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Synthesis and surface properties of a series of surfactants based on *O*-alkyl and *O*-perfluoro-*N*,*N*′-diisopropylisoureas

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ABSTRACT

O-Dodecyl-*N*,*N*′-diisopropylisourea and *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea were synthesized by reaction of hydrogenated or fluorinated alcohols onto diisopropylcarbodiimide in *quasi*-quantitative yields. Adding various hydrogen halides (HCl, HBr, or HI) onto these isoureas enabled one to obtain isoureas hydrohalides with tensioactive properties. The surface properties of both series of hydrogenated and fluorinated surfactants were studied and compared. The influence of the counter-ions onto the surface properties showed that the tensioactive properties were improved in the following increasing order: I < Cl < Br. Fluorinated isourea hydrohalides exhibited better surfactant properties than their hydrogenated homologues.

1. Introduction

Hydrochloride and hydrobromide cationic surfactants in water exhibit interesting surface properties [1] that showed various applications as anti-corrosion additives [2–4]. Indeed, corrosion inhibitors, especially those based on hydrochloride cationic surfactants, are the most interesting because of the small size of the chlorine atom, improving their adhesion to metal [5]. Moreover, these surfactants can be used as adhesion agents between the asphalt, resulting from the crude oil refinery, and gravels, which is a mixture of acidic (granite and quartz) and basic (lime and marble) minerals. Scheme 1 illustrates the adhesion between asphalt and gravels in the presence of surfactants. As the deterioration of road pavement often arises from a lack of adhesion, this drawback can be overcome by the use of a small amount of surfactants in the binder, at a low cost compared to the pavement itself [6–9].

Fluorinated surfactants are well known and currently used in more than 200 applications (including paints, cosmetics, anti-misting agents, emulsifiers for aqueous polymerization of fluorinated monomers, firefighting agents in extinguishers, etc.) [10–16]. These surfactants contain a perfluorinated chain as hydrophobic group and exhibit special properties such as high thermal and chemical stabilities, high surface activity, and low critical micelle concentration [12,16–23]. The fluorinated chains are much more hydrophobic than their hydrogenated homologues, and their introduction in surfactants enhances their amphiphilic character, improving the surface activity, which is about 27 and 15 mN m^{-1} for hydrogenated and fluorinated surfactants, respectively [24–28].

As a matter of fact, a series of *O*-alkyl-*N*,*N*′-dialkylisoureas was synthesized by Vowinkel [29] from an hydrogenated alcohol and a carbodiimide (Scheme 2). *O*-alkylisoureas have also been used for the preparation of esters and alkyl halides [30–32].

According to the literature [33,34], copper(I) chloride is the most widely used catalyst for the synthesis of *O*-alkyl-*N*,*N*′-dialkylisoureas. Palladium salts [35], tin salts [36] and acids [37] have also been used as catalysts but copper(I) chloride led to the best yields. In previous works, *O*-alkyl [38] and *O*-perfluoroalkyl-*N*,*N*′-dialkylisourea hydrochloride [28] were synthesized and their surface properties were assessed. Table 1 lists some characteristics of these hydrogenated and fluorinated isoureas [28,38].

Table 2 lists the values obtained for surface tension and critical micelle concentration of the *N*,*N*′-hydrogenated and *N*,*N*′-fluorinated diisopropylisourea hydrochlorides [28,38].

The present article deals with the synthesis of new surface active molecules and the study of their properties, aiming at developing new synthetic pathways and to optimize the surface properties. It was worth synthesizing both hydrogenated and

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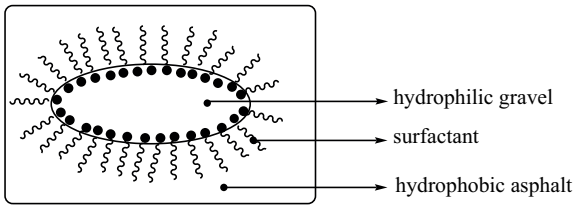
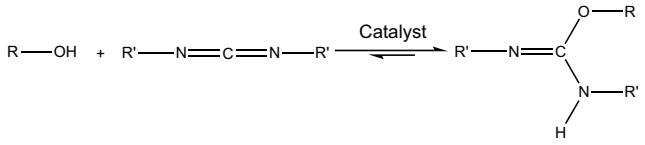


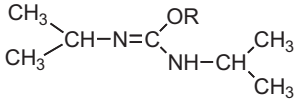
Scheme 1. Sketch of adhesion between asphalt and gravels in the presence of a surfactant.



Scheme 2. Synthesis of *O*-alkyl-*N*,*N*′-dialkylisourea from a hydrogenated alcohol and a carbodiimide.

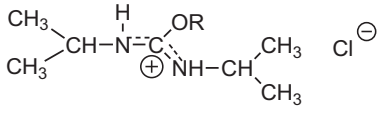
Table 1
Characteristics of some hydrogenated and fluorinated isoureas.

