New catanionic surfactants based on 1-alkyl-3-methylimidazolium alkylsulfonates, $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$: mesomorphism and aggregation[†]

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Anionic and cationic alkyl-chain effects on the self-aggregation of both neat and aqueous solutions of 1-alkyl-3-methylimidazolium alkylsulfonate salts ($[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$; n = 8, 10 or 12; m = 1 and n = 4 or 8; m = 4 or 8) have been investigated. Some of these salts constitute a novel family of pure catanionic surfactants in aqueous solution. Examples of this class of materials are rare; they are distinct from both mixed cationic-anionic surfactants (obtained by mixing two salts) and gemini surfactants (with two or more amphiphilic groups bound by a covalent linker). Fluorescence spectroscopy and interfacial tension measurements have been used to determine critical micelle concentrations (CMCs), surface activity, and to compare the effects of the alkyl-substitution patterns in both the cation and anion on the surfactant properties of these salts. With relatively small methylsulfonate anions (n = 8, 10 and 12, m = 1), the salts behave as conventional single chain cationic surfactants, showing a decrease of the CMC upon increase of the alkyl chain length (n) in the cation. When the amphiphilic character is present in both the cation and anion (n = 4 and 8, m = 4 and 8), novel catanionic surfactants with CMC values lower than those of the corresponding cationic analogues, and which exhibited an unanticipated enhanced reduction of surface tension, were obtained. In addition, the thermotropic phase behaviour of $[C_8H_{18}mim][C_8H_{18}SO_3]$ (n = m = 8) was investigated using variable temperature X-ray scattering, polarising optical microscopy and differential scanning calorimetry; formation of a smectic liquid crystalline phase with a broad temperature range was observed.

Introduction

The term 'ionic liquid' refers to the liquid state of matter exhibited by salts at, close to, or below 100 °C. Ionic liquids are typically organic salts, of which examples with 1,3-dialkylimidazolium cations have been the most extensively studied.¹ Computational² and direct experimental methods³ have shown that ionic liquid systems tend to exhibit bulk isotropy yet present relatively strong local structure correlations.

Structural modification of the individual ion components of an ionic liquid by, for example, increasing the length of alkylsubstituents in 1-alkyl-3-methylimidazolium cations can lead to increases in the structural anisotropy of the liquid with microbiphasic separation. In extremis, with decyl- or longer substituents, liquid crystalline phases can be formed. For instance, the thermotropic mesomorphism of 1-alkyl-3-methylimidazolium⁴ and quaternary phosphonium⁵ salts have been

widely studied. Evidence from molecular dynamics simulations⁶ and small-angle X-ray diffraction⁷ suggests that this separation of domains occurs even in ionic liquids with relatively short butyl, hexyl, and octyl substituents, although the lifetimes of some domains may be relatively small. It has also been recently reported that 1,3-dimethylimidazolium dodecylsulfonate exhibits a thermotropic liquid crystalline smectic A phase and that the phase behaviour can be tuned by modification of the substitution patterns on the imidazolium cation.⁸

The considerable interest in ionic liquid crystals is a consequence of the wide spectrum of potential applications: in sol-gel synthesis of macro and mesoporous silicas, hydrothermal synthesis of γ -alumina, preparation of gold and silver nanoparticles, or as stabilisers for suspension polymerisation.⁹

It has been anticipated that ionic liquid materials may have a significant potential impact on the field of surfactants.¹⁰ Three possible directions for development and application, namely using ionic liquids as solvents, surfactants, or as salt additives have been discussed. Ionic liquids can be added as co-surfactants or hydrotropes to aqueous solutions of common surfactants.^{11,12} They can be used directly as media for dissolution of many different common ionic and nonionic surfactants,¹³ amphiphilic polymers¹⁴ or ionic liquids.¹⁵ Moreover, due to the obvious structural similarities to conventional cationic surfactants, many ionic liquids exhibit surfactant-like

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| | Compound | n | т | n+m |
|---|----------|----|---|-----|
| | 1 | 8 | 1 | 9 |
| | 2 | 10 | 1 | 11 |
| | 3 | 12 | 1 | 13 |
| $N = N = C_n H_{2n+1} \left[C_m H_{2m+1} - SO_3 \right]$ | 4 | 4 | 4 | 8 |
| | 5 | 4 | 8 | 12 |
| | 6 | 8 | 4 | 12 |
| | 7 | 8 | 8 | 16 |

Fig. 1 General structure of 1-alkyl-3-methylimidazolium alkylsulfonate ionic liquids ($[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$); m + n is the sum of the number of carbon atoms in the two alkyl-substituents.

