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Aggregation behavior in water of new imidazolium and pyrrolidinium alkycarboxylates protic ionic liquids

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ABSTRACT

A novel class of anionic surfactants was prepared through the neutralization of pyrrolidine or imidazole by alkylcarboxylic acids. The compounds, namely the pyrrolidinium alkylcarboxylates ([Pyrr][$C_nH_{2n+1}COO$]) and imidazolium alkylcarboxylates ([Im][$C_nH_{2n+1}COO$]), were obtained as ionic liquids at room temperature. Their aggregation behavior has been examined as a function of the alkyl chain length (from $n = 5$ to 8) by surface tensiometry and conductivity. Decreases in the critical micelle concentration (cmc) were obtained, for both studied PIL families, when increasing the anionic alkyl chain length (n). Surprisingly, a large effect of the alkyl chain length was observed on the minimum surface area per surfactant molecule ($A_{\min}$) and, hence the maximum surface excess concentration ($\Gamma_{\max}$) when the counterion was the pyrrolidinium cation. This unusual comportment has been interpreted in term of a balance between van der Waals and coulombic interactions. Conductimetric measurements permit determination of the degree of ionization of the micelle (a) and the molar conductivity (Λ_M) of these surfactants as a function of n. The molar conductivities at infinite dilution in water (Λ_∞) of the $[Pyrr]^+$ and $[Im]^+$ cations have been then determined by using the classical Kohlrausch equation. Observed change in the physicochemical, surface, and micellar properties of these new protonic ionic liquid surfactants can be linked to the nature of the cation. By comparison with classical anionic surfactants having inorganic counterions, pyrrolidinium alkylcarboxylates and imidazolium alkylcarboxylates exhibit a higher ability to aggregate in aqueous solution, demonstrating their potential applicability as surfactant.

1. Introduction

Ionic liquids (ILs) are organic molten electrolytes, liquid near ambient temperature, and have gained attention as a new class of designer solvents [1]. Their physical and chemical properties can, effectively, be tailored by judicious selection of cation, anion, and substituent. Most ILs have low vapor pressures, outstanding catalytic properties, and high ion conductivities by comparison with traditional organic solvents. Thus ILs have attracted much attention as electrolytes [2] and solvent media for reactions and extractions [3,4]. Those formed by the transfer of a proton between a Brønsted acid and a Brønsted base form a protic subgroup in the class of ambient temperature fluid systems now referred to as “protic ionic liquids (PILs).” Proton conducting electrolytes are now emerging as useful materials owing to various possible applications such as electrolytes in aqueous batteries, fuel cells, double layer capacitors, dye-sensitized solar cells, and actuators [4–13]. Furthermore, they are relatively inexpensive to manufacture, promising large new fields of applications [14].

ILs possessing long aliphatic substituents have been reported to undergo micellization in aqueous solutions [15–18]. However, our current knowledge of IL micelle structure and behavior in aqueous solution is limited [15]. Due to their structural tuneability, ILs represent a unique class of “designer surfactants” in which the substituents on the head group can be widely varied.

The self-aggregation behavior of surfactant-like ILs in aqueous solutions has been a focus of recent investigations [16–18]. Micelle formation is undoubtedly important in relation to the future uses, applications, and environmental fate of ILs. Up to this time, more than 20 ILs have been described to form aggregates in aqueous solutions [19,20]. Alkylimidazolium-based ILs have been mostly studied in the field of colloid and interface science [17–19].

Knowledge of the aggregation behavior is a vital part of understanding how ILs participate as components in a mixed solvent system. Therefore, study of the interface and surface interactions is essential to understand micellar properties, technical applications, and environmental impacts of ILs. The critical micelle concentration (cmc) is an important factor in the characterization of the of

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amphiphilic compounds self-aggregation. The formation of micelles is due to the nature of ions constituting the ionic liquid, witch contain, generally, both hydrophobic and hydrophilic domains. Hence the cmc is dependent on the relative sizes of these domains [21]. A larger hydrophobic domain will result in a lower cmc.

As surfactant-based processes are found to be important in many fields (as pollution control, conventional ground water pump-and-treat processes, and wastewater purification), a promising future could be a link with the possibility of controlling the structure of the organized media of these designer solvents [22].

The behavior of *N*-alkyl-*N*-methylimidazolium ILs and *N*-alkyl-*N*-methylpyrrolidinium in aqueous solution has been studied by different groups [16,23], and it has been reported that the formation of the lyotropic liquid crystal and micelle occurs, respectively, at different concentrations on ILs. The aggregation behavior of long-chain imidazolium ILs in aqueous solutions has been investigated by using interfacial tension, ^{1}H NMR, steady-state fluorescence spectroscopy, and refractrometry [24,25].

The purpose of this study is to investigate the properties of eight new protonated pyrrolidinium and imidazolium ILs having alkyl carboxylate anions $C_nH_{2n+1}COO^-$ ($n = 5$–8) as counteranions. The aggregation behavior of these PILs in aqueous solutions has been investigated using surface tension and electrical conductivity measurements at room temperature (298 K).

