Journal of Fluorine Chemistry 132 (2011) 892–897

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Langmuir isotherm analysis of novel branched per-fluorinated surfactants and their interactions with single stranded DNA

Nicolas Dupuy [a], Andreea Pasc [a,*], Francis Baros [b], Christine Gérardin [a]

[a] LERMAB – EA 4370, Nancy-Université, BP 70239, F-54506 Vandoeuvre-lès-Nancy, France
[b] LRGP-UPR 3349 CNRS – INPL, Nancy-Université, ENSIC, 1 rue Grandville, BP 20451, F-54001 Nancy Cedex, France

ARTICLE INFO

Article history:
Received 16 March 2011
Received in revised form 28 June 2011
Accepted 28 June 2011
Available online 5 July 2011

Keywords:
Fluoroalkylated gemini surfactants
Fluorinated lipid
Langmuir monolayer
ssDNA binding

ABSTRACT

The efficient synthesis and surface properties of new fluorinated gemini surfactants are described. The aim of this study was to investigate the relationships between the molecular structure and the Langmuir layer properties of these fluorinated gemini lipids. The electrostatic ssDNA binding interactions of amino groups included on the spacer were also investigated. The synthesis corresponds to the substitution of vinyl fluorine atom of fluoro-unsaturated esters by a diethylene-oxide diamine *via* a Michael addition followed by a fluoride elimination reaction. For the spread layers, the measurements of surface pressure versus molecular area were performed with or without ssDNA in the subphase. The monolayers characteristics depend on the hydrophobic chain length, the polar-head, the pH of the subphase and the flexibility of the spacer. The introduction of ssDNA in the subphase seems to show a low interaction between the surfactants and the oligonucleotide.

1. Introduction

Since the experiment of Franklin in 1757, monolayers properties and applications have grown day by day [1–5]. The physicochemical characterization of Langmuir films [6] starts by adsorption measurements using a Langmuir trough and stability studies. Special interest is devoted to a better understanding of the interactions between DNA and amphiphilic monolayers [7]. The reason why its interactions with monolayers proved to be of great importance comes from the mimetic structure with cell membranes that contributes to the understanding of the interaction in cellular membranes concerning for example DNA delivery [8–11] in gene therapy or more recently RNA interference [12]. In this case, monolayers may so be also used as models for the study of the interactions between DNA and lipid vector structure. Recently, fluorinated surfactants have shown a better ability in transfection essay [13,14] than their hydrogenated analogs and have specific properties as synthetic vectors for gene delivery [13,14].

Geminis are special class of surfactants where two monomeric surfactants (two hydrophilic and two hydrophobic groups) are coupled together *via* a spacer. Fluorinated gemini surfactants containing two highly fluorinated hydrophobic chains and two polar heads covalently connected through a spacer group have been recently reported for their particular properties and their ability to form more stable monolayer [15,16]. Fluorinated surfactants [17,18] are chemically more inert and at the same time more hydrophobic and lipophobic than their hydrogenated counterpart. Because of the larger volume and higher electronegativity of fluorine than hydrogen, the introduction of fluorine atoms in hydrophobic chains of a surfactants greatly increase its amphiphilic character, resulting in enhanced surface activity [19], stability in the presence of biocoumpounds [20,21] and lower critical aggregative concentration (CAC) [19]. Furthermore, fluorocarbon chains are stiff and the Van der Waals interaction between the chains is weak and therefore fluorinated surfactants tend to form bilayer, vesicles and cylinders and their features are unmatched by their hydrocarbon analogs when they exist [19].

Fluorinated monolayers [22,23] properties and organization at the air/water interface depend on several parameters like the hydrophobic chain length and nature[24], the type of polar head groups [25,26], the nature and the length (flexibility) of the spacer [27,28] and the nature of the subphase. Generally, fluorinated gemini surfactants form more easily stable and ordered monolayer than their hydrogenated counterparts because of the rigidity of the chains and their high hydrophobicity. For gemini surfactants [29,30] it was observed that the area per molecule increases with the chain length, while the collapse pressure decreases. Moreover, the spacer plays a very important role [31,32] on the behavior of gemini surfactants at the air/water interface. The long and flexible spacers tend to decrease the area per molecule.

In the present study, we report the synthesis of new highly fluorinated gemini surfactants with a diamino diethyl-oxide spacer

* Corresponding author at: SRSMC – UMR 7565, Nancy-Université, BP 70239, F-54506 Vandoeuvre-lès-Nancy, France. Tel.: +33 0 383 684 330; fax: +33 0 383 684 322.
E-mail address: andreea.pasc@srsmc.uhp-nancy.fr (A. Pasc).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.06.037

and carboxylic acid or ester polar head groups respectively. The behavior of these compounds at the air / water interface was obtained from π–*A* isotherm curves, with the aim to determine the effect of the chain length, the pH and the polar head groups. The interaction of ssDNA with monolayers formed is also reported.

