



Alkylbetainate chlorides: Synthesis and behavior of monolayers at the air–water interface

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ABSTRACT

In this study, cationic alkylbetainate chloride surfactants (C_nBC , $n=10-16$) are synthesized using more environment-friendly reagents (glycine betaine, thionyl chloride and primary alcohols) than in previous works (chloroacetyl chloride, trimethylamine and primary alcohols). The interfacial behavior of the C_nBC monolayers is studied onto aqueous subphases at 20 °C using the Langmuir trough technique. Different experimental conditions including pH, temperature, sodium salts and Na_2SO_4 ionic strength are investigated. The results obtained have shown that the C_nBC with a hydrocarbon chain length ≥ 14 are able to form insoluble monolayers. The $C_{16}BC$ monolayer stability checked by the compression–expansion cycles has shown a superimposition of isotherms in the whole liquid-condensed region and an irreversible rearrangement of the molecules at high compression. The $C_{16}BC$ monolayer is not influenced by the pH and the presence of monovalent anions but it is influenced by the temperature, the divalent anions and the ionic strength. It has exhibited a great stability whatever the experimental conditions.

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1. Introduction

Surfactants are continuously being created in order to obtain materials with specific physicochemical properties for targeted applications [1]. Among them, cationic surfactants have shown their commercial potential as bacteriostatic agents [2]. They play an important role as sanitizing and antiseptic agents as well as components in cosmetic formulations as surfactants and antibacterial agents and are also used as cationic softeners, lubricants, retarding agents and antistatic agents in numerous sectors [3].

Quaternary ammonium surfactants are widely employed in pharmaceutical and cosmetic industries and in many applications where they come into contact with the skin. They are important ingredients that are frequently formulated into hair care products to modify the properties of hair surface [4]. Furthermore, these surfactants have been included in liposomes in order to obtain cationic liposomes which have the ability to transfer DNA into cells through fusion with the cell membranes [5] or to form spontaneously complexes with DNA and RNA [6].

As a consequence of their widespread use and strong resistance to biodegradation, chemical surfactants like quaternary ammonium ones may persist in wastewater treatment systems at relatively high concentrations [7,8]. They can cause a disturbance of the ecological

equilibrium, due to toxic impacts on aquatic organisms [9]. In order to meet legislative requirements and to discharge harmless effluents into the river, cleavable surfactants are of increasing interest today because of their higher biodegradability [10].

In this context, glycine betaine (N,N,N-trimethylglycine) also called betaine is an interesting candidate for the production of surfactants with a low environmental impact. It is present in various plants, animals and microorganisms and plays an important role in osmotic stress resistance in these organisms [11]. This molecule is a human nutrient and is used in the treatment of various diseases such as homocystinuria and homocystenemia [12,13], cardiovascular diseases, depression and other mental disorders, seizures and arthritis [14]. Furthermore, betaine supplementation decreased the hepatotoxicity induced by lipopolysaccharide in adult male rats [15].

Previous works have synthesized the alkylbetainates using chloroacetyl chloride (CAC with $LC_{50}=660$ ppm [16]), trimethylamine (TEA) and primary alcohols as reagents. CAC and TEA are respectively toxic and harmful by inhalation [17]. Wastewater containing TEA causes environmental pollution problems and adverse effects on aquatic ecology. In addition, TEA is malodorous, can endanger human health and has been considered to be a possible carcinogen [18,19].

Data concerning critical micelle concentration (CMC), foaming and dispersing properties of the alkylbetainates exist in the literature [20–25]. Their low CMC and their high foaming and dispersing powers demonstrate their high potential as formulating agents. Recently, a review of synthesis methods and potentialities of application of

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glycine betaine based surfactants has been published [26]. Data concerning the interfacial organization at the air–water interface of the alkylbetainates are not available. From a fundamental point of view, these data provide information on the molecular packing and on the intermolecular forces operating at the interface.

The objective of the present paper is twofold. First, the synthesis of the alkylbetainate chlorides (C_nBC , $n = 10–16$) is performed using more environment-friendly reagents than in previous works (glycine betaine, thionyl chloride (with $LC_{50} = 1277$ ppm [16]) and primary alcohols). The major factors affecting the esterification degree (the effect of basic catalysts, the nature of the solvent, the acid chloride/alcohol molar ratio, the temperature and the initial reactant concentration) are examined for the optimization of the hexadecylbetainate chloride ($C_{16}BC$) synthesis. Decylbetainate chloride ($C_{10}BC$), dodecylbetainate chloride ($C_{12}BC$) and tetradecylbetainate chloride ($C_{14}BC$) are synthesized using the optimum conditions obtained for the synthesis of the $C_{16}BC$. Second, surface pressure (Π)–molecular area (A) isotherms of the C_nBC are studied at the air–water interface by using the Langmuir trough technique. The influence of the environmental conditions (pH, temperature, anion types and ionic strength) on the monolayer interfacial properties of $C_{16}BC$, exhibiting the best foaming properties [25], is investigated. The study gives insights about the key parameters to take into account for the formulation of the alkylbetainate-based preparations for instance for cosmetic and pharmaceutical purposes.

2. Materials and methods

2.1. Materials

The following compounds are commercially available. Glycine betaine (99% purity), thionyl chloride, 1-decanol, 1-dodecanol, 1-tetradecanol and 1-hexadecanol are purchased from Aldrich. All the reagents and solvents used are of the highest grade and are used as received. Ultra pure water with a resistivity of 18.2 M Ω .cm is used in all the experiments.

