}{S_1} \tag{1}$$

where S_1 and S_2 are the respective dependence $\chi = f$(surfactant) below and above the cmc. (S_1 and S_2 are expressed in S m^2 mol^{-1}).

The values for counterion binding β were calculated according to the relation (2) [15–19]:

$$\beta = 1 - \alpha = 1 - \frac{S_2}{S_1} \tag{2}$$

The calculated values for the degree of ionization α and the counterion binding of the micelle β are summarized in Table 1. With increasing temperature the degree of ionization α rises slightly, whereas the counterion binding β decreases slightly. Generally, experimental data support

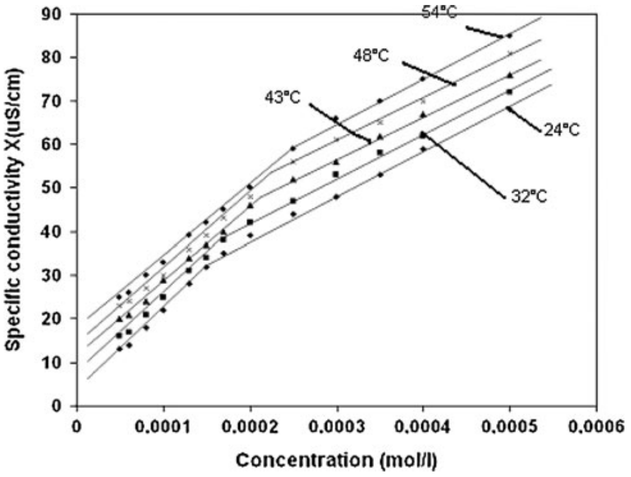


Fig. 1 Specific conductivity versus concentration for Gemini surfactant at 24, 32, 43, 48 and 54 °C

Table 1 Thermodynamic parameters of micellization of Gemini surfactant (14-2-N(CH3)-2-14) in aqueous solution determined by conductometry method

T (K)	CMC (mol/l)	α	B	ΔG_m^0(KJ mol^{-1})	ΔH_m^0(KJ mol^{-1})	ΔS_m^0(KJ/K mol)	$T\Delta S_m^0$ (KJ/K mol)
297	1.5×10^{-4}	0.28	0.72	−54.427	−12.998	0.140	41.580
305	1.8×10^{-4}	0.29	0.71	−54.657	−6.235	0.159	48.495
316	2.25×10^{-4}	0.31	0.69	−55.120	3.944	0.187	59.092
321	2.45×10^{-4}	0.32	0.68	−55.168	8.860	0.200	64.200
327	2.5×10^{-4}	0.33	0.67	−55.994	15.085	0.217	70.959

the suggestion that the nature of the counterion has a significant influence on the micellization of surfactants.

The cmc values determined at various temperatures were further used to calculate the thermodynamic parameters of micellization according to the Eqs. 3, 4, 5 and 6 [15–20]:

- For the standard molar Gibbs energy of micellization ΔG_m^0:

$$\Delta G_m^0 = (1+\beta)\mathrm{RTL}n\left(\frac{\mathrm{cmc}}{\rho}\right) \quad (3)$$

ρ equals to the moles of water per cubic decimeter ($\rho = 55.5$ mol/dm^3 at 25 °C).

- For the standard molar enthalpy of micellization ΔH_m^0

$$\Delta H_m^0 = -(1+\beta)RT^2\left(\frac{\delta \mathrm{Ln}(\mathrm{cmc})}{\delta T}\right) \quad (4)$$

Equation 4 could be also expressed in the form:

$$\Delta H_m^0 = -(1+\beta)RT^2(\mathrm{B}+2\mathrm{C}T)$$

where A, B and C are parameters of the second polynomial:

$$\mathrm{Ln}(\mathrm{cmc}) = f(T) = \mathrm{A} + \mathrm{B}T + \mathrm{C}T^2 \quad (5)$$

- For the standard molar entropy of micellization:

$$\Delta S_m^0 = \left(\frac{\Delta H_m^0 - \Delta G_m^0}{T}\right) \quad (6)$$

The values for the thermodynamic parameters of micellization are presented in Table 1. The standard molar Gibbs energy of micellization ΔG_m^0 was found to be negative in all cases, with only small differences over the given temperature range. The process of micellization is thus thermodynamically favored and spontaneous.

