Organoboron in organized molecular systems. I. Synthesis and surfactant properties of aminoalkylboronic acid salts

Jean-Brice Le Toumelin and Michel Baboulène*

Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique (CNRS UMR 5623), Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cédex, France. FAX: +33 5 61 25 17 33; E-mail: mbab@ramses.ups-tlse.fr.

Received (in Montpellier, France) 15th September 1998, Accepted 27th October 1998

To date there has been little use of organoboron compounds for construction of organized molecular systems. We describe here the synthesis and surface active properties of novel aminoorganoboron surfactants, which exploit certain physicochemical characteristics of the boron atom. Routes to the boranylalkylamines with a strong boron-nitrogen intramolecular complexation are described. They can account for the different strengths of intra- and intermolecular boron-nitrogen complexation in the molecules produced by hydroboration of long-chain unsaturated amines. Methanolysis followed by acid hydrolysis produced the salts of aminoalkylboronic acids in excellent yield. Study of the surface properties of these boron derivatives indicate that they would be good surfactants. The influence of the alkylboronic acid chain is discussed. This new family of surfactants opens perspectives in chemical synthesis and applications as surface active agents.

Le bore dans les systèmes moléculaires organisés. I. Synthèse et propriétés tensioactives de sels d'acides aminoalkylboroniques. Le développement de la chimie du bore n'a pas, à notre connaissance, suscité de recherches dans le vaste champ des systèmes moléculaires organisés. Ce travail se propose d'inclure les caractéristiques physico-chimiques du bore dans l'étude des synthèses et des propriétés de surface de nouveaux tensioactifs dérivés de composés aminoorganoborés. Dans ce but, les méthodes d'accès aux intermédiaires boranylalkylamines, présentant une forte complexation intra- et intermoléculaire bore-azote, sont décrites. Elles permettent d'expliquer les différentes forces de complexation intramoléculaire bore-azote présentent dans les molécules issues de l'hydroboration d'amines insaturées à longue chaîne. Une méthanolyse suivie d'hydrolyse acide donne accès, avec d'excellents rendements, aux sels d'acides aminoalkylboroniques. L'étude des propriétés de surface de tous ces composés borés les classent comme de bons tensioactifs. Le rôle de la chaîne acide alkylboronique est discuté. Ces nouvelles familles de tensioactifs ouvrent dès lors un vaste champ d'investigation.

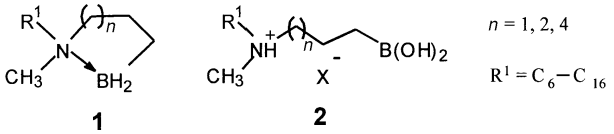
Amphiphilic molecules comprising a polar head linked to a hydrophobic tail are finding increasing applications as detergents and in cosmetic formulations.[1] A large number of studies have been devoted to the preparation and fundamental properties of these molecules, which are encountered in nearly all areas of scientific endeavour. Their structure lends itself to the generation of families of compounds with specific properties, which can now be produced by modular synthesis.[2] The quaternization of nitrogen and the ionic character of the carboxylic and sulfonic groups are essential components of the well-known families of cationic, anionic and zwitterionic surfactants,[3] but there has been little investigation to date of amphiphiles based on boron. However, organoboron compounds are now finding increasing applications as fuel additives and agrochemicals, as well as in cosmetic and biomedical formulations. The analogy of boronic acids with carboxylic acids has indicated a pharmacological application of aminoboronic acids and their peptide derivatives.[4] Boronic acids and their derivatives have been used as carriers in the transport of saccharide through membranes.[5] The lipophilic trioctylmethylammonium cation often accompanies the boronate ions.[6] More, Shinkai and coworkers[7] are investigating the recognition of saccharides by covalent bond formation with boronic acids. This concept suggests that saccharides may be useful as a trigger to change the aggregate morphology. This group has also studied[8] the aggregation properties of a boronic acid appended amphiphile with a chromophoric azobenzene moiety. The multiple valencies and electronegativity of boron along with its "hard atom" character confer specific properties to surfactant molecules, which can be exploited for structuration of the corresponding micellar media.

Encouraged by our preliminary results on the synthesis and surfactant properties of the (*N*-alkyl-*N*-methyl)-3-aminopropylboranes,[9] we present here a study of the synthesis and surfactant properties of a novel series of aminoalkylboronic acids **2** and their boranylalkylamines **1**.

Results and discussion

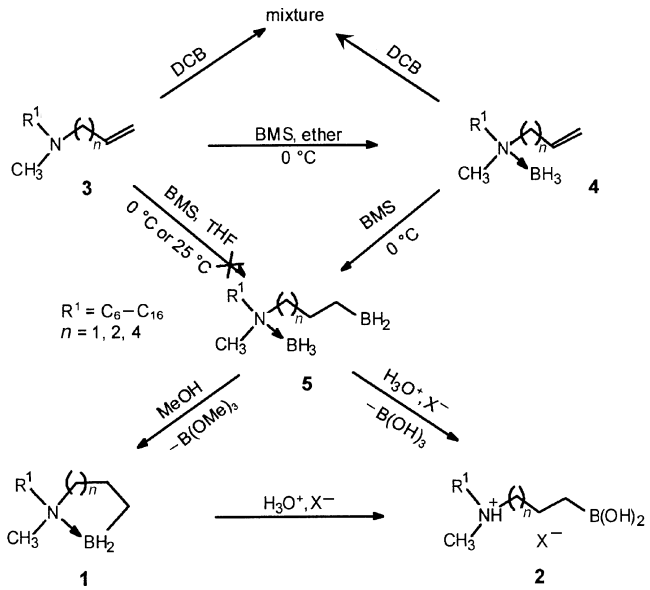
Synthesis

Numerous syntheses of alkyl- and arylboronic acids have been described.[10] The classical routes from corresponding halides *via* Grignard reagent[11] or lithiation,[12] followed by reaction with $B(OR)_3$, were the most useful. The approach using α-haloboronic esters[13] has favoured the synthesis of α-aminoboronic esters, biological compounds. But the hydroboration reaction, from diborane derivatives or dialkoxyboron hydrides, can lead to boronic esters.



