Colloids and Surfaces A: Physicochem. Eng. Aspects 507 (2016) 182–189

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Impact of organic solvents on the micellization and interfacial behavior of ionic liquid based surfactants

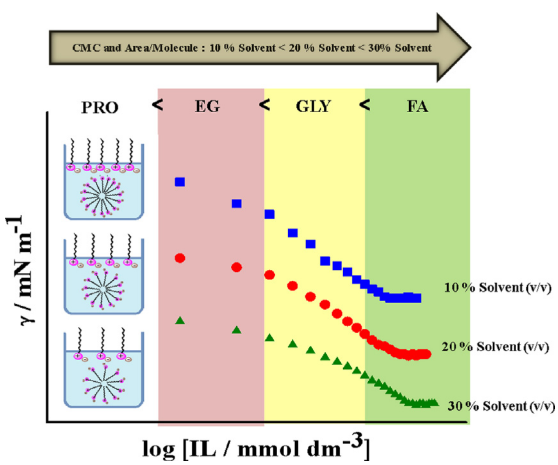
Sargam M. Rajput[a], Utkarsh U. More[a], Zuber S. Vaid[a], Kamlesh D. Prajapati[b], Naved I. Malek[a,*]

[a] Applied Chemistry Department, S. V. National Institute of Technology, Surat, 395 007, India
[b] V.S. Patel College of Arts and Science, Bilimora, 396 321, India

HIGHLIGHTS

- Organic solvent influences the micellization and surface activity of ionic liquid based surfactants.
- Increasing organic solvent composition in water, cmc increases.
- Organic solvent, disfavoring the micellization, displaces water layer at the interface.
- Comparative aggregation behavior of ILBSs with conventional cationic surfactants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 April 2016
Received in revised form 28 July 2016
Accepted 6 August 2016
Available online 8 August 2016

Keywords:
Critical micelle concentration
Relative permittivity of organic solvents
Ionic liquid based surfactants
1-Tetradecyl-3-methylimidazolium bromide
1-Hexadecyl-3-methylimidazolium bromide

ABSTRACT

To elucidate the role of organic solvents, in altering the micellization and interfacial behavior of Ionic Liquid based Surfactants (ILBSs), we had investigated the effect of formamide (FA), glycerol (GLY), ethylene glycol (EG) and 1-propanol (PRO) on the micellization and interfacial behavior of 1-tetradecyl-3-methylimidazolium bromide (C_{14}mimBr) and 1-hexadecyl-3-methylimidazolium bromide (C_{16}mimBr) ILs, in aqueous solution by conductometric and tensiometric techniques at 298.15 K. The micellization behavior has been determined by studying the changes in critical micelle concentration (cmc), degree of counter ion binding (β), gibbs free energy of micellization (ΔG_m^0) and interfacial behavior by studying various surface parameters. Micellization behavior was mainly studied in light of altering the relative permittivity of the medium and displacement of water layer, which disfavors the micellization and as a result increases cmc. Effect of solvophobic parameter (S_p) and packing parameter (P) on the micellization was also examined. Results have been compared with the conventional cationic surfactants with identical alkyl chain.

1. Introduction

Ionic liquids (ILs), consisting of larger organic cations and smaller organic/inorganic anions compared to traditional salts,

* Corresponding author.
E-mail addresses: navedmalek@ashd.svnit.ac.in, navedmalek@yahoo.co.in (N.I. Malek).

http://dx.doi.org/10.1016/j.colsurfa.2016.08.008
0927-7757/

are of interest to the research community due to their potential green characteristics. The unique physicochemical properties of ILs make them the best alternative to the traditional volatile organic compounds (VOCs) [1–4]. The long chain imidazolium based ionic liquids possesses better surface active properties than the traditional cationic surfactants [5–7] and are termed as Ionic Liquid Based Surfactants (ILBSs). These ILBSs found applications in various fields of science, including colloidal science [8,9], catalysis [10,11], nanotechnology [12,13] and biomedicine [14,15] to name a few. Among these bunches of applications, several applications need the media with no water or having water at the minimum level [16]. Among the possible alternatives, traditional strategy to synthesize newer ILs with structural variables such as alkyl chain length variations, various cations and/or anions [17–20] does not solve the purpose. The best possible way to alter the micellization behavior of these ILBSs and make them a better choice for such applications requiring water poor media is by changing the polarity of the aqueous medium by the addition of organic solvents.

The nature of surfactant-solvent interactions depends on the solvent environment and significantly influenced through changing the solvent relative permittivity. Introducing organic solvent improves the solvophobicity of the medium and makes the micellization process less favorable as compared to water. Several industrial applications use surfactants either in their aggregated form or they are subjected to the aggregation during the process. During the course of application, they come in contact with the organic solvents which have an impact on their overall aggregation behavior so on performance. Micellar liquid chromatography (MLC), dispersed or phase-separated systems, environmental pollution control, synthesis of reversible solvent-induced porous polymers, applications from battery design to reaction controlled, and extraction processes are among these applications [21,22]. MLC uses surfactants in the mobile phase (in their aggregated form). Polar and non-polar analysts are separated based on the interaction of the surfactant aggregates with the organic solvents [23]. Several conventional surfactants are been tested in MLC [24,25] but the data for the ILBSs are scared [26]. Several extraction processes, where surfactant solutions are used in the presence of organic solvents (ternary system) also find applications in recent times. The aggregated form of the surfactants reduces the efficiency of the process by partial extraction of the product. ILBSs are the best suitable alternative due to their better surface properties in such kind of applications. The knowledge of micellization and interfacial behavior of ILBSs in the presence of organic solvents could help us in designing such extraction systems [22,27]. Such systems also find their applications in high submicellar chromatography, where micellization of the surfactants occurred at high composition of the organic solvents [28]. Though several research groups had studied the influence of organic solvent on the micellization of ILBSs in aqueous medium, the data on the interfacial behavior is yet not studied systematically. Such data will provide researchers a handful of information in finding applications of ILBS.