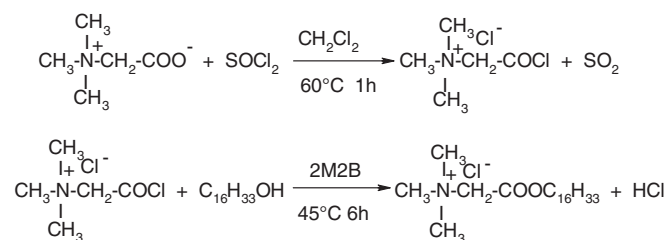
2.2. Methods

2.2.1. Synthesis of betainyl chloride

The first step of $C_{16}BC$ synthesis is the preparation of the betainyl chloride. Betainyl chloride is prepared according to the method described in the literature [27]. Anhydrous betaine (20.0 g, 0.171 mol) is suspended in 30 mL of dichloromethane in a three-necked round bottomed flask. Thionyl chloride (30 mL, 0.411 mol) is added dropwise under constant stirring during a period of 60 min. The reaction has proceeded at 60 °C in a water bath, until the emission of sulfur dioxide has ceased. Both thionyl chloride and solvent in excess are then removed by evaporation under reduced pressure. The product is washed four times with 100 mL of n-hexane with subsequent removal of the solvent by decantation. The crude product is dried in vacuum to afford 28.6 g of white powder.

2.2.2. Synthesis of $C_{16}BC$

Betainyl chloride, 1-hexadecanol and solvent (1,4-dioxan, acetonitrile, 2-methyl-2-butanol (2M2B), dichloromethane or n-hexan) are mixed at 200 rpm. The reaction mixture is heated up to different temperatures (25, 35, 45, 55 or 65 °C) in a water bath and stirred for 7.5 h at the most. Different catalysts (None, dimethylaminopyridine, pyridine or triethylamine), reactant concentrations and betainyl chloride/1-hexadecanol molar ratios are tested. The reaction mixture is allowed to cool to room temperature before the solvent is decanted. The crude product is purified by preparative HPLC (acetonitrile/water 10:90 v/v, 20 mL/min and 30 °C) to give $C_{16}BC$. Scheme 1 shows the reaction route for the synthesis of $C_{16}BC$.



Scheme 1. Synthesis route of cationic hexadecylbetainate chloride ($C_{16}BC$) with the optimal parameters.

2.2.3. Chemical characterization

The structure of the final product is confirmed by infrared spectroscopy (IR), mass spectrometry (MS) and nuclear magnetic resonance (NMR). The IR spectra are recorded with a Bruker IFS 25 instrument as KBr pellets. Mass spectra were acquired on a High Capacity Ion Trap mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an electrospray ionization source. Best results were obtained in positive mode with capillary, nebulizer pressure, drying gas flow, and drying gas temperature set to 66.0 nA, 40.0 psi (nitrogen), 9.0 L min⁻¹ (nitrogen) and 365 °C, respectively. The scan range was adjusted to m/z 50–3000 and the target mass set to m/z 500. MS data were recorded and processed using Bruker Daltonics data analysis software, version 3.0. NMR spectra (¹H, ¹³C, ¹H/¹H COSY, HSQC and HMBC) are recorded in deuteriomethanol (CD₃OD) at 600 MHz (¹H) and 150 MHz (¹³C) with a Varian instrument and are reported in ppm from internal tetramethylsilane on the δ scale. Data are reported as follows: chemical shift [multiplicity: singlet (s), triplet (t), quintuplet (quint), multiplet (m)].

2.2.4. Π -A isotherm

The Π -A isotherms are recorded by means of an automated Langmuir trough (KSV Minitrough, width: 75 mm, area: 24,225 mm², KSV Instruments, Helsinki, Finland) enclosed in a plexiglass box to reduce film contamination and equipped with a platinum plate attached to a Wilhelmy type balance. A symmetric compression is achieved with two moving barriers at a constant rate of 10 mm/min. Before each experiment, the trough is cleaned with 2-propanol and rinsed thoroughly with ultra pure water. The cleanliness of the system is confirmed by checking the surface pressure over the surface compression of the pure subphase. The temperature of the subphase is maintained at the desired value by circulating water through the base of the trough. The spreading solution is prepared in chloroform/methanol (2:1 v/v) and is dispensed as tiny droplets to produce a uniform monolayer. The compression is started 15 min after spreading the amphiphile solution to allow complete evaporation of the solvent and to reach equilibrium with the desired experimental temperature. The reproducibility of the Π -A isotherms is checked by repeated recordings and the relative standard deviation in surface pressure and area is found to be $\leq 3\%$.

