Surface active ionic liquids: Study of the micellar properties of 1-(1-alkyl)-3-methylimidazolium chlorides and comparison with structurally related surfactants

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A R T I C L E   I N F O

Article history:
Received 14 March 2011
Accepted 28 April 2011
Available online 10 May 2011

Keywords:
Surface active ionic liquids
1-Alkyl-3-methylimidazolium chlorides
1-Alkylpyridinium chlorides
Conductivity of micellar solutions
Isotermal titration calorimetry
Thermodynamic properties of micelle formation
Effect of temperature on micelle formation

A B S T R A C T

The impetus for the increasing interest in studying surface active ionic liquids (SAILs; ionic liquids with long-chain “tails”) is the enormous potential for their applications, e.g., in nanotechnology and biomedicine. The progress in these fields rests on understanding the relationship between surfactant structure and solution properties, hence applications. This need has prompted us to extend our previous study on 1-(1-hexadecyl)-3-methylimidazolium chloride to 1-(1-alkyl)-3-methylimidazolium chlorides, with alkyl chains containing 10, 12, and 14 carbons. In addition to investigating relevant micellar properties, we have compared the solution properties of the imidazolium-based surfactants with: 1-(1-alkyl)pyridinium chlorides, and benzyl (2-acylaminoethyl)dimethylammonium chlorides. The former series carries a heterocyclic ring head-group, but does not possess a hydrogen that is as acidic as H2 of the imidazolium ring. The latter series carries an aromatic ring, a quaternary nitrogen and (a hydrogen-bond forming) amide group. The properties of the imidazolium and pyridinium surfactants were determined in the temperature range from 15 to 75 °C. The techniques employed were conductivity, isotermal titration calorimetry, and static light scattering. The results showed the important effects of the interactions in the interfacial region on the micellar properties over the temperature range studied.

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1. Introduction

Ionic liquids, ILs, have generated an intense, and ever growing scientific and industrial interest because of their high polarity, chemical and thermal stability, and extremely low vapor pressure [1]. We concentrate here on imidazole-bearing ILs that carry long-chain alkyl groups. These are expected to be surface active (SAILs) this has been verified experimentally, e.g., for 1,3-dialkylimidazolium chlorides, bromides, and tetrafluoroborates [2–6].

The above-mentioned favorable characteristics of ILs are carried over to SAILs, as shown by the following representative examples of the applications of 1,3-dialkylimidazolium salts in the biomedical and nano-technological fields: inhibitors for acetylcholinesterase [7]; antibacterial, antifungal, and anti-cancer agents [8–10]; components of nanostructured particles [11–13]. These applications require understanding of the properties of their aqueous solutions, vide Tables SM-1 and SM-2 of Supplementary Material, as compared with those of “conventional” surfactants. Recently, we have investigated the micellar properties of the SAIL 1-(1-hexadecyl)-3-methylimidazolium chloride, C16MeMelmCl, in the temperature, T, range 15–75 °C. We have also compared the properties of its micellar solution with those of two (conventional) cationic surfactants that carry related structural moieties. The first is 1-(1-hexadecyl)pyridinium chloride, C16PyCl; this carries a heterocyclic head-group (pyridinium head-group, CONH(CH2)n, where A, Et, Bz stand for the acylamido group, CONH(CH2)2N2, ethyl and benzyl group, respectively. This carries an aromatic ring; its micellar properties have been explained based on the formation of direct- or water-mediated hydrogen bonding between the amide groups, plus hydrophobic interactions between its benzyl and the alkyl groups [14]. The molecular structures of the three surfactant series are depicted in Fig. 1.

