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Surfactant properties of ionic liquids containing short alkyl chain imidazolium cations and ibuprofenate anions†

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Interfacial tension, electrical conductivity, NMR self-diffusion and DLS experiments have been used to investigate the self-aggregation in water of ionic liquids associating an ibuprofenate anion and 1-alkyl-3-methylimidazolium $[C_nMIm]^+$ (n = 4, 6, 8) cations. Despite the short alkyl chain on imidazolium cations ($n \leq 8$), these ionic liquids exhibit particularly low Critical Aggregation Concentrations (CAC), significantly lower than their parent 1-alkyl-3-methylimidazolium chloride salts. This behaviour is attributed to the formation of catanionic pairs between ibuprofenate and imidazolium.

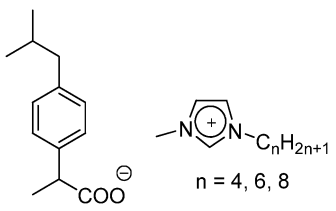
Introduction

The interest in ionic liquids (ILs) is motivated by their unique properties such as negligible vapour pressure, thermal stability and non-flammability, combined with high ionic conductivity and a wide electrochemical stability window.[1] These properties can be tuned by an appropriate choice of the anion/cation combination. A new formulation concept based on the design of active pharmaceutical ingredients in IL form has just emerged. It limits the polymorphism and improves the solubilization and dissolution rates.[2–4] Inclusion of such IL drug organic form in silica-based materials (*i.e.* ionogels) has been recently proposed as an alternative drug delivery system.[5] Ionogels were obtained by a one-step sol-gel synthesis using 1-methyl-3-butylimidazolium ibuprofenate. This method allows loading high amounts of drug. In these ionogels, the IL has two roles: it acts as a solubility promoting agent and as a templating agent for the silica structuration.[5] ILs have also been studied for their assembling properties[6] and mixed with oppositely charged surfactants to obtain mesophases.[7]

It is now accepted that 1-alkyl-3-methylimidazolium cations $[C_nMIm]^+$ undergo aggregation beyond a critical concentration called Critical Aggregation Concentration (CAC).

CACs of imidazolium based ILs have been determined through various methods such as surface tension, fluorescence, apparent molar volumes and electrical conductivities.[8–15] CAC depends on the cation alkyl chain length. For instance, long alkyl chain imidazolium chloride ILs ($n > 8$) unambiguously form aggregates in aqueous solutions whereas CAC of short alkyl chain imidazolium ILs is very high and hard to reach.[16,17] CAC also depends on the nature of the anion. Indeed, small polydisperse spherical aggregates were registered by SANS for $[C_4MIm][BF_4]$ for a concentration above 800 mM.[18] The effect of the anions nature on CAC has also been studied by Wang *et al.*[19] They demonstrated that the anionic effect correlates well with the Hofmeister series of the anions for cationic surfactants.[20,21] The position of an anion in this series is considered to be dependent on its charge, its hydrated radius/polarizability, hydrophobicity and bulkiness. Actually, one of the lower CACs (12 mM) was obtained by Blesic *et al.* using alkylsulfonate salts.[13] In this case, the striking low CAC value was ascribed to the catanionic behaviour of the IL. Related to the same catanionic behaviour, long-chain imidazolium ILs and an anionic surfactant, sodium dodecyl sulfate (SDS), have been reported to form vesicles which were used for the synthesis of hollow silica spheres.[22]

The aim of this paper is to investigate the aggregation behaviour in water of IL salts consisting of short alkyl chain $[C_nMIm]^+$ cations (n = 4, 6, 8) and ibuprofenate (Scheme 1).



Scheme 1 Structure of the investigated 1-alkyl-3-methylimidazolium ibuprofenate ionic liquids.

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The physicochemical behaviour of these ibuprofenate imidazolium ILs in water is one key point to control ionogels templating and drug release. Sodium ibuprofenate is an amphiphilic molecule, but its aggregation behaviour has been studied in few papers.[23] Ibuprofenate was reported to form catanionic mixtures with tetradecyltrimethylammonium bromide (TTAB) and a sugar-based surfactant and was used in drug formulation.[24,25] In the present paper, surface activities and CAC were determined by surface tension, conductimetry and by NMR self-diffusion measurements and compared with data obtained for long alkyl chain imidazolium chloride ILs. Aggregates size was estimated by DLS.