3. Results and discussion

3.1. Synthesis

Glycine betaine has a very low reactivity for direct esterification with alcohol [28]. Generally, esterification of a primary alcohol with betainyl chloride is proceeded in the presence of catalytic amount of one of the following basic catalysts (pyridine, dimethylaminopyridine, triethylamine, or N-bromosuccinimide) [27,29–31]. In this work, hexadecylbetainate chloride is synthesized from glycine betaine via betainyl chloride with 1-hexadecanol. The second step of the reaction (Scheme 1) is optimized. The use or not of basic catalyst, the initial reactant concentration, the betainyl chloride/1-hexadecanol molar ratio, the

nature of the organic solvent and the temperature are investigated. The combination of no basic catalyst (Fig. 1a), an initial concentration of reactants of 0.132 mol/L (corresponding to 45.19 mg/mL) (Fig. 1b), a 3:1 betainyl chloride/1-hexadecanol molar ratio (Fig. 1c), a temperature of 45 °C (Fig. 1d), the 2-methyl-2-butanol as organic solvent (data not shown) and a reaction time of 6 h has given the highest yield ($94 \pm 3\%$) of hexadecylbetainate chloride. Previous works have shown that acyl chlorides have high reactivity [28,32] and cationic esters are more stable in acidic medium [23,28]. The second step of the reaction (Scheme 1) produced a strong acid (HCl) which stabilized the final product and could play a role of acid catalyst. Other works have also shown that a high yield of ester (e.g., Octyl acetate) has been obtained with strong acid (sulfuric acid, p-toluenesulfonic acid) as catalyst [33,34]. The other alkylbetainate chlorides (decylbetainate chloride ($C_{10}BC$), dodecylbetainate chloride ($C_{12}BC$) and tetradecylbetainate chloride ($C_{14}BC$)) are synthesized using the optimized conditions for the synthesis of $C_{16}BC$.

3.2. Chemical characterization

The high purity ($\geq 97\%$) of C_nBC is checked by analytical HPLC-ELSD and confirmed by NMR (data not shown). The chemical characterization is done by Infrared and Mass Spectrometry. A typical spectrum of betainyl chloride has displayed bands at 2958 cm^{-1} (C–H), 1739 cm^{-1} (C=O), 675 cm^{-1} (C–Cl). IR spectra of the synthesized C_nBC have displayed bands at $2918\text{--}2962\text{ cm}^{-1}$ (C–H, stretching), $1738\text{--}1751\text{ cm}^{-1}$ (C=O, stretching), $1402\text{--}1477\text{ cm}^{-1}$ (C–H, bending), $1190\text{--}1205\text{ cm}^{-1}$ (C–O, stretching) (Fig. 2). Mass spectra have displayed the signals of the parent ions at $m/z = 258.1$ ($C_{10}BC$), 286.3 ($C_{12}BC$), 314.3 ($C_{14}BC$) and 342.4 ($C_{16}BC$) (Fig. 3).

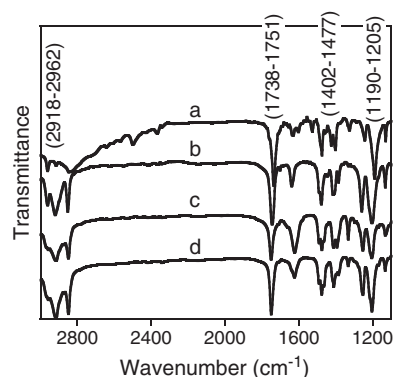


Fig. 2. Infrared spectra of alkylbetainate chlorides (C_nBC): (a) Decylbetainate chloride ($C_{10}BC$), (b) dodecylbetainate chloride ($C_{12}BC$), (c) tetradecylbetainate chloride ($C_{14}BC$) and (d) hexadecylbetainate chloride ($C_{16}BC$).

3.3. Interfacial properties of cationic alkylbetainate chlorides (C_nBC) at the air–water interface

Π -A isotherms of pure C_nBC are established at the air–water interface of a Langmuir trough to get insight into their interfacial organization. Four characteristic parameters are determined: the limiting area (A_0) (i.e., the extrapolation of the Π -A curve to $\Pi = 0$ mN/m corresponding to the theoretical area at which molecules leave the gaseous (G) state and adopt a liquid-expanded (LE) state [35]), the area (A_c) and the surface pressure (Π_c) at the collapse of the monolayer as well as the two-dimensional compressibility modulus (C_s^{-1}). C_s^{-1} is calculated from Π -A data according to the following Eq. (1):

$$C_s^{-1} = -A \cdot (\partial \Pi / \partial A). \quad (1)$$

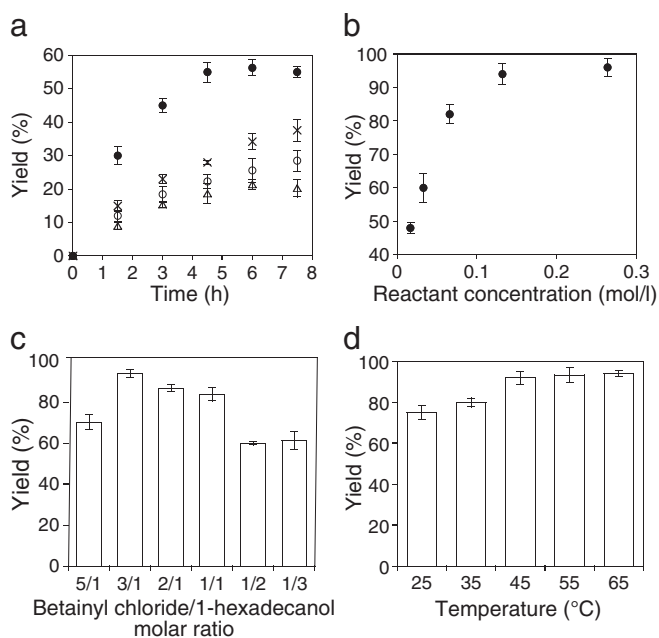


Fig. 1. Yield of hexadecylbetainate produced from betainyl chloride and 1-hexadecanol (a) Effect of basic catalysts at 0.066 mol/L – (●) No catalyst; (×) dimethylaminopyridine; (○) pyridine; (Δ) triethylamine; (b) Effect of reactant concentration (betainyl chloride and 1-hexadecanol at a molar ratio of 1:1); (c) Effect of molar ratio betainyl chloride to 1-hexadecanol; (d) Effect of temperature. When not specified, the reaction conditions are: betainyl chloride/1-hexadecanol molar ratio 1:1, concentration of reactants: 0.066 mol/L, solvent: 2-methyl-2-butanol, temperature: 45 °C, reaction time: 6 h and magnetic stirring: 200 rpm.