Based on our previous results,[9,14] we initially prepared compounds **1** and **2** by hydroboration of the unsaturated amines **3** according to Scheme 1. Addition of an equivalent of borane-methyl sulfide complex (BMS) to **3** at 0 °C led to excellent yields of the corresponding amine-boranes **4** (Table 1), in line with other reports in the literature.[14a] The IR spectra indicated the presence of vibration bands of the HC=CH bond at 3080 and 1645 cm^{-1} and the appearance of intense long bands between 2380 and 2480 cm^{-1} characteristic of the BH_2 moiety. The ^1H, ^{13}C and ^{11}B NMR spectra confirmed the structures proposed for these compounds.[15] The addition of a second equivalent of BMS led to complete hydroboration (disappearance of the double bond). Two boron signals were observed, consistent with the structure of compounds **5** (Table 1).

It should be noted that all attempts at hydroboration of compounds **4** with dialkylboranes gave rise to unworkable mixtures. Direct hydroboration of compounds **3** with two equivalents of BMS was also not favourable to production of the diboron derivative **5**. Compounds **5**, which are reactive and unstable in the absence of solvent, underwent attack by methanol exclusively at the amine–boron linkage (Table 2 and Scheme 1). The novel structure of the intramolecular amine-borane complex **1** was quite stable even in aqueous solutions.



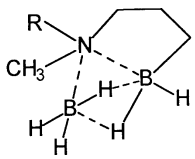
Scheme 1 Synthetic route to compounds **1** and **2**.

These reactivities can be interpreted in terms of the interactions between boron and nitrogen. In common with boron hydride, the amine-borane complex is quite reactive (*e.g.*, hydroboration), although it is less reactive than a dialkylborane.[16] The diboronated compounds **5** appear to be an exception as their transformation by methanolysis into the intramolecular amine-borane complexes can be explained by the similarity of the two boronated heads with respect to the nitrogen, as illustrated in Scheme 2. The intermolecular boron-nitrogen interaction becomes more accessible to attack by methanol. After the loss of methyl borate, the intramolecular boron-nitrogen interaction confers enhanced stability on the molecule. A similar case has recently been described for methanolysis of the disilylaminopropylboranes.[17]

By acid hydrolysis (40 °C for 3 h), compounds **1** led to the corresponding boronic acids **2** in quantitative yield (Table 3). The IR and NMR spectra were compatible with the structure of the amine salts, which could be employed as cationic surfactants. It should be noted that direct hydrolysis of compounds **5** (see Scheme 1) is possible, but the boric acid formed is not readily removed, which tends to be in favour of the methanolysis–hydrolysis route (see Scheme 1).

Surface properties

The surface active properties [18] of compounds **2** are illustrated in Fig. 1 and by the results listed in Table 4. Compound **2b**, which is soluble in aqueous medium, exhibited no breakpoint in the plot of surface tension against concentration,



Scheme 2 Boron-nitrogen interactions in compounds **5**.

Table 1 Yields and NMR data for compounds **4** and **5**

				NMR (ppm)					
				Compounds **4**			Compounds **5**[a]		
	R^1	*n*	Yield (%)	^{11}B	$^1H_{(NCH_3)}$	$^{13}C_{(NCH_3)}$	^{11}B	$^1H_{(NCH_3)}$	$^{13}C_{(NCH_3)}$
a	CH_3	1	98	−9.0	2.47	50.7	−10/+3.4	2.50	50.6
b	C_6H_{13}	1	91	−10.5	2.47	48.9	−11/−5.0	2.48	49.3
c	$C_{12}H_{25}$	1	96	−10.5	2.47	49.6	−10.5/−2.5	2.53	49.2
d	$C_{12}H_{25}$	2	100	−11.0	2.51	49.0	−11/−1.0	2.48	48.3
e	$C_{12}H_{25}$	4	100	−10.8	2.48	49.3	−11/+1.4	2.50	49.2
f	$C_{16}H_{33}$	1	100	−10.5	2.50	49	−10.7/+1.4	2.49	49.3

[a] Hydroboration was total and regioselective.

Table 2 Yields and NMR data of compounds **1**

				NMR (ppm)		
	R^1	*n*	Yield (%)	^{11}B	$^1H_{(NCH_3)}$	$^{13}C_{(NCH_3)}$
a	CH_3	1	90	−10.0	2.54	51.3
b	C_6H_{13}	1	75	−11.1	2.48	49.5
c	$C_{12}H_{25}$	1	92	−10.7	2.50	49.3
d	$C_{12}H_{25}$	2	80	−11.0	2.50	49.3
e	$C_{12}H_{25}$	4	95	−10.9	2.48	49.2
f	$C_{16}H_{33}$	1	90	−11.0	2.50	49.5