2. Experimental

2.1. Materials

All solvents were reagent grade unless otherwise specified and were used without further purification. NMR spectra were recorded on a Bruker AM 400 or an AC 200 instrument. Chemical shifts are reported in ppm relative to TMS as internal standard for the ^{1}H spectra and to $CFCl_3$ for the ^{19}F spectra. Melting points were determined using a Kofler bank and were not corrected. IR spectra were recorded on a Perkin–Elmer FTIR "spectrum one" in ATR mode. Ultrapure water (Elix 3 Millipore, surface tension of 72.5 mN m^{-1} at 20 °C, resistivity of at least 15 MΩ cm) was used for the Langmuir trough subphase and for surfactant solutions. ssDNA (M = 7404 Da, AAC-TCG-GAA-TGG-AGA-ACA-CAG-ATC) was purchased from Eurogentec.

2.2. Synthesis

2.2.1. General synthesis of dienamines

A mixture of 2 g of fluoroalkyl-2-enoic acid ethyl ester, 1 eq., 0.5 eq. of 2-[2-(2-amino-ethoxy)-ethoxy]-ethylamine and 30 eq. of Et_3N in 100 mL Et_2O was heated to reflux for 24 h. Et_2O and Et_3N were then removed under vacuum and the resulting mixture was redissolved in Et_2O and washed with 3 × 100 mL water. The organic phase was dried on $MgSO_4$ and the solvent was evaporated. The final product was purified on silica gel (hexane/AcOEt 9/1) or recristalized in hexane.

2.2.1.1. 3-(2-{2-[2-(1-Ethoxycarbonylmethylene-perfluoroalkylamino)-ethoxy]-ethoxy}-ethylamino)-perfluoro alk-2-enoic acid ethyl ester, **1**. IR (KBr) 3430, 1738, 1669, 1300–1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.57 (s, 2H, NH), 5.02 (s, 2H, Z CH=); 4.13 (q, 4H, CH_2OCO, $^3J_{HH}$ = 7 Hz); 3.66 (t, 4H, CH_2NH, $^3J_{HH}$ = 5 Hz); 3.63 (s, 4H, OCH_2CH_2O); 3.46 (t, 4H, CH_2CH_2NH, $^3J_{HH}$ = 5 Hz); 1.26 (t, 6H, CH_3, $^3J_{HH}$ = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 169.25 (COO); 147.75 (C=); 106 to 120 (m, CF_2 and CF_3); 88.39 (CH=); 70.20 and 70.81 (CH_2CH_2NH); 59.66 (CH_2OCO); 44.76 (CH_2NH); 14.04 (CH_3); ^{19}F NMR ($CDCl_3$) δ −81.20 (s, CF_3); −111.26 (m, CF_2C=); −121.44 to −126.00 (m, CF_2). For **1a**, yield 53%, white powder, mp 99 °C, Anal. Calcd for $C_{34}H_{26}F_{38}N_2O_6$: C, 31.87; H, 2.03; N, 2.18. Found: C, 31.55; H, 2.21; N, 2.15. For **1b**, yield 67%, white powder, Anal. Calcd for $C_{30}H_{26}F_{30}N_2O_6$: C, 33.33; H, 2.40; N, 2.59. Found: C, 33.01; H, 2.17; N, 2.86. For **1c**, yield 65%, colorless oil, Anal. Calcd for $C_{26}H_{26}F_{22}N_2O_6$: C, 35.45; H, 2.95; N, 3.18. Found: C, 35.17; H, 2.37; N, 2.89.

2.2.2. General reduction of dienamines

1 g of dienamine, 1 eq., was dissolved in 70 mL of a mixture of AcOEt/MeOH (2/1, v/v) and catalytic amounts of Ni Raney were introduced in a hydrogenation reactor working under 80 bar of H_2. After 24 h at 50 °C, the mixture was cooled down to room temperature, purged with N_2 and filtered on celite. The solvent was then removed under vacuum and the resulting product was redissolved in AcOEt and dried on $MgSO_4$. The final product was recovered after evaporation of the solvent, without further purification.

2.2.2.1. 3-(2-{2-[2-(1-Ethoxycarbonylmethyl-perfluoro-alkylamino)-ethoxy]-ethoxy}-ethylamino)-perfluoro-alkanoic acid ethyl ester, **2**. IR (KBr) 3366, 1740, 1300–1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.13 (q, 4H, CH_2OCO, $^3J_{HH}$ = 7 Hz); 3.82 (m, 2H, CH); 3.55 (s, 4H, $OC\underline{H}_2C\underline{H}_2O$); 3.50 (t, 4H, $C\underline{H}_2CH_2NH$, $^3J_{HH}$ = 5 Hz); 2.89 (t, 4H, $C\underline{H}_2NH$, $^3J_{HH}$ = 5 Hz); 2.72 (dd, 2H, CH_2COO, $^3J_{HH}$ = 5 Hz and 11 Hz); 2.55 (dd, 2H, CH_2COO, $^3J_{HH}$ = 8 Hz and 7 Hz); 1.72 (m, 2H, NH); 1.26 (t, 6H, CH_3, $^3J_{HH}$ = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 170.45 (COO); 106–120 (m, CF_2 and CF_3); 71.00 ($\underline{C}H_2CH_2NH$); 61.17 ($\underline{C}H_2OCO$); 56.42 (CH); 47.10 ($\underline{C}H_2NH$); 34.35 ($\underline{C}H_2COO$); 14.04 (CH_3); ^{19}F NMR ($CDCl_3$) δ −81.20 (s, CF_3); −115.98 and −117.17 (s, CF_2CH); −121.44 to −126.00 (m, CF_2). For **2a**, yield 94%, white powder, mp < 50 °C; Anal. Calcd for $C_{34}H_{30}F_{38}N_2O_6$: C, 31.77; H, 2.33; N, 2.18. Found: C, 31.46; H, 2.56; N, 2.45. For **2b**, yield 93%, white oil, Anal. Calcd for $C_{30}H_{30}F_{30}N_2O_6$: C, 33.21; H, 2.76; N 2.58. Found: C, 33.45; H, 3.02; N, 2.97. For **2c**, yield 83%, viscous oil, Anal. Calcd for $C_{26}H_{30}F_{22}N_2O_6$: C, 35.29; H, 3.39; N, 3.16. Found: C, 34.89; H, 2.93; N, 3.23.