–R



	Time (h)	$T_{reaction}$ (°C)	Boiling point (°C)	Yield (%)
$-C_{10}H_{21}$	4	50	125 @ 0.03 mbar	92
$-C_{12}H_{25}$	5	50	Undistilled	98 (Crude)
$-C_{14}H_{29}$	8	50	Undistilled	96 (Crude)
$-(CH_2)_2C_6F_{13}$	5	25	72	90
$-(CH_2)_2C_8F_{17}$	6	25	87	95
$-(CH_2)_2C_{10}F_{21}$	6	25	Undistilled	98 (Crude)

Table 2
Critical micelle concentration (CMC) and surface tension (γ) of hydrogenated and fluorinated isourea hydrochlorides.



R	γ (mN m^{-1})	CMC (mmol l^{-1})
$-C_{10}H_{21}$	31.17	1.030
$-C_{12}H_{25}$	31.05	0.844
$-C_{14}H_{29}$	33.90	0.841
$-(CH_2)_2C_6F_{13}$	20.55	0.457
$-(CH_2)_2C_8F_{17}$	20.85	0.245
$-(CH_2)_2C_{10}F_{21}$	Water insoluble	

fluorinated surfactants, comparing their surface properties by means of surface tension, conductimetry and to assess their critical micelle concentration (CMC).

The present manuscript describes the synthesis, the spectroscopic characterization, and the surface properties of the following cationic surfactants at various temperatures:

- *O*-Dodecyl-*N*,*N*′-diisopropylisourea hydrochloride, hydrobromide, and hydroiodide;
- *O*-Tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrochloride, hydrobromide, and hydroiodide.

It is worth indicating that *O*-$CH_2CH_2C_{10}F_{21}$-*N*,*N*′-diisopropylisourea hydrochloride is not soluble in water and thus its surface properties could not be assessed [28]. A study of the effect of the nature of the counter-ion (chloride, bromide, and iodide) on the surface properties was also investigated. In addition, to better understand the effect of the counter-ion, the surface tension and the CMC were assessed at various temperatures (15, 20, 25, and 30 °C).

2. Results and discussion

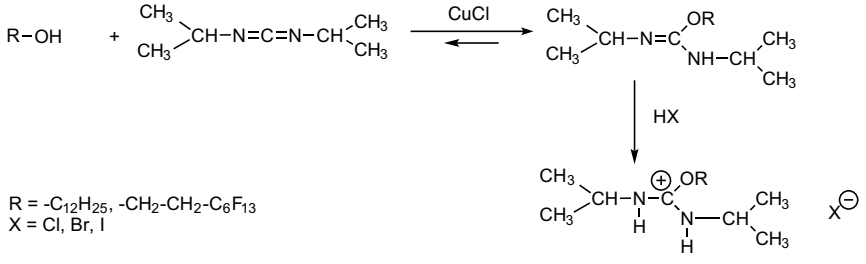
2.1. Synthesis

Cationic surfactants were synthesized under inert atmosphere from the condensation of an equimolar carbodiimide to alcohol ratio in the presence of copper(I) chloride as displayed in Scheme 3.

The reaction was monitored by infrared spectroscopy (Fig. 1). During the reaction, a new vibration frequency at 1660 cm^{-1} assigned to –N–C=N– was noted while that at 2100 cm^{-1} characteristic of -N=C=N- function vanished. In Fig. 1, the intensification of the bands in the 1000–1300 cm^{-1} range corresponds to the presence of C–F vibration bands.

The synthesis of these compounds was carried out in different conditions:

- At room temperature, for the hydrogenated isoureas, we found out that the reaction time was about 48 h [28,34]. Rising the temperature to 50 °C can decrease the reaction time to 4–6 h. In addition, and when temperature exceeded 80 °C, the corresponding urea formation was favored, thus reducing the yield. This is evidenced by a higher melting point and from ^{1}H NMR spectroscopic data. In the ^{1}H NMR spectrum, the methyl, methyne, and amine protons of diisopropylurea are located at 1.0, 3.15, and 3.4 ppm, respectively.
- Addition of dichloromethane as a solvent to the reaction mixture increased the reaction time to 24 h. Therefore, the reaction was carried out without any solvent, to achieve the best possible yield in a minimum of time. When fluorinated alcohols were used, the reaction was completed in few hours (at room temperature) instead of several days (reaction with hydrogenated alcohol). However, the chain length of the alcohol does not much influence the kinetics of the reaction.



Scheme 3. Synthesis of hydrogenated and fluorinated isoureas and isoureas hydrohalides.

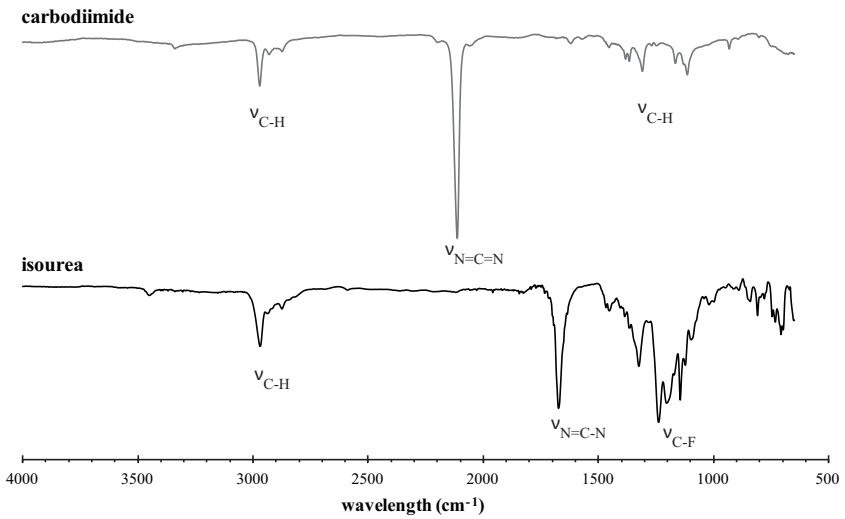


Fig. 1. FTIR spectra before (upper) and after (bottom) the reaction of synthesis of the fluorinated isourea.