Table 3 Yields and NMR data of compounds **2**

					NMR (ppm)		
	R^1	n	X^-	Yield[a] (%)	^{11}B	$^{1}H_{(NCH_3)}$	$^{13}C_{(NCH_3)}$
a	CH_3	1	Br	70	19.0	2.82	50.0
b	C_6H_{13}	1	Br	70	20.0	2.75	41.0
c	$C_{12}H_{25}$	1	Br	65	20.0	2.80	40.1
c′	$C_{12}H_{25}$	1	Cl	62	18.9	2.80	40.1
d	$C_{12}H_{25}$	2	Br	77	19.9	2.83	42.5
e	$C_{12}H_{25}$	4	Br	56	20.0	2.78	43.0
f	$C_{16}H_{33}$	1	Br	60	20.1	2.85	40.8

[a] Yield calculated from the corresponding compound **3**.

which would tend to rule out the possibility of micellization. The propylboronic acid chain thus did not appear to lengthen effectively the hexyl chain on the nitrogen atom of this compound. We found that a minimum chain length of eight carbon atoms was required for micellization behaviour.

On the other hand, all the other compounds **2** ($R' > 6$) synthesized gave rise to micellization (see Fig. 1), as they all led to a marked reduction in surface tension (γ) at the water–air interface ($27 < \gamma < 30$ mN m^{-1}). The cationic structure (amine salts) enabled comparison with their commercial analogs, dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB), and showed that the alkylboronic moiety enhanced certain surface parameters, especially the critical micellar concentration (CMC). In general, compounds **2** had a considerably lower CMC than that of the reference cationic surfactants [19] (*e.g.*, 2.51 mmol l^{-1} for **2c** *vs.* 14 mmol l^{-1} for DTAB). The area of the polar heads of these compounds is generally larger than that of the reference cationic surfactants, which would give rise to stronger repulsions between the polar heads and would therefore be expected to be less favourable for micellization. Our results are consistent with a participation of the alkylboronic moiety in the structure of the micelles due to: (*i*) its hydrophilic character (boronic acid function) in the neighbourhood of the polar heads and (*ii*) the additional hydrophobic character (alkyl chain) at the water–air interface. This can also explain why the Mukerjee and Mysels relationship[20] does not apply to these compounds (*e.g.*, for **2c** $\log CMC_{found} = -2.6$ *vs.* $\log CMC_{calculated} = -3.12$). It can also account for the lack of linearity in the relationship between CMC and length of the alkyboronic chain. The CMC of compound **2e** ($n = 4$) was lower than that of compound **2c** ($n = 1$), but higher than that of compound **2d** ($n = 2$).

From these results, we propose an explanation in terms of the hydrophobic nature of the hydrocarbon chain, the hydrophilicity of the boronic moiety and the flexibility of the alkylboronic acid linkage (Fig. 2). Compound **2c** with the short propyl chain has mostly hydrophobic chain–chain interactions confining the boronic acid group within the micelle core and preventing it from interacting with the polar heads of micellized molecules [Fig. 3(*a*)]. However, in compound **2d**, the butyl chain was thought to confer sufficient flexibility for an interaction between the boronic group and the Stern layer [Fig. 3(*b*)], thereby favouring micellization and leading to a lowering of the CMC, which was observed experimentally. Above a linkage of four carbons, the hydrophobic chain–chain interactions pull the hydrophilic moiety away from the polar heads, which would account for the intermediate value of CMC observed for compound **2e**. It has been found that the CMC of molecules with long hydrophobic chains ($>C_{16}$) do

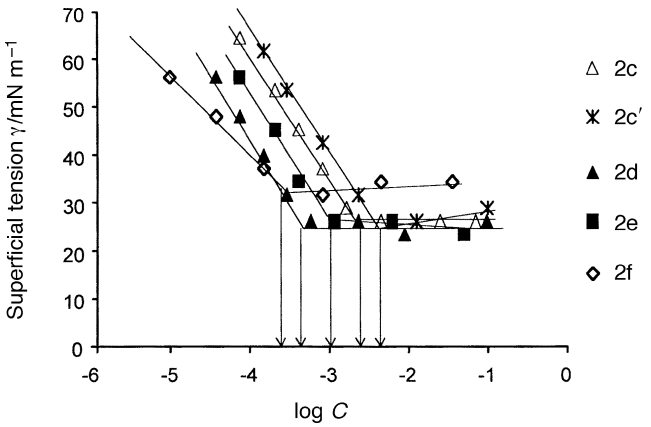


Fig. 1 Plots of surface tension (obtained by tensiometry) against log [surfactant mol l^{-1}] at 25 °C in water.

Table 4 Surface parameter of compounds **2**, DTAB and CTAB in water at 25 °C[a]

	CMC/ mmol l^{-1}	γ^b_{min}/ mN m^{-1}	$\Gamma^b/10^{-6}\times$ mol m^{-2}	A^b/ Å^2
c	2.51	27.0	2.09	79.2
c′	4.36	30.0	2.16	77.6
d	0.60	27.0	2.32	71.6
e	1.20	27.2	2.11	78.5
f	0.26	28.6	1.51	109.4
DTAB	14	—	2.64	63.0
CTAB	0.92	—	2.68	62.0

[a] Calculated from Gibb's equation.[23]
[b] γ: superficial tension, Γ: superficial excess, A: area of the polar head.