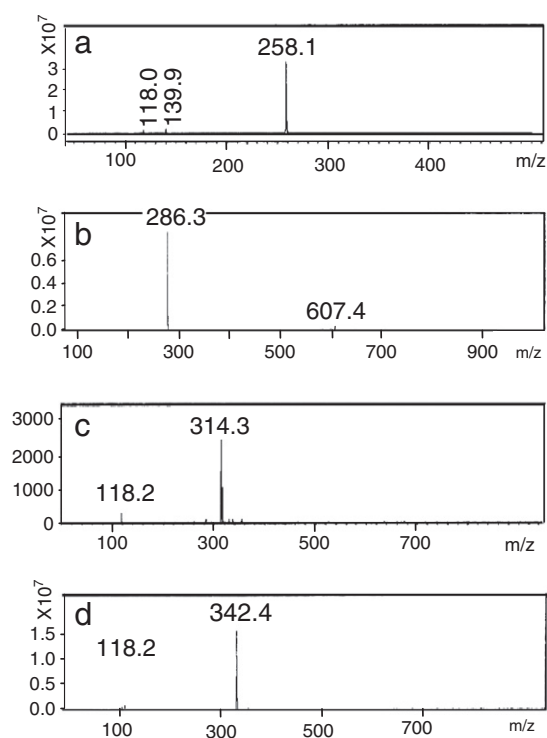


Fig. 3. Positive-ion ElectroSpray Ionization mass spectra of alkylbetainate chlorides (C_nBC): (a) Decylbetainate chloride ($C_{10}BC$), (b) dodecylbetainate chloride ($C_{12}BC$), (c) tetradecylbetainate chloride ($C_{14}BC$) and (d) hexadecylbetainate chloride ($C_{16}BC$).

Where A is the area per molecule at the indicated surface pressure and Π is the corresponding surface pressure. This parameter is useful to characterize the phase state of the monolayer and to more clearly detect the phase transitions [36]. The value of C_s^{-1} is approximately between 10–50 mN/m for a LE phase, 50–100 mN/m for an intermediate liquid (I), 100–250 mN/m for a liquid-condensed (LC) phase and 1000–2000 mN/m for a solid-condensed (S) monolayers [37,38]. The compressibility modulus is the inverse of the monolayer elasticity, i.e. a low compressibility modulus signifies a high interfacial elasticity [39], and consequently, a low monolayer stability.

Fig. 4a shows the Π - A isotherms of spread C_n BC monolayers on a water subphase at 20 °C. C_{10} BC monolayer exhibits only a G phase and Π does not exceed 0.5 mN/m. C_{12} BC monolayer shows a G phase and a LE phase confirmed by the C_s^{-1} values (inset in Fig. 4a). It is an indication of a certain degree of cooperative interaction between the molecules at the interface. Π starts deviating from zero at $A_0 \sim 30 \text{ \AA}^2/\text{molecule}$. At high compression, A and Π reach $13.8 \text{ \AA}^2/\text{molecule}$ and 16.9 mN/m , respectively (Table 1). Small monolayer areas and low surface pressures reached upon interface compression have been considered as characteristic of soluble monolayers at the air–water interface [40]. In our experimental conditions, C_{10} BC and C_{12} BC cannot form insoluble monolayers because the hydrophobicity of their alkyl chains is not high enough to prevent the progressive dissolving of the monolayer components into the subphase upon the interface compression as in the case of dodecyltrimethylammonium and sodium dodecyl sulfate monolayer at the air–water interface at 20 °C [41].

According to the shape of the isotherm and to the C_s^{-1} values (Fig. 4a and inset), C_{14} BC and C_{16} BC monolayers present a G phase, a LE phase, a LC phase and a collapse point with increasing of Π . It points out that C_n BC with hydrocarbon chain ≥ 14 are able to form an

Table 1

Molecular area at take-off (A_0), molecular area (A_c) and surface pressure (Π_c) at the collapse for the alkylbetainate chloride (C_n BC) monolayers on aqueous subphase (pH 5.7) at 20 °C.

Parameters	C_{10} BC	C_{12} BC	C_{14} BC	C_{16} BC
A_0 ($\text{\AA}^2/\text{molecule}$)	–	30.3	28.1	23.3
A_c ($\text{\AA}^2/\text{molecule}$)	–	13.8	16.6	17.6
Π_c (mN/m)	–	16.9	41.5	52.3

The relative standard deviation in A and Π was $\leq 3\%$.

insoluble monolayer at an air–water interface in spite of their high hydrophilic lipophilic balance value ($HLB = 24.3$) [42,43] classifying them as water soluble surfactants.