Experimental section

Materials

1-Butyl-3-methylimidazolium chloride [C_4MIm][Cl] (98%) was purchased from Solvionic whereas 1-hexyl-3-methylimidazolium chloride [C_6MIm][Cl] ($\geq$ 98%) and 1-octyl-3-methylimidazolium chloride [C_8MIm][Cl] ($\geq$ 98%) were purchased from Merck and used as received. Ibuprofen sodium salt was purchased from Aldrich (analytical standard). Deionised water was obtained from a Millipore Milli-Q water purification system.

Synthesis

The three ionic liquids used in this study were synthesised following the general procedure described below.

Sodium ibuprofen salt (1 eq.) was dissolved in ethanol ([Na][Ibu] = 0.73 mol L^{-1}). [C_4MIm][Cl] (1 eq.) was also dissolved in a minimum of ethanol and added slowly to the previous solution. The resulting mixture was stirred at 70 °C for 3 h and overnight at room temperature. The solution was filtered on Millipore (0.45 μm) and 100 mL of acetone was added leading to the precipitation of NaCl which was further filtered and the solvent was removed under vacuum. Addition of acetone was renewed until no further precipitation of NaCl could be detected. The products were then dried under vacuum at 343 K for 48 h. All products were obtained as a yellowish viscous liquid showing glass transition temperatures between −26 °C and −45 °C depending on the alkyl chain length.

The samples were characterized by ^{1}H and ^{13}C NMR, ESI, DSC and TGA (see ESI†).

Characterization

Interfacial tension measurements. Surface tension was measured using a tensiometer Krüss K100 by the plate method, at 25 °C (±0.5 °C). Each measurement was averaged over 30 values recorded for 120 s (stand. dev. = 0.02 mN m^{-1}). Samples have been prepared by successive dilutions with MilliQ water and carefully homogenized. The MilliQ water reference was 71.5 ± 0.8 mN m^{-1}. In order to avoid any contamination, the plate was systematically rinsed with alcohol and flame burned. The vessel was cautiously washed with alcohol and then dried.

Conductimetry. The conductivity of the IL solutions was measured on a NanoZS, Malvern Instrument at 25 °C. Measurements were performed on disposable folded capillary cells including the electrodes (Malvern, Instrument). The electric field was applied between the electrodes (inter-electrode distance of 61 mm). The current in the sample was measured between the same electrodes (sample volume of 750 μL). The surface of the electrodes was 29.25 mm^2.

Dynamic light scattering. DLS measurements were carried out at 25 °C using a NanoZS, Malvern Instrument. The NanoZS photospectrometer is equipped with a 532 nm laser beam. The detection angle was fixed to 173° to limit the multiple scattering of the concentrated sample and to measure very small particles (down to 0.6 nm). The correlation function was analyzed *via* the nonnegative least-squares method (NNLS) to obtain the distribution of diffusion coefficients (D) of the solutes, and then the apparent equivalent hydrodynamic radius (R_h) was determined using the Stokes–Einstein equation.

PGSE-NMR. All solutions were prepared in D_2O (99.95% Aldrich). PGSE-NMR diffusion measurements were carried out on a 9.4 T Bruker Avance 400 NMR spectrometer equipped with a Bruker 5 mm broadband probe with a z-axis gradient and a temperature controller. The self-diffusion measurements were performed with the pulsed field gradient stimulated echo and LED sequence using two spoil gradients (PGSE-NMR).[26] The magnitude of the pulsed field gradient was varied between 0 and 40 G cm^{-1}, the diffusion time, Δ, between two pulses was fixed at 200 ms, and the gradient pulse duration, δ, was set between 3 and 7 ms, depending on the diffusion coefficient of the mobile species. This enabled us to observe the attenuation of spin echo amplitude over a range of at least 2 decades, leading to good accuracy (<5%) of the self-diffusion coefficient values. These coefficients were determined from the classical relationship $\ln(I/I_0) = -Dg^2\gamma^2\delta^2(\Delta - \delta/3)$, where g is the magnitude of the two gradient pulses, γ is the gyromagnetic ratio of the nucleus under study and I and I_0 are the areas of the signal obtained with or without gradient pulses respectively.