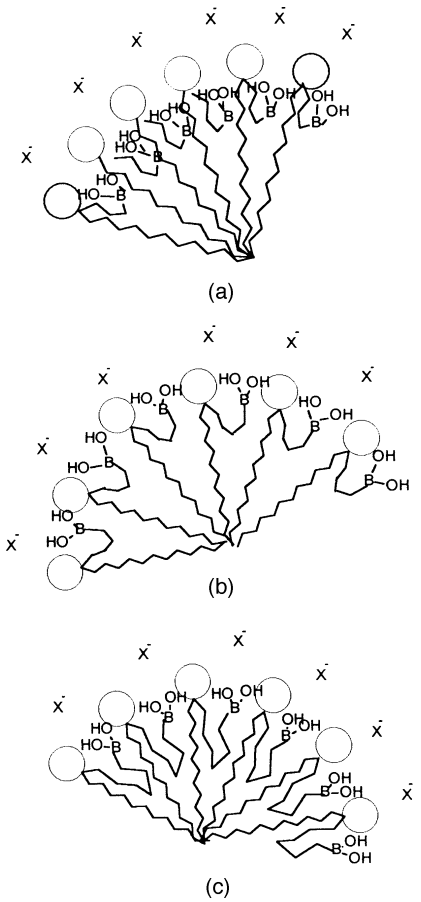


Fig. 2 Schematic representation of micellization of compounds **2c** (a), **2d** (b), **2e** (c).

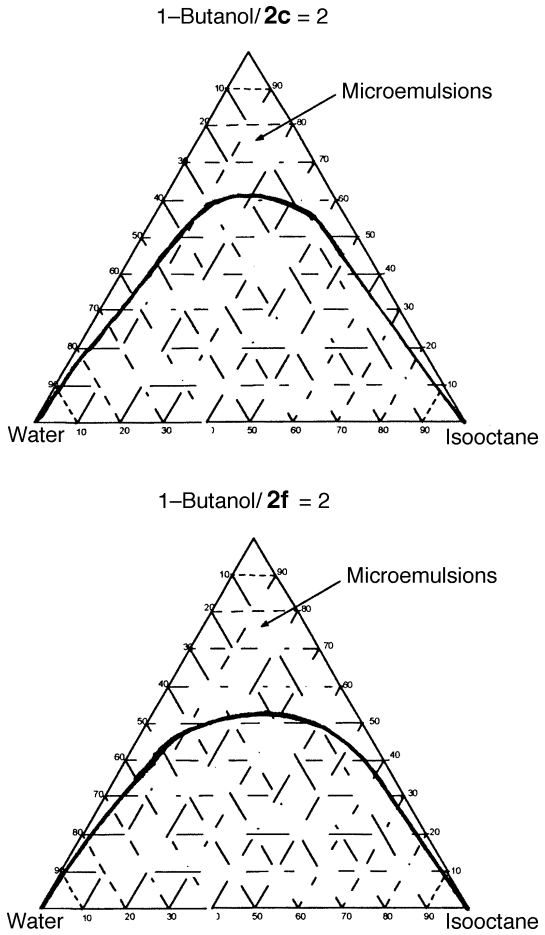


Fig. 3 Pseudo-ternary phase diagrams of the water–1-butanol–**2c**–isooctane and water–1-butanol–**2f**–isooctane systems at 20 °C (proportions by weight).

not always obey the Mukerjee and Mysels relationship, which is attributed to bending of the chains. It has also been shown that the influence on CMC of a polar group (*e.g.* alcohol) in a hydrophobic chain of a cationic surfactant depends on its position with respect to the amino group.[21]

The values of CMC of the boron derivatives are consistent with the rules governing the association of ions.[22] The CMC of compound **2c** (2.51 mmol l^{-1}) was less than that of compound **2c′** (4.36 mmol l^{-1}). For identical alkylboronic chains, the additional hydrophobicity with increasing carbon chain length was found to apply (see CMC of compounds **2c** and **2f**).

The existence of microemulsions was demonstrated by analysis of the phase diagrams in the water–butanol–isooctane system (Fig. 3). These diagrams show the boundaries of the direct and inverse micelles, and indicate the possibility of formation of lamellar structured media.

Conclusions

The chemical specificity of the boron atom was exploited for two main objectives. (*i*) Synthesis of aminoalkylboronic acids by hydroboration of long-chain unsaturated amines. This was made possible by exploiting the inter- and intramolecular interactions between the boron and nitrogen atoms. Preferential methanolysis of an intermolecular boron–nitrogen linkage gave rise to boranylalkylamine intermediates with a strong intramolecular boron-nitrogen interaction. (*ii*) Development of novel organoboron surfactants. They were found to have excellent surface active properties with a demonstrable influence of the alkylboronic acid group. These boron derivatives thus show promise for the constitution of novel structured organized media. Their structural characteristics combined with their surface active properties open new perspectives of enquiry and application.

Experimental

General

Reagents were of commercial quality and were used without purification. IR spectra (ν, cm^{-1}) were recorded on a Perkin-Elmer 683 spectrophotometer. ^{1}H, ^{13}C and ^{11}B NMR spectra (δ; J, Hz) were obtained on Bruker AC 80 or Bruker AC 200 instruments.

The surface active properties were calculated using Gibbs's equation[23] with the data obtained from measurements carried out on a Prolabo n°3 tensimat and a Dynamic Film Control KSV 2200 apparatus using Langmuir's balance procedures.

The ethylenic amines **3** were obtained according to Tweedie and Allabashi's method.[24] Only the amine **3c** was prepared from Cromwell and Hassner's method.[25]

The unsatisfactory elemental analysis ($\leqslant$1% error in carbon) found for compounds **2b–f** can have an explanation in the incomplete combustion often observed with boronic acids. But, the regular plotting of the curves at the time of determination of the surface parameters of compounds **2b–f** (see Fig. 1) is in favour of a good purity.