A_0 are $28.1 \text{ \AA}^2/\text{molecule}$ for C_{14} BC and $23.3 \text{ \AA}^2/\text{molecule}$ for C_{16} BC. A_c and Π_c of C_{14} BC are $16.6 \text{ \AA}^2/\text{molecule}$ and 41.5 mN/m while those of C_{16} BC are $17.6 \text{ \AA}^2/\text{molecule}$ and 52.3 mN/m (Table 1). C_{14} BC and C_{16} BC can thus adopt a tight packing at the interface. The small difference of interfacial occupation at low compression between C_{14} BC and C_{16} BC could be due to a better structuration of the molecules with a higher hydrocarbon chains due to van der Waals interaction increase. In the condensed state, the length of the hydrocarbon chain has no influence on the interfacial occupation suggesting that the chain is vertically oriented at the interface. Π_c increases with the hydrocarbon chain due to the increase of the van der Waals attractions.

Comparatively to other ammonium containing surfactants like alkyltrimethylammonium bromides C_{14} TAB and C_{16} TAB, C_n BC occupy an area twice smaller. C_{14} TAB and C_{16} TAB at the air–water interface at 23 °C have a A_c of 47 and $43 \text{ \AA}^2/\text{molecule}$ and a Π_c of 35 and 32 mN/m , respectively [44]. This is probably due to the difference of polarity between their head groups. The head groups of the C_n BC and the C_n TAB both contain a quaternary trimethylammonium group but the formers bear an additional carboxylate moiety. They are thus more polar and are probably more deeply immersed in the water subphase than the head groups of the C_n TAB.

The C_{16} BC monolayer exhibits a shape similar to the one of a non-ionic surfactant [45] in spite of the positive charge in their polar head groups. The isotherm is approximately linear (vertical) characterized by a steep slope with the occurrence of a superliquid phase between 18.7 and $17.8 \text{ \AA}^2/\text{molecule}$ corresponding to $\Pi = 30.0$ and 46.0 mN/m with a maximum of C_s^{-1} equal to 464.4 mN/m at $A = 18.3 \text{ \AA}^2/\text{molecule}$ and $\Pi = 36.6 \text{ mN/m}$. It suggests that the positive head is deeply immersed in the water subphase. The repulsive interactions between the C_{16} BC polar heads are thus screened by water solvation resulting in the increase of the van der Waals forces between hydrophobic chains, leading consequently to a high Π_c .

To get further information about the solubility of the monolayer-forming components in water, compression–expansion cycles of the C_{14} BC monolayer (data not shown) and C_{16} BC monolayer are performed (Fig. 4b). The isotherms of the compression and expansion of the C_{16} BC monolayer are superimposed in the whole LC region confirming that no C_{16} BC molecule leaves the interface. Interestingly, the plateau previously observed at $\sim 0 \text{ mN/m}$ still existed after expansion but has shifted to $\sim 8 \text{ mN/m}$. An irreversible ordered arrangement of surfactant molecules during the initial compression can be at the origin of this phenomenon. It was observed by Mallouri et al. [46] with the monolayer of surface-active metal organic complexes. Upon expansion intermolecular attraction forces between the arranged molecules are still present and irreversible, resulting in a plateau with an increased surface pressure. The result obtained from compression–expansion cycles proves that the C_{16} BC molecules are remained at the interface upon compression indicating a high stability of the C_{16} BC monolayer.

As C_{16} BC has been shown to develop the best performance as foaming agent [25], an in-depth interfacial analysis of this compound

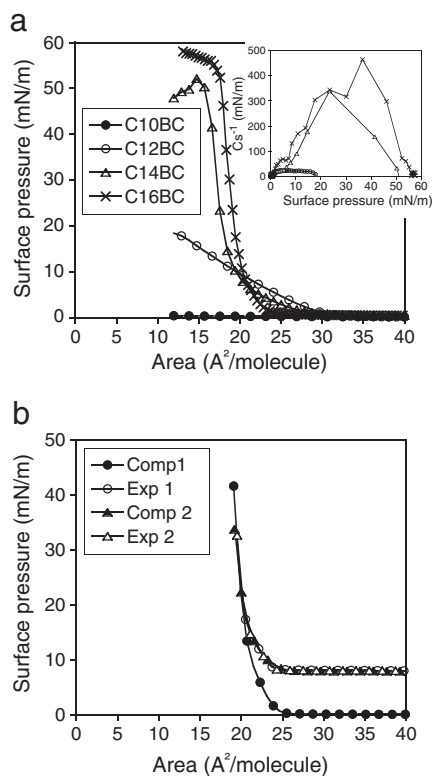


Fig. 4. (a) Surface pressure (Π)-molecular area (A) isotherm of alkylbetainate chlorides (C_n BC); Inset: compressibility modulus (C_s^{-1}) as a function of Π ; (b) Compression–expansion cycles of hexadecylbetainate chloride deposited onto an aqueous subphase (pH 5.7) at 20 °C.

is performed. The influence of the environmental conditions (pH, temperature, anion type and ionic strength) on its monolayer interfacial properties is investigated.

3.4. Influence of experimental conditions on the interfacial behavior of the $C_{16}BC$ monolayer

The structure and the stability of surfactant monolayers is known to be sensitive to the subphase pH particularly for ionic surfactants [47,48] and temperature. Anions influence a wide range of interfacial phenomena including surface properties of salt solutions, colloid stability and adsorption of cationic surfactant at the air-water interface [49].