Hydrogen bonding between the counter-ion and the relatively acidic H2 of the imidazolium ring is known to affect the properties of ILs [15], and is expected to be important for the formation and properties of micellar SAILs. In order to investigate the effects of the chain-length of the alkyl group on the micellar properties, we have extended our study to the C10, C12, and C14 members of the CnMelmCl and CnPyCl series, at T = 15–75 °C; the data for the corresponding amide group containing surfactants are published elsewhere [14]. (This comparative) approach had been employed before for the corresponding 1-hexadecyl surfactants [16] and
has shown to be very useful in explaining the relationship between the structure and properties of their micellar solutions. Using conductivity, we have calculated the critical micelle concentration, cmc, and the degree of counter-ion dissociation, ζmic. Application of Evans equation for the calculation of the latter parameter requires knowledge of the micellar aggregation number, Nagg [17], at different T. We have improved the relatively simple procedure employed before for carrying out this calculation [16], and demonstrate the validity of our approach by comparing theoretical and experimental results (static light scattering, SLS, measurements) in the temperature range from 15 to 45 °C. Values of the thermodynamic parameters of micellization, namely, the Gibbs free energy, ΔGmic; enthalpy, ΔHmic; entropy, ΔSmic; and heat capacity, ΔCp,mic, were calculated for the CnMeImCl and CnPyCl series, and the results were compared to those of the corresponding CnEtBzMe2Cl. The thermodynamic data of micellization are explained on the bases of effects on the micelle of the interactions in the interfacial region; the length of the alkyl group, and T.

2. Materials and methods

2.1. Materials

The reagents were purchased from Acros, Merck, or Tiririca Quimica (DF) and were purified as recommended elsewhere [18]. Repeated fractional distillation in a 50 cm long Vigreux column, under reduced pressure, was employed in order to purify 1-chloroalkanes; satisfactory purity was achieved (>99.9%) as shown by gas chromatographic analysis.

2.2. Equipment

The melting points were determined with IA 6304 apparatus (Electrothermal, London). For GC analysis we have employed Shimadzu 17A-2 gas chromatograph, equipped with an FID detector and Supelcowax 10 capillary column, or Shimadzu 14B/QP5050A GC/MS equipped with quadrupole analyzer. NMR spectra were recorded with Bruker DRX-500 NMR spectrometer (500.13 MHz for 1H); a Bruker Vector 22 spectrophotometer was employed for all the experiments. Elemental analyses were performed on Perkin-Elmer 2400 CHN apparatus at the Elemental Analyses laboratory of our Institute.

2.3. Surfactants

The surfactants CnMeImCl (n = 10, 12, 14, 16) and C16PyCl were available from previous studies [3,16]. We synthesized and purified CnPyCl (n = 10, 12, 14) by reacting pyridine (8.1 mL; 0.1 mol) with the corresponding 1-chloroalkane (21.8, 25.9, and 29.8 mL, for 1-chlorodecane, 1-chlorododecane, and 1-chlorotetradecane respectively; 0.11 mol) in 25 mL of toluene in a PTFE-lined stainless steel reactor for 16 h, under nitrogen pressure (15 atm), at 110 °C. The volatiles were removed under reduced pressure, the solid products were recrystallized several times from acetone and dried under reduced pressure, over P4O10, for at least 24 h. IR analyses (KBr pellet) have shown that the products do not contain water of hydration, unlike the commercially available C12PyCl and C16PyCl, which are monohydrates.

1-(1-Decyl)pyridinium chloride: (53%) mp 38–39 °C (synthesis given in [19,20], no mp available); elemental analysis (Found: C, 70.70, H, 10.35, N, 5.50. Calc. for C19H34ClN: C, 72.05, H, 10.70, N, 4.95).

1-(1-Dodecyl)pyridinium chloride: (55%) mp 66–67.5 °C (lit. [10], 71 °C); elemental analysis (Found: C, 72.45, H, 10.90, N, 4.90. Calc. for C21H38ClN: C, 72.05, H, 10.70, N, 4.95).

1-(1-Tetradecyl)pyridinium chloride: (55%) mp 75–76.5 °C (lit. [19–22] 75–76 °C); elemental analysis (Found: C, 73.40, H, 11.00, N, 4.40. Calc. for C15H30ClN: C, 73.25, H, 11.00, N, 4.50).

2.4. Measurement of the properties of surfactant solutions

2.4.1. Solution conductivity

Conductivity measurements were recorded at 15–75 (±0.1) °C with a PC-interfaced Fisher Accumet 50 ion-meter, provided with a DM-C1 (k = 1.0 cm−1) micro-conductivity electrode (Digimed, São Paulo) and Schott Titronic T200 programmed burette. Fig. SM-1 (Fig. 1 of Supplementary material) shows the home-built double-wall conductivity cell that we have employed. A home-developed software package was used for programmed dilution of the concentrated surfactant solution in H2O, acquisition of conductivity data, and calculations. Double-distilled, deionized water was used for all the experiments.

