Colloids and Surfaces A: Physicochem. Eng. Aspects 329 (2008) 146–152

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Effect of polyvinylpyrrolidone on the microstructure of 1-butyl-3-methylimidazolium tetrafluoroborate/Triton X-100/cyclohexane microemulsions

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ARTICLE INFO

Article history:
Received 11 December 2007
Received in revised form 1 July 2008
Accepted 6 July 2008
Available online 25 July 2008

Keywords:
Microemulsion
Ionic liquid
Polyvinylpyrrolidone
Dynamic light scattering
Conductivity
NMR spectroscopy
FTIR spectroscopy

ABSTRACT

The effect of the polymer polyvinylpyrrolidone (PVP) on the microstructure of reverse microemulsions consisting of the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4), the surfactant Triton X-100 and the component cyclohexane was investigated in the present work. The study of the phase behavior revealed that the existence region of the microemulsion state is remarkably decreased by the addition of PVP. Conductivity measurements showed that the threshold of electrical percolation is also slightly decreased with increasing PVP content, indicating an increase of the attractive interaction between the microemulsion droplets. The microemulsion droplets were gradually swollen by both, bmimBF_4 and PVP addition, and thereby the viscosity of the microemulsion solution was slightly increased. FTIR and NMR measurements revealed that there is no special interaction between the added PVP and Triton X-100, that is, PVP was only solubilized inside the polar IL-core of the microemulsion droplets.

1. Introduction

Ionic liquids (ILs) are receiving great attention as a class of neoteric solvents, due to their special physical and chemical properties, such as low volatility, non-flammability and high thermal stability [1–5]. They are also regarded as environmentally benign solvents for chemical reactions, separations, electrochemical applications, biopolymers, and interfacial synthesis [1,6,7]. Recently, microemulsions based on ILs as substitute for water or oil have been intensively investigated. Han and co-workers discovered that 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) can be dispersed as polar nano-sized droplets in a continuous hydrocarbon phase. Freeze-fracture electron microscopy (FFEM) indicated a droplet-like structure which has the same appearance as the structure known from water-in-oil (W/O) microemulsions [8]. Eastoe et al. have also investigated this microemulsion system by small-angle neutron scattering (SANS), which showed an increase of the droplet volume starting from micelles which were progressively swollen by addition of the IL bmimBF_4—a behavior which is consistent with W/O microemulsions [9]. The effect of confining the IL bmimBF_4 on the solvation dynamics and rotational relaxation of Coumarin 151 and Coumarin 153 in microemulsions has been explored [10]. In addition, the IL bmimPF_6 can substitute organic solvents to form "green" microemulsions with the aid of the surfactant Triton X-100 [11]. Electrochemical cyclic voltammetry was used to identify the microemulsion existence region [12,13]. Besides, a formation mechanism for IL microemulsions was proposed, based on the approach that the electrostatic interactions between the electronegative oxygen atoms of the oxyethylene (OE) units of Triton X-100 and the electropositive imidazolium ring are the driving force for the solubilization of bmimBF_4 in the core of the Triton X-100 aggregates [14]. It was also found that the addition of small amounts of water to IL microemulsions enhances the stability of the microemulsion. The added water molecules were located within the hydrophilic group domain of Triton X-100. They bridge the hydrogen bond network among the ethylene groups of Triton X-100, the cations and the anions of solubilized bmimBF_4. Such a hydrogen bond network is more stable than the electrostatic interaction and, as a result, the microemulsion becomes more stable in the presence of water [15].

It was found that IL microemulsions have potential as alternative reaction medium for the preparation of solid materials [10,11].

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doi:10.1016/j.colsurfa.2008.07.026

For example, in a recent report it has been shown that IL-based microemulsions can be used to produce polymer nanoparticles, gels, and open-cell porous materials [16]. Silica microrods with nano-sized pores were successfully fabricated in an IL microemulsion only, whereas in traditional W/O microemulsions compact nanoparticles were obtained [17]. Moreover, water-in-bmimPF_6 IL microemulsions were applied to prepare dispersed tetragonal ZrO_2 nanoparticles in which the highly thermostable IL prevents the particles form agglomeration during the subsequent calcination process [18].

The study of the effect of polymers on micellar solutions and microemulsions is interesting from both the fundamental and the applied point of view [19]. However, to the best of our knowledge, so far there is no study published on the role of polymers added to IL microemulsions. Polyvinylpyrrolidone (PVP) is a well-known homopolymer with a long and soft polyvinyl backbone and its individual monomer contains an amide group. As a commercially available material, PVP has been applied in many fields, such as pharmaceutical, biotechnology, even living goods. Numerous of nanomaterials synthesis strategies were reported by using PVP served as stabilizer, and shape-controller. For this reason, PVP was chosen in our work. This is why we investigated the effect of the solubilized polymer PVP on the behavior of bmimBF_4-in-cyclohexane (IL/O) microemulsions. The solubilization of PVP in IL microemulsions was characterized by conductivity measurements, dynamic light scattering (DLS), FTIR and NMR spectroscopic analyses. The current study is focused on a better understanding of the microstructure and the formation mechanism of IL microemulsions, aiming at establishing these solvents as novel reaction medium.