The standard molar enthalpy of micellization ΔH_m^0 and the standard molar entropy ΔS_m^0 increase with increasing the temperature; this indicates the formation of much ordered systems of micellization.

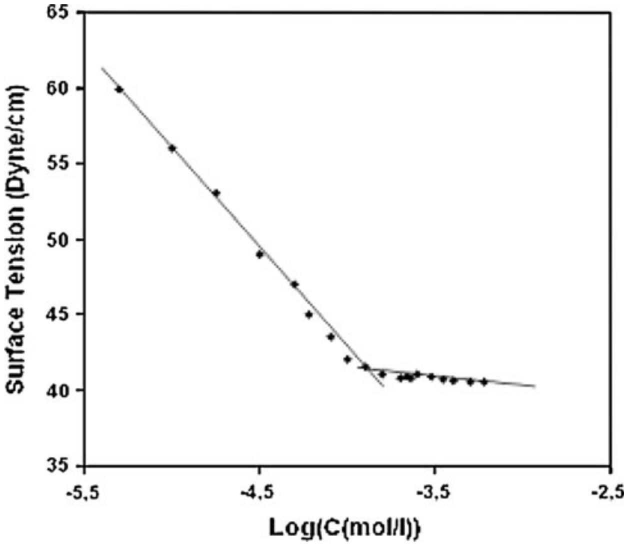


Fig. 2 Surface tension versus Log(C) of Gemini surfactant (14-2-N(CH3)-2-14) at 297 K

Surface Tension

Figure 2 shows the curve of the surface tension versus log (surfactant molar concentration) for the Gemini surfactant. The surface tension isotherm was used to determine several parameters according to the procedures described by Rosen [21]; critical micelle concentration (cmc), surface tension and the surface pressure at cmc (γ_{cmc}, Π_{cmc}, respectively), the maximum surface excess concentration ($\Gamma_{\max}$), the minimum area per molecule ($A_{\min}$), the logarithm of surfactant concentration required to reduce the surface tension by 20 mN/m (pC$_{20}$), the ratio cmc/C$_{20}$, the standard free energy of adsorption ($\Delta G_{\mathrm{ads}}^0$) and the standard free energy of micellization (ΔG_m^0).

The surface excess concentration $\Gamma_{\max}$ at the air/water interface and the minimum area per molecule, $A_{\min}$, were calculated according to the Eqs. 7 and 8 derived from the Gibbs adsorption isotherm [21]:

$$\Gamma_{\max} = -\frac{\left(\frac{\delta\gamma}{\delta \log(C)}\right)}{2.303 \times nRT} \tag{7}$$

$$A_{\min} = \frac{10^{16}}{N\Gamma_{\max}} \tag{8}$$

where $R = 8.\,31 \times 10^{7}$ ergs. Mol^{-1} K^{-1}, γ is in dyne/cm, and $\Gamma_{\max}$ is in mol/cm^{2}. The minimum area per molecule, A is in Å^{2}, N is Avogadro's number. The Gibbs pre-factor "n" in the equation represent the number of particles per surfactant molecule whose surface concentration changes with change in the bulk concentration of the surfactant. For monovalent ionic surfactant, $n = 2$. It is unclear which prefactor has to be used for a Gemini surfactant [8, 22, 23] but neutron reflectivity results from Thomas et al. [23] revealed that for a rigid xylyl spacer, a factor of 3 should be used.

However, for other Gemini surfactants with different structures, a pre-factor of 2 was found to be more appropriate.

The efficiency of adsorption pC$_{20}$ is the negative logarithm of the concentration of surfactant in the bulk phase required to produce 20 mN/m (dyn/cm) reduction in the surface or interfacial tension of water [21].

The Critical Packing Parameter CPP, which can provide a good idea of the shape of aggregates forming spontaneously [21], is given by Eq. 9:

$$\mathrm{CPP} = \frac{V_{\mathrm{H}}}{a_0 \times I_{\mathrm{c}}} \tag{9}$$

where $V_{\mathrm{H}}(\mathring{\mathrm{A}}^{3)}$ is the volume occupied by a saturated hydrocarbon chain containing n_{c} carbon atoms and I_{c} is the length of hydrocarbon groups in the micelle core. At saturation, a_0 can be replaced by $A_{\min}$ and V_{H} and I_{c} can be calculated by the following relation [24]:

$$V_{\mathrm{H}} = 27.4 + 26.9n_{\mathrm{c}}$$

$$I_{\mathrm{c}} = 1.5 + 1.265n_{\mathrm{c}}$$

The standard free energy of micellization was calculated using the equation:

$$\Delta G_{m}^{0} = (2-\alpha)RT\mathrm{Ln}\left(\frac{\mathrm{cmc}}{\rho}\right) \tag{10}$$