behaviour and similar aggregation phenomena in aqueous solution.^{10,11} Changes in the aggregation behaviour of a range of 1-alkyl-3-methylimidazolium halide, hexafluorophosphate and bis{(trifluoromethyl)sulfonyl}imide salts in aqueous solutions as a function of the alkyl chain length, concentration and nature of the anion have recently been reported by our group,^{10,11} and by others.¹⁶ The aggregation behaviour of aqueous solutions of dodecyl-substituted pyrrolidinium, pyridinium and piperidinium bromide salts has also been examined and compared as a function of head group type.¹⁰

1-Alkyl-3-methylimidazolium alkylsulfonate salts (see Fig. 1) are useful examples of ionic liquids in which it is simple to systematically vary the structure of both the cations and the anions by changing the number of carbons (n and m) of the two alkyl chains. The physical properties of a range of 1-alkyl-3-methylimidazolium alkylsulfonates with alkyl groups containing six or less carbon atoms in either the cation or anion and with a total of less than eleven carbon atoms in the two alkyl chains have been investigated recently.¹⁷

We report here the results of investigations of the structural and surfactant properties of seven 1-alkyl-3-methylimidazolium alkylsulfonate salts (Fig. 1) from two subsets of the $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$ (n + m) matrix: (a) salts with n = 8, 10 or 12 and m = 1, and (b) those with n = 4 or 8 and m = 4 or 8. In all cases, the total number of carbon atoms in the two side chains, n + m, is eight or more. By investigating the properties of these materials within this 2-D array of alkyl chains, it is possible to know whether systematic changes to the cation and anion structures induce serial (thus, merely cumulative) or synergistic variations in the structure–property relationship. In addition, the thermotropic mesomorphism of the catanionic 1-octyl-3-methylimidazolium octylsulfonate (7, n = m = 8) salt in the neat anhydrous state has been investigated.

The salts herein investigated have an amphiphilic character in either or both the cation and anion, and the results presented below demonstrate how these materials have exceptional performance characteristics which are comparable to those of mixed cationic–anionic surfactants¹⁸ (pseudocatanionic surfactants), as well as gemini¹⁹ surfactants.

Experimental

Materials

1-Methylimidazole (\geq 99%), dichloromethane, ethyl ethanoate, 1-butanesulfonyl chloride (\geq 98%), 1-octanesulfonyl chloride

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(98%), 1-butanol (\geq 99.8%), 1-octanol (\geq 99%), 1-decanol (\geq 99%), 1-dodecanol (\geq 99%), and trimethylamine (\geq 99%) were purchased from Aldrich. Methyl methanesulfonate (99%) was purchased from Acros Organics. 1-Methylimidazole was distilled from sodium hydride prior to use; all other reagents and solvents were used as received. Doubly-distilled deionised water was obtained from a Millipore Milli-Q water purification system (Millipore, USA). Pyrene (Fluka, Germany, 99%) was recrystallised from benzene.

¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker Avance spectrometer DPX 300, using CDCl₃ as solvent.

Synthesis

The seven ionic liquids used in this study (Table 1) were synthesised following the general procedure described below.

Alkyl alkylsulfonates ($C_nH_{2n+1}OSO_2C_mH_{2m+1}$). A solution of triethylamine (1.1 mol) and the desired alcohol ($C_nH_{2n+1}OH$; n = 4, 8, 10, 12) (1.1 mol) in dichloromethane (430 cm³) was cooled in an ice-bath. The respective alkylsulfonyl chloride ($C_mH_{2m+1}SO_2Cl$, m = 1, 4, 8; 1 mol. eq.) dissolved in dichloromethane (100 cm³) was added dropwise to the cooled, rapidly stirred reaction mixture while maintaining the temperature at 0 °C. The reaction mixture was then stirred for several hours at room temperature, filtered, and the solvent removed under reduced pressure. The filtrate was purified by fractional vacuum distillation to yield alkyl alkylsulfonate esters as transparent, colourless or slightly yellow liquids, except dodecylmethanesulfonate which was obtained as a colourless solid. All products were characterised by ¹H NMR spectroscopy.

1-Alkyl-3-methylimidazolium alkylsulfonates. A solution of freshly distilled alkylsulfonate ester $(C_nH_{2n+1}SO_3C_mH_{2m+1})$ (1.1 mol. eq.) and 1-methylimidazole (1 mol. eq.) in ethyl ethanoate (150 cm³) was heated under reflux with stirring overnight. The crude product formed as a dense layer and was removed, washed six times with ethyl ethanoate and any remaining solvent was removed under reduced pressure to give the corresponding ionic liquids $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$ (Fig. 1 and Table 1).