Results and discussion

Surface activity

Surface activities of [C_nMIm][Ibu] were investigated and compared to those of [C_nMIm][Cl] and [Na][Ibu] references (Fig. 1). Surface tensions of the solutions *versus* concentration in the logarithmic scale are displayed in Fig. 1. Short alkyl chain chloride salts showed a poor surface activity consistent with literature data.[16,17] The surface tension of [C_4MIm][Cl] did not significantly decrease below a concentration of 100 mM. Typically, a concentration of 0.5 M of [C_4MIm][Cl] was needed to decrease the surface tension to 50 mN m^{-1}.[16] [C_8MIm][Cl] and [C_{10}MIm][Cl] showed significant surface activity, confirming that imidazolium chloride ILs were surface active only for the long alkyl chain length ($n \geq 8$). By contrast, whatever the length of the alkyl chain, [C_nMIm][Ibu] aqueous solutions (n = 4, 6, 8) underwent a pronounced decrease in surface tension followed by a plateau indicative of aggregation. The pronounced minimum and the subsequent positive slope observed at higher concentrations might be ascribed to the presence of impurities in commercial IL

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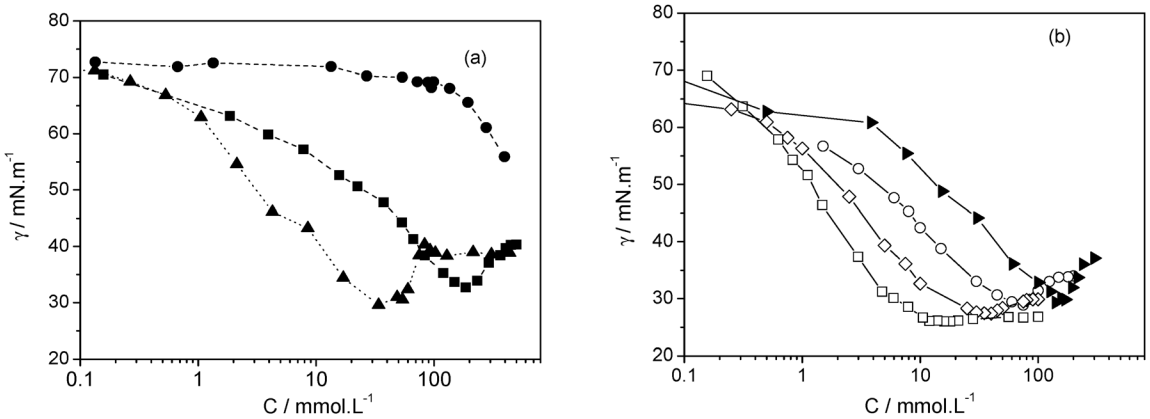

Fig. 1 Surface tension isotherms at 25 °C of (a) [C_nMIm][Cl] ● n = 4, ■ n = 8, ▲ n = 10, and (b) ▶ [Na][Ibu] and [C_nMIm][Ibu] ○ n = 4, ◇ n = 6, □ n = 8.

batches, or to a relative surface excess of water[18] or to coulombic interactions.[27] It is noteworthy that the plateau was reached directly for n = 8 suggesting more favorable aggregation in this case. The surface activities of [C_nMIm][Ibu] might be related to that of [Na][Ibu]. Indeed, this latter presented interfacial properties with a plateau region close to 36 mN m^{-1}. Thus, association of ibuprofenate and imidazolium cations could result in an ion pair amphiphile showing good interfacial activity.

The CAC was taken at the minimum surface tension which was considered to be the aggregation onset.[27] CAC data determined from surface tension measurements are set out in Table 1. CAC values turned out to be much lower for [C_nMIm][Ibu] than for [C_nMIm][Cl]. As a matter of fact, CAC obtained for [C_8MIm][Ibu] was 14 fold smaller than for [C_8MIm][Cl]. More interestingly, the short alkyl chain [C_4MIm][Ibu] possessed a CAC close to that obtained for [C_{10}MIm][Cl]. However, as for a classical ionic surfactant, a decrease of the CAC was observed when increasing the alkyl chain length of the imidazolium cation.

