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Ionic liquid bmimCl/formamide mixture as the polar phase of nonaqueous microemulsions

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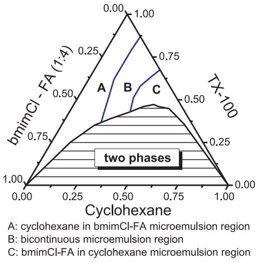
HIGHLIGHTS

- Microemulsions with ionic liquid and a nonaqueous polar solvent as the polar phase.
- Characterization by means of conductivity, DLS and UV–vis spectroscopy.
- Linear increase of the microemulsions droplet size by adding the polar phase.
- These nonaqueous microemulsions can dissolve metal salt.

GRAPHICAL ABSTRACT



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ABSTRACT

The solution of ionic liquid (IL) bmimCl and polar organic solvent formamide (FA) were used to form nonaqueous microemulsions in cyclohexane by the aid of surfactant Triton X-100 (TX-100). The phase behavior of the bmimCl–FA/TX-100/cyclohexane system at 25 ± 0.1 °C was studied. Electrical conductivity measurement was used to identify the microstructures of the nonaqueous microemulsions. Based on the phase diagram, the reverse microemulsions containing bmimCl–FA as the internal phase were investigated by the dynamic light scattering (DLS) and UV–vis spectroscopy. The result of DLS experiments confirmed the formation of reverse microemulsions of bmimCl–FA in cyclohexane. The UV–vis studies with methyl orange (MO) and methylene blue (MB) as absorption probes further confirmed the existence of reverse microemulsions. UV–vis studies using $CoCl_2$ as probe also indicated that the reverse microemulsions could dissolve metal salt.

1. Introduction

Microemulsions are transparent, isotropic and thermodynamically stable mixtures of two immiscible liquids (nonpolar and polar) stabilized by surfactants. The traditional reverse microemulsions use water as the polar component. The surfactant-covered water pools provide a unique microenvironment for reactions and nanoparticle preparation [1,2]. Reverse microemulsions can also be made using some polar organic solvents instead of water. These polar solvents have high dielectric constants and very low solubility in hydrocarbon solvents [3]. The most common polar solvents used for these nonaqueous microemulsions include formamide (FA), dimethylforamide (DMF), and ethylene glycol (EG) [4,5]. These waterless microemulsions have attracted much interest and have been widely applied in many fields.

Ionic liquids (ILs), which are typically composed of organic cations and organic/inorganic anions, are receiving much attention as neoteric solvents. They have many attractive properties, such as negligible vapor pressure, a wide electrochemical window, and high thermal stability. Particularly, the properties of ILs

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can be tuned by altering either the cation or the anion [6]. In the past decade, ILs have been used in various chemical applications including chemical reactions, separations, material preparation, and electrochemical applications. The unique properties of ILs are favored for increasing the efficiency of reaction and separation, and controllability of material preparation [7–10].

ILs can also play an important role in microemulsions [11–13]. Recently, using ILs instead of water to prepare nonaqueous microemulsions is an active subject. These new nonaqueous microemulsions expand the potential use of ILs in microheterogeneous systems as reaction or separation media [14]. Han and co-workers discovered that hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate ($bmimBF_4$) can substitute for water and act as polar nanosized droplets dispersed in cyclohexane with the surfactant Triton X-100 (TX-100) [15]. Eastoe et al. investigated the same microemulsions by small-angle neutron scattering (SANS), which showed a regular increase in droplet volume as the micelles were progressively swollen with added $bmimBF_4$, a behavior consistent with classic water-in-oil (W/O) microemulsions [14]. Zheng and co-workers found that $bmimBF_4$ can form nonaqueous microemulsions with benzene [16], toluene [17], *p*-xylene [18] or triethylamine [19] also using TX-100 as surfactant. The structure and properties of these microemulsions were further investigated using various methods by many groups [20–25]. Additionally, the hydrophobic ILs, such as 1-butyl-3-methylimidazolium hexafluorophosphate ($bmimPF_6$) can also form nonaqueous microemulsions [26–30]. The IL microemulsions have potential application in the production and processing of semiconductors, nanomaterials, enzyme-catalyzed reactions, and extraction [21]. Compared to traditional microemulsions, they have shown various advantages, especially in the preparation of nanostructures [31–33].

