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Phase behaviour and microstructure of the micro-emulsions composed of cholinium-based ionic liquid, Triton X-100 and water

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ABSTRACT

In this paper, micro-emulsions composed of cholinium-based ionic liquids (ILs), octylphenol ethoxylate (Triton X-100) and water were prepared. These ternary systems were found to be stable over 12 months at room temperature. Their phase behaviour was investigated by using cloud titrations, and their microstructures were characterised by means of cyclic voltammetry and electrical conductance measurements at $T = 298.15$ K. It was shown that the micro-emulsions exhibited IL-in-water, bi-continuous and water-in-IL microstructures. Dynamic light scattering data suggest that Triton X-100 forms micelles in water, which were swelled by the ILs added. Droplets with the size about 20 nm were formed in these IL-based micro-emulsions, and the droplet size increased with the increase of the IL concentrations. These IL-based micro-emulsions may have potential in drug delivery, chemical reactions and nanomaterial preparation as a new type of nanoreactors.

1. Introduction

Micro-emulsions (MEs) are thermodynamically stable and isotropic transparent mixtures composed of at least a hydrophobic, a hydrophilic and an amphiphilic component under certain conditions [1]. Owing to the advantages such as nanometer-sized aggregation, long-term stability, biocompatibility, and high solubilization capacity for polar and non-polar species, micro-emulsions have become increasingly important for applications in the areas such as separation, nanomaterials preparation, chemical reactions, cosmetic industry and drug delivery [2–6]. Depending on their composition, micro-emulsions exhibit different microstructures that crucially influence their properties and applications. In the majority of micro-emulsions, water has been used as polar phase to constitute aqueous micro-emulsions. Sometimes, non-polar compounds such as hydrocarbons can be used as oil phase to form nonqueous micro-emulsions.

During recent decades, a class of environmentally friendly solvents, ionic liquids (ILs), has received growing interest due to their fascinating and outstanding physicochemical properties such as non-volatility, high thermal and chemical stability, wide liquid range, and suitable polarity [7]. The diversity of cations and anions makes it possible to design ILs for specific applications. The most popular cationic components of ILs are the substituted imidazolium cations $[C_n\text{mim}]^+$ while hexafluorophosphate ($[PF_6]^-$) and tetrafluoroborate ($[BF_4]^-$) are most frequently used as anions. Although the properties of the imidazolium salts can be tuned easily by changing alkyl chain length of the cations and type of the anions, this class of ILs often exhibits high toxicity to ecosystems [8]. Therefore, less toxic or non-toxic ILs received much attention in recent years. It is known that choline derived ILs are less toxic, and the publications related to the synthesis, properties and applications of this class of ILs are rapidly growing [9–11].

Because of the amphiphilic nature, ionic liquids have been studied in classical colloid and surface chemistry [12–14], and IL-based micro-emulsions are the most popular. The first IL-based micro-emulsion where water was replaced by an IL was reported by Gao et al. [15]. In the subsequent investigations, various kinds of micro-emulsions containing IL have been prepared [16–20]. In most of the studies on IL-based micro-emulsions, the IL, such as 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4\text{mim}][BF_4]$, was used as a replacement for water [21–23]. Nevertheless, some ILs may serve as appropriate replacement for oil phase, such as 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4\text{mim}][PF_6]$ [24,25]. Sometimes, ILs with long alkyl chain can also be used as surfactants, which are named as surface active ionic liquids [26,27]. Recently, Porada and co-workers [28] prepared IL-based micro-emulsions by using a novel hydrophobic ionic liquid $[\text{Ali336}][Tf_2N]$ composed of a cheap and commercially available

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aliquat 336 cation and a bis(trifluoromethanesulfonyl)imide anion. Phase behaviour of these IL-based micro-emulsions has been studied as a function of surfactant concentration and temperature. Pramanik and co-workers [29] reported non-aqueous micro-emulsions containing pyrrolidinium ILs as polar phase. The micro-regions were identified by conductivity measurements based on percolation theory. Dynamic light scattering (DLS), *nuclear magnetic resonance* (NMR) and time-resolved fluorescence spectroscopy were also used to confirm microstructure of these micro-emulsions. Rojas and co-workers [30] investigated the ternary system composed of 1-ethyl-3-methylimidazolium ethylsulfate [C_2mim][$EtSO_4$], toluene and ionic liquid surfactant 1-butyl-3-methylimidazolium dodecylsulfate [C_4mim][$DodSO_4$]. The structure of micro-emulsions was identified by means of conductance, DLS and small-angle X-ray scattering. Klee and co-workers [31] studied magnetic micro-emulsions formed by magnetic ILs, cyclohexane and an appropriate mixture of ionic liquid surfactant and co-surfactant decanol. The structure of micro-emulsions was confirmed by small-angle neutron scattering (SANS) and conductivity. The most interesting characteristics of this kind of micro-emulsion is that properties of the micro-emulsion can be manipulated by a magnetic field. Ghosh and co-workers [32] examined the effect of alkyl chain length of ILs on the phase behaviour of 1-ethyl-3-methylimidazolium *n*-alkyl sulfate [C_2mim][C_nSO_4]/Triton X-100/cyclohexane systems. DLS results revealed the formation of highly stable nano-sized IL micro-emulsions. The size and physicochemical properties of such IL-based micro-emulsions can be tuned by chemical structure of the ILs. Therefore, these micro-emulsions share the advantages of ILs and traditional micro-emulsions, thus possessing various advantages over traditional water-based micro-emulsions. These outstanding properties render IL-based micro-emulsions excellent candidates for a variety of applications.

