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Dielectric analysis of the [Bmim][PF$_6$]/TX-100/ethyleneglycol nonaqueous microemulsions: Microstructures and percolation

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HIGHLIGHTS

- Microstructure and structural transitions vary with ethyleneglycol content.
- Dielectric parameters were obtained by fitting Cole–Cole equation.
- Hanai method was employed to estimate the phase parameters.
- Result of dielectric analysis was confirmed reasonable by interfacial polarization.

GRAPHICAL ABSTRACT

Dependence of (a) permittivity ε' and (b) dielectric loss ε'' spectra of ternary systems of EG/TX-100/[Bmim][PF$_6$] with different EG contents.
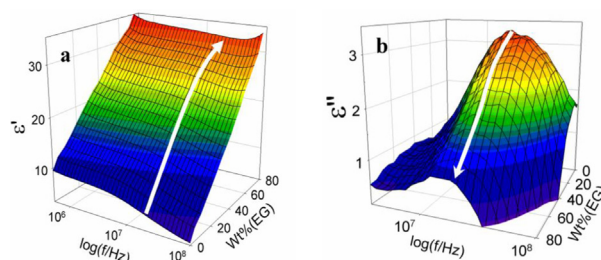
ABSTRACT

The ternary system consisting of ethyleneglycol (EG), an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, [Bmim][PF$_6$]) and a nonionic surfactant (p-(1,1,3,3-tetramethylbutyl)phenoxypolyoxyethyleneglycol, TX-100) was studied by dielectric measurements in the frequency range from 40 Hz to 110 MHz. A remarkable dielectric relaxations caused by interfacial polarization was observed around 10 MHz. The dielectric intensity $\Delta\varepsilon$ and the relaxation time τ could be obtained by fitting the experimental data using the Cole–Cole equation with one dispersion terms. The regions of EG-in-IL (EG/IL), bicontinuous phase (B.C.), IL-in-EG (IL/EG) microemulsions and dilute solution were identified by the dependence of direct current (dc) conductivity on the content of EG, where the dc conductivity was obtained from the total dielectric loss spectra. The scaling relation between conductivity and the content of EG was compared with the predictions of scaling theories. In the IL/EG micro-region, Hanai theory was used to calculate the phase parameters of the constituent phases. The trends of calculated relaxation time τ_{MW} and τ as a function of EG content in the IL/EG micro-region were almost the same, inferring that the dielectric relaxation probably arose from the interfacial polarization. In short, this work is helpful to understand the microstructures of different regions and percolation phenomenon in nonaqueous microemulsions.

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1. Introduction

Microemulsions are thermodynamically stable, isotropic mixtures of two immiscible liquids, a polar and a nonpolar, stabilized by a surfactant or by a surfactant/cosurfactant mixture [1]. Microemulsions are capable of solubilizing both polar and nonpolar substances, which are extensively used in separation [2], chemical reactions [3], synthesis of nanomaterials [4,5], drug delivery systems [6], etc. Most of microemulsions contain water as a component. However, there are many chemical reactions requiring water-free environment [7]. To overcome this limitation, polar solvents such as ethyleneglycol (EG), propyleneglycol (PG), glycerol

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(GY), formamide (FA), and dimethylformamide (DMF) can be used to prepare nonaqueous microemulsions [8–13]. Recently, nonaqueous microemulsions have attracted much more attention due to their specific ability to dissolve nonpolar and polar substances in water-free environment.

In addition to those conventional polar organic solvents, room temperature ionic liquids (ILs) are also feasible due to their unique properties, such as high electrical conductivity, high thermal stability, low volatility, nonflammability and adjustable salvation [14]. The combination of ILs and organic solvents enable significantly improved the properties of the microemulsions, which may have some potential applications [15,16]. Therefore, detailed understanding of the phase behavior and formation mechanism is of great importance, and many attempts have been made concerning the type and structural transitions of nonaqueous IL microemulsions by means of various methods, such as conductance [17–20], small-angle X-ray scattering [21–23], electrochemical cyclic voltammetry [19,24], microcalorimetry [25], dynamic light scattering [18,26–28], ultraviolet visible techniques [26], and freeze-fracture electron microscopy [29,30], etc. However, the relationship between the microstructural change and dynamic behavior of such systems are still far from being well understood, and more characterization methods are highly desired to be employed.

Dielectric relaxation spectroscopy (DRS), which usually measures permittivity and conductivity as a function of frequency in a noninvasive way, has been extensively used in the characterization of materials [31]. In the last two decades, DRS has become one of the most effective methods to detect the structural changes and electrical properties for microheterogeneous systems with great phase interface, such as emulsions and microemulsions [32–46]. The behavior of microemulsions and percolation process can be obtained by combining the experimental results with proper theories. As far as we know, most of these DRS studies are focused on the dependence of percolation process on temperature [33–41], but only a few are concentrated on the effects of composition on microemulsions percolation process [42–46]. Particularly, the well-established dielectric theory of microheterogeneous systems has never been applied to the nonaqueous microemulsions composed of hydrophobic ILs.