2. Experimental

2.1. Materials

Polyvinylpyrrolidone (PVP10, MW = 10,000) and non-ionic surfactant Triton X-100 were provided by Sigma–Aldrich. Triton X-100 was evaporated under vacuum at 80 °C for 4 h to remove excess water before use. Cyclohexane and d10-cyclohexane were purchased from Merck. IL, bmimBF_4 was synthesized according to the standard method by a quaternization reaction of 1-methylimidazole using 1-chlorobutane [20]. The imidazolium chloride salt was crystallized in ethyl acetate at −30 °C. The postmetathesis product was obtained by ion exchange of 1-butyl-3-methylimidazolium chloride and potassium tetrafluoroborate in distilled water and then washed with dichloromethane and dried under a high vacuum. To avoid water, the containers with the materials were sealed tightly to avoid any further contact with air before use.

2.2. Apparatus and procedures

A conductivity pocket meter (Model Cond 340i, Werkstätten GmbH & Co. KG, accuracy of ±0.5%) was used to measure the solution conductivities. The temperature of the solutions was controlled by a thermostat (F31C, Julabo, accuracy of ±0.01 °C). The diameters of the investigated microemulsions were determined by Nanotrac Particle Size Analyzers (Nanotrac NPA 250) using the microtrac FLEX application software program. The PSD was calculated by Brownian motion detection with an advanced power spectrum analysis of the Doppler shifts by the Controlled Reference Method. All measurements were made with laser diode 780 nm wavelength, 3 mW nominal, Class IIIB at the scattering angle of 180°. FTIR spectra were collected on a Nicolet Nexus 670 with continuum microscope, using OMNIC software. ^{1}H NMR measurements were carried out with a Bruker DPX 400 NMR spectrometer at 300 K. The instrument was operated at a frequency of 400.13 MHz using tetramethylsilane as an internal reference. The standard two-dimensional ROESY pulse sequence was used with a low power spin-lock pulse. The relaxation delay was 2 s. Complex data (2k) were collected in 256 increments with 8 transients each. The spin-lock field strength was 3200 Hz with a mixing time of 200 ms. Phase sensitive two dimensional time domain were recorded and processed using TPPI protocol. A pure squared cosine window function was used in both dimensions prior filling and Fourier transformation. The viscosities of samples are measured by a rheometer (HAAKE rheoStress RS75).

2.3. Sample preparation

The desired amount of polymer was first added to the IL bmimBF_4. A heating procedure can accelerate the dissolution of polymer in bmimBF_4. The IL microemulsions were prepared with IL solution of polymer. The mixtures were stirred until the dispersion becomes transparent. All samples used for characterizations were transparent and homogeneous. The weight ration of Triton X-100 and cyclohexane in the microemulsions is fixed at 11:9. The bmimBF_4 present in the microemulsions are referred to the surfactant concentration, and expressed as the molar concentration ratio. The polymer concentration is expressed by molar concentration ratio of polymer and bmimBF_4:

$$R = \frac{[\text{bmimBF}_4]}{[\text{Triton X-100}]},\ P = \frac{[P_\text{m}]}{[\text{bmimBF}_4]}$$

where P_m represents the monomer molar concentration of the polymer.

3. Results and discussion

3.1. Phase behavior

The ternary phase diagram of bmimBF_4/Triton X-100/cyclohexane has been studied in a recent report [8]. Temperature has a great effect on the phase behavior and the single-phase microemulsion region of the three-component system broadens with increasing temperature. Thus, it is necessary to study the effect of PVP on the IL microemulsion by the phase behavior involving temperature. The phase diagram of bmimBF_4-in-cyclohexane microemulsion at constant surfactant volume fraction, $\Phi_{\text{Triton X-100}} = 0.41$, and various ratios, $R = [\text{bmimBF}_4]/[\text{Triton X-100}]$ and different PVP content, P, was shown in Fig. 1. The phase boundaries were located by inspection. The single-phase microemulsion

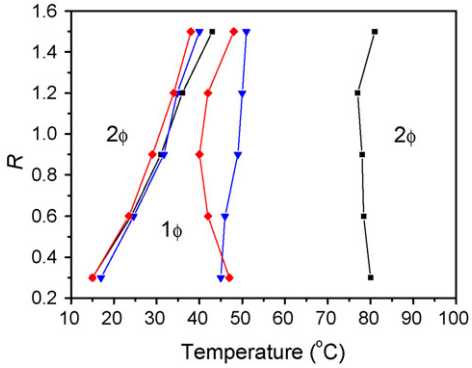

Fig. 1. Effect of PVP on the phase behavior of bmimBF_4-in-cyclohexane microemulsion at constant surfactant volume fraction, $\Phi_{\text{Triton X-100}} = 0.41$, and various R. The added polymer content, $P = 0$ (■), 0.18 (▼), and 0.31 (♦).