The ability to decrease surface tension was characterized by two other parameters: (i) the efficiency of adsorption pC_{20} defined as the negative logarithm of the amphiphilic molecules concentration required to reduce the surface tension of the pure solvent by 20 mN m^{-1}, (ii) the effectiveness of the surface tension reduction Π_{CAC} (see Table 1). From the measurements of pC_{20}, two points can be underlined. First, pC_{20} values increased with the alkyl chain length, which confirmed a higher efficiency of surfactant activity upon increasing n. Second, pC_{20} values were higher for [C_nMIm][Ibu] than for [C_nMIm][Cl], confirming the strong contribution of ibuprofenate anions to surface adsorption. Thus, the surface tension of short alkyl chain [C_4MIm][Ibu] was equal to that obtained for long alkyl chain [C_{10}MIm][Cl].

Table 1 Surface properties at 25 °C

Compound	CAC[a]/mM	pC_{20}	Π_{CAC}/mN m^{-1}	A_{min}/Å^2
[C_4MIm][Cl]	—	—	—	
[C_8MIm][Cl]	190	1.67	32.2	84
[C_{10}MIm][Cl]	45	2.55	33.7	92
[Na][Ibu]	142	1.92	35.4	95
[C_4MIm]Ibu]	75	2.42	38.5	105
[C_6MIm][Ibu]	38	2.74	42.5	82
[C_8MIm][Ibu]	12	3.00	45.5	62

[a] CAC determined at the minimum of γ values.

The surface tension reduction was defined as $\Pi_{CAC} = \gamma_0 - \gamma_p$, where γ_0 is the surface tension of water and γ_p the surface tension of the solution at the plateau. In the [C_nMIm][Cl] series Π_{CAC} was nearly constant, showing that the monolayer was essentially the same in terms of nature (imidazolium cations) and compactness (Table 1). However, the surface tension reductions for [C_nMIm][Ibu] series were different from that for [C_nMIm][Cl]. This confirmed that the monolayer at the water/air interface did not consist of only imidazolium cations, but rather of imidazolium/ibuprofenate ion pairs. Moreover, Π_{CAC} values of the ibuprofenate series dramatically increased from n = 4 to 8, revealing an increase in molecular packing at the film interface when increasing the chain length. This was demonstrated by estimating the area occupied by a surfactant molecule at the air–water interface A_{min} according to:

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad (1)$$

where N_a is the Avogadro constant (6.022×10^{23} mol^{-1}), Γ_{max} is the surface excess concentration calculated by applying the Gibbs equation:[28]

$$\Gamma_{max} = -\frac{1}{2RT}\left(\frac{\partial \gamma}{\partial \ln C}\right)_T \quad (2)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T the absolute temperature and C the surfactant concentration. Here adsorption of the ion pair (imidazolium + ibuprofenate) has been assumed.

A_{min} was observed to decrease as the alkyl chain length increased in the [C_nMIm][Ibu] series. This suggested that the interaction between imidazolium and ibuprofenate was not only electrostatic, but also hydrophobic. This is consistent with strong ion pairing under cooperative interactions, *i.e.* Coulombic interactions, π-stacking, strong hydrogen bonding between the carboxylate and the acidic proton on the imidazolium ring, and van der Waals interactions when increasing alkyl chain length on the cation.[29] The strong ion pairing associated

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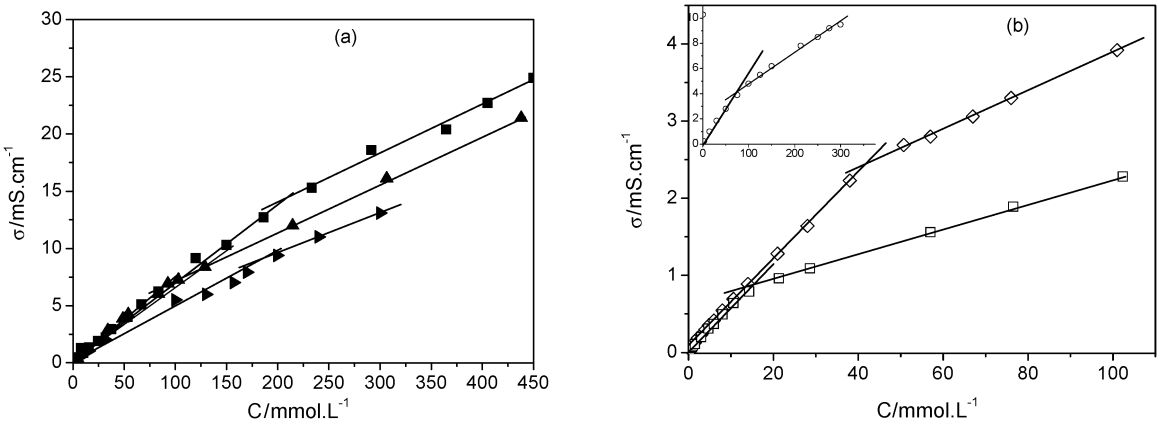