2.2.3. General synthesis of diacids

A mixture of 0.7 g of **2**, 1 eq., dissolved in 50 mL THF and 10 eq. of NaOH dissolved in 100 mL MeOH/H_2O (9/1, v/v) was stirred at room temperature for 4 h. A solution of HCl (1 N) was added until the pH becomes 1. The organic phase was extracted with 3 × 100 mL of ether and dried on $MgSO_4$. The solvent was then removed under vacuum. The final product was recristalized in hexane.

2.2.3.1. 3-(2-{2-[2-(1-Carboxymethyl-perfluoro-alkylamino)-ethoxy]-ethoxy}-ethylamino)-perfluoro-alkanoic acid, **3**. IR (KBr) 3420, 1731, 1300–1100 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 3.97 (m, 2H, $C\underline{H}NH_2$); 3.55 (m, 8H, $OC\underline{H}_2C\underline{H}_2O$); 2.94 (m, 4H, $CH_2C\underline{H}_2NH_2$); 2.70 (m, 4H, $CHC\underline{H}_2$); ^{13}C NMR (CD_3COCD_3) δ 171.45 (COO); 106–120 (m, CF_2 and CF_3); 71.33 ($OC\underline{H}_2C\underline{H}_2O$); 70.88 ($OC\underline{H}_2C\underline{H}_2O$); 56.93 ($\underline{C}HCH_2$); 47.73 ($CH_2C\underline{H}_2NH_2$); 33.73 ($\underline{C}HCH_2$); ^{19}F NMR ($CD_3COCD_3$) δ −76.91 (s, CF_3); −110 to −122 (m, CF_2). For **3a**, yield 87%, white powder, mp 60 °C; Anal. Calcd for $C_{30}H_{24}F_{38}N_2O_6Cl_2$: C, 27.67; H, 1.69; N, 2.15. Found: C, 27.54; H, 1.84; N, 1.98. For **3b**, yield 84%, white powder, mp 75 °C, Anal. Calcd for $C_{26}H_{24}F_{30}N_2O_6Cl_2$: C, 28.33; H, 2.17; N, 2.54. Found: C, 28.65; H, 2.01; N, 2.64. For **3c**, yield 84%, colored oil, Anal. Calcd for $C_{22}H_{24}F_{22}N_2O_6Cl_2$: C, 29.30; H, 2.44; N, 3.10. Found: C, 29.78; H, 2.11; N, 3.22.