2.2. Surface properties

All compounds except *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydroiodide were soluble in water and thus their surface properties could be assessed. Therefore, the evolution of their surface tension and conductivity versus the temperature (15–30 °C) were studied as well as the influence of the nature of the counter-ion (Cl^-, Br^- and I^-).

2.2.1. Surface tension and conductimetry

Surface properties of all these surfactants were assessed from tensiometry using the Wilhemy plate method. The following study shows that all products exhibit interesting surface properties (Fig. 2): the surface tension is in the order of 28–30 and 18–20 mN m^{-1} for hydrogenated and fluorinated surfactants, respectively, which is in agreement with the literature [12,14,15].

The same measurements were carried out on the fluorinated homologues. However, the *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydroiodide is very unstable, and turns into *N*,*N*′-diisopropylurea and tridecafluorooctyl iodide (Scheme 4). Fig. 3 represents the variation of the surface tension versus the log of the concentration for the *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisoureas hydrochloride and hydrobromide at various temperatures (15, 20, 25, and 30 °C).

2.2.2. Critical micelle concentration

The critical micelle concentration values were obtained from the inflection point on both surface tension and conductivity plots. Tables 3 and 4 show the values of the surface tension, γ, the critical micelle concentration (CMC), and the conductivity, σ, at various temperatures.

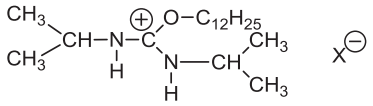
2.2.3. Interpretations

From Tables 3 and 4, the following conclusions can be drawn:

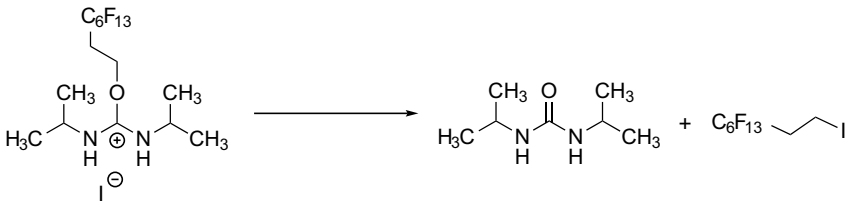
As expected, the fluorinated surfactants exhibit better surface properties than their hydrogenated homologues. For example, the *O*-dodecyl-*N*,*N*′-diisopropylisourea hydrochloride exhibits a surface tension of 32.0 mN m^{-1} at 20 °C, while that of its fluorinated homologue (*O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrochloride) worths 19.7 mN m^{-1}.

The surface tension and the conductivity do not vary significantly with the temperature, at least in the considered temperature range (15–30 °C). For example, the surface tension of the *O*-dodecyl-*N*,*N*′-diisopropylisourea hydrochloride varied from 32.5 to 30.7 mN m^{-1} while the temperature increased from 15 to 30 °C.

Table 3
Surface tensions (γ, mN m^{-1}), conductivities (σ, mS cm^{-1}), and critical micelle concentrations (CMC, mmol l^{-1}) deduced from both γ and σ for the various *O*-dodecyl-*N*,*N*′-diisopropylisourea hydrohalides at various temperatures (15, 20, 25, and 30 °C).



X	*T* (°C)	γ (mN m^{-1})	CMC (mmol l^{-1})	σ (mS cm^{-1})	CMC (mmol l^{-1})
Cl	15	32.5	5.5		
	20	32.0	1.2	0.31	1.70
	25	30.5	1.1		
	30	30.7	1.0		
Br	15	30.1	2.9		
	20	29.9	1.3	0.55	1.56
	25	29.5	1.2		
	30	29.5	1.4		
I	15	39.2	0.2		
	20	38.4	0.2	0.54	0.22
	25	36.0	0.4		
	30	35.6	0.2		



Scheme 4. Reaction of degradation of *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydroiodide.