All the salts 1–7 (see Table 1) were characterised by mass spectrometry and by ¹H and ¹³C NMR spectroscopy (see ESI†) and showed no impurities other than the presence of residual water (detected independently by Karl-Fischer analysis). All samples were then thoroughly degassed and

Table 1 Physical data collected for the $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$ salts 1–7; critical micelle concentration (CMC, mM) measured by interfacial tension, IFT, and fluorescence emission of pyrene, Fluor; absorption efficiency, pC_{20} , effectiveness of surface tension reduction, Π_{CMC} (mN m⁻¹), transition temperatures (°C) measured from the onset to the peak by DSC, and transition enthalpy (kJ mol⁻¹)

| Compound | п | т | CMC/mM | | | | | | | |
|----------|----|---|--------|-------|-----------------|---------------|---|-------------------------|------------------------|--------------------------------|
| | | | IFT | Fluor | Mean | pC_{20}^{a} | $\Pi_{\rm CMC}{}^b$ /mN m ⁻¹ | Transition ^c | $T/^{\circ}\mathbf{C}$ | $\Delta H/\ { m kJ\ mol}^{-1}$ |
| 1 | 8 | 1 | 220 | _ | 220 | 1.0 | 29.0 | $C \rightarrow iso$ | 40.3 | 39.3 |
| 2 | 10 | 1 | 60 | 65 | 62.5 ± 2.5 | 1.5 | 28.5 | $C \rightarrow iso$ | 53.6 | 40.5 |
| 3 | 12 | 1 | 14 | 19 | 16.5 ± 2.5 | 2.1 | 28.5 | $C \rightarrow iso$ | 64.9 | 47.5 |
| 4 | 4 | 4 | | | _ | 0.4 | _ | $C1 \rightarrow C2$ | 24.0 | 10.5 |
| | | | | | | | | $C2 \rightarrow iso$ | 60.1 | 18.3 |
| 5 | 4 | 8 | 135 | 130 | 132.5 ± 2.5 | 1.6 | 40.0 | $C \rightarrow iso$ | 56.3 | 29.1 |
| 6 | 8 | 4 | 140 | 155 | 147.5 ± 7.5 | 1.6 | 28.5 | $C \rightarrow iso$ | 54.1 | 32.3 |
| 7 | 8 | 8 | 12 | 17 | 14.5 ± 2.5 | 2.9 | 43.7 | $C1 \rightarrow C2$ | 68.4 | 22.5 |
| | | | | | | | | $C2 \rightarrow S_A$ | 78.9 | 28.2 |
| | | | | | | | | $S_A \rightarrow iso$ | 114.9 | 2.7 |

^{*a*} pC_{20} defined as the negative logarithm to the base 10 of the concentration of amphiphilic molecules required to reduce the surface tension of the pure solvent by 20 mN m⁻¹. ^{*b*} Effectiveness of the surface tension reduction, Π_{CMC} (defined as $\Pi_{CMC} = \gamma_0 - \gamma_{CMC}$, where γ_0 is the surface tension of the pure solvent (water), and γ_{CMC} is the surface tension of the solution at the CMC). ^{*c*} C is the crystal form, C1 and C2 designate lower and upper crystal phases when a crystal–crystal transition is observed, S_A is smectic liquid crystalline phase and iso designates the isotropic liquid state.

dried under vacuum (*ca.* 0.1 Pa) at moderate temperatures (60–80 $^{\circ}$ C) for typically 24 h before use.

Characterisation

Differential scanning calorimetry (DSC). Phase transition temperatures were measured using a TA Instruments DSC 2920 in modulated DSC mode. Cooling was accomplished by using a refrigerated cooling system capable of controlling the temperature down to 220 K. Dry dinitrogen gas, with a flow rate of approximately 20 cm³ min⁻¹, was purged through the DSC cell. Transition temperatures were determined from the onset points by initially heating the sample from room temperature at a rate of 10 °C min⁻¹ to beyond the clearing point, followed by cooling at a rate of 5 °C min⁻¹ to below the crystallisation temperature. The cooling–heating cycle was repeated three times. The transition temperatures and enthalpies of the transitions obtained from the second and subsequent cycles were reproducible.

Polarising optical microscopy (POM). Microscope observations were made using an Olympus BX50 microscope equipped with a Linkam TH600 hot stage and TP92 temperature controller. Neat samples were examined in the form of fine crystals placed between thin round glass plates. Contact experiments between the salts and water were performed using the Lawrence penetration experiment²⁰ by placing a few crystals of the salt between two glass slides and introducing a small drop of water in contact with the surfactant through capillary action.