2. Experimental

2.1. Materials

Pyrrolidine, imidazole, and carboxylic acids are commercially available from Fluka (>99.0%) and are used without further purification. Water is purified with Milli-Q 18.3 MΩ water system.

2.2. Preparation of pyrrolidinium and imidazolium alkyl carboxylates protic ionic liquids

The pyrrolidinium alkyl carboxylates [Pyrr][C_nH_{2n+1}COO] and imidazolium alkyl carboxylates [Im][C_nH_{2n+1}COO] ($n = 5$–8) are synthesized by neutralization reactions of pyrrolidine or imidazole by the corresponding Brønsted acid (molar ratio of amine/acid = 1/1) according to procedures described elsewhere (Scheme 1) [26–28].

The carboxylic acid was added slowly to amine with stirring in a tree-necked round-bottom flask immersed in an ice bath and equipped with a dropping funnel and then the stirred to $T = 298$ K for 4 h. The colorless (pyrrolidinium) or transparent (imidazolium) ionic liquids were obtained. All PILs synthesized were dried overnight at 343 K under high vacuum (0.1 Pa) prior to use. Ionic liquids were analyzed for water content using coulometric Karl-Fischer titration prior to any measurements. Water content of the PILs, measured just after distillation, is in the range 20–50 ppm, depending on the nature of PILs. Purity of ILs was checked by ^{1}H NMR spectrum using a Bruker 200 MHz spectrometer, $CDCl_3$ as solvent, and TMS as internal standard. PILs obtained are characterized by differential scanning calorimetry (DSC), pycnometry, and rheology by using a TA instrument rheometer (AR 1000) with conical geometry at various temperatures (from 298 to 333 K). Surface tension measurements show no minimum around the cmc, indicating that no unreacted products remain in the synthesized PILs.

2.3. Conductivity measurements

Conductivity measurements were performed by using a Crison (GLP 31) digital multifrequency conductimeter. The temperature control (at $T = 298.15$ K) is ensured by a JULABO thermostated bath. The conductimeter was calibrated with a standard solution of known conductivity (0.1 and 0.02) mol dm^{-3} KCl. The conductivity measurements of the [Pyrr][C_nH_{2n+1}COO] and [Im][C_nH_{2n+1}COO] in aqueous solutions were carried out by continuous addition of pure ILs into water. Each conductivity was recorded when its stability was better than 1% within 2 min.

2.4. Surface tension measurements

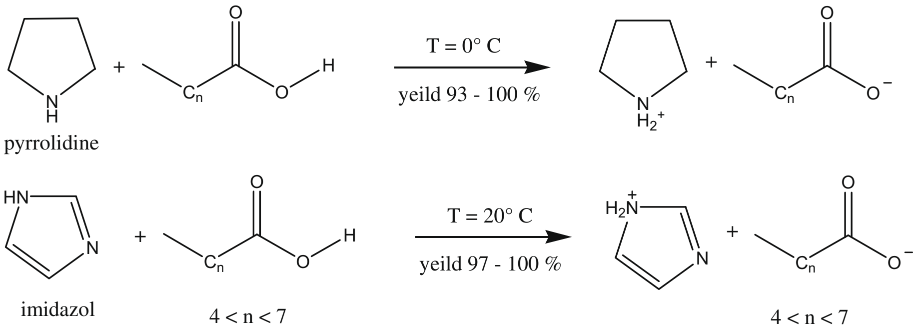
Surface tension measurements were performed with a Lauda tensiometer (accuracy ± 0.1 mN m^{-1}). Temperature was controlled at (298 ± 0.2) K using a JULABO thermostated bath. All measurements were repeated at least twice.

3. Results and discussion

3.1. Physical properties of pure PILs

The chemical formula of compounds investigated, pyrrolidinium alkyl carboxylates [Pyrro][$C_nH_{2n+1}CO_2$], $n = 5$ (**1a**), $n = 6$ (**2a**), $n = 7$ (**3a**), $n = 8$ (**4a**), and imidazolium alkyl carboxylates [Im][$C_nH_{2n+1}CO_2$] $n = 5$ (**1b**), $n = 6$ (**2b**), $n = 7$ (**3b**), $n = 8$ (**4b**), are represented in Fig. 1. Physicochemical characteristics, molar mass, density, molar volume, viscosity, specific and equivalent ionic conductivity and surface tension of PILs at 25 °C, are listed in Table 1.

The density of ionic liquids falls typically in the range from 0.9 to 1.6 g cm^{-3}. In general, the density of ionic liquids is very strongly affected by the nature of the anion. For the studied PILs in this paper, densities are related to the compactness of their structures. When the alkyl chain length increases, the density decreases for both series of alkyl carboxylate PILs. For example, [Pyrro][$C_nH_{2n+1}CO_2$], $\rho = 1.0246$ g cm^{-3} ($n = 5$), 1.0037 g cm^{-3} ($n = 6$), 0.9870 g cm^{-3} ($n = 7$), 0.9690 g cm^{-3} ($n = 8$). The nature of



Scheme 1. Preparation of pyrrolidinium and imidazolium carboxylate ionic liquids.