Colloids and Surfaces A: Physicochem. Eng. Aspects 369 (2010) 95–100

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

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

Lyotropic liquid crystalline phases formed in binary mixture of 1-tetradecyl-3-methylimidazolium chloride/ethylammonium nitrate and its application in the dispersion of multi-walled carbon nanotubes

Mingwei Zhao, Yanan Gao, Liqiang Zheng*

Key Laboratory of Colloid and Interface Chemistry, Shandong University, Ministry of Education, Shanda NanLu 27#, Jinan, Shandong 250100, People's Republic of China

ARTICLE INFO

Article history:
Received 27 May 2010
Received in revised form 24 July 2010
Accepted 4 August 2010
Available online 12 August 2010

Keywords:
Liquid crystalline
Ionic liquid
Multi-walled carbon nanotubes

ABSTRACT

The phase behavior of a surfactant-like ionic liquid 1-tetradecyl-3-methylimidazolium chloride (C_{14}mimCl) in a room-temperature ionic liquid ethylammonium nitrate (EAN) is studied. The lyotropic liquid crystalline (LLC) phases formed in the binary mixture are thoroughly investigated by polarized optical microscopy (POM) and small-angle X-ray scattering (SAXS) measurements, and the temperature effect on the LC phases is also elucidated. Then, a hexagonal (H_1) LC phase was used to disperse multi-walled carbon nanotubes (MWCNTs). Both POM images and SAXS patterns indicate that, the dispersion of MWCNTs cannot break the structure of H_1 phase. By comparing the rheological properties before and after dispersing, it could be found that the incorporation of MWCNTs has increased the viscosity of H_1 phase.

1. Introduction

Ionic liquids (ILs) are a class of compounds whose physical and chemical properties can be tailored by judicious selection of cation, anion, and substituent. They are generally liquid below 100 °C [1] and have many unique properties compared with traditional organic solvents, such as low melting temperature, nonflammability, high ionic conductivity, negligible vapor pressure, and wide electrochemical window [2]. In recent years, ILs have been widely used as solvents or surfactants to construct varied aggregates, including micelles, vesicles, microemulsions, and lyotropic liquid crystals (LLCs). Of all these aggregates, LLCs phases have attracted great attention for their long-range order, unique rheology properties and so on. Warr and Araos reported a variety of LLCs formed by a number of polyoxyethylene nonionic surfactants in a room-temperature ionic liquid ethylammonium nitrate (EAN) [3]. Drummond and co-workers studied the phase behavior of LC constructed by nonionic surfactants myverol 18–99 K (predominantly monoolein) and phytantriol in 40 protic ILs [4]. Except using as the solvents, some ILs with long alkyl chains have also been designed and used as surfactants, which indicate good amphiphilic behavior to form LCs [5–8]. Firestone et al. constructed the LLCs phases through the addition of water to 1-decyl-3-methylimidazolium bromide (C_{10}mimBr) [5]. Our group also investigated the phase behavior of ternary mixtures of 1-hexadecyl-3-methylimidazolium bromide (C_{16}mimBr)/*p*-xylene/water by polarized optical microscopy (POM), small-angle X-ray scattering (SAXS) and rheology measurements [6]. All these investigations have inordinately shown us the difference between the long alkyl chain ionic liquid and traditional cationic surfactants, which greatly stimulate us to further efforts, i.e. investigating the phase behavior of C_{14}mimCl in EAN and then using the formed H_1 phase to disperse carbon nanotubes (CNTs).

The discovery of CNTs has created a stir [9] and attracted many researchers to investigate the exotic physical and chemical properties of them in the last two decades. Due to their novel physical properties, such as good electrical conductivity and high tensile strength, CNTs can be widely used in the fields of transistors, chemical and biological sensors [10–13].

In general, CNTs can exist in two states: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). There have already been many methods to produce the CNTs [14–16]. However, there is an open problem for the freshly produced CNTs, which greatly hinders their wide applications. The freshly produced CNTs usually aggregated in ropes and bundles due to the van der Walls attraction between the adjacent nanotubes. Many groups have turned to this problem and carried out a series of work on the dispersion of CNTs. Of these investigations, the CNTs can associate to different molecules, such as polymers, surfactant, and biological molecules through covalent and noncovalent adsorption, which is considered as the main driving force for the dispersion of the CNTs [17–24]. Moore et al. successfully

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* Corresponding author. Tel.: +86 531 8836 6062; fax: +86 531 8856 4750.
E-mail address: lqzheng@sdu.edu.cn (L. Zheng).

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doi:10.1016/j.colsurfa.2010.08.015

dispersed the SWCNTs in solutions with different solutes including anionic, cationic, nonionic surfactants, and polymers [17]. Zheng and Jagota studied the dispersion and separation of the CNTs with DNA [18].

As reported previously, the LLCs exhibits long-range orientational order along a particular direction [25–27], which has led to their considerable applications for the dispersion of CNTs. Dierking and Scalia firstly dispersed the CNTs using LCs and found the CNT-LC composites showing interesting electrical switch phenomenon [28]. Through a large number of works about the dispersion of CNTs in LCs [29–31], we can see that, most of the LCs used are thermotropic liquid crystal. The dispersion of CNTs in LLCs has been rarely studied [32–36]. Regev and co-workers dispersed the SWCNTs in lyotropic hexagonal (H_1) LC for the first time [32].