X-Ray diffraction (XRD). X-Ray diffraction data were collected using a Siemens D5000 powder diffractometer equipped with a sealed Paar heating stage with Cu K α X-rays ($\lambda = 1.542$ Å). Data were recorded from between 2 and 30° in steps of 0.05° over the temperature range 25 to 120 °C.

Fluorescence spectroscopy. For the fluorescence measurements, aqueous stock solutions of salts 1–7 were prepared using water containing 1.74×10^{-6} M pyrene, and all studied solutions were prepared from the stock solutions, by diluting

with the same pyrene aqueous solution. Pyrene was used as a fluorescent probe to ascertain the onset of the aggregation of the ionic liquids in water. Steady-state fluorescence spectra of the pyrene-containing solutions in 1 cm quartz cuvettes were recorded at room temperature with a Cary Varian Eclipse Fluorescence Spectrometer collected at a 90° angle. Excitation was set to a wavelength of 337 nm. The intensities of the first (I1) and third (I3) vibronic bands in the pyrene emission spectra located around 373 and 384 nm, respectively, were measured and used to determine the ratio I3/I1.

Interfacial tension (IFT). Interfacial tensions were measured using a Drop Shape Analysis Tensiometer (Contact Angle System OCA, Carl Stuart Ltd) working in the pendant drop mode at a constant temperature of 23 ± 2 °C. IFT is derived from the fit of the pendant drop profile, and care was taken to ensure that the apparatus was calibrated with several solvents of known IFT in the range of interest. The drops were left to equilibrate close to the rupture point and at least three consistent measurements per solution were recorded.

Results and discussion

and solution behaviour The thermal of seven $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$ salts (1–7) have been investigated. The salts comprised two sets; a series of three salts (1-3) with methylsulfonate (m = 1) anions and different alkyl chain lengths on the cation (n = 8, 10, and 12, respectively), and a matrix of four salts with intermediate length of alkylsubstituents on both cation and anion, 4 (n = m = 4), the cross terms 5 (n = 4, m = 8) and 6 (n = 8, m = 4), and 7 (n = m = 8). Thermophysical data for two of the salts, 1 and 2, have been previously reported,¹⁷ whereas the remainder (3-7) are new and were synthesised and characterised here for the first time.

All salts were readily soluble in water at room temperature, and produced surface active solutions. The CMCs of the salts in water were determined at room temperature using both interfacial surface tension and fluorescence spectroscopy.

Self-aggregation of neat $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$ salts and thermal behaviour

The thermal behaviour of the salts was investigated using modulated DSC. First order endothermic transition temperatures, enthalpies, and assignments from the onset temperatures of the heating cycle from the second and subsequent cycles are given in Table 1. On the cooling cycles, all salts showed thermal hysteresis and supercooling for the liquid-to-crystal transition. For 7, the liquid crystalline phase to crystal transition shows an average temperature depression of 15 °C. Similar phenomena were observed in the case of crystal-crystal transformations.

1–6 melted directly to form ionic liquids at less than 100 °C; **4** (n = m = 4) also showed a reversible crystal–crystal phase transition at 24 °C before melting at 60 °C. 7 (n = m = 8) exhibits a crystal–crystal transition at 70 °C and then melts to a smectic liquid crystal phase at 79 °C, clearing to the isotropic liquid (iso) at 115 °C. Confirmation of the character of the DSC transitions was made by comparison with observations from hot-stage polarising optical microscopy; and, for 7, also by small-angle X-ray diffraction to elucidate the nature of the mesophase formed.

Upon heating a crystalline sample of 7 from ambient temperature on the hot-stage of the polarising optical microscope, a crystal-crystal transition was observed consistent with the DSC data, followed by melting of the solid into the enantiotropic liquid crystalline phase, which cleared to the isotropic liquid at 115 °C. Cooling from the isotropic liquid yielded the phase sequence, iso $\rightarrow S_A \rightarrow C2 \rightarrow C1$. The mesophase forms a dark homeotropic texture under crossed polarisers, both on heating and cooling from the isotropic liquid, characteristic of the smectic A bilayer structure commonly found for neat amphiphilic salts, especially for the imidazolium-type ionic liquid crystals.⁴

X-Ray diffraction data were collected for 7. The sample, initially in the crystalline state at ambient temperature, was heated to the liquid state at 120 °C; then, the temperature was decreased to 40 °C in 10 °C steps, and equilibrated for 20 min at each temperature. Both phase transitions iso $\rightarrow S_A$ and $S_A \rightarrow C2$ were observed with a significant degree of supercooling such that the iso $\rightarrow S_A$ transition occurred between 110–100 °C and the $S_A \rightarrow C2$ transition between 60–50 °C. This is to be compared with the corresponding transition temperatures in the heating cycle of 115 and 79 °C, respectively. Typical X-ray diffraction patterns for each phase region are shown in Fig. 2a with polarising optical micrographs of the three phases shown in Fig. 2b.