Typical procedure for the synthesis of compounds 4

To a solution of ethylenic amine **3** (0.025 mol) in 20 ml of anhydrous ether was added BMS solution (0.03 mol) at 0 °C and under inert atmosphere. The mixture was stirred for 1 h. An excess of MeOH was added. The mixture was left to warm to room temperature and was stirred for 30 min. After removing the solvent *in vacuo*, the residual oil was purified by trituration with anhydrous petroleum ether and evaporated *in vacuo*.

***N*,*N*-Dimethyl allylamine-borane, 4a.** Yield: 98%. Colourless oil. IR (neat): ν 3080 (=CH), 2970–2860 (CH), 2378 (BH), 1650 (C=C); ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.47 (s, 6H, CH_3), 3.30 (d, J = 7.2, 2H, CH_2N), 5.30 (m, 2H, $=CH_2$), 6.0 (m, 1H, =CH); ^{13}C NMR (200 MHz, $CDCl_3$): δ 50.7 (CH_3N), 67.0 (CH_2N), 123.3 ($=CH_2$), 129.5 (=CH); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 9.0 (q, J = 90 Hz)

***N*-Hexyl-*N*-methyl allylamine-borane, 4b.** Yield: 91%. Colourless oil. IR (neat): ν 3080 (=CH), 2960–2860 (CH), 2360 (BH), 1640 (C=C); ^{1}H NMR (80 MHz, $CDCl_3$): δ 0.86 (t, J = 6, 3H, CH_3—C_5), 1.25 (m, 6H, $(CH_2)_3$), 1.70 (m, 2H, NC—CH_2—C_4), 2.47 (s, 3H, CH_3N), 2.70 (t, J = 6, 2H, NCH_2—C_5), 3.35 (d, J = 7, 2H, NCH_2—C—C=), 5.25 (m, 2H, $=CH_2$), 6,05 (m, 1H, =CH); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 (CH_3—C_5), 22.6–31.5 ($(CH_2)_4$), 48.9 (CH_3N), 61.5 (NCH_2—C_5), 64.3 (NCH_2—C—C=), 122.3 ($=CH_2$), 130 (=CH); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 10.5.

***N*-Dodecyl-*N*-methyl allylamine-borane, 4c.** Yield: 96%. Colourless oil. IR (neat): ν 3080 (=CH), 2950–2850 (CH), 2400–2280 (BH), 1640 (C=C); ^{1}H NMR (80 MHz, $CDCl_3$): δ 0.86 (t, J = 6, 3H, CH_3—C_{11}), 1.25 (m, 20H, $(CH_2)_{10}$), 2.47 (s, 3H, CH_3N), 2.65 (m, 2H, NCH_2—C_{11}), 3.33 (d, J = 7, 2H, NCH_2—C—C=), 5.3 (m, 2H, $=CH_2$), 6.02 (m, 1H, =CH); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 (CH_3—C_{11}), 22.6–31.7

($(CH_2)_{10}$), 49.6 (CH_3N), 61.4 ($NCH_2—C_{11}$), 64.1 ($NCH_2—C—C=$), 122.3 ($=CH_2$), 129.8 (=CH); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 10.5.

***N*-(1-Butenyl)-*N*-dodecyl-*N*-methylamine-borane, 4d** Yield: quantitative. Colourless oil. IR (neat): ν 3080 (=CH), 2960–2860 (CH), 2360 (BH), 1640 (C=C); ^1H NMR (80 MHz, $CDCl_3$): δ 0.88 (t, $J = 6$, 3H, $CH_3—C_{11}$), 1.26 (m, 18H, $(CH_2)_9$), 1.70 (m, 2H, $NCH_2—C_{11}$), 2.51 (s, 3H, CH_3N), 2.70 (m, 6H, $(CH_2)_3$), 5.05 (m, 2H, $=CH_2$), 5.70 (m, 1H, =CH); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 ($CH_3—C_{11}$), 22.7–29.7 ($(CH_2)_{10}$), 32.0 ($NCH_2—C—C=$), 49.0 (NCH_3), 60.3 ($NCH_2—C_{11}$), 61.6 (NCH_2), 117.2 ($=CH_2$), 134.3 (=CH); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 11.0.

***N*-Dodecyl-*N*-(1-hexenyl)-*N*-methylamine-borane, 4e.** Yield: quantitative. IR (neat): ν 3080 (=CH), 2950–2850 (CH), 2370 (BH), 1640 (C=C), 1465 (CH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.90 (t, $J = 6$, 3H, $CH_3—C_{11}$), 1.25 (m, 20H, $(CH_2)_{10}$), 1.55 (m, 4H, $NC—(CH_2)_2—C—C=$), 2.05 (q, $J = 6$, 2H, $CH_2—C—C=$), 2.48 (s, 3H, CH_3N), 2.71 (m, 4H, CH_2N), 4.90 (m, 2H, $=CH_2$), 5.75 (m, 1H, =CH); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 ($CH_3—C_{11}$), 22.7–33.3 ($(CH_2)_{13}$), 49.3 (CH_3N), 61.1 ($NCH_2—C_{11}$), 61.4 (NCH_2), 115.1 ($=CH_2$), 138.1 (=CH); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ—10.8.