Fig. 2 Conductivities *vs.* concentrations at 25 °C of (a) [C_nMIm][Cl] ■ $n = 8$, ▲ $n = 10$, ▶ [Na][Ibu] and (b) [C_nMIm][Ibu] ○ $n = 4$ (onset), ◇ $n = 6$, □ $n = 8$.

Table 2 CAC determined by conductimetry and NMR with the corresponding degree of ionization and free energy of aggregation

Compound	CAC[a]/mM	α	ΔG^0_m/kJ mol^{-1}	CAC[b]/mM
[C_4MIm][Cl]	—	—	—	—
[C_8MIm][Cl]	205	0.65	−18.7	—
[C_{10}MIm][Cl]	78	0.54	−23.8	—
[Na][Ibu]	187	0.86	−16	—
[C_4MIm]Ibu]	75	0.45	−25.4	72
[C_6MIm][Ibu]	41	0.44	−27.9	—
[C_8MIm][Ibu]	14	0.30	−34.8	14

[a] Determined by conductivity. [b] Determined by PGSE-NMR.

to low critical aggregation concentrations is characteristic of catanionic surfactant-systems in water.[30] Catanionic systems consist of mixtures of anionic and cationic surfactants that reveal enhancement of their interfacial properties (compared to the individual molecules).[31]

Electrical conductivity measurements

Conductivities of aqueous solutions of [C_nMIm][Ibu] ($n = 4$, 6, 8) were compared with those of [C_nMIm][Cl] ($n = 8$, 10) and [Na][Ibu], used as references. As it can be seen in Fig. 2, there were two linear regimes in the concentration dependence of the conductivity. The difference in these regimes was not well marked for the references [C_nMIm][Cl] and [Na][Ibu]. On the other hand, the slope change was well pronounced for the [C_nMIm][Ibu] series. The slope break was assigned to the onset of the critical aggregation concentration (CAC) due to the decrease of free charged species in the bulk. Data obtained by this method are collected in Table 2. The latter were consistent with the values obtained by surface tension measurements. Application of the pseudo-phase model of micellization allowed determining the Gibbs energy of aggregation (ΔG^0_m) according to the following equation:[28]

$$\Delta G^0_m = (2 - \alpha)RT\ln\chi_{CAC} \qquad (3)$$

where χ_{CAC} is the critical aggregation concentration expressed in mole fraction, α is the degree of ionization determined by Frahm's method *i.e.* as the ratio of the slopes of the linear fragments above and below CAC.[32]

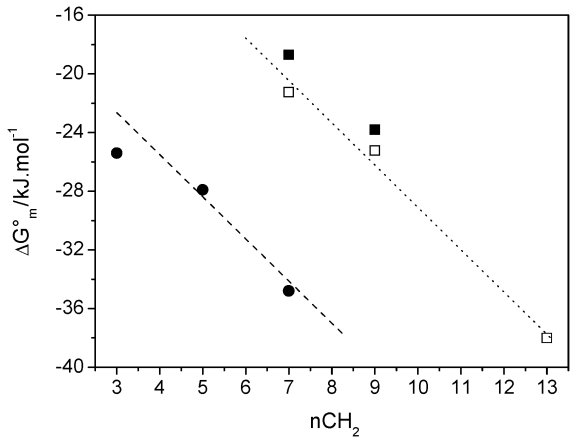

Fig. 3 ΔG^0_m as a function of the number of CH_2 groups of ■ [C_nMIm][Cl] and of ● [C_nMIm][Ibu]. Data in empty squares are those from Jungnickel *et al.*[17] Dashed and dotted lines represent the expected linear variation with ($\Delta G^0_{m,CH_2} = -2.85\,kJ\,mol^{-1}$) for [$C_n$MIm][Cl] and [$C_n$MIm][Ibu], respectively.

