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Phase behavior of epoxidized soybean oil-based ionic liquid microemulsions: Effects of ionic liquids, surfactants, and co-surfactants

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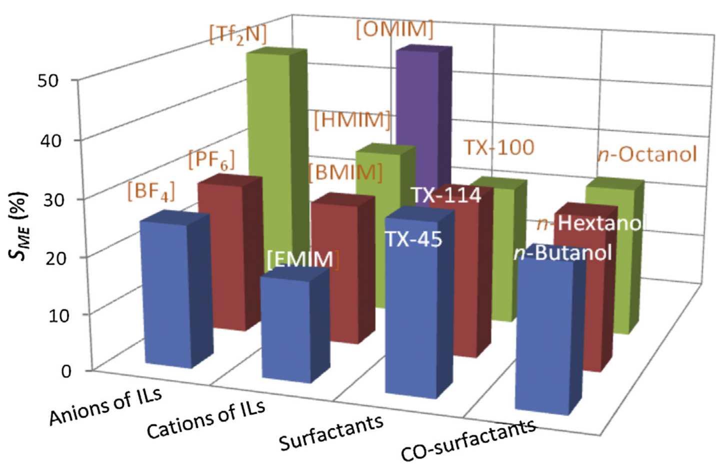
HIGHLIGHTS

- The phase behavior of ESBO-based ionic liquid microemulsions was investigated.
- Ionic liquids, surfactants and co-surfactants influenced the phase behavior significantly.
- ESBO-based ionic liquid microemulsions exhibit potential in biolubricant application.

GRAPHICAL ABSTRACT



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ABSTRACT

Epoxidized soybean oil (ESBO)-based ionic liquid microemulsions are promising alternatives for petroleum-based lubricants. This study presents the phase behavior of these microemulsions through phase manifestation, and the areas of the single-phase domain were accordingly calculated to illustrate the phase-forming capacities of the designed microemulsions. Effects of ionic liquid anions and cations, surfactant and co-surfactant chain lengths on the phase behavior, and phase-forming capacities of ESBO-based ionic liquid microemulsions were investigated. Results showed that the phase-forming capacities of the ESBO-based ionic liquid microemulsions with different ionic liquid anions and cations showed the following sequence: Tf_2N^--based > PF_6^--based > BF_4^--based, $OMIM^+$-based > $HMIM^+$-based > $BMIM^+$-based > $EMIM^+$-based. Given the presence of ionic liquid–ESBO amphiphilic balance in the designed systems, the ESBO–surfactant micelles achieved maximum solubilization capacity for 1-butyl-3-methylimidazolium tetrafluoroborate when the surfactant had approximately eight ethoxylated groups. In addition, ESBO-based microemulsion containing *n*-hexanol showed a higher phase-forming capacity than that containing *n*-butanol, and *n*-octanol caused a different phase behavior for the ESBO-based microemulsion because of its oilier nature than a co-surfactant.

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1. Introduction

Non-aqueous ionic liquid microemulsions, which comprise a system of oil, ionic liquid, surfactant, and co-surfactant (added optionally) [1], provide numerous benefits in various applications, such as a reaction medium for nanomaterials, solubilizing agent for drug molecules, and direct utilization as potential bio-products [2–5]. In the past decades, ionic liquid microemulsions have been increasingly investigated. The interfacial composition, thermodynamic properties, and structural parameters for certain ionic liquid microemulsions have been explored through dilution method [6]. Prior to the investigation of ionic liquid microemulsions, the phase-forming capacity of each component, which is expressed by the areas of the single-phase domain (S_{ME}) in pseudo ternary phase diagrams, should be determined [7]. Moreover, the microstructures and properties of the ionic liquid microemulsions are substantially influenced by the nature and concentration ratio of the components [8]. Accordingly, determining the effects of polar phase structure, surfactant and co-surfactant on the phase behavior of ionic liquid microemulsions is important.