The initial crystal form (C1) has a highly ordered layer structure, with a strong small-angle diffraction peak $\langle 100 \rangle$ at $2\theta = 3.42^{\circ}$, corresponding to a layer spacing of 25.81 Å. A second set of intense peaks in the wide angle region at *ca*. 13.12, 16.36, and 19.64° show a high degree of structure in the other two dimensions.

In the isotropic region, 7 shows a small residual peak in the small-angle region at 6.5° and a characteristic broad diffraction band centred around 22° (~4 Å) consistent with fully mobile liquid alkyl chains. The S_A mesophase region is characterised by the presence of a sharp peak in the low angle region $(2\theta = 2-5^{\circ})$ and a broad band centred at 22°, consistent with fully mobile alkyl chains. The change in the layer spacing (*d*), determined from the position of the most intense peak in the low angle region, as a function of temperature through the different phase regions is shown in Fig. 3.

In the S_A phase, the layer spacing *d* decreases from 23.11 Å at 60 °C to 21.75 Å at 100 °C, corresponding to an interlayer contraction of 0.034 Å K⁻¹ consistent with the decreasing mobility of the alkyl chains as temperature is reduced. Unusually, the layer spacing in the mesophase is larger than



Fig. 2 Development of the smectic (S_A) and two consecutive solid crystalline (C2 and C1) phases for 7 (n = m = 8) on cooling from the molten isotropic (iso) state: (a) XRD data in which the iso spectrum is scaled by 10×; and (b) photomicrographs of 7 in the three phase regions; C1 (20 °C), C2 (72 °C) and S_A (82 °C).

27 26 25 ¥1 p 23 22 C1 C2 iso 21∟ 20 40 80 100 120 60 Temperature /°C

Fig. 3 Change in the layer spacing (*d*) of 7 in the liquid crystalline (S_A, \bigcirc) and two crystalline phase $(C1, \diamondsuit; C2, \Box)$ regions as a function of temperature, determined from the position of the peak at the lowest value of 2θ in the XRD data.

the sum of the lengths of the two amphiphiles, and suggests the formation of a double-bilayer structure. This may be a result of the high density packing of the surfactant headgroups (calculated from the surface tension data, *vide infra*). Further cooling leads to crystallisation from the S_A to the crystalline C2 phase, this transition being characterised by a discontinuous increase in *d* (from *ca*. 23.11 Å at 60 °C in the S_A phase to 25.96 Å at 50 °C in the C2 crystalline phase, see Fig. 3) and the appearance of well defined diffraction peaks in the wide angle region that support the formation of a crystalline phase. In contrast to the mesophase region, the *d*-spacing in the crystalline phases shows a typical contraction on cooling (0.015 Å K⁻¹).

The C2 \rightarrow C1 transition was not observed directly when samples were cooled *in situ* on the diffractometer hot stage. This is, in part, due to an absence of active cooling in the diffractometer which limits the effective minimum temperature that could be achieved in a cooling cycle to *ca*. 40 °C. In order to demonstrate that the C2 \rightarrow C1 transformation is enantiotropic, a sample of **7** was heated externally until molten, then allowed to cool to room temperature and was then left to stand at room temperature overnight. The powder diffraction pattern subsequently measured was consistent with that collected on the initial crystalline sample prepared.

$Self-aggregation \ of \ neat \ [C_8H_{17}mim][C_8H_{17}SO_3] \ (7) \ as \ predicted \ by \ molecular \ simulations$

Preliminary simulation results at 400 K of $[C_8H_{17}mim]$ -[$C_8H_{17}SO_3$] (performed specifically at this temperature to match the bulk isotropic liquid phase of 7) reveal a nano-segregated structure (Fig. 4) similar to that found in other ionic liquids with significant (large) low-charge density regions:²¹ a polar network (coloured red for the positively charged, and blue for negatively charged groups), permeated by non-polar regions



Fig. 4 Snapshot of a simulation box containing 396 ions of $([C_8H_{17}mim][C_8H_{17}SO_3])$ at 400 K. The application of a coloring code enables one to identify the positively charged (*blue*), negatively charged (*red*) polar and nonpolar (*green*) domains that form the nano-segregated structure of the bulk isotropic liquid phase of the ionic liquid. The yellow lines—separated by ~20 Å—are guides to the eye that help to recognize the partially layered distribution of the polar liquid network. Details concerning the molecular dynamics simulations can be found elsewhere.⁶