The standard free energy of adsorption was calculated according to the equation:

$$\Delta G_{\mathrm{ads}}^{0} = (2-\alpha)RT\mathrm{Ln}\left(\frac{\mathrm{cmc}}{\rho}\right) - \Pi A_{\min} \tag{11}$$

$$\Delta G_{\mathrm{ads}}^{0} = \Delta G_{m}^{0} - \mathrm{P}A_{\min}$$

Values for cmc, γ_{cmc}, $\Gamma_{\max}$, $A_{\min}$, pC$_{20}$, Cmc/C$_{20}$, CPP, ΔG_{m}^{0} and $\Delta G_{\mathrm{ads}}^{0}$ at 25 °C are presented in Table 2.

In the order to compare the performance of the studied Gemini surfactant, we have collected from the literature the surface properties data for similar Gemini species (14-4-14) as well as the corresponding monomeric compound. The only difference between the Gemini synthesized and 14-4-14 is the presence of the amine function in the spacer. The surface properties of these compounds will be discussed.

Microscopical Observation

Optical microscopy was employed to study the behavior of anhydrous surfactant and for binary water/surfactant systems as the function of temperature. For the water mixture system, the optical observations were performed according to the "flooding" penetration method [14]. The main observations are summarised in Fig. 3.

Table 2 Surface properties of Gemini surfactant (14-2-N(CH3)-2-14) at $T = 297$ K: critical and surface properties of Gemini surfactant 14-4-14 and mono surfactant for comparison

Surface properties	Values for Gemini surfactant (14-2-N(CH3)-2-14)	Values for Gemini surfactant (14-4-14)	Values for monosurfactant C14T
cmc (mol/L)	1.3×10^{-4}	$1.9 \times 10^{-4\mathrm{a}}$	$36 \times 10^{-4\mathrm{b}}$
Surface excess concentration $\Gamma_{\max}$ (mol/cm^{2})	1.51×10^{-10}	$1.75 \times 10^{-10\mathrm{a}}$	$2.8 \times 10^{-10\mathrm{c}}$
Surface tension at cmc γcmc (mN/m)	31.4	35$^{\mathrm{a}}$	38$^{\mathrm{b}}$
pC20	4.5	4.85$^{\mathrm{a}}$	2.8$^{\mathrm{b}}$
Cmc/C20	4.11		2.1$^{\mathrm{b}}$
Interfacial area $Amin$ (Å2)	110	95$^{\mathrm{a}}$	61$^{\mathrm{c}}$
Surface pressure Π (mN/m)	27.5	25$^{\mathrm{a}}$	22
Critical packing parameter CPP	0.19	0.22$^{\mathrm{a}}$	0.34
Free energy of micellization ΔG_{m}^{0} (KJ/mol)	−47.15		
Free energy of adsorption $\Delta G_{\mathrm{ads}}^{0}$ (KJ/mol)	−65.36		

Ref. $^{\mathrm{a}}$[25]; $^{\mathrm{b}}$[26]; $^{\mathrm{c}}$[8]