In this context, the aggregation behavior of imidazolium based ILBSs having long alkyl chain in the head group (1-dodecyl-3-methylimidazolium bromide, C_{12}mimBr) in various water-organic solvents mixtures was reported by Wang et al. [29,30]. The study reported that with increasing the organic solvent proportion in water, there appears significant increase in cmc and decrease in size of the aggregates as well as in aggregation number (N_{agg}). Recently, micellization and surface adsorption behavior of C_{12}mimBr was studied in aqueous solution in the presence of several organic solvents and the results have been compared with the traditional cationic surfactant with identical alkyl chain length. The results show that the solvents having larger dielectric constant act as co-solvents and the more hydrophobic solvents acts as co-surfactants [31]. To the best of our knowledge, this is the first report that comprehensively studies the effect of the organic solvent additives on IL aggregation for these two ILBSs (C_{14}mimBr and C_{16}mimBr) in aqueous solutions. Our data for C_{14}mimBr and C_{16}mimBr therefore, complete these published work on the 1-R-3-methylimidazolium bromide series [29–31], in addition to demonstrating the effects of organic solvents on (conventional) TTAB and CTAB surfactants. Han and his co-workers [32] studied aggregation behavior of ILs in organic solvents by applying several analytical tools and found that aggregation depends on the dielectric constant of the solvents. Polarized optical microscopy and small-angle X-ray scattering was used to investigate the phase behavior of ternary mixtures including IL, water and alcohols (long chain) [33]. Pino et al. [26] studied the impact of various organic solvents on the aggregation behavior of long chain aqueous ILs (1-hexadecyl-3-butylimidazolium bromide and 1,3-didodecylimidazolium bromide) solution. The aggregation behavior of 1-dodecyl-3-methylimidazolium chloride was studied in various concentrations of water-methanol mixtures and the role of methanol as co-surfactant at lower concentration and as co-solvent at higher concentration [34]. During the preparation of this manuscript, a publication appeared on the determination of cmc of reverse micelle in the anionic surfactant AOT [35] in various nonpolar hydrocarbon solvents. Day et al. studied the aggregation behavior of the anionic surfactant sodium dioctylsulphosuccinate (AOT) in the presence of water-acetonitrile mixture [36]. As per our knowledge, further literature studying the aggregation behavior of ILBSs in presence of organic solvents in aqueous medium is not available.

In the present investigation, we have studied the micellization and interfacial behavior of 1-tetradecyl-3-methylimidazolium bromide (C_{14}mimBr) and 1-hexadecyl-3-methylimidazolium bromide (C_{16}mimBr) in water in the presence of different organic solvent with variable polarity (Formamide (FA), glycerol (GLY), ethylene glycol (EG) and 1-propanol (PRO)) by electrical conductivity and surface tension measurements at 298.15 K. The micellization and interfacial properties of the studied ILBSs are compared with the conventional cationic surfactants having similar carbon chain length i.e. Tetradecyltrimethylammonium bromide, (C_{14}TAB) and Cetyltrimethylammonium bromide, (C_{16}TAB). The aim of the present work is to understand the factors influencing the micellization of ILBSs in different composition of solvents. The data are helpful in various filed of applications including extraction, synthesis of various organic molecules and in various separation methods to name a few.

2. Materials and methods

The cationic surfactants tetradecyltrimethyl ammonium bromide (C_{14}TAB) and cetyltrimethyl ammonium bromide (C_{16}TAB) were purchased from Aldrich LTD (≥99%) and used as received. ILBSs (C_{14}mimBr and C_{16}mimBr) were synthesized as per the procedure published elsewhere [37–40]. Briefly, N-methyl imidazole (0.10 mol) and respective alkyl bromides (0.13 mol) were taken in three necks round bottom flask and toluene as the solvent. The reaction was preceded for 24 h at 80 °C by continuously observing the progress of reaction through Thin Layer Chromatography (TLC). Product was washed three times by ethyl acetate and the resulting white crystalline solids were dried in vacuum for 48 h before the preparation of the respective solution. Water content was found to be less than 100 ppm (Karl-Fischer, Metrohm, 890 Titrando). The probable impurities in the products were analyzed through ^{1}H NMR (Bruker 400 MHz) spectra and 99.5% purities (on mass fraction basis) were obtained. ^{1}H NMR data for the synthesized ILBSs are reported in ESI as Figs. S1 and S2 . Further, absence of minimum near the breakpoint in the surface tension graph confirms the absence of any surface impurity in the synthesized ILs.