***N*-Hexadecyl-*N*-methyl allylamine-borane, 4f**. Yield: quantitative. Colourless gel. IR (neat): ν 3080 (=CH), 2960 − 2860 (CH), 2480–2280 (BH), 1640 (C=C); ^1H NMR (80 MHz, $CDCl_3$): δ 0.84 (t, $J = 6$, 3H, $CH_3—C_{15}$), 1.23 (m, 28H, $(CH_2)_{14}$), 1.7 (m, 2H, $CH_2—CN$), 2.50 (s, 3H, CH_3N), 2.70 (m, 2H, $NCH_2—C_{15}$), 3.28 (d, $J = 7$, 2H, $NCH_2—C—C=$), 5.30 (m, 2H, $=CH_2$), 6.0 (m, 1H, =CH); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.0 ($CH_3—C_{15}$), 22.3–32 ($(CH_2)_{14}$), 49.0 (NCH_3), 61.3 ($NCH_2—C_{15}$), 64.0 ($NCH_2—C—C=$), 122.4 ($=CH_2$), 129 (=CH); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 10.5.

Typical procedure for the synthesis of compounds 1

To a solution of amine-borane **4** (0.025 mol) in 50 ml of anhydrous THF was added BMS solution (0.03 mol) at room temperature for 90 min. The mixture was concentrated *in vacuo*. After cooling at 10 °C, 20 ml of methyl alcohol were slowly added. The mixture was stirred for 1 h at room temperature. Them, the solvent was evaporated *in vacuo*. The residual oil was triturated from petroleum ether. Compounds **1** were obtained by evaporation *in vacuo*.

***N*,*N*-Dimethyl-1,2-azaborolidine, 1a.** Yield: 90%. Colourless oil. IR (neat): ν 2960 (CH), 2360–2280 (BH), 1475 (CH), 1170 (BH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.88 (m, 2H, CH_2B), 1.78 (m, 2H, $CH_2—CN$), 2.54 (s, 6H, CH_3), 2.78 (t, $J = 5$, 2H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 18.5 (CH_2B), 51.3 (CH_3N), 66.7 (CH_2N), 65.0 (CH_2CN); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ −10.0.

***N*-Hexyl-*N*-methyl-1,2-azaborolidine, 1b**. Yield: 75%. IR (neat): ν 2950–2850 (CH), 2480–2280 (BH), 1475 (CH), 1180 (BH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.88 (m, 5H, $CH_3—C_5$, CH_2B), 1.28 (m, 6H, $CH_3—C_5$), 1.66 (m, 4H, $C_4—CH_2—C—N—C—CH_2$), 2.48 (s, 3H, CH_3N), 2.71 (m, 4H, CH_2CN); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.0 ($CH_3—C_5$), 22.4–31.5 ($(CH_2)_4$, CH_2B, $CH_2—CN$), 49.5 (CH_3N), 60.1 (CH_2N), 63.5 (CH_2N); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 11.1.

***N*-Dodecyl-*N*-methyl-1,2-azaborolidine, 1c.** Yield: 92%. Colourless gel. IR (neat): ν 2950–2850 (CH), 2380–2280 (BH), 1470 (CH), 1175 (BH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.81 (m, 5H, $CH_3—C_{11}$, CH_2B), 1.20 (s, 18H, $(CH_2)_9$), 1.6 (m, 4H, $CH_2—CN$), 2.50 (s, 3H, CH_3N), 2.67 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 ($CH_3—C_{11}$), 22.7–31.9 ($(CH_2)_{10}$, CH_2B), 49.3 (CH_3N), 61.5 ($C_{11}—CH_2N$), 62.7 (CH_2N); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 10.7.

***N*-Dodecyl-*N*-methyl-1,2-azaborocyclohexane, 1d.** Yield: 80%. Colourless oil. IR (neat): ν 2940–2850 (CH), 2380–2280 (BH), 1475 (CH), 1170 (BH); ^1H NMR (80 MHz, $CDCl_3$): δ 0,87 (t, $J = 6$, 3H, $CH_3—C_{11}$), 1.0 (m, 2H, CH_2B), 1.26 (m, 18H, $(CH_2)_9$), 1.57 (m, 4H, $CH_2—CN$), 2.50 (s, 3H, CH_3N), 2.70 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14,1 ($CH_3—C_{11}$), 22.7–31.9 ($(CH_2)_{12}$), 49.3 (CH_3N), 61.15 (CH_2N), 61.4 (CH_2N); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 11.0.

***N*-Dodecyl-*N*-methyl-1,2-azaborocyclooctane, 1e.** Yield: 95%. Colourless oil. IR (neat): ν 2960 (CH), 2940–2850 (CH_2, CH), 2380–2280 (BH), 1470 (CH_2), 1170 (BH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.86 (m, 5H, $CH_3—C_{11}$, CH_2B), 1.25 (m, 24H, $(CH_2)_9$, $(CH_2)_3$), 1.63 (m, 4H, $CH_2—CN$), 2.48 (s, 3H, CH_3N), 2.68 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 (CH_3C_{11}), 22.5–32.2 ($(CH_2)_{15}$), 49.2 (CH_3N), 62.35 (CH_2N); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 10.9.

***N*-Hexadecyl-*N*-methyl-1,2-azaborolidine, 1f.** Yield: 90%. White powder. IR (KBr): ν 2950–2850 (CH), 2380–2280 (BH), 1475 (CH), 1170 (BH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.87 (m, 5H, $CH_3—C_{15}$, CH_2B), 1.26 (m, 26H, $(CH_2)_{13}$), 1.74 (m, 4H, $CH_2—CN$), 2.50 (s, 3H, CH_3N), 2.70 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.13 ($CH_3—C_{15}$), 22.7–31.9 ($(CH_2)_{14}$, CH_2B), 49.5 (CH_3N), 55.9 ($C_{15}—CH_2N$), 61.4 (CH_2N); ^{11}B NMR (200 MHz, $CDCl_3$–BF_3, Et_2O): δ − 11.0.