2.4.2. Isothermal titration calorimetry (ITC)

The experiments were carried out in the temperature range 15–75 (±0.1) °C. Heat flow was measured with a power-compensated VP-ITC microcalorimeter (Microcal, Northampton). The titrant, a concentrated surfactant solution (ca. 20 × cmc; value known from solution conductivity) was injected with a syringe into 1.4 mL of degassed, deionized water. The injections were maintained at adequate time intervals, i.e., when the tracer of heat flow has dropped back to base line. Each injection resulted in a peak, whose corresponding area was calculated (Origin version 5.0 software, Microcal).

2.4.3. Static light scattering, SLS

SLS measurements were recorded at 90° scattering angle, at 15, 25, 35, and 45 °C (±0.1 °C) by employing Malvern 4700 light-scattering system, operating with a tunable-power Ar ions laser source (Spectra Physics model 177, 488 nm). In order to attenuate...
inter-micelle interactions, the “solvent” employed in these experiments was NaCl solution \([\text{[NaCl]} = 8 \times \text{cmc for C}_{12}\text{MeImCl and C}_{14}\text{MeImCl and [NaCl]} = 4 \times \text{cmc for C}_{12}\text{MelmCl]}\); all solutions were filtered through 0.35 \(\mu\)m membrane. A home-developed software package was used for acquisition of the scattering data and calculation of the (weight-averaged) micellar molecular weight from the Debye plot [23]. Solution refractive indices at the above-listed temperatures were measured with J357-NDS digital refractometer operating at 470 nm (Rudolph Research Analytical, Hackettstown). Solution refractive index increments \(\left(\text{n}\text{H}_2\text{O}/\text{[Surf]}\right)\) were calculated from the slopes of the plots of refractive index versus \([\text{Surf}], 2-40 \text{g L}^{-1}\); these were strictly linear \((r \geq 0.997)\).

3. Results and discussion

Note: Calculations of all micellar properties are detailed in the “Calculations” section of the Supplementary Material.

3.1. Calculation of the thermodynamic parameters of micellization from conductivity and ITC data

The only member of the C\(_{16}\)PyCl series that has been studied in detail is C\(_{16}\)PyCl [16,24–36]. As can be seen from the data of Table SM-3, the other members have not received much attention. In particular, they have been studied at a single temperature, e.g., entry 22; over a rather narrow temperature range, e.g., entry 9, or in temperature range smaller than the one employed in the present work, e.g., entries 7 and 13 (all of Table SM-3). More importantly, however, is that the values of \(\alpha_{\text{mic}}\) have been calculated from Frahm’s approximation [37]. As discussed in details recently [16], the latter approach super-estimates the degree of counter-ion dissociation. The reason is that it ignores the contribution of the micelle (a “macro-ion”) to solution conductivity above the cmc; this contribution is far from being negligible [38]. Super-estimation of \(\alpha_{\text{mic}}\) leads to smaller \(\Delta G_{\text{mic}}^{\text{cm}}\), see Eq. (14) below; the error is then carried over to \(\Delta H_{\text{mic}}^{\text{cm}}\). In view of this fact; and the unavailability of \(N_{\text{agg}}\) as a function of \(T\) – both parameters are required for a correct comparison of this series with \(\text{C}_m\text{MelmCl} – \) we have synthesized and determined the micellar parameters of the \(\text{C}_{10-\text{C}_{14}}\) members of C\(_{16}\)PyCl.

3.2. Procedures employed for the calculations of the micellar parameters

We have determined the cmc values from ITC and conductivity data; representative examples for both techniques are shown in Figs. 2 and 3 respectively, for the \(\text{C}_m\text{MelmCl} \) series. Figs. SM-2 and SM-3 present the corresponding plots for the C\(_{16}\)PyCl series, whereas Fig. SM-4 illustrates the manipulation of the ITC data in order to obtain the values of cmc and \(\Delta H_{\text{mic}}^{\text{cm}}\). The experimentally measured enthalpy is that of demicellization, \(\Delta H_{\text{mic}}^{\text{demic}}\). It is more convenient, however, to discuss \(\Delta H_{\text{mic}}\), whose magnitude is equal to \(\Delta H_{\text{mic}}^{\text{demic}}\), but with an opposite sign. The value of \(\Delta H_{\text{mic}}^{\text{demic}}\) can be calculated either directly from the ITC curves, Fig. 3, or indirectly from the (approximately U-shaped) dependence of cmc on \(T\) [39–41], according to van’t Hoff treatment. The value of \(\Delta G_{\text{mic}}\) is calculated from the values of cmc and \(\alpha_{\text{mic}}\). \(\Delta S_{\text{mic}}\) is then calculated from Gibbs free energy relationship.

