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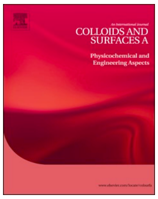

Comparison of ionic liquid and salt effects on the thermodynamics of amphiphile micellization in water

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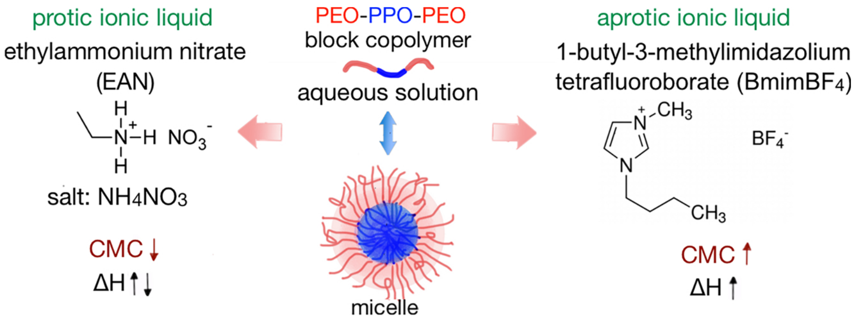
GRAPHICAL ABSTRACT



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ABSTRACT

Ionic liquids are low-melting salts that have novel properties and are very useful as solvents or additives on the basis of the intermolecular interactions operating between the ionic liquid ions and various solute or solvent molecules. In this work, we compare the effects of ionic liquids and salt on the micellization of a representative amphiphilic block copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO), Pluronic P123 ($EO_{20}PO_{70}EO_{20}$). Ethylammonium nitrate (EAN) is used as a representative protic ionic liquid, to compare with its corresponding classic salt, ammonium nitrate (NH_4NO_3), and with 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) as a representative aprotic ionic liquid. The protic ionic liquid EAN is similar with the classic salt NH_4NO_3 in promoting PEO-PPO-PEO micellization; they both increase the micellization entropy and lower the micellization enthalpy at higher concentration. The hydrogen bonding between EAN and PEO, and the ethyl group on the EAN cation, both assist the solvation of PEO-PPO-PEO molecules, which partially offsets their dehydration caused by the ionic liquid ions. These lead to a less significant change of the micellization thermodynamics parameters by EAN compared to NH_4NO_3. The aprotic ionic liquid $BmimBF_4$ exhibits effects that are opposite to those of the protic ionic liquid EAN. The micellization enthalpy of PEO-PPO-PEO significantly increases in the presence of $BmimBF_4$. The hydrogen bonds formed between $BmimBF_4$ and PEO-PPO-PEO, along with nonpolar butyl clusters formed by Bmim cations assist the solvation of Pluronic P123, which in turn hinders micellization. This work compares for the first time the effects of a protic ionic liquid with a classic salt and with an aprotic ionic liquid on amphiphile micellization in aqueous solution in terms of thermodynamics.

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1. Introduction

Ionic liquids are salts that are liquid at ambient conditions, consist of organic cations and inorganic or organic anions, [1–3] and find potential applications [4] in diverse fields such as electrochemistry [5], separations [6,7], biomass processing [8], catalysis [9], drug delivery [10], and space technology [11]. Ionic liquids can be classified into protic and aprotic. Protic ionic liquids are prepared through a stoichiometric neutralization reaction that transfers protons from Brønsted acids to Brønsted bases. Having proton(s) on their cations, protic ionic liquids can donate such protons to form X-H…Y hydrogen bonds with cations or anions that contain proton acceptors such as halogen. [12] Aprotic ionic liquids can also form hydrogen bonds; for example those aprotic ionic liquids based on 1-alkyl-l-3-methylimidazolium can hydrogen bond through the carbons on the C2 (most acidic), C4 and C5 positions of the imidazolium rings [1].

Imidazolium-based ionic liquids having long alkyl side chains can segregate to form apolar and polar domains comprising the alkyl chains and the other ionic liquid parts, respectively. [13] The less polar domains increase in size and become more connected as the length of the alkyl chain increases [14]. The highly hydrogen-bonded networks and the microdomains promote the dissolution in aprotic ionic liquids of various substances, including several that are insoluble in most solvents [15–17]. With their ionic nature, intensive hydrogen bonding and micro-domain segregation, ionic liquids have generated great interest as media for amphiphile self-assembly [18–20].

Water is the typical solvent for amphiphile self-assembly. [21] However, some ionic liquids can completely replace water to play the role of a solvent [19,22] in which some amphiphiles self-assemble into various structures including micelles and lyotropic liquid crystals [19,20,23]. Hydrophobic interactions between water and the hydrophobic part of the amphiphile tend to drive self-assembly in water. The driving force of amphiphile self-assembly in ionic liquids is presumed analogous to that in water, however the solvophobic effect is weaker in ionic liquids than in water (ionic liquids appear better solvents than water for amphiphiles), thus higher concentrations are typically required to amphiphiles to self-assemble in ionic liquids. [24] The temperature effect on micellization and the micellization thermodynamics of silicone surfactants in the protic ionic liquid ethylammonium nitrate (EAN) suggested an entropy-driven micellization at low temperature similar to that in water [25], whereas the micellization was found enthalpy driven at higher temperature (> 35 °C). [26]. The exothermic micellization of imidazolium-based long-alkyl chain ionic liquids in EAN exhibited no significant dependence on temperature, which is in contrast to the behavior of the same surfactants in aqueous solutions [27]. The micellization of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymers in the aprotic ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) and 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) was found entropy-driven, [28] which is analogous to that observed in aqueous solutions [29].

