



Aggregation behavior of dodecyltriphenylphosphonium bromide in aqueous solution: Effect of aromatic ionic liquids



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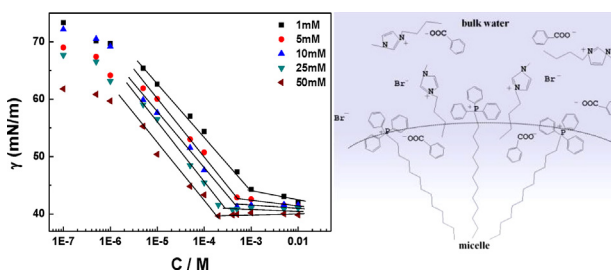
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HIGHLIGHTS

- A kind of room-temperature ILs with aromatic anions was successfully synthesized.
- The aromatic ILs affect the micellization of a surfactant with aromatic headgroups.
- The enhanced π - π stacking interaction and hydrophobic interaction play a key role.

GRAPHICAL ABSTRACT

Surface tension curves of C₁₂TPB/[Bmim][PhCOO] system and the proposed mechanism.



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ABSTRACT

The effects of ionic liquids (ILs), 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) and 1-butyl-3-methylimidazolium benzoate ([Bmim][PhCOO]) on the aggregation behavior of dodecyltriphenylphosphonium bromide (C₁₂TPB) in aqueous solution were investigated by surface tension measurements, dynamic light scattering (DLS) measurements and ¹H NMR spectroscopy. The introduction of benzene rings in the anions of [Bmim][PhCOO] can promote the micellization of C₁₂TPB more efficiently with a smaller CMC value and a bigger micellar size. The ¹H NMR spectra revealed that [Bmim][PhCOO] can participate in the micelle formation. The combined effect of intermolecular interactions, such as electrostatic attraction, hydrophobic effect and π - π stacking interaction is proposed to be responsible for the enhancement in the micellization of C₁₂TPB.

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1. Introduction

Ionic liquids (ILs), as a class of compounds composed of ions with melting points at or near room temperature, have unusual physicochemical properties including low volatility, high thermal stability, high ionic conductivity and easy recyclability [1,2]. Thus ILs have been applied widely in the range of organic synthesis and catalysis [3–7], inorganic synthesis [8], chromatography [9], analysis systems [10,11] and biochemistry [12]. Perhaps the

most unique capability of ILs is to support the self-assembly of amphiphiles [13,14]. The physicochemical properties of ILs can be easily modulated by altering the substituents or anions. Based on this characterization, a large variety of ILs with different structures have been designed for various applications [15–19].

As is known universally, surfactants can self-assemble into micelles in aqueous solutions when the surfactant concentration is above the critical micelle concentration (CMC). The microstructures, shapes, and properties of the micelles in aqueous solutions mainly depend on the structures of the surfactant molecules. In addition, the physicochemical properties of the given surfactant solutions can be modified by the addition of external additives, including inorganic or organic salts, co-solvents, and co-surfactants

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[20–26]. Recently, the utilization of ILs to modify the properties of aqueous surfactant solutions has attracted extensive attention. The special properties of ILs would play a unique role in altering the aggregation behavior of surfactant solutions.

Many works have concentrated on the effects of ILs on the aggregation behavior of surfactant in aqueous solution. Pandey et al. have systematically investigated the effects of various ILs on the aggregation behavior of a series of surfactants [27–33]. They have reported that the addition of 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) to aqueous Triton X-100 solution results in a decreased micellar size, an increased CMC value, and a decreased aggregation number N_{agg} . While the hydrophobic ILs 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) have no significant change in CMC value. They have also observed that the addition of IL to aqueous *N*-dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (SB-12) solution results in decreased N_{agg} ; and the decrease in N_{agg} is significantly drastic for the [Bmim][PF₆] addition as compared with that for [Bmim][BF₄]. They have explained this fact on the basis of simple packing considerations and the differences in the size of the two anions. Recently Pandey et al. have found that the addition of ILs in sodium dodecyl benzene sulfonated (SDBS) aqueous solutions can give rise to a sudden aggregate size enhancement. Aromaticity of the IL cation alongside the presence of sufficiently aliphatic (butyl or longer) alkyl chains on the IL appear to be essential for this dramatic critical expansion in self-assembly dimensions within aqueous SDBS solution. The effects of ILs 1-hexyl-3-methylimidazolium bromide ([Hmim][Br]) and co-surfactant *n*-hexyltrimethylammonium bromide (HeTAB) on the aggregation behavior of aqueous cetyltrimethylammonium bromide (CTAB) solution were also investigated, and they found that [hmim][Br] appears to be more effective in altering the properties of aqueous CTAB solution. In addition, Sarkar et al. have also investigated the micellization of CTAB in aqueous solution with the addition of two protic ILs dimethylethanol ammonium hexanoate (DAH) and dimethylethanol ammonium formate (DAF) [34]. The location of the anions is different due to the different alkyl chain length, resulting in different micellar size of CTAB. The addition of functional ILs with special groups was also studied by our group [35]. The introduction of acidic, basic and neutral groups in the IL cations has different effects on the micellization of SDS and the aggregation behavior was also dependent on the pH values. It can be deduced from the previous reports that ILs have significant effects on the aggregation behavior of surfactant in aqueous solution.