The determination of the cmc of the \(\text{C}_{16}\text{MelmCl}\) surfactant by ITC proved to be difficult, because of the high values of heat involved. If a concentrated surfactant stock solution is employed, the generated heat pulse that is released on addition to water is outside the range of the calorimeter. On the other hand, if a more diluted solution is employed, the final solution volume required to carry out the experiment is larger than the volume capacity of the syringe. Therefore, we determined their enthalpograms in two steps, as follows: first we added surfactant solution \((C \approx 15 \times \text{cmc}; \text{value of cmc taken from conductivity data})\) to water until the syringe was empty. Then we refilled the syringe and added the \((C \approx 15 \times \text{cmc})\) solution to the surfactant solution at 75 \(^\circ\)C because the heat evolved was too high, even by using this two-step procedure; the reported values of cmc and \(\Delta H_{\text{mic}}^{\text{cm}}\) at 75 \(^\circ\)C were calculated by extrapolation. The combined results of the two additions were plotted together as a full titration curve. Although this should not affect the value of \(\Delta H_{\text{mic}}^{\text{cm}}\), it could, in principle, have some effect on the cmc, as a consequence of small variations of the heats of dilution in the cmc region. Because of the high viscosity of (relatively concentrated) C\(_{16}\)PyCl solution, and the small volume of the syringe, it was not possible to use ITC to determine its cmc and \(\Delta H_{\text{mic}}^{\text{cm}}\). These parameters were calculated by extrapolation from the data of the other members of the series, i.e., C\(_{12}\)PyCl, C\(_{14}\)PyCl and C\(_{16}\)PyCl.

As can be seen in Fig. 3, the plots can be subdivided into two concentration ranges, with a transition at the cmc region. Their shapes are clearly dependent on the length of the surfactant hydrophobic tail; this dependence has been discussed elsewhere in terms of cmc, \(N_{\text{agg}}\) and \(\alpha_{\text{mic}}\) [42–44]. Small cmc and \(\alpha_{\text{mic}}\), and a large \(N_{\text{agg}}\) result in an intense heat pulse, exothermic or endothermic, detected by the calorimeter. A small cmc also means that the solutions in both sample cell and the injection syringe are essentially ideal (concentrations are equal to activities), and that the parts of the plot before and after the cmc are independent of surfactant concentration, as shown for C\(_{10}\)MelmCl and C\(_{12}\)MelmCl. Decreasing the length of the surfactant tail results in an increase of cmc and \(\alpha_{\text{mic}}\), and a decrease of \(N_{\text{agg}}\) [45–47]. Consequently, the surfactant solution in the syringe and, with increasing number of injections, in the sample cell, cannot be assumed to be ideal. This results in concentration-dependent heat evolution, and a smaller enthalpy variation at the cmc, as can be seen, especially for C\(_{10}\)MelmCl.

Whereas the ITC experiment allows accurate determination of cmc and \(\Delta H_{\text{mic}}^{\text{cm}}\), conductivity is an appropriate technique to determine cmc and \(\alpha_{\text{mic}}\). We, and others have pointed out to the deficiency of the van’t Hoff treatment for the determination of \(\Delta H_{\text{mic}}^{\text{cm}}\) [16,48]. From Gibbs free energy relationship, any uncertainty introduced in the calculation of \(\Delta H_{\text{mic}}^{\text{cm}}\) will be carried over to \(\Delta G_{\text{mic}}\), so that \(\Delta G_{\text{mic,ITC}}^{\text{cm}} > \Delta G_{\text{mic,Good}}^{\text{cm}}\) [16]. For the present surfactant series, therefore, conductivity data does not offer reliable \(\Delta H_{\text{mic}}^{\text{cm}}\); this quantity has been calculated from ITC-data.