3.4.1. Influence of pH

Fig. 5a shows the Π -A isotherms of the $C_{16}BC$ monolayers on water subphases with different pH values. The global shape is not greatly affected by the pH of the subphase. At pH below 7, the shape of the isotherms is slightly more tilted than at higher pH. Some small differences are observed for the characteristic parameters in Table 2a. A_0 increases slightly but significantly with the addition of HCl in the subphase. The addition of NaOH has no significant effect on A_0 , A_c and Π_c are not significantly or very slightly influenced by the addition of chloride or hydroxide anions. The C_s^{-1} values obtained between 20 and 30 mN/m (Inset Fig. 5a) show that the $C_{16}BC$ monolayer is less ordered at pH < 7 and more ordered at pH > 7 than in pure water. In other words, in presence of anions, the monolayer is more ordered with the hydroxide than with the chloride. For one specific anion, the order increases with its concentration in the medium. Although the charge of the quaternary ammonium cation is permanent and independent of the pH of the solution, the presence of anions like Cl^- and OH^- has a small but significant influence on the $C_{16}BC$ interfacial organization and more particularly on its compressibility.

Table 2

Molecular area at take-off (A_0), molecular area (A_c) and surface pressure (Π_c) at the collapse for the hexadecylbetainate chloride ($C_{16}BC$) monolayer on aqueous subphase (a) with various pH, (b) with various temperatures, (c) with various anions and (d) with various Na_2SO_4 ionic strengths.

Parameters	Water 20 °C	pH (with HCl or NaOH)				
		3	5	7	9	12
A_0 ($\text{\AA}^2/\text{molecule}$)	23.3	26.1	28.1	23.9	24.2	25.8
A_c ($\text{\AA}^2/\text{molecule}$)	17.6	18.4	17.9	18.0	18.8	19.5
Π_c (mN/m)	52.3	51.1	54.2	51.5	51.9	52.1
Parameters	Temperature (°C)					
	15	20	25	30		
A_0 ($\text{\AA}^2/\text{molecule}$)	20.2	23.3	24.0	29.5		
A_c ($\text{\AA}^2/\text{molecule}$)	16.5	17.6	18.7	19.1		
Π_c (mN/m)	48.2	52.3	53.3	51.4		
Parameters	Anion (Sodium salts, 2 mM)					
	HPO_4^{2-}	SO_4^{2-}	OH^-	Br^-	NO_3^-	ClO_4^-
A_0 ($\text{\AA}^2/\text{molecule}$)	32.3	31.3	25.9	24.5	25.5	24.3
A_c ($\text{\AA}^2/\text{molecule}$)	26.6	20.7	17.9	17.7	18.0	18.4
Π_c (mN/m)	54.2	54.6	52.3	46.5	52.1	52.4
Parameters	Ionic strength (Na_2SO_4 , mM)					
	0.5	1	2	5	10	
A_0 ($\text{\AA}^2/\text{molecule}$)	26.2	26.5	31.3	34.5	32.5	
A_c ($\text{\AA}^2/\text{molecule}$)	18.0	19.1	20.7	22.5	23.6	
Π_c (mN/m)	51.7	53.4	54.6	51.3	53.3	

The relative standard deviation in molecular area and surface pressure was $\leq 3\%$.

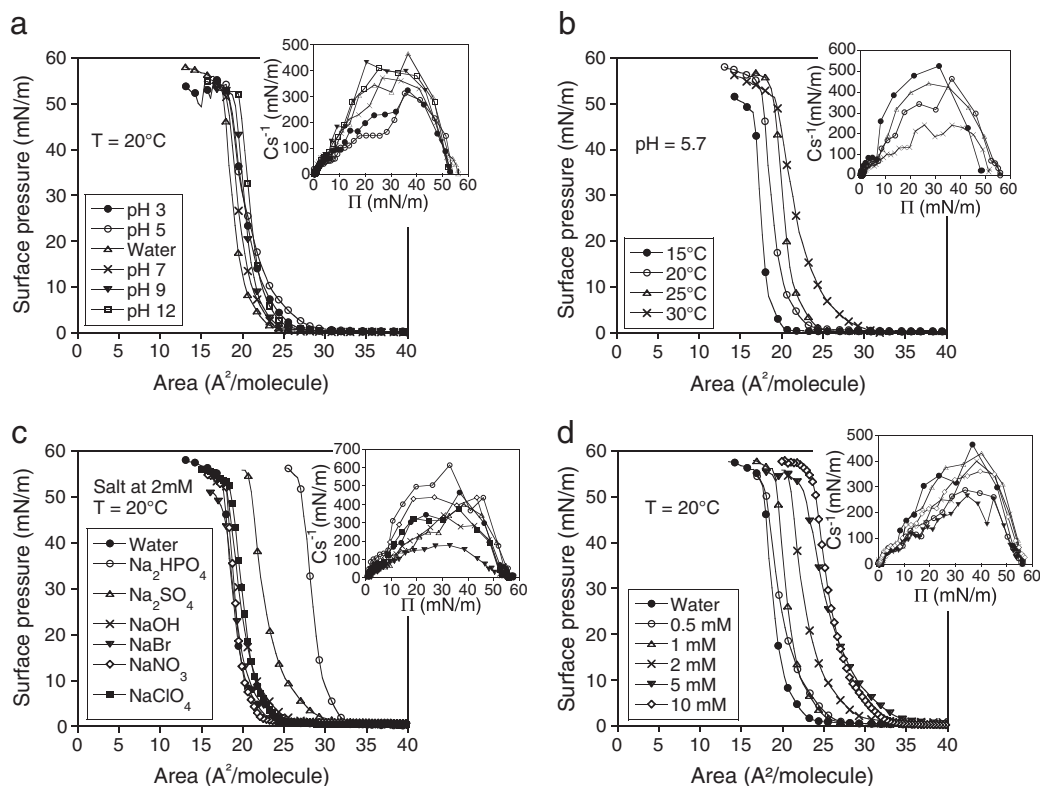


Fig. 5. Surface pressure (Π)-molecular area (A) isotherm of hexadecylbetainate chloride ($C_{16}BC$) monolayers deposited onto an aqueous subphase of different (a) pH, (b) temperatures, (c) sodium salts and (d) Na_2SO_4 salt concentrations. Insets: compressibility modulus (C_s^{-1}) as a function of Π for the corresponding subphase conditions.