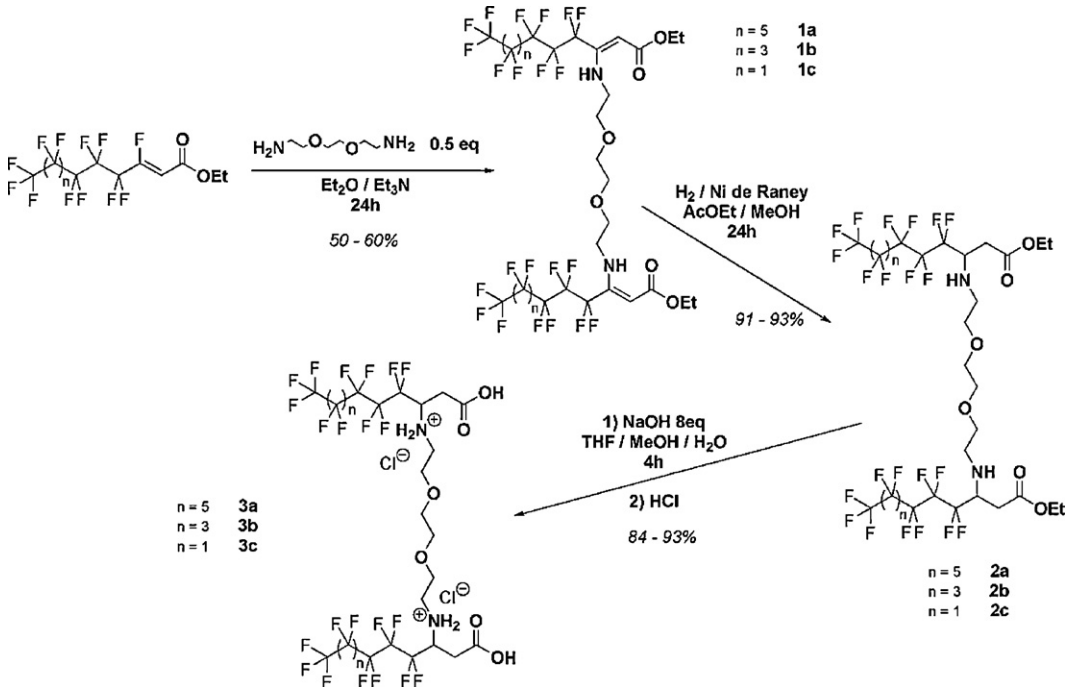
2.3. Compression isotherms

Surfactant solutions were prepared in 10% F-113 (Fluka)/chloroform (HPLC grade) and kept at −18 °C between experiments to limit solvent evaporation. Compression isotherms were obtained with a KSV Minithrough. Temperature was kept constant at 20 °C. Surface film equilibration time before compression was 10 min. The compression rate of the monolayer was maintained constant at 750 mm^2 min^{-1}.

3. Results and discussion

3.1. Synthesis of fluorinated lipids

The structure of the compounds described herein is entirely adjustable: the hydrophobic part, the spacer and the polar head. Fluorinated chains were choosen for their ability to form stable monolayers. The spacer, with two amino groups, can interact with oligonucleotides by electrostatic interactions or by hydrogen bonds. The polar head group was choose in order to allow the facile introduction of functional groups such as polyethylenglycol (PEG), which is able to modulate the hydrophilic lipophilic balance (HLB) of the molecule and to enhance its life time *in vivo*. Using this synthesis strategy, it is possible to introduce a cell-receptor for further specific cells recognition.



Scheme 1. General synthesis of gemini-type surfactants.

Starting deshydrofluorinated esters were prepared as previously reported [33]. This type of compounds can react with different nucleophiles by a Michael addition and fluoride elimination [34–38].

Fluorinated lipids reported in this paper result from the reaction between esters of 3-perfluoroalkyl 3-fluoroprop-2-enoic acid and ethoxylated diamines. The addition of 0.5 eq. of diamines to the double bond and the elimination of the fluorine give the corresponding enamines which are hydrogenated under relatively hard conditions (80 bar H_2, 50 °C) and Raney Nickel as catalyst (Scheme 1). Diesters were then saponified under basic conditions in a mixture of methanol and THF. Target compounds are obtained with good overall yields (Table 1).

3.2. 2D self-assembling. Compression isotherms

The amphiphilic behavior of gemini-type diesters **2** or diacides **3** was studied at the air/water interface by means of the Langmuir trough technique.

The compression isotherm carried out on pure water or buffered subphase shows that **2** can form a stable monolayer at the air/water interface for any chain length; we can note that the compression isotherm carried out on pure water subphase or on aqueous solution (NaCl 150 mM) subphase shows a similar profile. On pure water, the collapse pressure varies from 37 mN m^{-1} to 42 mN m^{-1} and reveals a relatively high dynamic stability of the monolayer which increases with the length of the hydrophobic part. The apparent molecular area of 74 $Å^2$, 78 $Å^2$ and 169 $Å^2$ respectively for **2a**, **2b** and **2c** (more than twice the molecular area of a fluorinated chain, 27–30 $Å^2$) seems to be governed by the polar ethylene-oxide spacer. Usually, due to their intrinsic rigidity and absence of any gauche defects, when compressed at the interface, fluorinated chains present a quasi-orthogonal orientation regarding the interface, in a liquid-condensed state. However, in our case, the compressibility modulus (C_s^{-1}) value of 86, 94 and 85 mN m^{-1} reveals that the film is macroscopically in a liquid-expended state, showing the main contribution of the polar head, regulating thus the interdistance between fluorinated segments. This result may originate from the rigidity of the spacer, which forces the two

Table 1
Yields of synthetic gemini-type surfactants.

Compound	Yield (%)	Compound	Yield (%)	Compound	Yield (%)
1a	53	**2a**	94	**3a**	87 (30)[a]
1b	67	**2b**	93	**3b**	84 (29)[a]
1c	65	**2c**	83	**3c**	84 (16)[a]

[a] Total yield to respect to the starting fluorinated alcohol.

Table 2
Characteristic parameters of compression isotherms of gemini diesters (A_c is the molecular area at the collapse and A_{30} is the molecular area at 30 mN/m).

Compound	Subphase	A_c/molecule ($Å^2$)	π_c (mN/m)	A_{30}/molecule ($Å^2$)	C_s^{-1}
2a	Pure water	74	**42**	84	86
2a	NaCl 0.15 M	69	42	81	88
2a	pH 10 NaCl 0.15 M	70	41	82	84
2a	pH 2 NaCl 0.15 M	73	**47**	91	88
2b	Pure water	78	**40**	88	94
2b	NaCl 0.15 M	81	40	91	96
2b	pH 10 NaCl 0.15 M	82	39	93	98
2b	pH 2 NaCl 0.15 M	79	**45**	94	100
2c	Pure water	169	**37**	190	85
2c	NaCl 0.15 M	169	37	190	87
2c	pH 10 NaCl 0.15 M	163	37	183	85
2c	pH 2 NaCl 0.15 M	165	**42**	196	90

Table 3
Characteristic parameters of compression isotherms of gemini diacids.

