Application of surface active amino acid ionic liquids as phase-transfer catalyst

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ABSTRACT

Five structurally related morpholinium derived ionic liquids containing N-acetyl-glycinate anion were synthesized and their thermal stability, surface properties and activity as phase transfer catalysts investigated. The thermal properties were studied by differential scanning calorimetry, while the adsorption at the air/water interface and micellization behavior was analyzed by surface tension measurements, conductometry and isothermal titration calorimetry. The catalytic activity was assessed in two model reactions that were N-alkylation of dibenzoazepine and C-alkylation reaction of fluorene derivatives. The effect of the chain length, thus surface activity of the newly synthesized ionic liquids on the yields of N- and C-alkylation reactions was discussed.

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1. Introduction

Ionic liquids (ILs) are not just solvents and may play multiple roles in chemical processes such as functional compounds or reacting species. According to the widely accepted definition, ILs are salts with melting temperature below 100 °C, characterized by high enthalpies of vaporization (negligible volatility). The interest in this group of compounds is also related with the easiness to fine-tune their physical and chemical properties by modification/selection of ion moieties (“designer compounds”), thus adjusting the properties for specific application.

Ionic liquids due to their amphiphilic structure (presence of charged hydrophilic headgroup and hydrophobic alkyl substituent) in these applications may be used in a manner analogous to conventional surfactants. In this regard, studies on the surface properties of ionic liquids have been developed extensively for many years with using various experimental and theoretical methods [1–10]. The relationship between alkyl chain length in the IL’s cation as well as an anion structure and ILs’ susceptibility to form micellar aggregates in solutions was described. This phenomenon was mainly observed for the long-chained IL’s derivatives, usually containing eight or more carbon atoms in the cation’s substituent. In that case, the micellar structures were formed by ILs composed of simple anions (Cl, Br, HSO4) [7–9], whereas the low solubility of ionic liquids containing hydrophobic ions such as [PF6] and [Te2N] [11] resulted in phase separation prior to the formation of aggregates. Fewer studies were performed for ionic liquids with surface-active anions toward formation of anionic micelles [11,12].

The surface activity of ILs was used in some synthetic, catalytic and separation processes. Micellar aggregates in aqueous media provide an environment different from the bulk water, therefore they influence kinetics of the reactions and effectiveness of separation processes. For example, Bica et al. revealed that aqueous solutions of amphiphilic ionic liquids can be efficiently applied as micellar reaction media in Diels–Alder synthesis [13] (1,3-cyclohexadiene with N-benzylmaleimide) and in nucleophilic substitution of the organophosphorus compounds [14]. It was found that the rate of Diels–Alder reaction occurring in micellar solutions can be enhanced compared to than in water [13]. In another example, the effect of the IL’s anion structure (halides and sulfonates), thus effectiveness of anion binding to the cationic micelle, on the acceleration of the nucleophilic substitution reaction rate was observed [14]. Moreover, the same group revealed also a correlation between extraction yield and the critical micelle concentration (CMC) of ILs in a micellar extraction of Piperine from black pepper [15]. Ionic liquids with amphiphilic structures can be also used in organic synthesis to facilitate biphasic reactions as phase transfer catalysts (PTC). The PTC in the liquid/liquid system facilitates migration of anionic reagents between phases and thus accelerates the reaction. The tetraalkyammonium salts have been used as PTCs in liquid/liquid systems, starting from the pioneering works of Starks [16], Małkowska [17] and Brändström [18]. Such salts when used as PTCs exhibit high