For a better understanding of the percolation process and relaxation mechanisms of IL-containing nonaqueous microemulsions, in this work, the dielectric properties were measured for the EG/p-(1,1,3,3-tetramethylbutyl)phenoxypolyoxyethyleneglycol (TX-100)/1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]) system with the increase of EG content when the weight ratio of TX-100/[Bmim][PF$_6$] was fixed. A relaxation due to interfacial polarization can be observed around 10 MHz and it was analyzed by Hanai theory. The phase parameters reflecting the internal properties of the constituent phases were calculated. Percolation models were adopted to explain the percolation phenomenon based on the conductivity data. Furthermore, the percolation threshold was obtained basing on the logarithmic derivative of EG content, and percolation models were adopted to explain the percolation phenomenon on the basis of dc conductivity.

2. Materials and methods

2.1. Materials and sample preparation

TX-100 (p-(1,1,3,3-tetramethylbutyl)phenoxypolyoxyethyleneglycol) (A.R. grade) was purchased from Amresco Chemical Inc. America. 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]) (purity > 99.2%) was purchased from Shanghai
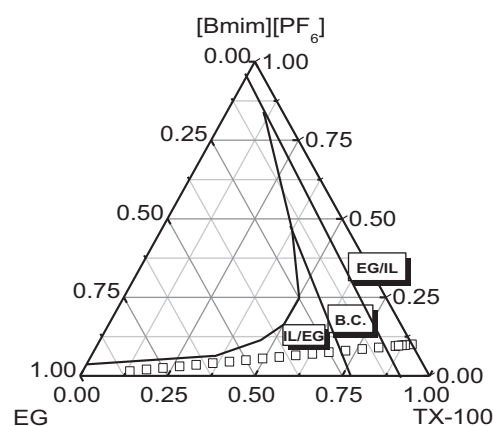
Fig. 1. Experimental path (square) in this work for EG/TX-100/[Bmim][PF$_6$] systems. The path denotes the change of EG content in the ternary systems when the weight ratio of [Bmim][PF$_6$]/TX-100 is fixed as 1:9; the phase diagram at 30.0 °C is cited from [29].

Cheng Jie Chemical Co., China. Ethylene glycol (EG) (A.R. grade) was obtained from Beijing Chemical Works. They were dried under vacuum at 80 °C for 12 h before use.

The microemulsions were prepared by mixing EG, TX-100 and [Bmim][PF$_6$] in appropriate weight fractions. The experimental path is shown in Fig. 1 in which the boundaries are drawn according to the work of Han et al. [29]. First, the mixture of TX-100 and [Bmim][PF$_6$] with the weight ratio of [Bmim][PF$_6$]/TX-100 is fixed to 1:9 was prepared. After the mixture was fully homogenized, EG was added to prepare EG/TX-100/[Bmim][PF$_6$] ternary mixtures with different weight fraction of EG (Wt%(EG)) ranging from 0% to 85%. According to the phase diagram, it can be seen that the path crosses three different sub-regions, i.e., this ternary mixture is in the EG-in-IL (EG/IL) microemulsion phase when Wt%(EG) ≤ 10.3%, in the bicontinuous (B.C.) phase when 10.3% < Wt%(EG) < 31.2%, and in the IL-in-EG (IL/EG) microemulsion phase when Wt%(EG) ≥ 31.2%.

2.2. Dielectric measurements

The dielectric measurements were performed on a 4294A precision impedance analyzer (Agilent Technologies) that allowed a continuous frequency measurement from 40 Hz to 110 MHz. A dielectric measurement cell with concentrically cylindrical platinum electrodes was employed and connected to the impedance analyzer by a 1607E spring clip fixture. The amplitude of the applied alternating field was 500 mV, and the measurement temperature was (30 ± 0.5) °C. In order to submerge the electrodes, the mass of solutions used in the experiment was 2.0 g. The experimental data errors arising from the residual inductance and measurement cell were corrected by Schwan's method [47]. The cell constant C_l, stray capacitance C_r and residual inductance L_r that had been determined by several standard substances (air, pure ethanol, and pure water) were 0.45 pF, 3.17 pF, and 1.13×10^{-8} F S^{-2}, respectively. The permittivity and total dielectric loss at each measured frequency were calculated from the corrected capacitance and conductance.

2.3. Dielectric analysis

In an applied electric field of frequency *f*, the dielectric properties (permittivity ε and conductivity κ) of microemulsions can be