In the present work, we have focused on the aggregation behavior of a cationic surfactant dodecyltriphenylphosphonium bromide (C₁₂TPB) in aqueous solution upon the addition of an aromatic IL 1-butyl-3-methylimidazolium benzoate ([Bmim][PhCOO]). For comparison, the effect of IL 1-butyl-3-methylimidazolium acetate

([Bmim][OAc]) was also investigated. The chemical structures of the surfactant and ILs are shown in Fig. 1. The aim of this work seeks to explore the role of benzene rings of added ILs on the aggregation behavior of C₁₂TPB in aqueous solution. We expected the introduction of aromatic structures can generate distinct π – π stacking interaction and tune the physicochemical properties of the surfactant solution.

2. Materials and methods

2.1. Materials and synthesis

Triphenylphosphine (99%), 1-bromododecane (97%), 1-methylimidazole (98%), 1-chlorobutane (99%), D₂O (99.96%) and CDCl₃ (99.96%) were purchased from Sigma–Aldrich. Sodium benzoate (98%), ammonium acetate (98%), sodium acetate (99%) and sodium bromide (99%) were the products of Sinopharm Chemical Reagent Co. Toluene (99%), pentane (99%), acetonitrile (99%) and isopropanol (99%) were obtained from Beijing Chemical Reagent Co. Triply distilled water was used throughout all the experiments.

The surfactant dodecyltriphenylphosphonium bromide was synthesized according to the previous literature [36] and the purity of the product was ascertained by the ¹H NMR spectrum in D₂O. The ILs ([Bmim][PhCOO]) and ([Bmim][OAc]) were prepared based on the procedures reported previously [37,38] and the purity of the obtained ILs was ascertained by the ¹H NMR spectrum in CDCl₃.

2.2. Sample preparation

Certain amount of additives was dissolved in triplydistilled water in a 250 mL volumetric flask and this additive solution with definite additive concentration was used to dissolve an appropriate amount of C₁₂TPB to obtain the stock solution. Next, the stock solution of C₁₂TPB was diluted in turn by the above additive solution instead of water. Finally, a series of C₁₂TPB solutions with different concentrations and a definite additive concentration were prepared.

2.3. Methods

Surface tension measurements were carried out by a surface tensiometer (Model JYW-200B, Chengde Dahua Instrument Co.) using the ring method. Temperature was controlled at 25 ± 0.1 °C by a thermostatic bath. The sizes and size distributions of the micelles were determined by dynamic light scattering (DLS) using a Nanotracc Particle Size Analyzer (Nanotracc NPA 250) and the microtracc FLEX application software program. All measurements

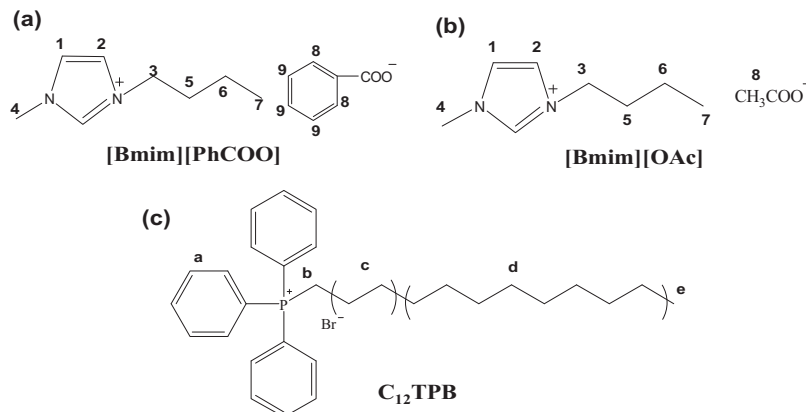


Fig. 1. The chemical structures and ¹H NMR signal assignment of the surfactant and ILs.

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