As mentioned above, Frahm’s approximation leads to an over-estimation of \(\alpha_{\text{mic}}\); we used Evans equation [6,14]. As shown in Eq. (9) below, solving the latter requires knowledge of the values of \(N_{\text{agg}}\) at different temperatures. These, in principle, can be determined from SLS experiments but the number of runs required is prohibitive (6 surfactants; 10 solutions each; 7 temperatures = 420 runs!). Recently, we have introduced a hybrid theoretical/experimental approach in order to calculate \(N_{\text{agg}}\) of C\(_{10}\)MelmCl and C\(_{16}\)PyCl, at different \(T\). Briefly, \(N_{\text{agg}}\) was calculated from the (theoretically optimized) volume and length of the monomer, \(V_{\text{mon}}, l_{\text{mon}}\), respectively; this was taken as the aggregation number at 25 \(^\circ\)C. A value of \(\Delta H_{\text{agg}}^\text{ITC} = (0.84134 \text{ C}^{-1} \pm 0.14)\) was extracted from the literature data of seven (anionic and cationic) surfactant series, in the temperature range from 20 to 60 \(^\circ\)C. This coefficient was then applied to \(N_{\text{agg}}\) in order to calculate the corresponding aggregation numbers at other temperatures. In the present work, this approach gave good \(N_{\text{agg}}\) for the C\(_{10}\) and C\(_{14}\) surfactants but not for their C\(_{12}\) and C\(_{16}\) counterparts. Namely a negative (!) aggregation number was calculated for C\(_{10}\)MelmCl surfactants at 75 \(^\circ\)C. A collection of available literature data for ionic C\(_{12}\) surfactants (C\(_{12}\)SO\(_4\)Na, \(T = 20–51.4\) \(^\circ\)C [45]; C\(_{12}\)NMe\(_3\)Cl, \(T = 15–45\) \(^\circ\)C [45]; C\(_{12}\)NMe\(_3\)Br, \(T = 20-50\) \(^\circ\)C [45]) indicated a lower mean value of \(\Delta H_{\text{agg}}^\text{ITC} = 0.86221 \text{ C}^{-1} \pm 0.17\). Its use,
however, still gave unreasonable values of \( N_{agg} \) at higher temperatures (\( N_{agg} = 1 \), for C\(_{10}\)MeImCl at 75°C), associated with an unacceptable standard deviation (±27%).

In order to solve this problem, we proceeded as follows: Values of \( N_{agg} \) were theoretically calculated as given above, these were taken as valid at 25°C. For each surfactant, the value of \( \partial N_{agg} / \partial T \) was extracted from the corresponding SLS data, in the temperature range from 15 to 45°C. The latter coefficients were then applied to (theoretically calculated) \( N_{agg} \) in order to obtain the aggregation numbers at temperatures different from 25°C. The previous approach can be tested by comparing the calculated and experimental \( N_{agg} \); in the T range from 15 to 45°C. Eqs.(1)–(4) show excellent linear correlations with slope close to unity; this corroborates the validity of our procedure. For consistency, we have employed the same values of \( \partial N_{agg} / \partial T \) in order to calculate \( N_{agg} \) as a function of (\( T \)) for the C\(_n\)MeImCl and C\(_n\)PyCl series.

Table 1 shows the properties of micellar solutions, calculated for C\(_n\)MeImCl and C\(_n\)PyCl. Eq. (5) shows the dependence of \( \partial N_{agg} / \partial T \) on the number of carbon atoms in the surfactant hydrophobic tail (n).

\[
N_{agg}(calc; C_{10}MeImCl) = 10.36 + 0.95N_{agg}(exp; C_{12}MeImCl), \quad r^2 = 0.962
\]

\[
N_{agg}(calc; C_{12}MeImCl) = 1.95 + 1.01N_{agg}(exp; C_{14}MeImCl), \quad r^2 = 0.982
\]

\[
N_{agg}(calc; C_{14}MeImCl) = 7.10 + 0.98N_{agg}(exp; C_{16}MeImCl), \quad r^2 = 0.988
\]

\[
N_{agg}(calc; C_{16}MeImCl) = 3.70 + 0.95N_{agg}(exp; C_{18}MeImCl), \quad r^2 = 0.952
\]

\[
\frac{\partial N_{agg}}{\partial T} = 1.38 - 0.165C_n, \quad r^2 = 0.943
\]