However, in current studies, the ILs used are room-temperature ILs [34], which possess relatively small viscosity. As we known, ILs are often extraordinarily viscous or even solid near room temperature [35]. Take the chloride anion-based ILs as an example, they are solid near room temperature and should be diluted with traditional molecular solvents in some applications [9,36]. Therefore, the broader use of ILs to form nonaqueous microemulsions is limited. Using the mixture of an IL and nonaqueous polar solvents instead of pure ILs may be a prospective approach to this problem. The addition of polar solvents can significantly reduce the viscosity of the IL phase [37]. Moreover, this type of nonaqueous microemulsions may have advantages in tuning the properties of the polar microenvironment as the chemical properties of the solution of IL and polar solvent can be adjusted by altering the IL or polar solvent [38].

The present work investigates the formation of nonaqueous microemulsions containing the mixture of IL and polar solvent as the polar phase. For this purpose, a chloride anion-based IL 1-butyl-3-methylimidazolium chloride (bmimCl) was chosen as a model IL. Formamide, which has very low solubility in hydrocarbon solvents [39], was chosen as the polar solvent. Then, in this work, these nonaqueous microemulsions were prepared and characterized using different techniques, including electrical conductivity, dynamic light scattering (DLS) and UV–vis spectroscopy.

2. Experimental

2.1. Materials

TX-100 was obtained from Sigma–Aldrich and dried under vacuum at 80 °C for 4 h before use. The IL bmimCl (purity > 99%) was provided by Lanzhou GreenChem ILS, LICP, CAS (China). Formamide (purity > 99%) was purchased from Lingfeng Co., Ltd. (Shanghai, China). Cyclohexane (purity > 99.5%) and methyl orange (MO) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methylene blue (MB) was produced by Dongsheng Chemical Reagents Co. (Zhejiang, China). $CoCl_2$ was a product of Jingchun Reagent Co., Ltd. (Shanghai, China).

2.2. Apparatus and procedures

The phase diagram of the system was determined by direct visual observation at 25 ± 0.1 °C. In a typical experiment, bmimCl–FA and cyclohexane were added into a thermostated glass vessel; the sample was then agitated. After thermal equilibrium, the sample was then titrated with TX-100 until the hazy and milky liquid solution became transparent, which was indicative of the formation of the single phase. The corresponding composition of the solution was remarked as the phase boundary. The bmimCl–FA was a solution of IL bmimCl in FA with a fixed bmimCl to FA molar ratio (1:4), which was regarded as pseudo one component.

Conductivity measurement was performed with a DDS-11 A conductivity meter (Shanghai Precision & Scientific Instrument Co., Ltd.). In the experiment, the desired amounts of bmimCl–FA and TX-100 were mixed in a thermostated glass vessel at the temperature of 25 ± 0.1 °C. Then a certain amount of cyclohexane was added. After thorough mixing and thermal equilibrium, the electrical conductivity was recorded. The cyclohexane was successively added to the mixture with a transferpette (Brand Co., Ltd., Germany) until the transparent liquid solution became turbid. The conductivity was measured after each addition of cyclohexane.

The diameters of the microemulsion droplets were determined by dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern Instruments, UK) with a laser light wavelength of 633 nm and a scattering angle at 173°. The sample was filtered through 0.45 μm millipore membrane filter to remove possible dusts prior to measurement. All measurements were conducted at 25 °C.

The UV–vis spectra were performed on a Shimadzu UV-2550 spectrophotometer at 25 ± 0.1 °C. The path length of the quartz cell used in this experiment was 1 cm. The solutions were prepared in advance and then added to the quartz cell.

3. Results and discussion

3.1. Phase diagram and microregions of the microemulsions

The phase diagram of the bmimCl–FA/TX-100/cyclohexane system at 25 ± 0.1 °C is illustrated in Fig. 1. The shadow area of the diagram marked “two phases” is a turbid region. Above the phase separation boundary curve, the system exists as a single phase. Generally, the single phase region of microemulsions can be divided into different microregions, such as water (or polar solvent)-in-oil microemulsions region, bicontinuous microemulsions region and oil-in-water (or polar solvent) microemulsions region [26]. In this work, the microregions were identified by electrical conductivity measurement, which was frequently used to investigate the structure and structural changes in aqueous and nonaqueous microemulsions [26]. Thus the electrical conductivity as a function of cyclohexane weight fraction at different fixed weight ratios of bmimCl–FA to TX-100 (1:9, 2:8, 3:7, 4:6, 5:5) was investigated. The test samples are shown in Fig. 1 (lines a–e).

Two typical curves of conductivity versus cyclohexane concentration are shown in Fig. 2. As an example, Fig. 2a illustrates how to distinguish the microregions of the microemulsions on the basis of the conductivity data. The initial conductivity increases with the increase of the content of cyclohexane, due to the successive increase of conductive microemulsion droplets, which indicates the formation of cyclohexane in bmimCl–FA microemulsions. After