Ionic liquids in aqueous solutions have been studied for their effects on amphiphile self-assembly. Due to the hydroscopic character of ionic liquids, their properties can change dramatically in the presence of even small amounts of water. [30] Overall, mixing water with ionic liquids can enhance the mobility of all ions and contribute to higher ionic conductivities [12]. A comparison of protic and aprotic ionic liquids and their aqueous solutions indicated a lower ionicity (defined as the molar conductivity ratio: molar conductivity obtained from impedance divided by molar conductivity from NMR self-diffusion coefficients) of pure protic ionic liquids compared to aprotic ionic liquids due to stronger ion-ion interactions, and the ionicity of protic ionic liquids increased upon water addition. The degree of ionicity increase varies, depending on the specific ionic liquid. For example, the ionicity of the protic ionic liquid 1-ethylimidazolium bis(trifluoromethanesulfonyl) imide, ($C_2HImTFSI$) increased from 0.54 to 0.65 when the water-ionic liquid molar ratio increased from 0 to 1, which is quite close to the ionicity of its aprotic analogue, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_2C_1ImTFSI$). In contrast, an aprotic ionic liquid with a similar cation, 1-ethylimidazolium trifluoromethanesulfonate ($C_2HImTfO$), exhibited an ionicity increase from 0.49 to 0.53 when the water-ionic liquid molar ratio increased from 0 to 1, still lower than the ionicity of its aprotic analogue, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (C_2C_1ImTfO), which is around 0.63. [31] The addition of protic ionic liquids into aqueous solutions of PEO-PPO-PEO amphiphilic block copolymer was found to decrease the critical micelle temperature (CMT) and increase the micelle radius; the CMT was primarily affected by the anion type and the ionic liquid concentration [32,33]. The critical micelle concentration (CMC) of N-hexadecyl-trimethylammonium bromide (CTAB) in aqueous solutions containing imidazolium-based aprotic ionic liquids increased; this was attributed to the hydrogen bonding network formed by aprotic ionic liquids with ionic liquid and water [34].

Ionic liquids are involved in amphiphile micellization in different ways: they mostly act as solvents and/or as additives that may alter the solvent properties and/or interact with the amphiphiles. [27,32,35] It is known that addition of salts or organic solvents can tune the properties of aqueous solutions [36]. Ionic liquids exhibiting features of inorganic salts as well as solvents are anticipated to affect micellization. The cosolvent effect, as observed also for polar organic solvents such as glycerol, ethanol, and propanol, alters the amphiphile micellization depending on the solvent quality of the mixed solvents. For example, the addition to water of ethanol or 1-propanol decreases the cohesive forces in the solvent mixture and increases the solubility of amphiphilic molecules, which increase critical micelle concentration (CMC) as a consequence, while the addition of glycerol favors micellization and decreases CMC [25,37,38]. Ionic liquids may also act as cosolutes during micellization, which is similar to classic salts such as alkali-halide salts promoting micellization [36]. Due to the flexible design of the ionic liquid chemical structure, the effects of ionic liquids on micellization can emanate primarily from certain functional groups, for example, the long alkyl chain ionic liquid 1-hexyl-3-methyl imidazolium bromide (HmimBr) formed mixed micelles with CTAB, whereas N-butyl imidazolium chloride (N-BimCl) behaved partly as a solvent [34]. Ionic liquids with different anions follow the Hofmeister series [39] on salting out effects. [32] The available literature on amphiphile micellization in aqueous solutions containing ionic liquids focuses mostly on the effects of different ionic liquid anions or side-chain length, and the CMC is typically used for comparison. [32] The need for improved understanding of ionic liquids interacting with solvents and solutes during amphiphile micellization motivates the present work.

We select here a model polymeric amphiphile (PEO-PPO-PEO block copolymer [36,40,41]), on which to examine the effects of the widely used protic ionic liquid ethylammonium nitrate (EAN), and to compare with a classic salt having a similar molecular structure, ammonium nitrate (NH_4NO_3), in order to elucidate the unique role of ionic liquids on micellization. 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$) is used here as a representative aprotic ionic liquid to compare with EAN in order to probe the differences between protic and aprotic ionic liquids on micellization. PEO-PPO-PEO block copolymer micellization in water is an endothermic entropy-driven process. [42] The modification of the water solvent properties by addition of electrolytes [39] or polar organic solvents [37,38] is expected to change the thermodynamics of PEO-PPO-PEO micellization [39,43,44]. Isothermal titration calorimetry (ITC) has been utilized to assess the thermodynamics of PEO-PPO-PEO micellization [45–48]. In a recent study [49], we employed ITC to probe enthalpy changes during micelle dilution and micelle dissociation of a representative PEO-PPO-PEO block copolymer in aqueous EAN solutions, and showed EAN to play the role of inorganic salt and co-solvent during the micellization process. However, the mechanism behind the effects of ionic liquids on amphiphile micellization in aqueous solution is still not well understood,