With regard to the results of Table 1, the following is relevant:

i. Except for the C\(_{10}\) surfactants, there is an excellent agreement between the cmc values calculated from the data of both techniques; the differences vary between 0.3 and 39%. The reasons for the observed dependence of cmc on the technique employed have been discussed in details elsewhere [51]. The differences observed in the cmc values determined for the C\(_{10}\) surfactants are acceptable because of procedure employed for the ITC experiment, as outlined above. Note that the break in the enthalpogram may affect the value of the cmc, but not that of \( \Delta H_{mic} \) value. This is due to the fact that the break is located in the cmc region and does not interfere with the lines before and after micellization.

ii. Plots of cmc versus \( T \) show approximate U-shape graphs, with minima between 25 and 35°C. An increase in \( T \) causes two interactions that affect the cmc in opposite directions: A decrease in hydrophilicity of the surfactant molecule (in particular, a decrease in the hydration of its head-group), this favors micellization, decreasing the cmc; a decrease in water structure, corresponding to a decrease in hydrophobic hydration of the alkyl group, this disfavors micellization, i.e., increases the cmc. Therefore, as \( T \) is increased, the
contribution of the latter effect increases, and finally pre-
dominates as the cmc reaches a minimum value, increasing
with temperature [41, 52, 53].

iii. As expected, $x_{mic}$ was found to increase as function of
decreasing the chain length, and of increasing $T$. Both effects
are consequences of the larger surface area of the shorter-
chain surfactants, and the decreased interaction of the
head-ions as a function of increasing $T$ [54].

3.3. Thermodynamic parameters of micelle formation: dependence on
the length of alkyl chain and the temperature

The thermodynamic data were calculated as follows: conductivity-
based cmc and $x_{mic}$ were employed in order to calculate $\Delta G^{0}_{mic}$;
ITC-based $\Delta H^{0}_{mic}$ was employed; $\Delta S^{0}_{mic}$ was calculated from Gibbs
free energy equation; $\Delta C^{0}_{mic}$ was calculated from the dependence
of $\Delta H^{0}_{mic}$ on $T$. The results are presented in Table SM-4 and Figs. 4
and 5.

Regarding these data, the following can be concluded:

iv. Except for C16AEtBzMe2Cl, whose micellization enthalpy is
always exothermic, in the temperature range studied, the
values of $\Delta H^{0}_{mic}$ decrease as $T$ increases, then change sign.
That is the micellization enthalpy is endothermic at lower
temperatures, turning exothermic at higher temperatures.
On the other hand, $\Delta S^{0}_{mic}$ is always positive and decreases
as a function of increasing $T$. Hydrophobic and electrostatic
interactions contribute to $\Delta H^{0}_{mic}$ [23, 39–41, 55, 56]. The main
contribution to the enthalpy of micellization is associated
with the transfer of the hydrocarbon chain of the surfactant
monomer from the aqueous environment to the micelle,
with concomitant release of solvating water molecules; this
effect is expected to be exothermic [57, 58]. Electrostatic
interactions involve (exothermic) repulsion between the
(similarly charged) head-ions, between the counter-ions,
and (endothermic) attraction between the head-group and
the counter-ion. Because electrostatic repulsive interactions
involve a larger number of ions than the attractive counter-
part, the net contribution of electrostatic interactions to
$\Delta H^{0}_{mic}$ is expected, to a first approximation, to be exothermic.
The $\Delta S^{0}_{mic}$ term, associated with the transfer of the surfactant
monomers from the aqueous pseudo-phase to the micelle
contains contributions from the following: Release of a sub-
stantial fraction of the water “frozen” around the surfactant
hydrophobic tail; readjustment of hydration of the head-
group according to the surface charge density, due to mono-
mer association and counter-ion condensation; increase in
the degrees of freedom of the surfactant molecules in the
micelle; decrease in the degrees of freedom of the head-
groups at the interface. The sum of these processes is an
increase in the degrees of freedom of the system,
i.e., positive
entropy. The same line of reasoning explains the change of
$\Delta H^{0}_{mic}$ and $\Delta S^{0}_{mic}$ to $\Delta G^{0}_{mic}$ as a function of increasing $T$. That
is, the contribution of the entropic term that dominates the
hydrophobic effect at room temperature is reduced and mic-
ellization may become (at high $T$) driven by an exothermic
association enthalpy [50, 59]. Although the contribution of
alkyl group dehydration to $\Delta H^{0}_{mic}$ decreases at higher $T$, it
is more than compensated for by increased (exothermic)
head-group repulsion, and decreased (endothermic)
The degree of counter-ion dissociation, \( a \), is determined by calorimetry by using Király's approach \([50]\). \( a \) is determined by conductivity by using Carpena's method \([49]\).