(in green). The red polar regions are assigned both to the imidazolium and sulfonate headgroups, with the green non-polar areas corresponding to the alkyl chains. The relative sizes and distributions of the two regions, compared with other previously studied ionic liquids,^{2,6} are unusual. Due to the existence of two rather long alkyl chains in [C₈H₁₇mim]- $[C_8H_{17}SO_3]$, the polar network occupies a relative volume smaller than that of the non-polar regions and seems to be constrained to form thread-like or lamellar-like structures, some of which becoming almost parallel and showing a laver spacing of ca. 20 Å. This value is commensurate with that of d = 21.75 Å for the high temperature portion of the S_A phase, suggesting a pre-aggregation of the ionic liquid forming local structures, i.e., anticipation of the formation of a liquid crystal at lower temperatures. In other words, the simulations demonstrate that the tendency of 7 to form a structured liquid crystal mesophase is related to the nano-segregated nature of the ionic liquid already present in the bulk isotropic liquid phase, and to the interplay between the sizes and distributions of the two segregated domains (polar network versus non-polar region).

Self-aggregation of $[C_nH_{2n+1}mim][C_mH_{2m+1}SO_3]$ salts in aqueous solution

Contact experiments²⁰ (introducing a droplet of water into contact with the $[C_8mim][C_8SO_3]$ salt over the temperature range 25–80 °C) revealed a slight swelling of both the crystalline solid and the supercooled mesophase domains on addition of water, rapidly followed by dissolution to form a fluid homogeneous solution as the contacting aqueous phase penetrated the salt. Thus, 7 showed no tendency to form lyotropic mesophases, despite the formation of a neat, anhydrous smectic (lamellar) thermotropic mesophase.

Self-aggregation of the salts in water over the lower concentration regimes was studied by surface tension and fluorescence spectroscopy with pyrene as a probe molecule. The air-water interfacial tension of aqueous solutions of the salts 1-7 was measured as a function of concentration. Surfactant aggregation in solution leads to a decrease in the surface tension with increasing concentration, followed by a change to almost constant surface tension as the CMC is reached and the concentration of surfactant molecules in solution remains static. Data for the salts, 1-3, 6 and 7, are shown in Fig. 5a and b. The surface tension data were used to determine the CMC from the intersection of a linear extrapolation of the two differing regions. The two adsorption parameters: efficiency of adsorption, pC_{20} , (defined as the negative logarithm to the base 10 of the concentration of amphiphilic molecules required to reduce the surface tension of the pure solvent by 20 mN m⁻¹) and the effectiveness of the surface tension reduction, $\Pi_{\rm CMC}$, (defined as $\Pi_{CMC} = \gamma_0 - \gamma_{CMC}$, where γ_0 is the surface tension of the pure solvent (water), and γ_{CMC} the surface tension of the solution at the CMC) were calculated from the data.²²

Fluorescence spectroscopy, using pyrene as a molecular probe, was used to investigate the polarity of the probe domains in the solutions as a function of surfactant concentrations. By comparing the intensities of the first, I1, and third, I3, vibronic bands of the pyrene emission spectrum, changes to the local environment of the probe molecule, and hence the bulk solution, can be monitored. The intensity ratio I3/I1 varies as a function of the polarity of the pyrene environment and increases with decreasing solvent polarity. Fig. 5c and d show the pyrene response (I3/I1) for the aqueous solutions of the salts, **1–3**, **6** and **7**, as a function of concentration. The CMC is determined from the intersection points between that plateau and the descending part of the fluorescence profile.

Experimental CMC values are presented in Table 1, calculated from both interfacial tension and fluorescence experiments. The data from the two approaches are in good agreement.

The decrease in the CMC of aqueous solutions of 1-3 containing a methylsulfonate anion is a consequence of the increased alkyl chain in the cation and follows the empirical rule that the CMC decreases by a factor of two for each CH₂ group added to the alkyl chain of a single chain ionic surfactant, Fig. 5a. The dependencies, and CMC values, found here for salts 1-3 are almost identical to those reported for the corresponding 1-alkyl-3-methylimidazolium chloride systems in water.¹¹ This fact indicates that the chloride and methylsulfonate anions are equally efficient in decreasing the electrostatic repulsion between head groups and, consequently, have very similar values of adsorption efficiency and effectiveness of the surface tension reduction.

The solutions of the short alkyl chain ionic liquid 4 (n = m = 4) showed reduced surface tensions with increasing concentration of ionic liquid. However, at concentrations up to 2 M in solution no aggregation behaviour was observed (data are not shown).