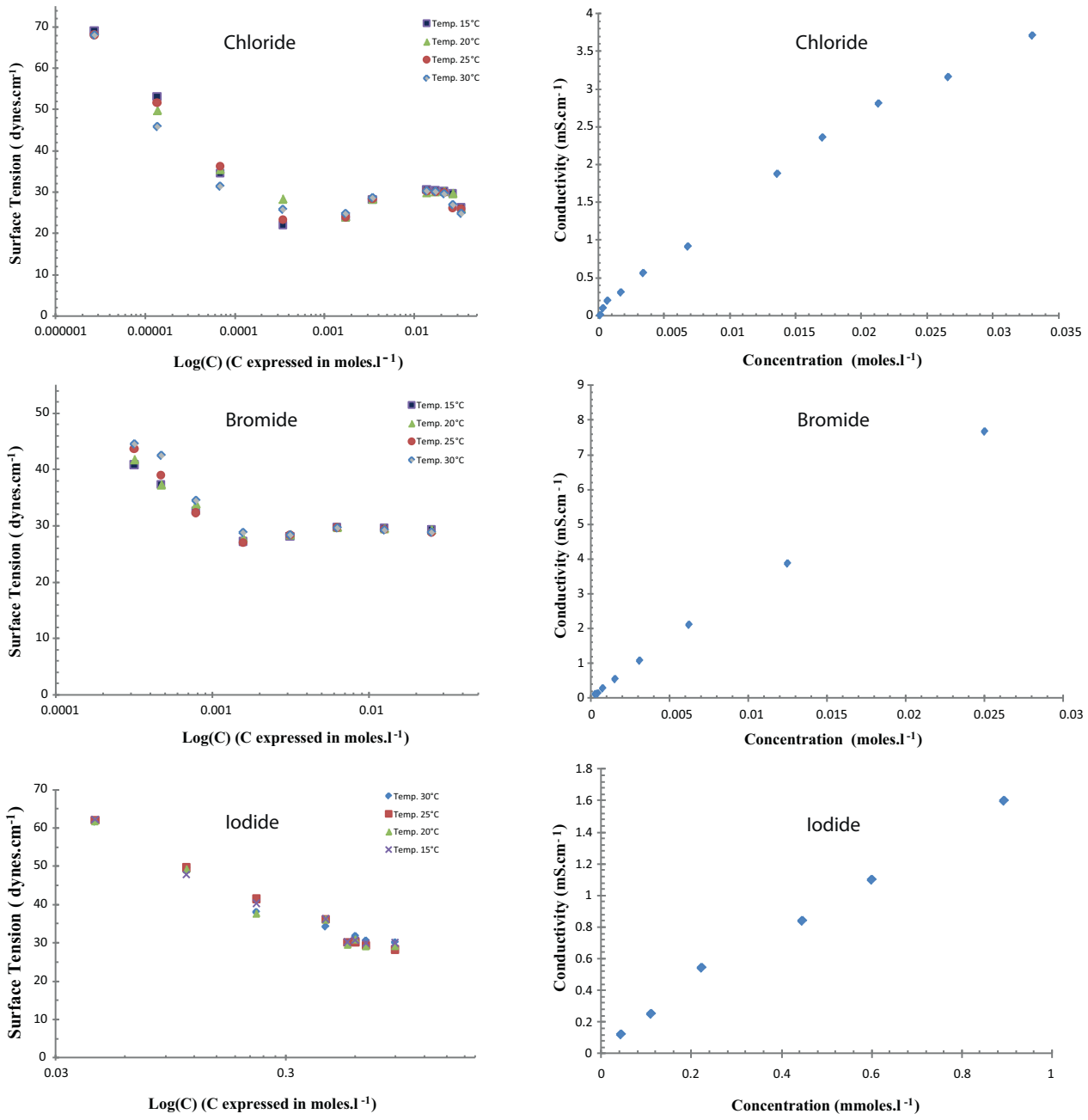


Fig. 2. Variation of the surface tension (left, mN m^{-1}) at various temperatures (15, 20, 25, and 30 °C) and of the electrical conductivity (right, mS cm^{-1}) at 20 °C of *O*-dodecyl-*N*,*N*′-diisopropylisourea hydro-chloride, -bromide, and -iodide (from top to bottom, respectively) versus the isourea concentration (mol l^{-1}).

Regarding the influence of the nature of the counter-ion, it is observed that the bigger the counter-ion, the higher its polarizability, the larger the impact of the temperature on the surface tension value. For example, for *O*-dodecyl-*N*,*N*′-diisopropylisourea hydrohalides, the surface tension increased from 29.9 (bromide) to 38.4 mN m^{-1} (iodide) at 20 °C. When the temperature increased, the surface tension slightly decreased in the considered temperature range (15–30 °C). For example, surface tension of the *O*-dodecyl-*N*,*N*′-diisopropylisourea hydroiodide decreased from 39.2 to 35.6 mN m^{-1} while the temperature increased from 15 to 30 °C.

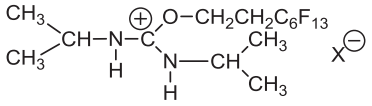
The influence of the temperature was more pronounced for the fluorinated surfactants: for example, when the temperature increased from 15 to 30 °C, the surface tension of the *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrobromide increased from 16.2 to 21.0 mN m^{-1} (30% increase).

These results confirm what has been reported in the literature [39]. The movement of the surface-active molecules increases with temperature. Thus, they tend to go toward the surface, hence reducing the surface tension value [12].

Moreover, the critical micelle concentrations (CMCs) for both hydrogenated and fluorinated surfactants is affected to the same extent by the change of temperature, at least in the considered temperature range. For example, the CMC of *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrobromide varied from 0.20 to 0.26 mmol l^{-1} (also 30% increase) in the 15–30 °C temperature range. The variation of the CMC with the temperature is however less important for the fluorinated surfactants than for the hydrogenated ones.

