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Effect of alkyl chain length and head group on surface active and aggregation behavior of ionic liquids in water

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ABSTRACT

A series of surfactant-like ionic liquids (ILs), typically consisting of a long hydrocarbon tail and an ionic head group have been synthesized by a direct reaction of 1-methylimidazole and 1-choloroalkane, RCl, R = C_{10}, C_{12}, C_{14}, C_{16} and C_{18}, 1-methylpipridine or 1-methylpyrrolidine and 1-chlorooctadecane respectively. Surface activity and aggregation of these surfactants have been explored by surface tension and solution conductivity measurements. New results (critical aggregation concentrations (cac), and surface active parameters (at 298.15 K), thermodynamic parameters of aggregation (at 298.15, 303.15 and 313.15 K)) are reported. The increase in length of *R* decreased cac, minimum area/surfactant molecule at air/water interface and while the adsorption efficiency, surface excess concentrations, standard entropy of aggregation were increased indicating that the aggregation with in the temperature limits of present study is an entropy driven process. The analysis of the small angle neutron scattering (SANS) curves revealed that the aggregates are of oblate ellipsoidal shape and the aggregation numbers increased with the increase in the chain length (C_{10}–C_{18}) of alkyl branch and therefore it is suggested that the longer the alkyl chains, parallel would be their alignment in the core part of the aggregates. Comparison of surface active parameters for the three ILs with a common octadecyl chain but different cationic head groups revealed that the methylimidazolium moiety is more effective than methylpiperidine and methylpyrrolidine at air/water interface. Similarly, the number of molecules in an aggregate was found to be more, when the cationic head group is made up of π electron ring systems as compared to the one with point charge.

1. Introduction

Ionic liquids (IL) consist entirely of ions and are emerging as an important class of compounds with unique properties such as negligible vapor pressure, wide liquidous range, excellent solvation, high thermal stability, ionic conductivity, selective catalytic behavior and wide electrochemical windows etc. [1–8]. The chemical structure of ionic liquids mimic that of amphiphilic cationic surfactants consisting of a non-polar hydrophobic tail and a polar cationic head group. Therefore based on structure activity relationship, a typical long alkyl chain IL could possess surface active properties similar to the conventional cationic surfactants and have tendency to associate in to nano micellar structures [9]. A long alkyl chain based IL, when dissolved in water thus exhibits amphiphilic character. Very little is known about the surface active and micellization features of such ILs and it is unclear as how the surfactant-like tendency of ILs depends upon their molecular characteristics, concentration, temperature and additives etc. In view of this, the study on the relationship between the molecular structural features and microstructural characteristics of micellar associates of ILs in aqueous solutions is always an interesting and an important subject area of investigation in the discipline of colloid and interface science.

The understanding of the solution behavior of surfactant-like ionic liquids in aqueous media is highly necessary to invent and propose very useful and still yet fully unexplored applications such as wetting, dispersion, emulsification, detergency, solubilization, catalysis of chemical reactions, etc. ILs have already been emerging as one of the alternatives to volatile organic solvents because of their negligible vapor pressure. Similarly, ILs can be potential green surface active agents especially to replace the cationic surfactants of alkyltrimethylammonium bromide type that are widely used in hair conditioning products and reported to be toxic to micro-organisms inhabiting activated sludge systems [10,11]. A proper and comprehensive understanding, especially of the adsorption behavior at air/water interface, and aggregation or association phenomenon in aqueous and non-aqueous solutions is a prerequisite before ILs are explored for surfactant based applications [9]. The surface, interfacial and aggregation characteristics of ILs based

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on 1-alkyl (butyl to hexadecyl)-3-methylimidazolium bromide, or chloride in water have been extensively studied by using various methods such as surface tension [12,13,16,21–23,25–27], electrical conductivity [14–25,31,32], fluorescence [16,20,21,25,26], ^{1}H NMR [19,26,28], steady state fluorescence spectroscopy [25,29], isothermal titration calorimetry [30]. The main focus of these investigations were to determine the critical aggregation concentrations (CAC) mostly at 298.15 K. Some discrepancies between the CAC data as determined from different methods for the same IL were noted [31] and these discrepancies can be attributed to the presence of impurities of the sample as well as to the sensitivity of the method used. The CAC values of ILs with bromide counter anion were found to be lower than that of with chloride counter anion. Bromide ions, being larger have weaker hydration and hence are easily adsorbed on the surface of the aggregates and effectively decrease the electrostatic repulsions between the head groups which eventually facilitate the onset of aggregation at much lower concentrations.