Compound	Subphase	A_c/molecule ($Å^2$)	π_c (mN/m)	A_{30}/molecule ($Å^2$)	C_s^{-1}
3a	Pure water	61	49	75	112
3a	NaCl 0.15 M	62	50	77	106
3a	pH 10 NaCl 0.15 M	63	54	81	103
3a	pH 2 NaCl 0.15 M	59	53	75	101
3b	Pure water	66	54	80	115
3b	NaCl 0.15 M	66	55	84	121
3b	pH 10 NaCl 0.15 M	71	52	89	114
3b	pH 2 NaCl 0.15 M	62	56	80	130

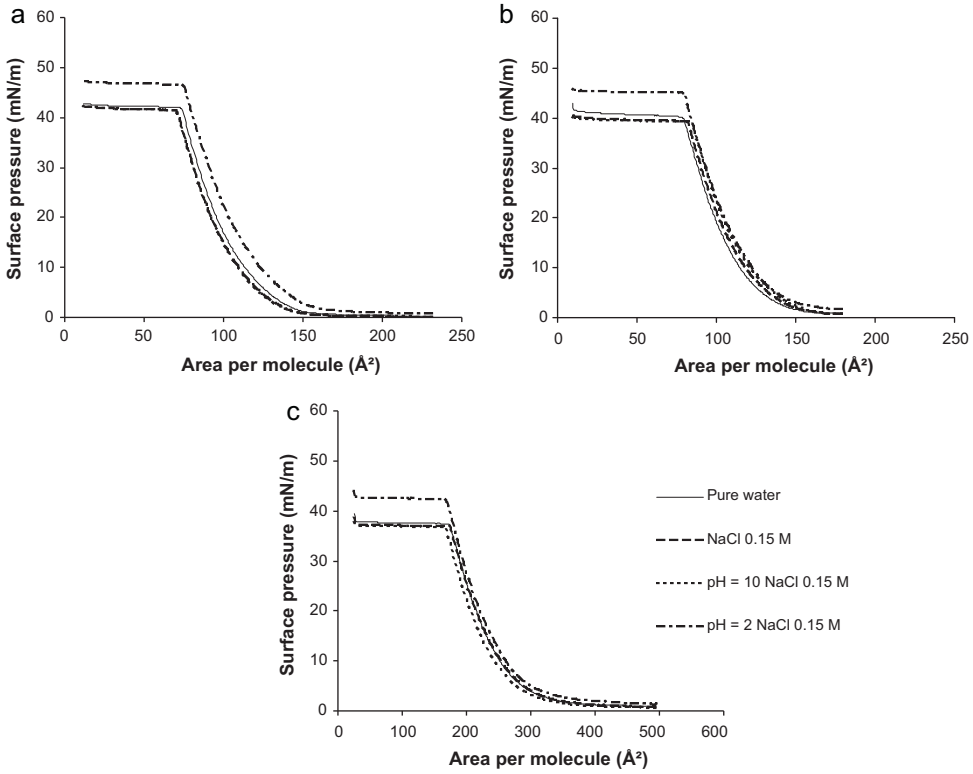


Fig. 1. π–A isotherms curves for **2a** (a), **2b** (b) and **2c** (c) on different subphases.

chains to be separated and has a significant effect on the molecular orientation. The molecular area decreases when the fluorinated chain length increases because of the interaction between them. This interaction becomes likely weak for the shortest fluorinated segment which allow a higher control of the organization by the spacer (Table 2).

The amine group is positively charged only at low pH, due to the withdrawing effect of the fluorinated backbone and ester group. At