The variations of the CMC values (Table 3) are quite small in the considered temperature range, especially for surfactants that have

Table 4
Surface tension (γ, mN m^{-1}), conductivity (σ, mS cm^{-1}), and critical micelle concentrations (CMC, mmol l^{-1}) deduced from both γ and σ for the various *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrohalides at various temperatures (15, 20, 25, and 30 °C).



X	*T* (°C)	γ (mN m^{-1})	CMC (mmol l^{-1})	σ (mS cm^{-1})	CMC (mmol l^{-1})
Cl	15	19.1	1.364		
	20	19.7	1.325	0.186	1.18
	25	19.2	1.421		
	30	17.9	1.715		
Br	15	16.2	0.258		
	20	18.2	0.228	0.517	0.26
	25	20.7	0.211		
	30	21.0	0.204		

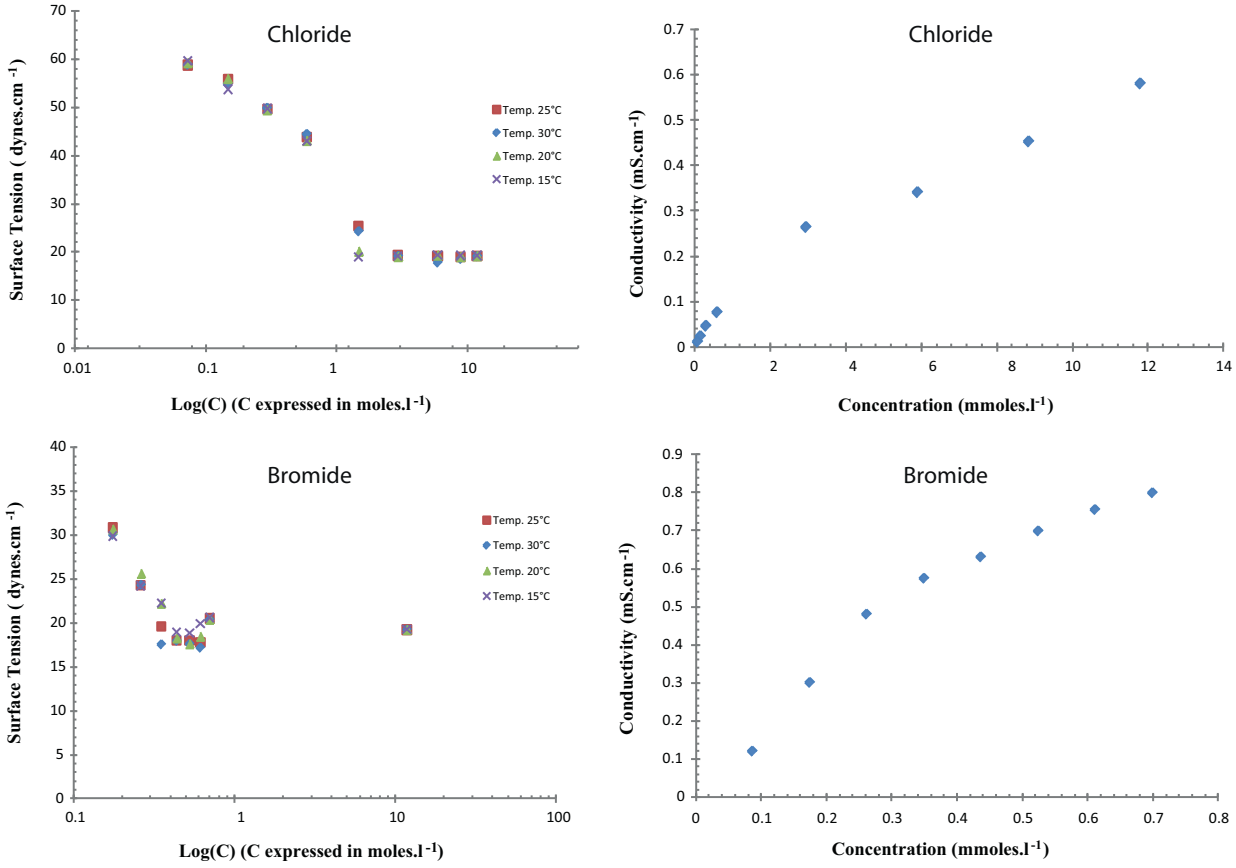


Fig. 3. Variation of the surface tension (left, mN m^{-1}) at various temperatures (15, 20, 25, and 30 °C) and of the electrical conductivity (right, mS cm^{-1}) at 20 °C of *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrochloride and -bromide (upper and lower graphs, respectively) versus the isourea concentration (mol l^{-1}).

low CMC values (i.e. hydroiodide). On the contrary, for surfactants based on hydrochlorides, which exhibit the highest CMC values, their CMC decreased to a minimum before increasing again with temperature. This is not unexpected as it has been previously observed on cationic surfactants bearing chloride or bromide as counter-ions [40].