Luczak et al. [9] and Smirnova et al. [31] have collected the literature CAC data of homologous ILs based on alkylmethylimidazolium of type [C$_n$mim][Cl] or [C$_n$mim][Br] and examined the dependence of their CAC on the alkyl chain length. It was observed that the variation of log CAC values with the alkyl chain can be fitted to an empirical Stauff–Klevens rule, $\log \text{CAC} = A - Bx$, where A and B are constants at a given temperature and x is the number of carbon atoms in the alkyl chain. The CAC values of ILs otherwise were found to lie in between the values of molecularly comparable cationic and anionic surfactants. As compared to extensive data on the CAC, there exists very little information on the surface active and morphological features such as size and the shape of the aggregates formed by homologous ILs in general and their variation with the molecular characteristics, i.e. alkyl chain length, type of ring cation, nature of anion and solution conditions such as concentration of IL, temperature and presence of additives etc. in particular. Our laboratory has recently reported the surface active features and aggregation characteristics of surfactant-like ionic liquids based on 1-alkyl-3-methylimidazolium or 1-alkyl-1-methylpyridinium halides of type. [C$_n$mim][X] or [C$_n$py][X], where $n = 4$, 6 or 8 and X = Cl$^-$, Br$^-$ and I$^-$ in water as well as in aqueous solutions containing sodium chloride, sodium sulfate and 2-butoxyethanol as additives, by employing surface tension, electrical conductance, ^{1}H NMR and SANS methods [32–34]. Even though the studied ILs displayed characteristic CAC, the analysis of the results especially from the latter two methods revealed that true micelle-like aggregates are not evident in ILs when $n = 4$. 1-Octyl-3-methylimidazolium or -pyridinium chloride aqueous solutions do contain aggregates but the structural organization is far different from conventional micelles formed by amphoteric surfactant substances. The ionic liquids with hexyl chains are found to be of transitory type with no detectable aggregate structures. This prompted us to take up systematic investigations with a focus mainly on examining the surface activity and aggregate formation of ionic liquids based on 1-alkyl-3-methylimidazolium halides of type, [C$_n$mim][Cl], where $n = 10$, 12, 14, 16 and 18, 1-octadecyl-1-methylpiperidinium chloride, [C$_{18}$mpip][Cl] and 1-octadecyl-1-methylpyrrolidinium chloride, [C$_{18}$mpyrro][Cl] and access the effect of chain length and head group nature on (i) the critical aggregation concentration, (ii) the surface active properties such as the effectiveness of surface tension reduction, γ_{CAC}, adsorption efficiency, pC_{20}, surface excess, $\Gamma_{\max}$ and minimum area per ionic liquid molecule, a_1^s, (iii) thermodynamic parameters of aggregation and (iv) size and shape of the aggregate structures, by surface tension, electrical conductance and SANS measurements. SANS profiles at different concentrations for a given ionic liquid were measured and analyzed through model fits to ascertain the effect of concentration on the geometrical features of the aggregates. To the best of our knowledge, this is the first report that describes the geometrical features for homologous series of ILs of type, [C$_n$mim][Cl] where $n \geq 10$ in water.

2. Experimental

2.1. Reagents

Acetonitrile (GR reagent grade, Merck 99.5%) was used as such without any further purification. Ethyl acetate (Merck, ≥98%) was dried over fused calcium chloride and distilled and the fraction boiling in the temperature range of 349.15–350.15 K was collected. 1-methylimidazole (Alfa Aesar, 99%), 1-methylpyrrolidine (Fluka, ≥99%), and 1-methylpiperidine (Merck, ≥98%), were dried over potassium hydroxide and freshly distilled. The liquids were fractionally distilled. 1-Chlorodecane (≥98%), 1-chlorododecane (95%), 1-chlorohexadecane (96%) and 1-chlorooctadecane (98%) were of Merck make (with the purities shown in the parenthesis) and used as received. The water was triple distilled over potassium permanganate and the samples with a conductivity of 1.2×10^{-6} S/cm were used in the solution preparation.

2.2. Synthesis and characterization of ionic liquids

The ionic liquids were prepared by carrying out a direct reaction between 1-methylimidazole, or 1-methylpyrrolidine, or 1-methylpiperidine with an excess amount of respective 1-chloroalkane in acetonitrile under reflux at 353.15 K for 48 h. The reactions were conducted under nitrogen blanket in a round bottom flask equipped with reflux condenser and magnetic stirrer. The resulting product in its solution form was cooled. The product was crystallized from ethylacetate under vigorous stirring in the temperature range of 273.2–278.2 K depending upon the reactants. The crystallized products were further dissolved in acetonitrile and recrystallize them once again. This process was repeated for four times to remove the un-reacted reagents. The solvent residues were finally removed by placing the product solution under vacuum at 343.2 K over a period of 12 h.

The structures of the products were confirmed by ^{1}H and ^{13}C NMR spectra in CDCl$_3$. The melting points of the ILs were obtained from differential scanning calorimetry (DSC) traces. The results of ^{1}H and ^{13}C NMR spectra are summarized in Table S1

1-Decyl-3-methylimidazolium chloride: [C$_{10}$mim][Cl]: colorless liquid: yield, 90%.
1-Dodecyl-3-methylimidazolium chloride: [C$_{12}$mim][Cl]: white waxy solid: yield, 91%: m.pt. 317.2 K.
1-Hexadecyl-3-methylimidazolium chloride: [C$_{16}$mim][Cl], white waxy solid: yield, 91%: m.pt. 332.8 K.
1-Octadecyl-3-methylimidazolium chloride: white waxy solid: yield, 95%: [C$_{18}$mim][Cl], m.pt. 343.1 K.
1-Octadecyl-1-methylpyrrolidnium chloride: white waxy solid: [C$_{18}$mpyrro][Cl], m.pt. 324.1 K.
1-Octadecyl-1-methylpiperdinium chloride: white waxy solid: [C$_{18}$mpip][Cl], m.pt. 365.2 K.

The water content of ILs was determined by using Karl Fischer titrator and the results showed that mass fractions of water ranged from 5.3×10^{-6} to 8.2×10^{-6}. The purity of the ionic liquids was adjudged by potentiometric titration using argentometric method in which 10 cm^3 of IL aliquot solution was titrated with a sodium