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<th>( T (^\circ C) )</th>
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Where “terminal CH\(_3\)”, (N) and CH\(_2\) refer to the methyl group of the hydrophobic chain, the number of methylene groups of the latter and each methylene group, respectively. The analysis is simplified because the contribution of the terminal CH\(_3\) is independent of the chain length; hence it can be taken as constant along the surfactants series. Consequently, the intercept of Eq. (6) reflects essentially the effects of the transfer of the head-groups from bulk solution to the micelle, and the slope reflects the transfer for one methylene group \([23,36]\).

Figs. SM-5 and SM-6 show the (linear) correlations between the thermodynamic parameters of micellization and \(N_{mic}\) for C\(_{10}\)MelmCl and C\(_{10}\)PyCl, respectively, in the \( T \) range 15–75 \(^\circ C\); the results for the three surfactant series at 25 and 45 \(^\circ C\) are shown in Table 2. The contribution of one methylene group to \(\Delta G_{mic}^{0}\) is expected to be close to \(-3 \text{kJ mol}^{-1}\) and is independent of the surfactant head-group structure \([23]\); Table 2 shows that this is indeed the case. At both temperatures, the \(\Delta G_{mic}^{0}\) values show the order: \(\Delta G_{mic}^{0}\) C\(_{12}\)MelmCl > C\(_{12}\)PyCl \(>\) C\(_{10}\)MelmCl and C\(_{10}\)PyCl almost compensate, resulting in small values of \(\Delta G_{mic}^{0}\). The difference of \(\Delta G_{mic}^{0}\) is a linear function of \(c_{mic}c^2\) and \(T\). At both temperatures, the \(\Delta G_{mic}^{0}\) values show the order: \(\Delta G_{mic}^{0}\) C\(_{12}\)MelmCl > C\(_{12}\)PyCl \(>\) C\(_{10}\)MelmCl and C\(_{10}\)PyCl almost compensate, resulting in small values of \(\Delta G_{mic}^{0}\). The difference of \(\Delta G_{mic}^{0}\) is a linear function of \(c_{mic}c^2\) and \(T\).
Fig. 4. Thermodynamic parameters of micellization of C\textsubscript{n}MeImCl. The following are the symbols employed, the corresponding parameters and the techniques used to determine them: $\Delta G_{\text{mic}}^0$, calorimetry-based cmc and conductivity-based $a_{\text{mic}}$; $\Delta H_{\text{mic}}^0$, directly from calorimetry; and $\Delta T S_{\text{mic}}^0$, from the difference between $\Delta G_{\text{mic}}^0$ and $\Delta H_{\text{mic}}^0$. Part A: C\textsubscript{10}MeImCl; Part B: C\textsubscript{12}MeImCl; Part C: C\textsubscript{14}MeImCl and Part D: C\textsubscript{16}MeImCl.

Fig. 5. Thermodynamic parameters of micellization of C\textsubscript{n}PyCl. The following are the symbols employed, the corresponding parameters and the techniques used to determine them: $\Delta G_{\text{mic}}^0$, calorimetry-based cmc and conductivity-based $a_{\text{mic}}$; $\Delta H_{\text{mic}}^0$, directly from calorimetry; and $\Delta T S_{\text{mic}}^0$, from the difference between $\Delta G_{\text{mic}}^0$ and $\Delta H_{\text{mic}}^0$. Part A: C\textsubscript{10}PyCl; Part B: C\textsubscript{12}PyCl; Part C: C\textsubscript{14}PyCl and Part D: C\textsubscript{16}PyCl.

Table 2
Contribution of the discrete surfactant segments, CH\textsubscript{2} and CH\textsubscript{3} + head-group (CH\textsubscript{3} + HG), to the thermodynamic parameters of micellization, in the temperature range 15–75 °C.