The CMC values obtained from the conductimetry are slightly different from those assessed via the surface tension. This difference has been explained by Mukerjee in a detailed study [41]. Tensiometry, using the Wilhemy plate, measures surface tension from the interphase air/liquid. Thus, as it is very likely that the micelles do not have a surface activity, surface tension is proportional to the unimers at the surface only. On the other hand, the conductivity, at a given concentration, is related with bulk properties and relies on both species: the unimers at the surface and the micelles in the bulk. The intrinsic differences between both methods may have a small incidence on the CMC value.

3. Conclusions

Two series of *O*-dodecyl- and *O*-tridecafluorooctyl-*N*,*N*′-diisopropylisourea hydrohalides have been synthesized by the reaction

of a hydrogenated or fluorinated alcohol onto diisopropylcarbodiimide in high yields. These products were characterized by the usual spectroscopic techniques and elemental analysis. The use of hydrobromic, hydriodic, or hydrochloric acids on these hydrogenated and fluorinated isoureas enabled the preparation of products with surface-active properties. These cationic surfactants contain either a hydrogenated or a fluorinated hydrophobic chain. The synthesized fluorinated surfactants exhibit more interesting surface properties than their hydrogenated homologues. These compounds were chosen from different hydrogenated or fluorinated chains lengths as they exhibit the best surface properties [28,38]. It was worth focusing on the assessment of the surface tension and conductivity to study the impact of counter-ion (chloride, bromide and iodide) as well as the effect of the temperature (15–30 °C) on the surface properties. For the hydrogenated series, a 12-carbon alkyl chain was the best choice while for the fluorinated series, the tridecafluorooctyl group was chosen.

The results presented in this work show that surface tension, conductivity and critical micelle concentration values are somewhat affected by a change of temperature, at least in the considered temperature range (15–30 °C). Considering a wider temperature range would probably be interesting to show the impact of temperature on the surface properties and the thermal stability of these surfactants. However, it was observed that the higher the polarizability of the counter-ion, the higher the impact of temperature on the surface tension (chloride < bromide < iodide). The variation of the critical micelle concentration with the temperature was stronger for the fluorinated surfactants than for the hydrogrenated ones. Further properties (in acidic and basic media) of these original surfactants are under investigation. Also, if the counterion is exchanged for other anions such as PF_6^- or BF_4^-, it might be possible to use these compounds as ionic liquids, actually under investigation.

4. Experimental

4.1. Materials

N,*N*′-diisoproprylcarbodiimide (99%), copper(I) chloride (96%), hydrogenated alcohols (>95%), hydrochloric acid (37%), hydrobromic acid (47%), hydriodic acid (99.5%), dichloromethane (99.5%), ammonia (32%), sodium sulfate (99.5%) were purchased from Sigma–Aldrich and used as received. Fluorinated alcohols were generously provided by Elf Atochem (Paris, France). Deuterated chloroform used for the nuclear magnetic resonance spectroscopy was purchased from Euroiso-top (Grenoble, France) (purity > 99.8%).

4.2. Characterizations

4.2.1. Nuclear magnetic resonance (NMR)

The NMR spectra were recorded on Bruker AC 200 instruments, using deuterated chloroform as the solvent and tetramethylsilane (or trichlorofluoromethane) as the references for ^1H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording ^1H [or ^{19}F] NMR spectra were as follows: flip angle 90° [or 30°], acquisition time 4.5 s [or 0.7 s], pulse delay 2 s [or 5 s], number of scans 32 [or 64], and a pulse width of 5 μs for ^{19}F NMR.

4.2.2. Fourier transform infrared (FTIR) spectroscopy

Infrared spectra were recorded on a Nicolet 510P Fourier transform infrared (FTIR) spectrometer from KBr pellets (10 wt%), and the intensities of the absorption bands (cm^{-1}) were labeled strong (s), medium (m), or weak (w). The accuracy was ±2 cm^{-1}.

4.2.3. Gas chromatography coupled with mass spectrometry (GC–MS)

GC–MS chromatograms were recorded on an Agilent 6890 N gas chromatographer integrated with an Agilent 5973A quadrupole mass spectrometer. The chromatographer is equipped with a HP-1 non polar column (polydimethylsiloxane, 25 m × 0.20 mm, 0.33 μm), a flame ionization detector, the temperature of the injector is set at 250 °C, and the oven is heated from 50 °C to 250 °C at 10 °C min^{-1} during the experiment.

4.2.4. Tensiometry

Surface tensions were measured by means of a Dataphysics DCAT 21 Tensiometer using the Wilhemy plate method at different concentrations to assess the critical micelle concentration (CMC) of the surfactant in water. Each concentration was prepared at least 24 h prior to measurement. The solution was allowed to equilibrate in the apparatus and the surface tension was considered stable when the difference is less than 0.03 mN m^{-1}. The value for the surface tension was determined as the average of the last 200 points. The critical micelle concentration (CMC) was calculated as the intersection between the two straight lines emerging from high and low concentrations.

4.2.5. Conductimetry

It is also possible to assess the critical micelle concentration by conductimetry, where an inflection point can be observed on the conductivity versus concentration curve. Conductivity was measured on a CDM210 conductimeter from MeterLab equipped with a two poles conductivity cell (CDC745-9 from Radiometer Analytical).