As expected from surface tension measurements, an increase in the alkyl chain length on an imidazolium ring resulted in a decrease of ΔG^0_m. The variations of ΔG^0_m with the nature of the anion are represented in Fig. 3. As previously reported,[33] ΔG^0_m could be divided into contributions from the head group $\Delta G^0_{m,head\ group}$, the methylene group of the hydrophobic chain $\Delta G^0_{m,CH_2}$ and the terminal CH_3 group of the alkyl chain $\Delta G^0_{m,CH_3}$. These contributions express the fact that aggregates form under the influence of both attractive and repulsive forces. Attractive forces are associated with the poor solubility of alkyl chains, while effective repulsive forces result from the high solubility of head groups.

$$\Delta G^0_m = \Delta G^0_{m,head\ group} + \Delta G^0_{m,CH_3} + nCH_2\Delta G^0_{m,CH_2} \qquad (4)$$

A plot of ΔG^0_m *versus* nCH_2 should give a straight line with an intercept equal to $\Delta G^0_{m,head\ group} + \Delta G^0_{m,CH_3}$ and a slope equal to $\Delta G^0_{m,CH_2}$. Since $\Delta G^0_{m,CH_3}$ is independent of the chain length in a homologous series, differences in the intercept essentially reflected the reluctance of the head group to aggregate.

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Data obtained for [C_nMIm][Cl] series were compared with those described by Jungnickel *et al.*[17] They followed the same linear variation with $\Delta G^0_{m,CH_2} = -2.85\,kJ\,mol^{-1}$ (dotted line in Fig. 3). The $\Delta G^0_{m,CH_2}$ value is generally close to $-3.0\,kJ\,mol^{-1}$ since the transfer of a CH_2 group from water to the micelle is independent of the head-group structure.[28] The dashed line in Fig. 3 represented the variation ($\Delta G^0_{m,CH_2} = -2.85\,kJ\,mol^{-1}$) for [$C_n$MIm][Ibu] series. [$C_6$MIm][Ibu] and [$C_8$MIm][Ibu] followed the same linear variation of ΔG^0_m, while [C_4MIm][Ibu] showed a slight deviation from it. The intercept corresponding to $\Delta G^0_{m,head\ group} + \Delta G^0_{m,CH_3}$ was equal to -0.6 kJ mol^{-1} for [C_nMIm][Cl] series and to -10.6 kJ mol^{-1} for [C_nMIm][Ibu]. This confirms that imidazolium and ibuprofenate salts aggregate as ion pairs and it is consistent with the low ionization degree observed for these salts as compared to the parent chloride salts (Table 2).[28]

PGSE-NMR

Pulsed gradient stimulated echo NMR (PGSE-NMR) was used to determine self-diffusion coefficients of [C_4MIm][Ibu] and [C_8MIm][Ibu] in aqueous solutions. Interestingly, the presence of protons on both the cation and the anion allowed measuring the diffusion coefficients of both species D^{Ibu}_{meas} for the anion and D^{Im}_{meas} for the cation. For each species, the diffusion coefficients obtained from different protons were the same within ± 5%.