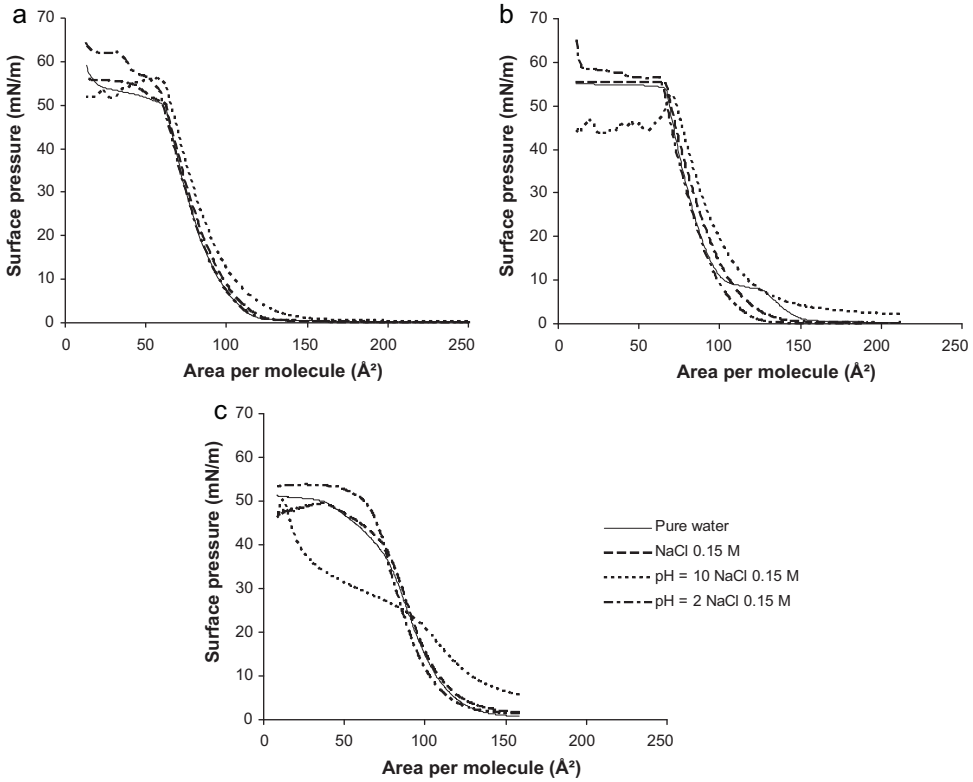


Fig. 2. π–A isotherms curves for **3a** (a), **3b** (b) and **3c** (c) on different subphases.

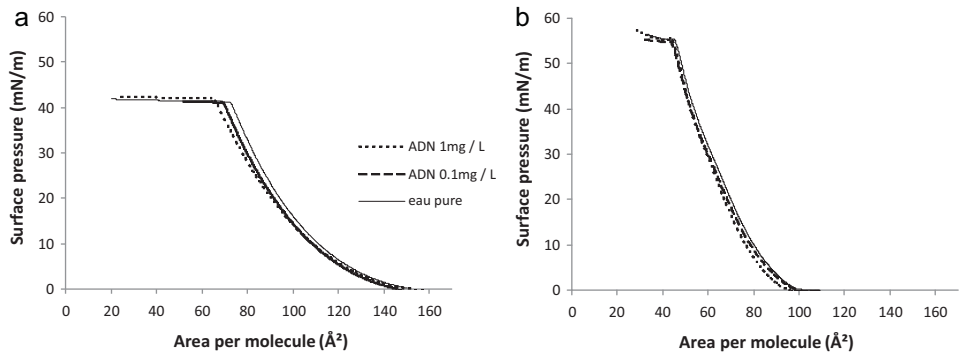
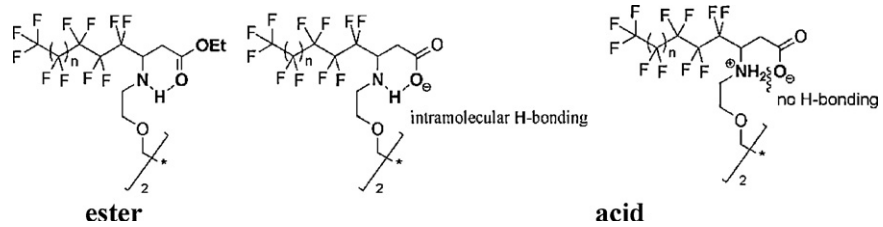


Fig. 3. π–A isotherms curves of **2a** (a), **3a** (b) with different concentrations of DNA in the subphase.

Table 4
Compression isotherms measurements values of **2a** on aqueous subphase (pH 7.4; NaCl 0.15 M) with and without ssDNA, respectively.

Subphase	A_c/molecule (Å^2)	π_c (mN m^{-1})	C_s^{-1} (mN m^{-1})
Without DNA	73	40	88
1 mg L^{-1} DNA	67	42	92

this pH the most polar NH_2^+ group interacts strongly with the water layer destructuring it and thereby the surface pressure increases, from 42 to 47 mN m^{-1} for **2a** from 40 mN m^{-1} to 45 mN m^{-1} for **2b** and from 37 mN m^{-1} to 42 mN m^{-1} for **2c** whereas the minimal molecular area is the same. The increase of molecular area is certainly due to the electrostatic repulsion between cationic amino groups. The compression isotherms show that compound **3** can form stable monolayers except for **3c** especially at high pH (Table 3). For these compounds, the results



Scheme 2. Schematic representation of the intramolecular H-bonding.