Typical procedure for the synthesis of compounds 2

To a solution of compound **1** (0.025 mol) in 10 ml of THF was added slowly 20 ml of HCl (2 N) or HBr (2 N) at 10 °C. The mixture was left to warm to room temperature and was stirred for 3 h. Sometimes, it is necessary to heat (40 °C) the mixture. The solvent was evaporated *in vacuo*. An azeotropic distillation with toluene give the crude boronic acids. By recrystallization from ether–acetone (9 : 1), pure compound **2** obtained as solids that decompose during the melting point determination.

***N*,*N*-Dimethyl-*N*-(propyl-3-boronic acid)ammonium bromide, 2a.** Yield: 70%. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 1.05 (m, 2H, CH_2B), 1.72 (m, 2H, CH_2CN), 2.82 (s, 6H, CH_3N), 3.10 (m, 2H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 17.3 ($CH_2—C$), 19.8 (CH_2B), 50.0 (CH_3N), 64.5 (CH_2N); ^{11}B NMR (200 MHz, D_2O–BF_3, Et_2O): δ + 19.0; Anal. calc. (%) for $C_5H_{15}BBrNO_2$ (211.86), C: 28.34; H: 7.14; N: 6.61; found, C: 27.83; H: 7.40; N: 6.92.

***N*-Hexyl-*N*-methyl-*N*-(propyl-3-boronic acid)ammonium bromide, 2b.** Yield: 70%. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.84 (t, $J = 6$, 3H, $CH_3—C_5$), 0.96 (m, 2H, CH_2B), 1.26 (m, 6H, $(CH_2)_3$), 1.81 (m, 4H, $CH_2—CN$), 2.75 (s, 3H, CH_3N), 2.95 (m, 4H, CH_2N); ^{13}C NMR (200

MHz, $CDCl_3$): δ 13.9 (CH_3—C_5), 22.3–31.1 (CH_2B, $(CH_2)_5$), 41.0 (CH_3N), 49.6 (C_5—CH_2N), 56 (CH_2N); ^{11}B NMR (200 MHz, D_2O–BF_3, Et_2O): δ + 20.0. Anal. calc. (%) for $C_{10}H_{25}BBrNO_2$ (282.03), C: 42.59; H: 8.93; N: 4.93; found, C: 41.48; H: 9.28; N: 4.71.

***N*-Dodecyl-*N*-methyl-*N*-(propyl-3-boronic acid)ammonium bromide, 2c.** Yield: 65%. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.82 (t, $J = 6$, 3H, CH_3—C_{11}), 0.94 (m, 2H, CH_2B), 1.20 (m, 18H, $((CH_2)_9)$, 1.79 (m, 4H, CH_2—CN), 2.80 (s, 3H, CH_3N), 2.95 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 (CH_3—C_{11}); 21.5–31.9 ($(CH_2)_{11}$, CH_2B), 40.1 (CH_3N), 56 (C_{11}—CH_2N), 58.5 (CH_2N); ^{11}B NMR (200 MHz, D_2O–BF_3, Et_2O): δ +20.0. Anal. calc. (%) for $C_{16}H_{37}BBrNO_2$ (366.19), C: 52.48; H: 10.18; N: 3.82; O: 8.74; found, C: 51.53; H: 10.34; N: 3.74; O: 8.86.

***N*-Dodecyl-*N*-methyl-*N*-(propyl-3-boronic acid)ammonium chloride, 2c′.** Yield: 62%. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.82 (t, $J = 6$, 3H, CH_3—C_{11}), 0.96 (m, 2H, CH_2B), 1.20 (m, 18H, $(CH_2)_9$), 1.79 (m, 4H, CH_2—CN), 2.80 (s, 3H, CH_3N), 2.95 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.1 (CH_3—C_{11}), 21.5–31.9 ($(CH_2)_{11}$, CH_2B), 40.1 (CH_3N), 56.0 (C_{11}—CH_2N), 58.5 (CH_2N); ^{11}B NMR (200 MHz, D_2O—BF_3, Et_2O): δ + 18.9. Anal. calc. (%) for $C_{16}H_{37}BClNO_2$ (321.74), C: 59.73; H: 11.59; N: 4.35; found, C: 58.70; H: 12.05; N: 4.21.

***N*-Dodecyl-*N*-methyl-*N*-(butyl-4-boronic acid)ammonium bromide, 2d.** Yield: 77%. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.82 (t, $J = 6$, 3H), 0.92 (m, 2H, CH_2B), 1.20 (m, 20H, $(CH_2)_{10}$), 1.81 (m, 4H, CH_2—CN), 2.83 (s, 3H, CH_3N), 2.92 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 16.0 (CH_3—C), 22.2–34.71 ($(CH_2)_{13}$), 42.5 (CH_3N), 58.3 (C_{11}—CH_2N), 63.34 (CH_2N); ^{11}B NMR (200 MHz, D_2O–BF_3, Et_2O): δ + 19.9. Anal. calc. (%) for $C_{17}H_{39}BBrNO_2$ (380.22), C: 53.70; H: 10.34; N: 3.68; found, C: 52.87; H: 10.48; N: 3.64.