4.3. Synthesis

An example of the preparation of the *O*-dodecyl-*N*,*N*′-diisopropylisourea hydrobromide is provided and such procedure can be applied to all other molecules.

The reaction is an equimolar reaction between diisopropylcarbodiimide (0.1 mol, 6.1 g) and dodecanol (0.1 mol, 12.6 g) in the presence of CuCl in catalytic quantity (0.2 g). The reaction mixture was stirred away from moisture in a round-bottom flask. Once the reaction completed, the catalyst was eliminated by filtration using dichloromethane as the solvent. The filtrate was treated with a solution of ammonia. This will retrieve the copper ions that were complexed with the isourea $[Cu(NH)_3]^{2+}$ (ammonia is a stronger ligand than isourea for copper). The filtrate was then washed with water to eliminate all mineral ions. This treatment was repeated several times until the aqueous phase was colorless and its pH was neutral. The organic phase was dried over anhydrous magnesium or sodium sulfate. After the dichloromethane evaporation, a colorless oil (0.098 mol, 30.6 g) was obtained. Products were purified by distillation under reduced pressure.

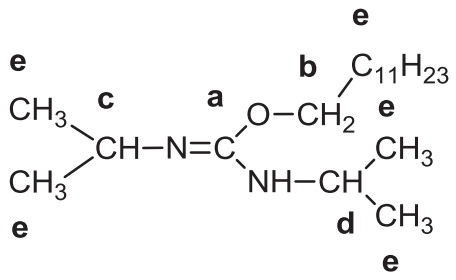
Isourea hydrochlorides were obtained by bubbling gaseous hydrochloric acid generated from the reaction of sodium chloride (NaCl) onto sulfuric acid (H_2SO_4). The preparation of the hydrobromide and hydroiodide homologues required hydrobromic acid and hydriodic acid, respectively. The reactions were carried out without solvent, and were quite instantaneous leading to quantitative yields. All products were waxy.

4.3.1. Hydrogenated isoureas

FTIR 3440 (N–H), 3000–2800 (C–H), 1655 (C–O–C and C=N), 1400 (C–N).

^1H NMR ($CDCl_3$) δ = 4.0 (2 H, triplet of triplets, O–C**H_2**–), 3.7 (1 H, heptuplet, $(CH_3)_2$C**H**–N=, $^3J_{HH}$ = 7.0 Hz), 3.4 (1 H, multiplet, –N**H**–), 3.1 (1 H, heptuplet, $(CH_3)_2$C**H**–NH–, 1.26 (2n H, multiplet, O–CH_2–C_n**H_{2n}**–CH_3), 1.1 ppm (12 H, d, 2[(CH_3)$_2$C**H**-], $^3J_{HH}$ = 6.9 Hz), 1 ppm (3H, triplet, O–CH_2–C_nH_{2n}–C**H_3**).

^{13}C NMR ($CDCl_3$) δ = (a) 153.0, (b) 66.1, (c) 47.2, (d) 44.4 and (e) 32.1.



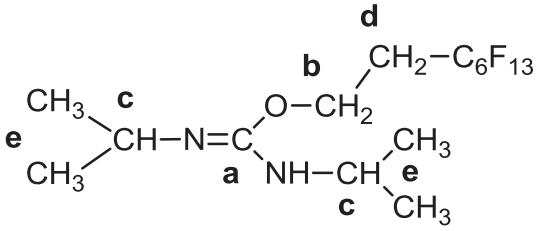
GC–MS *m*/*z*: 90 [$(CH_3)_2$CH–N=C(OR)–NH–CH–$(CH_3)_2$]; 100 [$(CH_3)_2$CH–N=C(O–)–NH–CH–$(CH_3)_2$].

4.3.2. Fluorinated isoureas

FTIR 1674 (N–C=N), 1325 C–N and 1240 (C–F).

^{1}H NMR ($CDCl_3$) δ = 1.0 (multiplet, $^{3}J_{HH}$ = 6.4 Hz, (C**H$_3$**)$_2$CH–, 12H), 2.4 (triplet of triplets, $^{3}J_{HF}$ = 18.9 Hz, $^{3}J_{HH}$ = 6.5 Hz, –O–CH_2–C**H$_2$**–C_6F_{13}, 2H), 3.15 (heptuplet, $^{3}J_{HH}$ = 6.4 Hz, $(CH_3)_2$C**H**–NH–, 1H), 3.8 (heptuplet, $^{3}J_{HH}$ = 6.4 Hz, $(CH_3)_2$C**H**–N=, 1H), 4.0 (triplet of triplets, $^{3}J_{HF}$ = 18.9 Hz, $^{3}J_{HH}$ = 6.5 Hz, –O–C**H$_2$**–CH_2–C_6F_{13} 2H), 3.3 (J_{HH} = 6.4 Hz, $(CH_3)_2$CH–N**H**–, 1H).

^{13}C NMR: δ = (a) 159, (C_nF_{2n+1}) 110–140, (b) 64–65, (c) 45–46, (d) 30–31 $^{2}J_{CF}$ = 32 Hz and (e) 21–22.



Elemental analysis: %C calc./meas. (36.73/36.83), %H calc./meas. (3.87/3.93) and %N calc./meas. (5.71/5.63).