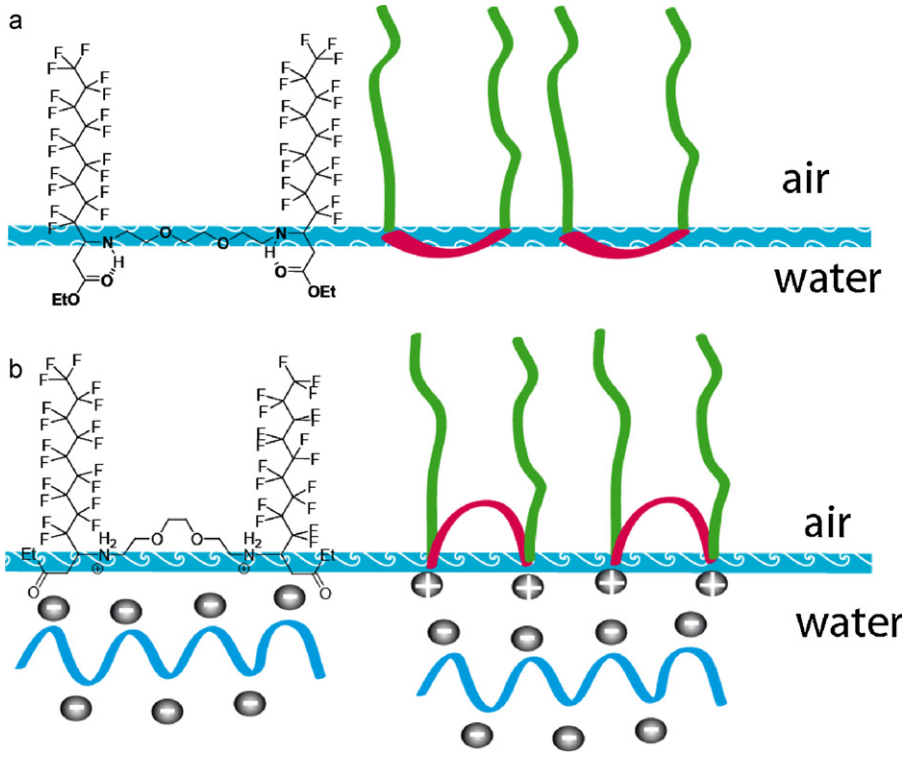


Fig. 4. Schematic representation of monolayers of **2a** compressed on an aqueous subphase with (a) and without DNA (b).

show a better surface activity by increasing the chain length whereas the area per molecule decreases. The reasons are the same as previously. However, the molecular area is nearer twice the molecular area of a fluorinated chain suggesting that the spacer have a minor role in the organization at the interface. Variation of pH, in this case, leads to more important changes in the organization, certainly due to the protonation of the carboxylic group (see Figs. 1 and 2).

3.3. Gemini monolayer/ssDNA interactions

In order to investigate the interactions of **2a**-based monolayers and **3a**-based monolayers with single-stranded low molecular weight DNA, compression isotherms were carried out on buffered subphases with DNA concentrations of 0.1 and 1 mg L^{-1}. For the diester **2a**, when ssDNA was added to the subphase, the molecular area at the lift-off (A_0) also remains constant but the compressibility decreases, and a smaller molecular area, 67 $Å^2$ versus 73 $Å^2$, was reached at the collapse for DNA concentration 1 mg L^{-1}. The compression isotherms measured on an aqueous solution (Tris pH 7.4, 150 mM NaCl) containing or not ssDNA are presented in Fig. 3 (Table 4).

This behavior is contrary to what is classically observed with dsDNA where the interaction of the DNA with the lipid monolayer is accompanied by an expansion of the film. This result could be explained by the fact that at small surface density, the molecules most likely reside with their ethyleneoxide moiety in the subphase, whereas NH group might be masked by the intramolecular H-bond with the ester group (Scheme 2), and therefore no interaction with DNA could be seen. By increasing the surface pressure, DNA molecules can interact with the lipid, stabilizing thus the ammonium form and undergoing thus the polar head phase transition from an extended ethyleneoxide moiety to a U-shape. This behavior of gemini surfactants is not unusual and seems to depend on the rigidity and length of the spacer. No significant changes in the surface pressure at the collapse were registered.

In the case of diacid **3a**, no significant interaction with DNA was observed, compression isotherm curves being similar. This result could be explained by electrostatic repulsions between DNA and carboxylate groups (Fig. 4). Moreover, NH groups might be masked also by intramolecular H-bond with the carboxylate group and therefore prevent interaction with DNA.

4. Conclusion

We report the synthesis of gemini-type fluorinated surfactants with ester and acid polar heads connected with diaminoethoxylated spacer. These compounds were obtained in good yields from commercial perfluoroalkylethanols.

The high hydrophobicity of the fluorocarbon chains allows the formation of stable 2D monolayers at the air/water interface except for the diacid with the shortest chain. The properties for the obtained Langmuir films were studied by changing the chain length and the nature of the subphase. For all products, one can note that the surface activity increases and the molecular area decreases with the chain length. The organization at the air/water interface seems to be governed by the rigidity of the spacer and the interaction between the fluorocarbon segments. This result is less marked with diacids. By changing the pH, variations can be observed on the isotherm curves, certainly due to the ionization of amino groups and carboxylic groups which create electrostatic interactions.

Their interactions with short, 23 bases, ssDNA were investigated in 2D systems. It was observed that the ssDNA complexation induces the contraction of the film with diesters, which is contrary to the classical behavior with dsDNA. Moreover, it was suggested that the aminoethoxylated polar head might undergo conformational changes so that the DNA complexation could occur. For diacids, no significant interaction with DNA was observed certainly due to the repulsive electrostatic interaction between the carboxylate groups and DNA. These results show that fluorous tag lipids appear as good models for DNA/surfactant interactions studies.

Acknowledgment

ND thanks the French Ministry of Education and Research for his PhD grant.