Initial Cl^- ions in the subphase are in competition with water molecules. Additional Cl^- appear to dehydrate the C_{16}BC head groups by substitution of water molecules by Cl^- , inducing a steric effect in the interfacial film. This behavior was already observed for dodecylphosphocholine in the presence of Cl^- ions [50].

In water subphase (pH 5.7), the addition of OH^- ions (low concentration) leads to their neutralization by protons forming water molecules. As the concentration of OH^- ions increases, the subphase is neutralized and initial Cl^- in competition with OH^- are progressively replaced by the latter which interact with C_{16}BC head groups. The final behavior of the monolayer is governed by the type of the counterion which is present in excess in the solution. The OH^- ions are highly hydrated in water [51] and may interact strongly with the C_{16}BC head groups similar to that of 1,2-diacyl-3-trimethylammonium-propane which was found to be a strong water adsorber [52]. More hydrated ions seem to influence positively the order of C_{16}BC molecules at the interface.

3.4.2. Influence of temperature

Fig. 5b shows the Π -A isotherms of the C_{16}BC monolayer at different temperatures. The shape of the isotherms is not globally influenced by the temperature. The different states described for Fig. 4a are observed whatever the temperature between 15 and 30 °C. General interfacial organization of C_{16}BC molecules is thus not considerably modified by the heat input. However, significant differences are observed for the characteristic parameters (Table 2b). A_0 increases from 15 to 30 °C and A_c increases with raising temperature up to 25 °C. The Brownian motion contributes to a higher surface occupied by the molecule up to 25 °C as would be expected from the increased thermal agitation of the molecules in the surface film [53]. Above 25 °C, a partial desorption of the molecules from the monolayer or a molecule aggregation into “surface micelles” at the interface can occur as discussed by Knauf and coworkers for alkyltrimethylammonium bromides [54] and for alkylaminomethyl rutin [55]. Π_c shows a maximum at 25 °C reflecting a maximal stability of the film to the compression at this temperature. The sharp decrease of the C_s^{-1} values above 25 °C confirms this result (Inset Fig. 5b). Above this temperature, the interactions between the monolayer-forming components are strongly reduced due to high thermal agitation.

3.4.3. Influence of anions

The influence of anion types on C_{16}BC monolayer isotherms is investigated using different sodium salts. All the monolayer isotherms have exhibited the three phases (G, LE and LC) (Fig. 5c). Nevertheless, the characteristic parameters of the isotherms are in some cases different suggesting different types of interaction between the C_{16}BC head groups and the additional anions in competition with chloride anions in the subphase. Two different trends are observable. Divalent anions (HPO_4^{2-} , SO_4^{2-}) shift the isotherm to the right resulting in a higher A_0 and A_c (Table 2c) while monovalent anions (OH^- , Br^- , NO_3^- , ClO_4^-) do not influence the isotherms in comparison with the one recorded on pure water (Table 2a). This trend was also observed previously for monovalent anions in the case of viologen dication (1,1'-dioctadecyl-4,4'-bipyridilium) [56].

SO_4^{2-} and HPO_4^{2-} give rise to a steric effect by penetrating within the interface between the C_{16}BC head groups. Indeed, these anions have a high number of tightly bound water molecules, also called the apparent dynamic hydration number (ADHN) compared to the monovalent anions [57]. The ADHN is 1.83 for SO_4^{2-} and 3.95 for HPO_4^{2-} . This can explain the difference observed in the expansion of the C_{16}BC monolayer in the presence of these two anions. The ADHN is zero for Cl^- , Br^- , NO_3^- and ClO_4^- while it is 2.8 for OH^- which has the smallest ionic radius among the monovalent anions investigated [58].

Π_c is not influenced by the presence of the monovalent and divalent anions in the subphase, except for Br^- (Table 2c). The interactions involved at this high compression state are thus not

affected by them. It indicates that the stability of the monolayer at high compression is mainly governed by interactions between the hydrocarbon chains. The lower Π_c value for Br^- can be due to the formation of a structure other than a monolayer.