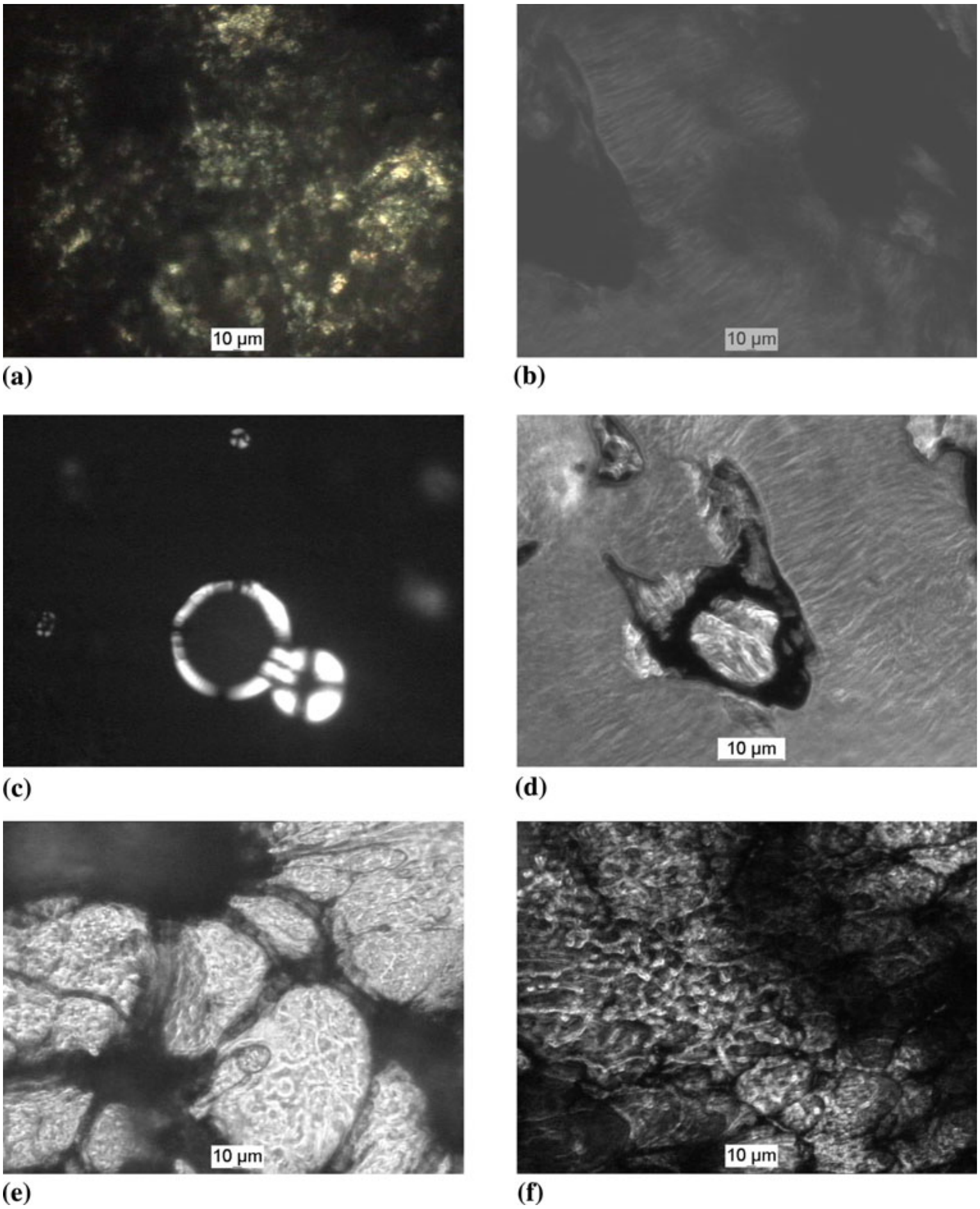


Fig. 3 Optical micrograph illustrating different phases for the anhydrous product and the phases formed by the penetration of water as function of temperature “Flooding method. **a** Optical micrograph for anhydrous product $t = 20$ °C, **b** Optical micrograph, flooding method, $T = 45$ °C, **c** Optical micrograph, flooding method, $T = 60$ °C, **d** Optical micrograph, flooding method, $T = 70$ °C, **e** Optical micrograph, flooding method, $T = 80$ °C, **f** Optical micrograph, flooding method, $T = 85$ °C

For the anhydrous product and before the melting point, a thermotropic liquid crystal phase has been observed (Fig. 3a). When small quantities of water were added (“flooding method”) and when the temperature increased and reached 45 °C, we observed the appearance of a lamellar phase together with a solid, while in the other region we observe a lamellar phase structure, Fig. 3b. This lamellar phase structure persisted up to 60 °C, where a typically lamellar phase (Fig. 3c) was observed. At 65 °C, a mesophase was observed in polarized light: a cubic phase inside and a lamellar phase outside (Fig. 3d). The phenomenon persisted with the increase of temperature and when the temperature attained 70 °C, we noted the appearance of a typical millenic phase in a certain region (Fig. 3e) and a lamellar phase elsewhere. At temperatures near the 80 °C, we only observed the millenic phase structure (Fig. 3f).