***N*-Dodecyl-*N*-methyl-*N*-(hexyl-6-boronic acid)ammonium bromide, 2e.** Yield: 56%. White powder. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.87 (t, $J = 6$, 3H, CH_3—C_{11}), 1.22 (m, 26H, $(CH_2)_{12}$, CH_2B), 1.85 (m, 4H, CH_2—CN), 2.78 (s, 3H, CH_3N), 3.01 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 16.5 (CH_3—C_{11}), 25.0–34.7 ($(CH_2)_{15}$), 43.0 (CH_3N), 58.2 (CH_2N); ^{11}B NMR (200 MHz, D_2O–BF_3, Et_2O): δ + 20.0. Anal. calc. (%) for $C_{19}H_{43}NBBrNO_2$ (408.28), C: 55.90; H: 10.62; N: 3.43; found, C 56.90; H: 10.75; N: 3.39.

***N*-Hexadecyl-*N*-methyl-*N*-(propyl-3-boronic acid)ammonium bromide, 2f.** Yield: 60%. White powder. IR (KBr): ν 3400 (BOH); ^1H NMR (80 MHz, $CDCl_3$): δ 0.87 (t, $J = 6$, 3H, CH_3—C_{15}), 1.24 (m, 28H, $(CH_2)_{13}$, CH_2B), 1.83 (m, 4H, CH_2—CN), 2.85 (m, 3H, CH_3N), 3.05 (m, 4H, CH_2N); ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.5 (CH_3—C_{15}), 19.8 (CH_2B), 23.7–33.1 ($(CH_2)_{15}$), 40.8 (CH_3N), 57.5 (CH_2N), 61.4 (CH_2N); ^{11}B NMR (200 MHz, D_2O–BF_3, Et_2O): δ + 20.1. Anal. calc. (%) for $C_{20}H_{45}BBrNO_2$ (422.30), C: 56.88; H: 10.74; N: 3.32; found, C: 57.4; H: 10.86; N: 3.4.

Acknowledgements

We thank Professor R. Nagarajan (Dept. of Chemical Engineering, Pennsylvania State University) for helpful discussions on to the interpretation of the surface properties.

Notes and references

1 *4th World Surfactants Congress: Proceedings*, C.E.D., Barcelona, Spain, 1996.
2 Images de la Recherche, *De la Matière au Vivant: les Systèmes Moléculaires Organisés*, CNRS, Paris, France, 1994.
3 (*a*) R. Zana., *Heterogen. Chem. Rev.*, 1994, **1**, 145; (*b*) B. Lindman. and H. Wennerström., in *Solution Behavior of Surfactants*, ed. K. L. Mittal and R. Fender, Plenum Press, New York, 1982, vol. 1.
4 *Interbiotech Review*, Boron Biologicals Inc., Raleigh, North Carolina, USA, 1990, September, n° 2664, and references therein.
5 M. J. Karpa, P. J. Duggan, G. J. Griffin and S. J. Freudigmann, *Tetrahedron*, 1997, **53** , 3669 and references therein.
6 (*a*) T. Sinbo, K. Nishimura, T. Yamaguchi and M. Sugiura, *J. Chem. Soc., Chem. Commun.*, 1986, 349; (*b*) S. Shinkai, K. Tsukagoshi, Y. Ishikawa and T. Kumitake, *J. Chem. Soc., Chem. Commun.*, 1991, 1039.
7 M. Takeuchi, S. Yoda, T. Imada and S. Shinkai, *Tetrahedron*, 1997, **53** , 8335 and references therein.
8 T. Kimura, M. Takeuchi, I. Hamachi and S. Shinkai, *Isr. J. Chem.*, 1996, **36**, 379.
9 J. B. Le Toumelin and M. Baboulène, *Langmuir*, 1996, **12**, 2128.
10 D. S. Matteson, *Tetrahedron*, 1989, **45**, 1859.
11 R. M. Washburn, E. Levens, C. F. Albright and F. A. Billing, *Organic Synthesis*, Wiley, New York, 1963, **Collect. vol. 4**, p. 68.
12 H. C. Brown and T. E. Cole, *Organometallics*, 1983, **2**, 1316.
13 D. S. Matteson, *Tetrahedron*, 1998, 54, 10555.
14 (*a*) M. Baboulène, J. L. Torregrosa, V. Spéziale and A. Lattes, *Bull. Soc. Chim. Fr.*, 1980, **II**, 565; (*b*) A. Dicko, M. Montury and M. Baboulène, *Synth. Commun.*, 1988, **18**, 459.
15 H. Nöth and B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, Springer Verlag, New York, 1978.
16 W. Sieberg, *Advances in Boron Chemistry*, Royal Society of Chemistry, London, UK, 1997.
17 B. Goeller, A. Dicko and M. Baboulène, *Main Group Met. Chem.*, 1997, **20** , 795.
18 M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1988, 2nd edn.
19 R. Zana, *J. Colloid Interface Sci.*, 1980, **78**, 330.
20 P. Mukerjee and K.J. Mysels, *Critical Micelle Concentrations of Aqueous Surfactant Systems*, National Bureau of Standards, Washington D.C., 1971, NSRDS-NBS 36.
21 M. J. Rosen, L. Liu and L.D. Song, in *4th World Surfactants Congress: Proceedings*, C.E.D., Barcelona, Spain, 1996, p. 416.
22 B. Lindman and H. Wennerström, in *Topics in Current Chemistry Micelles*, ed. F. L. Boschke, Springer Verlag, Heidelberg, 1980, vol. 1, p. 85.
23 J. W. Gibbs, *The Collected Works of J. W. Gibbs*, Longmans and Green, London, 1928, vol. 1, p. 119.
24 V. L. Tweedie and J. C. Allabashi, *J. Org. Chem.*, 1961, **26**, 3676.
25 N. H. Cromwell and A. Hassner, *J. Am. Chem. Soc.*, 1955, **77**, 1568.

Paper 8/07205A