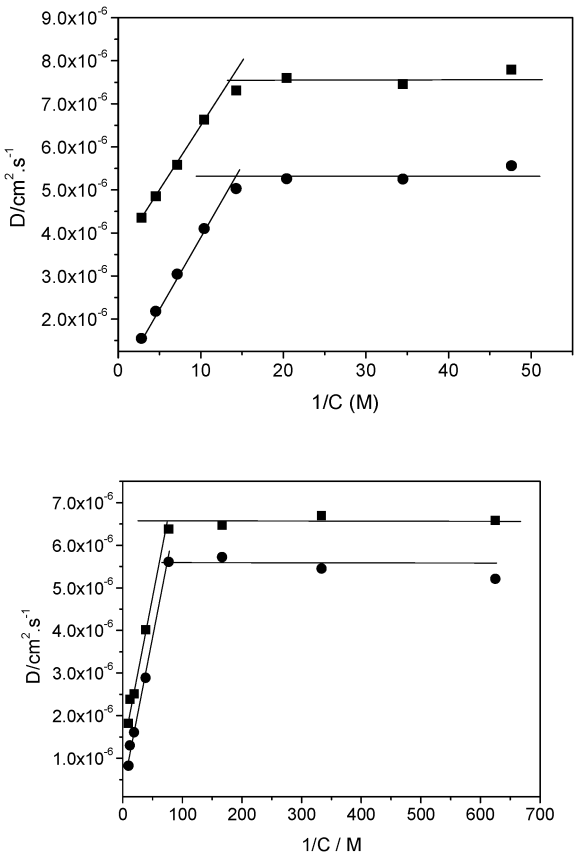

Fig. 4 Variation of self-diffusion coefficients (● D^{Ibu}_{meas}, ■ D^{Im}_{meas}) of [C_4MIm][Ibu] (top) and [C_8MIm][Ibu] (bottom) as a function of the reciprocal concentration at 25 °C.

Table 3 Monomer and micellar diffusion coefficients obtained by PGSE-NMR at 25 °C

Compound	CAC/mM	D^{Ibu}_{mon} [a]	D^{Im}_{mon} [a]	D^{Ibu}_{agg} [a]	D^{Im}_{agg} [a]
[C_4MIm][Ibu]	71	5.2 ± 0.2	7.4 ± 0.2	0.8 ± 0.6	3.6 ± 0.4
[C_8MIm][Ibu]	14	5.5 ± 0.1	6.5 ± 0.2	0.3 ± 0.3	1.2 ± 0.2

[a] 10^{-6}/cm^2 s^{-1}.

Fig. 4 depicts a plot of the measured diffusion coefficients D^{Ibu}_{meas} and D^{Im}_{meas} of [C_4MIm][Ibu] and [C_8MIm][Ibu] as a function of the reciprocal total surfactant concentration. This representation was chosen to analyze the results according to the pseudo-phase model.

In the low concentration range, the surfactant molecules were in dynamic equilibrium between monomeric and micellar states. If the exchange kinetics between the monomeric and micellar states was fast on the diffusion time scale, the measured diffusion coefficient D_{meas} could be expressed as:[34]

$$D_{meas} = D_{agg} + \frac{CAC}{C_t}(D_{mon} - D_{agg}) \text{ for } C_t > CAC \quad (5)$$

$$D_{meas} = D_{mon} \text{ for } C_t \leq CAC \quad (6)$$

where D_{mon} and D_{agg} represent the monomer and aggregates diffusion coefficients respectively, and C_t is the total surfactant concentration. Below the CAC, the pseudo-phase transition model accounted well for the fact that the measured diffusion coefficient was independent of the concentration and equal to the diffusion coefficient of monomers. Above the CAC, for concentrations sufficiently close to CAC, it was supposed that the free monomer concentration remained constant.[35] According to eqn (5), variation of D_{meas} against $1/C_t$ consisted of two straight lines and the point of intersection of these two lines was 1/CAC. CAC values obtained from the diffusion measurements for the cation and the anion were identical, confirming that they were both participating in the aggregates formation (Table 3). Furthermore, the CAC values were in good agreement with those obtained by other techniques (Table 2). As expected, below the CAC, diffusion coefficients appeared constant within the experimental error.

Below CAC, D^{Ibu}_{mon} of [C_4MIm][Ibu] and [C_8MIm][Ibu] was nearly identical, whereas D^{Im}_{mon} of [C_8MIm][Ibu] was lower than D^{Im}_{mon} of [C_4MIm][Ibu] as expected from the increase in the alkyl chain length. Micellar coefficients D_{mic} were obtained by introducing the values of CAC and D_{mon} in eqn (5). Fig. 4 reveals that diffusion coefficients of imidazolium and ibuprofenate decreased similarly upon aggregation, suggesting the formation of mixed micelles. It should also be noticed that the slowing down was more pronounced for [C_8MIm][Ibu], demonstrating easier aggregation in this case, due to the alkyl chains interactions.

The fact that D_{agg} differed from one species to another (it was higher for Im than for Ibu) suggested that the residence time of the Ibu anion in the micelle was larger than that of the Im cation. This means that the composition of the micelles was richer in Ibu than in Im.