The influence of increasing alkyl chain length in the anion on the CMC is shown in Fig. 5b comparing the 1-octyl-3methylimidazolium salts **1**, **5** and **7**. A non-linear dependence is found. For comparison purposes, the surface tension of the



Fig. 5 Determination of CMC by surface tension (a) and (b), and fluorescence (c) and (d) for the alkylsulfonate salts: $\mathbf{1}$ ($n = 8, m = 1; \blacktriangle$), $\mathbf{2}$ ($n = 10, m = 1; \blacklozenge$), $\mathbf{3}$ ($n = 12, m = 1; \blacklozenge$), $\mathbf{6}$ ($n = 8, m = 4; \bigcirc$), and $\mathbf{7}$ ($n = m = 8; \blacksquare$), and for comparison [C₁₀H₂₁mim]Cl (\Box).¹¹

aqueous solution of 6 (n = 4, m = 8) as a function of concentration was measured as well and showed almost identical aggregation behaviour to the corresponding cross-term 5 (n = 8, m = 4).

Fig. 5a and b clearly illustrate that (i) increasing the alkyl chain length in the cation is the most efficient way to decrease CMC values, and (ii) increasing the alkyl chain length in the anion (along with long alkyl chain in the cation) leads to lower CMCs and, more significantly, to higher effectiveness in surface tension reduction.

In common with the previously reported fluorescence studies on 1-octyl-3-methylimidazolium chloride in water,¹¹ the I3/I1 ratios for solutions of 1 show the typical increase with increasing surfactant concentration in solution indicating the formation of hydrophobic domains; however, a plateau is not reached. This may be due to the progressive dense packing of monomers in elongated aggregates without the formation of a well defined micellar structure. For 7 (n = m = 8), the plateau region of the I3/I1 ratio is significantly higher than that of the single chain surfactants (1–3) and implies the formation of micellar aggregates with a different structure, probably cylindrical or lamellar rather than spherical. Further investigation by light scattering and cryo-TEM techniques are required in order to clarify whether dense packed micelles, or other type of aggregates are formed.

Surface adsorption of surfactants

The lowering of the surface tension γ is a consequence of the increased concentration of surfactant at the air–water surface. At concentrations greater than that of the CMC, the interfacial composition and consequently the chemical potential change only slightly.²³ Values for the efficiency of adsorption at the surface (pC₂₀) and effectiveness of surface tension reduction (Π_{CMC}) calculated in each case from the change in, and absolute values of, surface tension as a function of surfactant concentrations are listed in Table 1. The salts **1–3** (with methylsulfonate anions) show an increase in pC₂₀ with increasing alkyl chain length, with only a small variation in

the final value of Π_{CMC} between them. This tendency was previously described for classical cationic surfactants.²²

In contrast, it was observed that both pC_{20} and Π_{CMC} increase with the sum of the cation and anions alkyl-substituent carbon atoms, for **5**, **6** and **7**. So that, on increasing the alkyl-chain in the cation and the anion in unison, substantial surface tension reductions are observed, see for example, Fig. 5b.

In order to explore whether the two structural variations in the salts, namely changing the lengths of the alkylsubstituents on the cation and anion, lead to any obvious cooperativity effects on the surface activity, the CMC, pC_{20} and Π_{CMC} data were examined as a function of the sum of the number of carbons on the two alkyl chains, n + m. The trends are shown in Fig. 6. The CMC values show as distinct sets for the cationic and catanionic surfactants, with the CMC varying by approximately the same amount (slope of the line) with n + m for the two sets. pC_{20} varies proportionally with n + mirrespective of the relative lengths of the two alkyl-chains contribution to the parameter. The Π_{CMC} parameter also shows two separate sets of data: for the (i) cationic surfactants, Π_{CMC} is invariant with n + m, and for the (ii) catanionic systems, Π_{CMC} increases with n + m.

It should be noted that each molecule of catanionic surfactant yields two surface active monomers on dissolution. This is the reason why, for the same concentration of surfactant, a much lower value of surface tension and higher absorption efficiency, pC_{20} , were obtained for 7 in comparison to 1.