Here, in our study, the LLC phases are constructed in the binary mixture of 1-tetradecyl-3-methylimidazolium chloride (C_{14}mimCl)/EAN. Our major focus is paid on the different LLC phases formed in this binary system, which may enrich our knowledge on the LLCs completely composed of ILs and then the formed H_1 phase was used to disperse the MWCNTs. To the best of our knowledge, this may be the first time to disperse the MWCNTs in the LLCs constructed by two ILs. Due to their great electrical conductivities, such CNTs-LC composite is expected to show the super electrical conductivity.

2. Experimental

2.1. Material

C_{14}mimCl was synthesized according to the procedures reported previously [37]. The methylimidazole and an excess amount of tetradecyl chloride were mixed in dichloromethane, refluxed under nitrogen atmosphere at about 80 °C for 48 h. Then, the solvent was removed under reduced pressure. The residue was cooled to room temperature and purified by recrystallization in fresh diethyl ether at least four times. Finally, the products were dried under vacuum conditions for 48 h. The C_{14}mimCl was characterized by ^{1}H NMR spectrum.

EAN was prepared according to the procedures presented by Evans et al. [38]. In a typical synthesis, a portion of nitric acid was slowly added to ethylamine solution dropwise under stirring and cooling in an ice bath. Then water in the resulting mixture was removed through a rotary evaporator. The purity of the products was ascertained by ^{1}H NMR spectrum in D_2O.

MWCNTs are purchased from Shenzhen Nanotech Port Co., Ltd. China, with the diameter of 10–20 nm and the length of 10–15 μm, and used as received.

2.2. Preparation

2.2.1. Phase diagram

The process of mapping the phase diagram has been described elsewhere [6,7]. The samples were prepared by weighing the appreciate amount of C_{14}mimCl and EAN (in weight percent, wt.%, herein after) in a well-closed glass vials to avoid evaporation. The mixture was homogenized and equilibrated by repeated vortex mixing and centrifuging. Then they were kept in a thermostat at least 1 month for equilibration. The phase diagram was mapped between 30 and 140 °C in the whole EAN-C_{14}mimCl concentration range.

2.2.2. Dispersion of MWCNTs in the H_1 phase

The stock solutions were prepared at first by dispersing the MWCNTs (2 mg) in EAN (5 g) with the aid of C_{14}mimCl (0.05 g). The mixture was sonicated for 120 min with an ultrasonic instrument operating at 100 W and 40 kHz. Then it was centrifuged to remove the non-dispersed MWCNTs. In our study, the H_1 phase was selected to disperse the MWCNTs. According to the phase diagram, a H_1 phase composed of 65 wt.% C_{14}mimCl and 35 wt.% EAN was employed. In a typical experiment, a certain amount of the stock solutions with dispersed MWCNTs were added to the preformed LLC phase. Then C_{14}mimCl was also added to the mixture to maintain the compositions of the LLC phase. After homogenizing, repeatedly vortex mixing and centrifuging, the mixture was kept in a thermostat at least 1 month for equilibration. The concentration of MWCNTs in our study is calculated to be about 0.014%.

2.3. Characterization

2.3.1. Polarized optical microscopy

A polarized optical microscope equipped with a charge-coupled device camera (Panasonic Super Dynamic II WV-CP460) was employed. In the measurements, the sample was confined between a glass slide and a cover-slip, then examined with the digital microscope (Zeiss AxioShop 40) by using an Axio Vision Image Analysis System. Birefringent textures allow the determination of particular LC phase. In general, the H_1 phase indicates a fanlike and angular texture, while the lamellar (L_α) phase shows a distinct woven structure or a Maltese cross texture. The isotropic cubic phases are not birefringent [39–41].

2.3.2. Small-angle X-ray scattering

The samples (LCs and MWCNTs-LC composites) were characterized using an HMBG-SAX X-ray small-angle scattering system (Austria) with a Cu Kα radiation operating at 2 kW (50 kV and 40 mA). To remove the Kβ radiation, a 10-μm thick nickel filter was employed and a 2-mm tungsten filter was used to protect the detector from the primary beam. The distance between the sample and detector was about 278 mm. All samples were held in a vacuum steel holder to provide good thermal contact to the computer-controlled Peltier heating system (Hecus MBraun Austria) with the aid of the Kapton window.

2.3.3. Rheology measurement

The rheological properties of the samples were performed with a HAAKE RS 75 rheometer. A cone-plate sensor was used with 20 mm diameter and 1° cone angle. The cone-plate distance was adjusted to 52 μm for all measurements. The temperature was kept at 30 ± 0.1 °C. Each sample was inserted onto the top of the cone-plate and then the plate was slowly elevated to its measuring position at a constant velocity. Any excess sample squeezed out from the sensor system was gently removed. Dynamic oscillation-shear measurements were employed, in which the stress (σ) was varied while the frequency was kept at 1.0 Hz. Once the linear viscoelastic region was determined, frequency sweep measurements were performed as a function of frequency at a constant stress.

3. Results and discussion

3.1. Phase behavior of C_{14}mimCl/EAN binary mixture

The temperature–composition (T–X) phase diagram of C_{14}mimCl/EAN in the range of 30–140 °C is shown in Fig. 1. Four single-phase LC regions can be recognized: one H_1 phase, two L_α phases, and one isotropic cubic LC (V_2) phase. At low C_{14}mimCl concentration (less than 55 wt.%), a homogeneous and isotropic solution phase is shown, which is normally considered to be micellar solution phase for that there is only one wide scattering peak observed in its SAXS curve. With the increase of the C_{14}mimCl concentration, various LC phases including H_1, L_α, and V_2 can be formed and go through different concentration and temperature range. Their corresponding POM images and SAXS patterns are shown in Fig. 2, which can be used to classify the LC