Considering the fact that choline derivative-based ILs can be readily prepared from cheap, renewable natural compounds and other non-toxic materials, the aim of this work is to prepare aqueous cholinium-based ILs micro-emulsions and to investigate their phase behaviour and microstructure. In the design of the cholinium salts, bis(trifluoromethanesulfonyl)imide ([Tf_2N]$^-$) was chosen as the anion. Chemical structures of such ILs are shown in figure 1. These ILs are found to serve as polar oil phase in the micro-emulsions. The phase equilibrium, cyclic voltammetry, electrical conductance and DLS measurements have been used to understand the phase behaviour, the sub-regions and the droplet size of the micro-emulsions.

2. Experimental

2.1. Materials

All the ILs used in this work, [$N_{1,1,n}C_2OH$][Tf_2N] (n = 1,4,6,8,10) and [Bet][Tf_2N], were synthesized according to the procedures described in the literature [9]. These ILs were analysed by ^{1}H-NMR (Bruker, AV-400) to confirm the absence of any major impurities

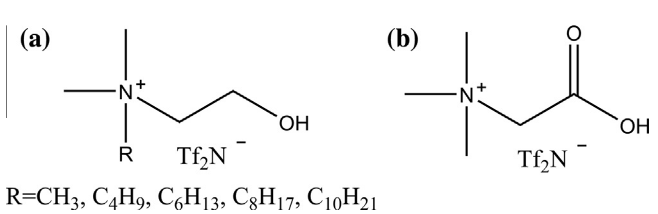

FIGURE 1. Chemical structure of the ionic liquids: (a) cholinium-based ionic liquids [$N_{1,1,n}C_2OH$][Tf_2N] (n = 1,4,6,8,10); and (b) [Bet][Tf_2N].

and the purity of these ILs is found to be greater than 0.99 in mass fraction. Deionised water was double distilled and used throughout the experiments, and its conductivity was less than 1.0 $\mu S \cdot cm^{-1}$ at room temperature. Triton X-100 was purchased from Alfa Aesar and used as received, and $K_4Fe(CN)_6$ was obtained from Aladdin and used without further purification. The details of the compounds used in the present work are given in table 1.

2.2. Phase diagrams of the micro-emulsions

Phase diagrams of the micro-emulsions were constructed by titration of Triton X-100 into the mixtures of IL and water at T = (298.15 ± 0.05) K. For this purpose, different ratios of the IL to water were prepared in the concentration range from (0 to 100) wt%. Then, the surfactant Trition X-100 was added drop wise by vortexing the mixtures vigorously. The mass fractions at which turbidity-to-transparency occurred were derived from precise weight measurements using a Sartorius ALC-210.4 balance with an accuracy of ±0.0001 g. Based on critical values obtained at different mass ratios, the phase boundary was determined.

2.3. Diffusion coefficients of $K_4Fe(CN)_6$ in the micro-emulsions

Diffusion coefficients of the probe molecule $K_4Fe(CN)_6$ were determined according to the procedure reported in the literature [24]. The three-electrode system consisted of a glassy carbon working electrode and an Ag/AgCl reference electrode. A platinum flake counter electrode was used for cyclic voltammetric measurements. The cyclic voltammogram of the probe was recorded on an electrochemical analyzer (CHI 660D, Shanghai Chenhua Co., China) over −0.5 V to 0.5 V at T = (298.15 ± 0.05) K with the scan rate varied between (20 and 100) $mv \cdot s^{-1}$. The diffusion coefficients (D) of the probe in different micro-emulsions were calculated from the peak currents (i_p) according to Randles–Sevcik equation [24]:

$$i_p = (0.447F^{1.5}An^{1.5}D^{0.5})/(RT)^{0.5}, \tag{1}$$

where n is the number of electrons involved in oxidation or reduction reaction, A is the area of the working electrode, C is concentration ($mol \cdot L^{-1}$) of the probe in solution, V is the scan rate, F is the Faraday constant, R is the gas constant, and T is the temperature. All the experimental data were determined in triplicate. In most cases, the D values were reproducible, in general, within an experimental error less than 5%.

2.4. Electrical conductivity measurements of the micro-emulsions

The electrical conductivity measurements were performed at T = (298.15 ± 0.05) K by using a conductivity meter (DDSJ-308A, Shanghai Leici Precision Instrument Co., Ltd., Shanghai, China) with an accuracy of ±0.5%. The temperature was controlled by a precision bath circulator (THD-2006, Tianheng Precision Instrument Co., Ltd., Ningbo, China).

2.5. Droplet size measurements of the micro-emulsions

The size and size distribution of the micro-emulsions were measured by DLS technique using a Malvern Zetasizer Nano-90 light scattering instrument (Malvern Instrument Ltd., Worcester, UK). The scattering angle was set at 90°. After the micro-emulsion samples were equilibrated for 24 h, the samples were filtered through a 0.45 μm Millipore filter to remove the dust or contaminants. Measurements were performed at T = (298.2 ± 0.1) K. The measurement errors were less than 5%.