 Π_{CMC} , the effectiveness parameter,²² is important for surface activity and reflects the detergency, foaming, emulsification, and wetting properties of surfactants. In the case of single chain ionic surfactants, the repulsion between polar head groups inherently establishes a limit to the dense packing of amphiphiles at the interface. In contrast, the surface tension reduction is dramatically increased for those surfactants containing both amphiphilic cations and anions. Since both the cations and anions incorporate hydrophobic alkyl chains, they both take part in the surface monolayer formation. The



Fig. 6 CMC (left, with error bars arising from the two results derived from IFT and fluorescence measurements), pC_{20} (middle) and Π_{CMC} (right) plotted as a function of n + m, the total number of carbons in the two alkyl-substituents in the 1-alkyl-3-methylimidazolium alkylsulfonate. Data for the methylsulfonate systems (m = 1) are shown as circles and the remainder ($m \neq 1$) as squares.

net electrostatic attraction between the positively and negatively charged amphiphile head groups, facilitated by van der Waals attractions between hydrophobic alkyl chains, enhances the dense packing of monomers in the monolayer and, consequently, leads to lowering the surface tension in the plateau region. The magnitude of the reduction reflects the efficiency of packing at the interface. From the surface tension data, by assuming that for these low concentration regimes the interfacial structure at the surface is a monolayer, the minimum area per ionic liquid molecule, a_0 , can be calculated using the well known Gibbs equation.²² A very low value of 0.7 nm² per ionic pair was calculated for solutions of 7, demonstrating that, at the interface, the amphiphiles are extremely close-packed.

Closer packing increases the coherency of the interfacial film and this usually results in superior emulsifying and foaming properties. Additionally, for these catanionic surfactants, since they contain both cationic and anionic amphiphiles, they will be adsorbed at both negatively and positively charged surfaces, similar to zwitterionic surfactants. Much lower values of surface tension were obtained in the plateau region for 7 as compared with that for 1,3-didodecylimidazolium bromide,²⁴ which illustrates the dominance of the electrostatic effect over the combination of hydrophobic and van der Waals effects.

During the reviewing process of the current manuscript we became aware of the work by Santos and Baldelli²⁵ concerning 1-alkyl-3-methylimidazolium alkylsulfates in the neat state. These are also potentially interesting, catanionic ionic liquids, even though their thermal and chemical stabilities are inferior to those of their alkylsulfonate-based counterparts.¹⁷ Nonetheless, it is interesting to note that at high surfactant concentrations, *i.e.* above the CMC, the interfacial surface tensions measured here (shown in Fig. 5) approach those reported in ref. 25 for the structurally similar sulfate-based ionic liquids. This also suggests bulk aggregation of the surfactants at the air–liquid interface at high concentration.

Gemini surfactants,¹⁹ containing two, or more, hydrophilic head groups covalently connected, have been shown to have superior properties to traditional cationic or anionic surfactants with significantly reduced surface tensions at low concentrations. Gemini surfactants have many applications, for example as solubilisers of water-insoluble materials and as agents for removal of pollutants from water.²² 7 displays a high effectiveness parameter for reduction of surface tension, and has a CMC which is lower than those reported for comparable gemini surfactants with identical alkyl chain lengths.²⁶ Consequently, there is real potential to explore the design and preparation of new surfactants with lower CMCs and even greater efficiencies.

Low CMC values are also associated with reduced adverse responses to biological systems, since less material is required to achieve an equivalent performance. In addition, the aquatic toxicity of surfactants (and ionic liquids) has been shown to decrease with decreasing alkyl chain length, so new surfactants such as 7 with octyl substituents may prove to have significantly lower environmental impact than single-chain cationic surfactants with equivalent activity containing dodecyl or tetradecyl substituents.

Conclusions

The surfactant properties of 1-alkyl-3-methylimidazolium alkylsulfonate ionic liquid surfactants have been investigated. In general, the low melting points and high solubility in water combine to give materials with excellent surfactant characteristics. The ionic liquids with methylsulfonate anions (1-3, n = 8, 10, and 12) behave as conventional cationic surfactants, showing CMC values comparable with those of the corresponding imidazolium halide salts and having equivalent surface activity, reducing water-air interfacial tension from 72.5 to a minimum of ca. 44 mN m⁻¹.

In contrast, when an amphiphilic character is imparted into both the cation and anion, a synergistic packing effect appears to lead to the formation of novel catanionic surfactants with both CMC values lower than anticipated, and enhanced surface activity. The large effect on the surface tension is interpreted in terms of a cooperative effect with both cations and anions forming the interfacial layer.

Two features of these ionic liquids, low melting points and high water solubilities, were combined with a synergistic surfactant effect. This enhancement of properties obtained from the combination of two relatively poor surface active amphiphiles (1-octyl-3-methylimidazolium and octylsulfonate) provides great opportunities to develop new, molecularly simple yet functionally complex, modern high performance ionic surfactants that outperform gemini and zwitterionic surfactants. The presence of an amphiphilic structure, in which both the cation and the anion contain a hydrophobic chain, leads to significant surface tension reduction, as compared with structures in which both chains are appended to the same ion, or where there is only a single chain. An additional interesting feature in systems such as these is that the alkyl chains on the individual ions are relatively small which may improve biodegradability and lower the overall environmental and toxicological impact.

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