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References

[1] S. Singh, A. Bhadani, H. Kataria, G. Kaur, R. Kamboj, Ind. Eng. Chem. Res. 48 (2009) 1673–1677.
[2] M.A. Deyab, Corros. Sci. 49 (2007) 2315–2328.
[3] D. Asefi, M. Arami, N.M. Mahmoodi, Corros. Sci. 51 (2009) 1817–1821.
[4] D. Asefi, M. Arami, N.M. Mahmoodi, Corros. Sci. 52 (2010) 794–800.
[5] M.M. Saleh, Mater. Chem. Phys. 98 (2006) 83–89.
[6] T.E. Havre, J. Sjöblom, Colloids Surf. A: Phys. Eng. Aspects 228 (2003) 131–142.
[7] A. Jada, C. Florentin, S. Mariotti, Adv. Colloids Int. Sci. 108–109 (2004) 127–132.
[8] F.B. Richardson, Spec. Publ. R. Soc. Chem. 107 (1992) 161–183.
[9] L.A. Mikeska. US Patent-1994/2,361,488, assigned to Sandard Oil Development Company, Delaware, USA.
[10] J. Scheirs, Modern Fluoropolymers, John Wiley and Sons Ltd., New York, 1997.
[11] G. Hougham, Fluoropolymers, Plenum Press, New York, 1999.
[12] E. Kissa, Fluroinated Surfactants: Synthesis, Properties and Applications, 2nd ed., CRC Press, New York, 2001.
[13] B. Ameduri, B. Boutevin, Well-Architectured Fluoropolymers: Synthesis, Properties and Applications, Elsevier, Amsterdam, 2004.
[14] M.-P. Krafft, J.G. Riess, J. Polym. Sci. Part A: Polym. Chem. 45 (2007) 1185–1198.
[15] M.-P. Krafft, J.G. Riess, Chem. Rev. 109 (2009) 1714–1792.
[16] G. Kostov, F. Boschet, B. Ameduri, J. Fluorine Chem. 130 (2009) 1192–1199.
[17] J.C. Ravey, M.-J. Stebe, Colloids Surf. A: Phys. Eng. Aspects 84 (1994) 11–31.
[18] N. Yoshino, M. Morita, A. Ito, M. Abe, J. Fluorine Chem. 70 (1995) 187–191.
[19] T.H.V. Ngo, C. Damas, R. Naejus, R. Coudert, J. Fluorine Chem. 131 (2010) 704–708.
[20] A. Pasc-Banu, M. Blanzat, M. Belloni, E. Perez, C. Mingotaud, I. Rico-Lattes, T. Labrot, R. Oda, J. Fluorine Chem. 126 (2005) 33–38.
[21] M. Pabon, J.M. Corpart, J. Fluorine Chem. 114 (2002) 149–156.
[22] F. Guittard, S. Geribaldi, J. Fluorine Chem. 107 (2001) 363–374.
[23] P. Vierling, C. Santaella, J. Greiner, J. Fluorine Chem. 107 (2001) 337–354.
[24] E.G. Schwartz, W.G. Reid, J. Ind. Eng. Chem. 56 (1964) 26–31.
[25] S. Szonyi, F. Szonyi, I. Szonyi, Revue Générale de sécurité 88 (1989) 49–53.
[26] S. Szonyi, R. Vandamme, A. Cambon, J. Fluorine Chem. 30 (1985) 37–57.
[27] S. Cosgun, C. Gérardin-Charbonnier, J. Amos, C. Selve, J. Fluorine Chem. 125 (2004) 55–61.
[28] L. Badache, G. Bauduin, B. Boutevin, S. Rahal, J. Fluorine Chem. 92 (1998) 53–58.
[29] E. Vowinkel, Chem. Ber. 99 (1966) 1479–1484.
[30] A. Chighine, S. Crosignani, M.-C. Arnal, M. Bradley, B. Linclau, J. Org. Chem. 74 (2009) 4753–4762.
[31] S. Crosignani, B. Nadal, Z. Li, B. Linclau, Chem. Commun. (2003) 260–261.
[32] S. Crosignani, P.D. White, B. Linclau, J. Org. Chem. 69 (2004) 5897–5905.
[33] E. Schmidt, F. Moosmuller, Liebigs Ann. Chem. 597 (1955) 235–240.
[34] L.J. Mathias, Synthesis (1979) 561–576.
[35] E. Vowinkel, J. Bluethe, Chem. Ber. 107 (1974) 1353–1359.
[36] X. Schaffer. German Patent-1979/29,41,253.
[37] K. Hartke, F. Rossbach, Angew. Chem. Int. Ed. Engl. 7 (1968) 72.
[38] W.N. Abderrahmane, L. Badache, F. Boschet, J. Soc. Alg. Chim., in press.
[39] F. Puisieux, M. Seiller, in: Galenica (Ed.), Agent de surface et émulsion: les systèmes dispersés, vol. 5, Lavoisier, Paris, 1983.
[40] J.J. Galan, A.-G. Perez, J.L.D. Castillo, J.R. Rodriguez, J. Therm. Anal. Calorim. 70 (2002) 229–234.
[41] P. Mukerjee, Adv. Colloid. Interface Sci. 1 (1967) 241–275.