<table>
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<tr>
<th>T (°C)</th>
<th>$\Delta G_{\text{CH}_{\text{2}}+\text{HG}}^0$</th>
<th>$\Delta G_{\text{CH}_{\text{2}}}^0$</th>
<th>$\Delta H_{\text{CH}_{\text{2}}+\text{HG}}^0$</th>
<th>$\Delta H_{\text{CH}_{\text{2}}}^0$</th>
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<td>$-3.16 \pm 0.08$</td>
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<td>$-0.97 \pm 0.1$</td>
<td>$13.10 \pm 2$</td>
<td>$2.19 \pm 0.2$</td>
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<tr>
<td>45</td>
<td>$-1.99 \pm 0.9$</td>
<td>$-3.22 \pm 0.07$</td>
<td>$17.43 \pm 2$</td>
<td>$-2.22 \pm 0.2$</td>
<td>$19.41 \pm 2$</td>
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<td>C\textsubscript{12}PyCl$^b$</td>
<td>$-1.22 \pm 4$</td>
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$^a$ The correlation coefficients were $\geq 0.998$, 0.94, and 0.92 for plots of $\Delta G_{\text{mic}}^0$, $\Delta H_{\text{mic}}^0$ and $T\Delta S_{\text{mic}}^0$, respectively. $\Delta G_{\text{mic}}^0$, $\Delta H_{\text{mic}}^0$ and $T\Delta S_{\text{mic}}^0$ are in kJ mol$^{-1}$.

$^b$ The correlation coefficients were $\geq 0.97$, 0.97, and 0.93 for plots of $\Delta G_{\text{mic}}^0$, $\Delta H_{\text{mic}}^0$ and $T\Delta S_{\text{mic}}^0$, respectively. $\Delta G_{\text{mic}}^0$, $\Delta H_{\text{mic}}^0$ and $T\Delta S_{\text{mic}}^0$ are in kJ mol$^{-1}$.

$^c$ The correlation coefficients were $\geq 0.988$, 0.993, and 0.999 for plots of $\Delta G_{\text{mic}}^0$, $\Delta H_{\text{mic}}^0$ and $T\Delta S_{\text{mic}}^0$, respectively. $\Delta G_{\text{mic}}^0$, $\Delta H_{\text{mic}}^0$ and $T\Delta S_{\text{mic}}^0$ are in kJ mol$^{-1}$.
the benzyl group and the micellar interior; appreciable for C\textsubscript{8}MeImCl, because of the relatively acidic H2 of the imidazolium ring, and normal for pyridinium ring for a lack of relatively acidic hydrogens. This conclusion agrees with the partial atomic charges calculated, 0.410 (amide N–H), 0.237 (H2 of the imidazolium ring) and 0.182 (H6 of the pyridinium ring) [16].

A most important characteristic regarding SAILs is their structural versatility. Practically unlimited combinations of counterions and substituted head-groups can be envisaged. For example, using the same counter-ion and long-chain “tail”, C\textsubscript{12} = 10, 12, 14 and 16, it is possible to synthesize four pyridine-based surfactants and 16 imidazole-based counterparts, based on methyl to 1-butyl group attached to the second nitrogen atom of the imidazolium ring. This offers exciting possibilities for applications, because the interactions, e.g., electrostatic and hydrophobic, in the interfacial region can then be “fine-tuned” according to one’s needs by a judicious combination of the head-cation (nature of the substituents introduced) and the counter-ion (charge density, hydration). Another advantage is that SAILs share with ILs the same favorable characteristics, high polarity, thermal and chemical stability, low m.p., and negligible vapor pressure. Therefore, SAILs can be industrially used, inter alia, as “solvents” and in separation processes. Understanding their behavior in solution and the main forces driving micellization is important, therefore, in order to select the best structure(s) for the desired application.

Acknowledgments

We thank FAPESP (State of São Paulo Research Foundation) for financial support; the CNPq (National Council for Scientific and Technological Research) for a pre-doctoral fellowship to P.D. Galgano, and a research productivity fellowship to O. A. El Seoud. We are indebted to Profs. Hernan C. Guralnik and Iolanda M. Cuccovia (IQ-USP) for making the ITC equipment available to us. We thank Dr. Paulo A.R. Pires (IQ-USP), and Prof. Kátia R.P. Daghastanli for their help with theoretical calculations, and interpretation of ITC data, respectively, and the LCCA-USP for making the computing programs available to us. The help of Tayla C. Perfeito, Alannah S. Guerrero, and Cezar Guizzo is appreciated.

Appendix A. Supplementary material


References