Discussion

From conductivity measurements, Fig. 1 reflects the variation of specific conductivity versus concentration of Gemini surfactant 14-2-N(CH_3)-2-14 in the temperature range [24–54 °C]; these curves showed all a single break unlike Frindi et al. [27] who found two breaks for Gemini (8-3-8) and (8-6-8). The cmc is determined at the breakpoint in the specific conductivity versus concentration curve. According to Table 1, the cmc increases slightly with increasing temperature. The reports of temperature dependence of cmc are scarce. Such a report on 12-s-12 ($s = 2, 3, 4$) is available in the literature [28]. The cmc values increased with temperature for the three surfactants studied, which is in good agreement with our results. The effect of temperature on the micellization process is quite complex, and typically the cmc is minimal around 25 °C for ionic surfactants and at about 50 °C for nonionic surfactants [21]. The length of the alkyl chain and the nature of the counterion influence significantly the temperature dependence of cmc [29, 30]. The increase in temperature causes a decrease in hydration of polar heads that promotes micellization and also a greater disorder in the structure of water in the vicinity of the hydrophobic parts which disadvantages the micellization. As a consequence, the balance between these opposing effect determines the evolution of the cmc with temperature [16, 21].

As can be seen from the Table 1, the α values determined for the Gemini surfactant 14-2-(CH$_3$)-2-14 are in good agreement with the results of Manet [31], the author found the α values of 0.27 at 303 K and 0.32 at 333 K for the Gemini surfactant 14-2-14, 2Br$^-$.

It is worth noting that the α values found in the literature are quite method dependent. A recent work by Geng et al. [32] used a chemical trapping technique and to study dodecyl cationic Gemini surfactants having bromide as the counterion. They found that micelles of the Gemini surfactant with two, three and four methylene groups in the spacer had all α values of around 0.2.

We also observed that the variation of the degree of ionization α of the Gemini surfactant with temperature is insignificant; this result agrees with the finding of Tehrani et al. [33] who determined the α values at different temperatures for the monomeric surfactant and the corresponding Gemini surfactant having two and three methylene groups as the spacer and bromide as the counterion, and found that the α values were virtually independent of temperature.

All values of the free energies of micellization of the Gemini surfactants were negatives, which means that the process of micellization is spontaneous; the variation of free energy of micellization with temperature is low because the existence of an entropy-enthalpy compensation phenomenon.

The standard molar entropy of micellization ΔS_m^0, is largely positive. The standard molar enthalpies of micellization ΔH_m^0 can be positive or negative. The result shows that $\left|T\Delta S_m^0\right| > \left|\Delta H_m^0\right|$, indicating that the process of micellization is entropy driven. It has been shown that the weak variation in ΔG_m^0 with increasing temperature arises from the compensation of the variation in the standard enthalpy ΔH_m^0 and entropy of micellization ΔS_m^0. Thermodynamics parameters for micellization of the Gemini surfactants with varying spacer length (m-s-m, $m = 12$) obtained by calorimetry were reported by Bai et al. [34]. They compared the results with conventional surfactants. It was found that the determined cmc values are in good agreement with those obtained by the other methods, with a maximum at $s = 4$–6. The enthalpies of micellization, ΔH_m are all exothermic and show a marked minimum at s = 4–6. The variation of ΔH_m and ΔS_m shows that the balance between enthalpic and entropic contributions to the micellization process changes substantially with s.

From surface tension measurements, the plot of surface tension versus the logarithm of the concentration of the Gemini 14-2-N(CH$_3$)-2-14 surfactant exhibits an abrupt change in the slope at a concentration corresponding to the cmc. The cmc value and surface parameters derived from the plot are listed in Table 2, which also includes bisquaternary Gemini 14-4-14 without amine function in the spacer, and monoquaternary ammonium bromides C14 for comparison purpose.

According to Table 2, the value of cmc determined for the Gemini 14-2-NCH$_3$)-2-14 is slightly lower than the value corresponding to the Gemini 14-4-14, and much lower than the cmc of the monomeric surfactant C$_{14}$TAB. Devinsky et al. [35] reported the same result for homologous series of Gemini surfactants with flexible hydrophobic spacers (CH$_2$)$_2$ -Y(CH$_2$)$_2$, i.e., the cmc of these surfactants does not depend significantly on the chemical nature of the Y. The cmc values of Gemini surfactant [(C$_{12}$H$_{25}$(CH$_3$)$_2$N$^+$, Br$^-$)$_2$ (CH$_2$)$_2$Y(CH$_2$)$_2$] were found to be 1.2, 1.1, 1.0 and 0.84 mM for Y=N(CH$_3$), O, CH$_2$ and S respectively.