References

[1] H.M. Mc Connell, A. Radhakrishnan, Biochem. Biophys. Acta 1610 (2003) 159–173.
[2] J.P. Folkers, C.B. Gorman, P.E. Laibinis, S. Buchkolz, G.M. Whitesides, R.G. Nuzzo, Langmuir 11 (1995) 813–824.
[3] A.R. Parker, C.R. Lawrence, Nature 414 (2001) 33–34.
[4] Y. Masuda, K. Tomimoto, K. Koumoto, Langmuir 19 (2003) 5179–5183.
[5] R.G. Nuzzo, Nat. Mater. 2 (2003) 207–208.
[6] J.H. Clint, Surfactant Aggregation, Blackie, New York, 1992.
[7] T. Lopes-Costa, F. Gamez, S. Lago, J.M. Pedrosa, J. Colloid Interface. Sci. 354 (2011) 733–738.
[8] J.G. Riess, Curr. Opin. Colloid Interf. Sci. 14 (2009) 294–304.
[9] P. Chabaux, M. Camplo, D. Payet, G. Serin, L. Moreau, L. Barthélémy, M.W. Grinstaff, Bioconjug. Chem. 17 (2006) 466–472.
[10] C. McGregor, C. Perrin, M. Monch, P. Camilleri, A.J. Kirby, J. Am. Chem. Soc. 123 (2001) 6215–6220.
[11] H. Wang, S.D. Wettig, Phys. Chem. Chem. Phys. 13 (2011) 637–642.
[12] J. Wang, Z. Lu, M.G. Wientjes, J.L.S. Au, Am. Assoc. Pharm. Sci. 12 (2010) 492–503.
[13] J. Gaucheron, C. Santaella, P. Vierling, Bioconjug. Chem. 12 (2001) 114–128.
[14] C. Boulanger, C. Di Giorgio, J. Gaucheron, P. Vierling, Bioconjug. Chem. 15 (2004) 901–908.
[15] H.M. Courrier, T.F. Vandamme, M.P. Krafft, S. Nakamura, O. Shibata, Colloids Surf. A: Physicochem. Eng. Aspects 251 (2003) 33–41.
[16] S. Nakamura, H. Nakahara, M.P. Krafft, O. Shibata, Langmuir 23 (2007) 12634–12644.
[17] M.P. Krafft, Adv. Drug Deliv. Rev. 47 (2001) 209–228.
[18] J.G. Riess, M.P. Krafft, Biomaterials 19 (1998) 1529–1539.
[19] E. Kissa, Fluorinated Surfactants and Repellents, 2nd ed., Marcel Dekker, New York, 2001.
[20] I. Huc, R. Oda, Chem. Commun. (1999) 2025–2026.
[21] M. Gaysinski, L. Joncheray, F. Guittard, A. Cambon, P. Chang, J. Fluorine Chem. 74 (1995) 131–135.
[22] M.K. Bernett, W.A. Zisman, J. Phys. Chem. 67 (1963) 1534–1540.
[23] S. Shin, S.A. Rice, Langmuir 10 (1994) 262–266.
[24] K.M. Jenkins, S.D. Wettig, R.E. Verrall, J. Colloid Interface Sci. 247 (2002) 456–462.
[25] H.J. Lehmler, P.M. Brummer, J. Fluorine Chem. 117 (2002) 17–22.
[26] T. Takiue, D.J. Vollhardt, Colloids Surf. A: Physicochem. Eng. Aspects 198–200 (2002) 797–804.
[27] Y. Li, P. Li, C. Dong, X. Wang, Y. Wang, H. Yan, R.K. Thomas, Langmuir 22 (2006) 42–45.
[28] S.D. Wettig, X. Li, R.E. Verrall, Langmuir 19 (2003) 3666–3670.
[29] F.M. Menger, J.S. Keiper, Angew. Chem. Int. Ed 39 (2000) 1906–1920.
[30] M.J. Rosen, D.J. Tracy, J. Surfact. Deterg. 1 (1998) 547–554.
[31] Q. Chen, D. Zhang, R. Li, H. Liu, Y. Hu, Thin Solid Films 516 (2008) 8782–8787.
[32] R. Zana, J. Colloid Interface Sci. 248 (2002) 203–220.
[33] S. Achilefu, L. Mansuy, C. Selve, S. Thiébaut, J. Fluorine Chem. 70 (1995) 19–26.
[34] S. Thiebaut, C. Gérardin, J. Amos, C. Selve, J. Fluorine Chem. 73 (1995) 179–184.
[35] S. Thiébaut, C. Gérardin-Charbonnier, C. Selve, J. Fluorine Chem. 82 (1997) 131–138.
[36] S. Cosgun, C. Gérardin-Charbonnier, J. Amos, C. Selve, J. Fluorine Chem. 125 (2004) 55–61.
[37] M.S. Özer, C. Gérardin-Charbonnier, S. Thiébaut, L. Rodehüser, C. Selve, Amino Acids 16 (1999) 381–389.
[38] N. Dupuy, A. Pasc, E. Mayot, S. Cosgun, C. Gérardin-Charbonnier, J. Fluorine Chem., doi:10.1016/j.jfluchem.2011.03.019, in press.