Significant differences between the C_s^{-1} values are noticed for investigated anions (Inset Fig. 5c). At 30 mN/m, the C_s^{-1} of the monolayer in the presence of different anions can be classified as follows: $\text{HPO}_4^{2-} > \text{NO}_3^- > \text{ClO}_4^- \approx \text{Cl}^- (\text{water}) \approx \text{OH}^- \approx \text{SO}_4^{2-} > \text{Br}^-$. According to the Hofmeister anion series ordered as follows: SO_4^{2-} , HPO_4^{2-} , OH^- , Cl^- , Br^- , NO_3^- , ClO_4^- [59], anions on the left of Cl^- , which represents a borderline case, are water-structure-makers and reduce the solubility of macromolecules by inducing their crystallization while those on the right of Cl^- are water-structure-breakers and increase the solubility of macromolecules. They are respectively called kosmotrope and chaotrope. The result obtained in the present study show that HPO_4^{2-} and NO_3^- have increased the C_{16}BC monolayer C_s^{-1} . ClO_4^- , OH^- and SO_4^{2-} have slightly influenced the monolayer C_s^{-1} while Br^- has decreased it. According to Aroti et al. [50], Br^- and NO_3^- are consider as hydrophilic and kosmotropic ions. This consideration corroborates the result obtained in this work for NO_3^- , which has a stabilizing effect on C_{16}BC monolayer. The result obtained with Br^- ions is not obvious and may be due to dehydration of the C_{16}BC molecules with a decrease of the monolayer stability. ClO_4^- ions are hydrophobic ions and do not compete with hydrophilic Cl^- . The kind of interaction, the ionic radius, the ADHN and the hydrophobicity of the anion may explain the behavior of the C_{16}BC monolayer in the presence of the investigated anions. To further understand the effect of divalent anions on the interfacial behavior of C_{16}BC monolayer, different Na_2SO_4 concentrations are investigated in the following section.

3.4.4. Influence of ionic strength

To investigate the influence of the subphase ionic strength on C_{16}BC monolayer, Π -A isotherms of C_{16}BC for five Na_2SO_4 concentrations (0.5, 1, 2, 5 and 10 mM) is considered (Fig. 5d). As it can be seen, the general trend of the isotherm of C_{16}BC in pure water is retained in the presence of different Na_2SO_4 concentrations. Some differences are observed for the characteristic parameters (Table 2d). An expansion of A_0 and A_c is generally observed as the concentration of Na_2SO_4 increases. Π_c is not greatly affected. According to the C_s^{-1} values between 20 and 35 mN/m, the films are in a LC state which condenses more from 0.5 to 1 mM, decreases from 1 to 5 mM and then increases again at 10 mM (Inset Fig. 5d). The expansion of the monolayer observed can be a result of SO_4^{2-} anions penetrating between the C_{16}BC head groups. The cationic component undergoes a large change in area per head group upon oppositely charged polyion adsorption as the polyelectrolyte concentration in the subphase strongly influences the conformation of an adsorbed layer [60]. A similar behavior has been observed for monolayers of cationic surfactant didodecyltrimethylammonium bromide [61]. Further increase of SO_4^{2-} results in the formation of a less ordered monolayer. It can arise from the repelling of SO_4^{2-} from the air-water interface as they prefer bulk salvation [62]. Another possible mechanism is that the larger space of the C_{16}BC head groups due to SO_4^{2-} hydration [63] reduces C_{16}BC chain-chain interactions which decrease the monolayer C_s^{-1} . The more condensed state observed at 10 mM than at 2 and 5 mM may be due to the screening of the C_{16}BC head group charges after the saturation of the bulk water.

4. Conclusion

Synthesis of the cationic alkylbetainate chlorides (C_nBC , $n = 10$ –16) has been accomplished using more environment-friendly reagents (glycine betaine, thionyl chloride and primary alcohols) than in previous works (chloroacetyl chloride, trimethylamine and primary alcohols). The combination of no basic catalyst, an initial reactant concentration of 0.132 mol/L, a 3:1 betainyl chloride/1-hexadecanol molar ratio, a temperature of 45 °C, the 2-methyl-2-butanol as organic

solvent and a reaction time of 6 h has given the highest yield ($94 \pm 3\%$) of hexadecylbetainate chloride.

The II-A isotherms of spread cationic alkylbetainate chloride (C_nBC) monolayers on the water subphase at 20°C have shown that the $C_{10}BC$ and $C_{12}BC$ are not able to form insoluble monolayers because of the weak hydrophobicity of their alkyl chains. The $C_{14}BC$ and $C_{16}BC$ monolayers have shown the characteristics of insoluble monolayers. However, at high compression, an irreversible rearrangement or interaction of the molecules within the $C_{16}BC$ monolayer has occurred preventing its complete relaxation. This result is in correlation with that obtained by Itoh et al. [25] for the foaming powers of the alkylbetainate chlorides (C_nBC) in aqueous solutions. $C_{10}BC$ and $C_{12}BC$ have almost no foaming powers while $C_{14}BC$ and $C_{16}BC$ are interesting foaming agents with the latter being the most efficient.

The influence of different factors (pH, temperature, sodium salts concentration of monovalent and divalent anions belonging to the Hofmeister series and Na_2SO_4 ionic strength) on the $C_{16}BC$ monolayer interfacial properties has been studied. The interfacial organization of the $C_{16}BC$ monolayer is not greatly influenced by the pH and the monovalent anions but is influenced by the temperature, the divalent anions and the ionic strength mainly in term of interfacial area occupation. The whole results suggest that the C_nBC molecules interact mainly via the van der Waals forces at the air–water interface and that the polar heads are deeply immersed into the water subphase. This accounts for the poor influence of the experimental conditions on the molecule organization at the air–water interface. These surface-active agents issued from the green chemistry can be thus useful for the formulation of products with a wide range of applications. Similarly to the conventional quaternary ammonium surfactants, they could be used in the cosmetic industry as hair conditioner or in the pharmaceutical field as DNA delivery agent for example. Additional works are, however, required to better define the fields of application for these alkylbetainate surfactants.

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