Cmc values found for these compounds were lower than those corresponding to the monomer, meaning that the two alkyl chains of the Gemini surfactants facilitate the micellization, when compared to the hydrophobic single chain in their conventional counterparts. Aratani et al. [36] have suggested two hypotheses to explain this difference:

1. The first is a repulsion between the hydrophilic cationic heads which hinders the aggregation and the formation of micelles for mono-quat, while in the bis-quat, this constraint is reduced by the covalent bonds between these two hydrophilic heads in the spacer.
2. The presence of two hydrophobic chains in the structure of the bis-quat is itself a phenomenon of premicellization.

The formation of micelles in an aqueous solution of dimeric surfactant has been much investigated. In all instances, where the comparison is possible, the cmc(s) of dimeric surfactants have been found to be at least one order of magnitude smaller than the corresponding value for a monomeric surfactant. The most likely explanation for these low cmc values is that in solution of dimeric surfactants, two alkyl chains are simultaneously transferred from water to the micellar phase, resulting in a nearly double free energy change of transfer, and thus in a much lower value of the cmc [21].

The surface excess Γ_{max} is a measurement of how much the air/solution surface has been modified by the surfactant adsorption. It depends on the molecular structure of a surfactant molecule. Adsorption behavior at the air/solution surface of the Gemini surfactant with a hydrophobic spacer is determined mainly by the hydrophobicity of the two alkyl chains and the spacer length [35, 36]. When the length of the spacer increases, it begins to exert an important influence on adsorption: Γ_{max} decreases and consequently A_{min} increases.

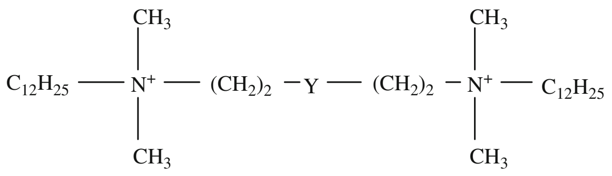
The value of Γ_{max} determined for the Gemini 14-2-N(CH_3)-2-14 was slightly lower than the one for 14-4-14 and much lower than the surfactant monomeric C14TAB value. This means that the Gemini 14-2-N(CH3)-2-14 produces a strong modification at the air/solution surface, greater than those produced by Gemini 14-4-14 and monomeric surfactant C14TAB.

The value of A_{min} obtained for the Gemini 14-2-N(CH_3)-2-14 is slightly higher than that obtained for the Gemini 14-4-14, thus indicating a looser packing of the former at the air/solution surface.

The main factors that determine the variation of A_{min} with spacer S were found to be the spacer conformational entropy and the attractive and repulsive interactions between surfactant molecules. Devinsky et al. [35] have studied the effect of flexible spacers type $(CH_2)_2$-Y$(CH_2)_2$ on the area per molecule A_{min} in the case of the Gemini surfactants in C12 series. They found that A_{min}, depends on the chemical nature of the group Y and increases in the order S (84) < N(CH_3) (108) < CH2 (114) < O (128). The values of A_{min} in parentheses are in Å^2 for cationic Gemini surfactants with the following chemical structure (Scheme 3):

Y=S; N(CH_3); CH_2; O

A useful measure of the efficiency of a surfactant in reducing the surface tension of water is the surfactant concentration C_{20} required to reduce the surface tension by 20 mN/m or the logarithm of C_{20} (pC_{20}). Molecules with high efficiency partition adsorb strongly at the interface even at low concentrations. Our results show that the value of pC20 obtained for the 14-2-N(CH_3)-2-14 species is similar to that obtained for the Gemini 14-4-14.



$$C_{12}H_{25}-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N^+}}-(CH_2)_2-Y-(CH_2)_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{N^+}}-C_{12}H_{25}$$

Scheme 3 Structure of the Gemini surfactant with flexible hydrophobic spacers

Surfactant effectiveness is also measured by the maximum reduction of surface tension reached at the cmc (γ_{cmc}). The value of surface tension at the cmc for the Gemini studied was slightly lower than that of Gemini 14-4-14. The ratio cmc/C20 value is a measure of the surfactant preference for adsorption relative to micellization. The high value of this cmc/C20 ratio determined for the studied Gemini 14-2-N(CH_3)-2-14 indicates that this surfactant shows a great preference for adsorption at the interface. This result was confirmed by the values of free energies of adsorption and micellization. Indeed, the free energy of adsorption is higher in absolute values to the free energy of micellization.