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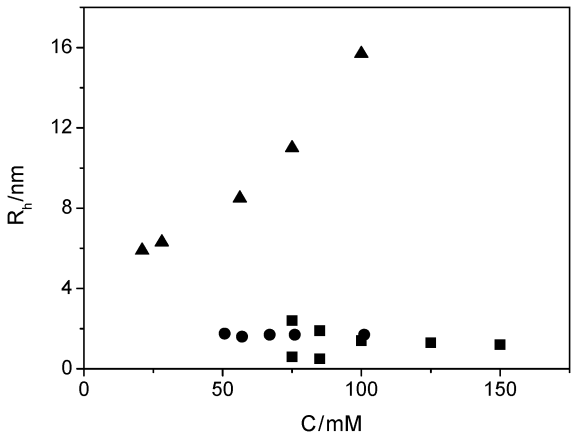

Fig. 5 Hydrodynamic mean radius of ■ [C_4MIM][Ibu], ● [C_6MIM][Ibu] and ▲ [C_8MIM][Ibu] with concentration above CAC.

Diffusion coefficients D_{agg} arising from NMR were used to determine the hydrodynamic radius R_h according to Stokes–Einstein equation:

$$D_{agg} = \frac{kT}{6\pi\eta R_h} \quad (7)$$

where T is the absolute temperature, k the Boltzmann constant, η the solvent viscosity ($\eta(D_2O)$ = 1.0511 cP at 300 K).

For [C_4MIm][Ibu], R_h calculated from D^{Ibu} was 2.7 nm, whereas that calculated from D^{Im} was 0.6 nm. For [C_8MIm][Ibu], R_h calculated from D^{Ibu} was 7.5 nm, whereas that calculated from D^{Im} was 1.8 nm. These results show that the exact hydrodynamic radius of our complex aggregates can be hardly assessed from NMR data.

Dynamic light scattering

Dynamic Light Scattering (DLS) studies were carried out on the [C_nMIm][Ibu] series above the CAC. Fig. 5 displays the variation of the hydrodynamic radius with concentration. At concentrations close to the CAC, two populations were observed for [C_4MIm][Ibu], a very small one with $R_h \approx 0.5$ nm and another one with R_h = 1.5–2 nm. On increasing concentration, only one population was observed, with R_h = 1.2 nm. This suggested that aggregates were not stable close to the CAC. For [C_6MIm][Ibu], only one population was observed just above the CAC with R_h = 1.7 nm. Finally, an exponential increase in the mean hydrodynamic radius was observed with [C_8MIm][Ibu], which ranged from 6 to 16 nm. The evolution of the hydrodynamic radius is typical for micelles growing from spheres to cylinders. The latter radius was larger than those usually obtained for micelles which generally range from 2 to 10 nm, and suggested the formation of different types of aggregates. However, as pointed by Leaist *et al.*,[36] DLS measurements have to be considered cautiously in the case of ionic surfactants. Actually, this technique measures surfactant mutual diffusion coefficients, including both contributions from micelles and relatively mobile free surfactant monomers. Due to the catanionic behaviour of [C_nMIm][Ibu] solutions, complex aggregated structures are expected, such as mixed-micelles and vesicles.[37] This could also explain the difficulty of correlating these results with those arising from PGSE-NMR.

Conclusion

The surfactant properties of 1-alkyl-3-methylimidazolium ILs (n = 4, 6, 8) containing an ibuprofenate anion have been investigated using various techniques. The CAC values turned out to be very low compared to the parent imidazolium chlorides. This behaviour was ascribed to the surfactant activity of ibuprofenate anions, through the formation of catanionic pairs between ibuprofenate and imidazolium ions. Actually, determination of surface parameters, Gibbs energy of aggregation and diffusion coefficients allowed concluding that both ions were involved in the aggregates. These aggregates were richer in ibuprofenate anions. The here observed catanionic behaviour took place with short alkyl chains on the imidazolium cation, even though it was shown to be reinforced on increasing the alkyl chain length. This result is all the more interesting as catanionic pairing is usually observed only with long alkyl chains ($n > 8$). Further studies as SANS analysis are needed to determine the exact shape of the aggregates. The use of these ILs as structuring agents in ionogels synthesis is currently under investigation.

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