The packing parameter calculated for the Gemini 14-2-N(CH_3)-2-14 is less than 1/3 indicating the formation of spherical micelles, as Gemini 14-4-14.

In order to compare the investigated compound 14-2 N(CH3)-14 with other Gemini surfactants, we have compiled in Table 3 the physicochemical parameters of some dimeric and trimeric Gemini surfactants. We first compared the cmc of the dimeric studied surfactant 14-2-N(CH3)-14 with the homologous Gemini m-4-m with $m = 10.12.14$; we found that the cmc of the Gemini 14-2N(CH3)-14 is smaller than the cmc(s) of the dimeric species 10-4-10, 12-4-12 and 14-4-14. The same trend is observed in the case of two series of homologous dimeric surfactants 10-2-10, 12-2-12, 14-2-14 [26, 37] and 8-3-8,10-3-10 and 12-3-12 [38, 39]. This fact is due to the well known phenomenon. i.e., the linear decrease of cmc with the length of the alkyl tail at constant spacer length [26, 37–41]. The decrease of cmc with the length of the alkyl chain is also observed for

Table 3 Some physicochemical parameters of dimeric and trimeric surfactants

Surfactant	CMC (mmol/L)	α	γcmc (mN/m)	106 Γ (mol/m^2)
10-4-10[a]	7.04		38	1.37
12-4-12[a]	1.11		39	1.47
14-4-14[a]	0.19		35	1.75
14-2-NCH3)-2-14[b]	0.15	0.28	31.4	1.51
10-2-10[c]	6.5		32	
12-2-12[c]	1.1		40	
14-2-14[a]	0.14		34	1.76
8-2-8-2-8[c]	14		35.1	1.07
10-2-10-2-10[c]	0.95		25.8	1.38
12-2-12-2-12[c]	0.065		36.4	1.11
8-3-8[d]	54	0.28		
10-3-10[d]	6.1	0.24		
12-3-12[e]	0.96	0.22		2.3
12-3-12-3-12[e]	0.16	0.24		1.75

Ref. [a][26]; [b]present study; [c][37]; [d][38]; [e][39]

the trimeric Gemini surfactants [37]. We have also observed that the studied Gemini 14-2N (CH3)-14 has the lowest surface tension at the cmc (γ_{cmc}), and is more effective at reducing surface tension than the Gemini species10-4-10, 12-4-12 and 14-4-14.

By comparing some thermodynamic parameters listed in Table 3 for the investigated Gemini 14-2N (CH3)-14, with the trimeric 12-2-12-2-12 synthesized by Yoshimura et al. [37] and the trimeric 12-3-12-3-12 synthesized and studied by Zana et al. [39], we can see that the studied Gemini has roughly the same performance as the trimeric 12-3-12-3-12, while the trimeric 12-2-12-2-12 seems more efficient than the studied dimeric.

From polarized light microscopy, we observed the behavior of anhydrous surfactant and the binary water/surfactant system as function of temperature. Only few phase diagrams have been reported for dimeric surfactants, though the m-s-m, 2Br- surfactants have been investigated systematically. It was first shown that the pure dimeric surfactants do not give rise to thermotropic liquid crystals, a rather unexpected behavior, as the corresponding conventional monomeric surfactant show liquid crystalline thermotropic behavior. This result agrees with our finding. The absence of the thermotropic liquid crystal was tentatively attributed to the geometric constraint introduced by the spacer on the arrangement of the charged groups. For these surfactants, the concentration range of the lyotropic mesophases was found to decrease as the spacer carbon number "*s*" increased and completely disappeared at $s = 10$ and 12. These surfactants only give micellar solutions even at concentrations as high as 90%. The observed mesophases had the texture of the conventional lamellar and cylindrical phases.

Eastoe et al. [42], in their study on sugar Gemini surfactants found the following phase sequence with decreasing surfactant concentration: hydrated crystals → lamellar (Lα) → Cubic (V1) → Hexagonal (H1) → micellar (L1).

In our case, we observed the following sequence with increasing the temperature:

Hydratedcrystal → Lamellar → Cubic → millenic.

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