Vegetable oil has a notable role in a sustainable industrial development because of their renewable and biodegradable nature [9]. We presented in our previous study a successful formulation of microemulsions with vegetable oil as the continuous phase and with room-temperature ionic liquid as the polar phase. We showed that the ionic liquid microemulsification of vegetable oil effectively reduced the high viscosity of the oil and improved its friction-reduction property [5]. Traditional vegetable oils with lubricating feature, such as castor, jatropha, and soybean, have been confirmed to be capable of producing isotropic microemulsions with ionic liquids, and the phase behavior of vegetable-oil based ionic liquid microemulsions have been previously reported [10].

Epoxidized vegetable oils, which are biodegradable and have the potential as biolubricants, have recently attracted much attention [11–14]. Exploring efficient and environment-friendly alternative resources is essential given the decreasing fossil fuel resources and worsening environmental conditions. Ionic liquid microemulsions containing epoxidized soybean oil (ESBO) may be beneficial as lubricants because of their unique features. We have previously shown that ESBO-based ionic liquid microemulsions could be successfully produced. In addition, the influences of K_m and temperature on the phase behavior of ESBO-based ionic liquid microemulisons had been initially investigated [15]. In this study, we further investigated the effects of the ionic liquid structure, surfactant type and co-surfactant chain length on the phase behavior of ESBO-based ionic liquid microemulsions.

1-Ethyl-3-methyl-imidazolium tetrafluoroborate ([EMIM][BF_4]), 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF_4]), 1-hexyl-3-methyl-imidazolium tetrafluoroborate ([HMIM][BF_4]), and 1-octyl-3-methyl-imidazolium tetrafluoroborate ([OMIM][BF_4]) were used as ionic liquid phases to investigate the influence of ionic liquid cations on the phase behavior of ESBO-based ionic liquid microemulsions. 1-Butyl-3-methyl-imidazolium hexafluorophosphate ([BMIM][PF_6]) and 1-butyl-3-methyl -imidazolium bis[(trifluoro-methyl) sulfonyl]imide ([BMIM][Tf_2N]), together with [BMIM][BF_4], were used to determine the influence of ionic liquid anions. Triton X series nonionic surfactants with five (Triton X-45), eight (Triton X-114), and ten (TX-100) oxyethylene (OE) groups were investigated. Co-surfactants with different chain lengths were *n*-butanol, *n*-hexanol, and *n*-octanol. The phase behavior of the aforementioned ESBO-based microemulsions was explored through pseudo-ternary phase diagrams.

2. Experimental

2.1. Materials

ESBO (>99 wt%) was purchased from Sigma–Aldrich (Shanghai, China). The ESBO physicochemical properties had been presented in our previous study [15]. All the ionic liquids, including [EMIM][BF_4] (>99 wt%), [BMIM][BF_4] (>99 wt%), [HMIM][BF_4] (>99 wt%), [OMIM][BF_4] (>99 wt%), [BMIM][PF_6] (>99 wt%) and [BMIM][Tf_2N] (>99 wt%) were provided by the Center of Green Chemistry and Catalysis at the Lanzhou Institute of Chemical Physics (Lanzhou, China). *n*-Butanol (>99 wt%), *n*-hexanol(>99 wt%), *n*-octanol (>99 wt%) and TX-100 (>99 wt%) were purchased from Kermel (Tianjin, China). TX-45 (>99 wt%) and TX-114 (>99 wt%) were bought from J&K Scientific (Guangzhou, China) and Aladdin (Shanghai, China), respectively.

2.2. Methods

Pseudo-ternary phase diagrams of ESBO, ionic liquid, surfactant, and co-surfactant were constructed through titration and direct observation. Mixtures of the ESBO and surfactants/co-surfactants with varying mass ratios from 1:9 to 9:1 were prepared in a series of stoppered test tubes. The samples were placed in a thermostatic water bath at 298 ± 0.5 K for 10 min, and then titrated with the ionic liquid under moderate agitation. The ionic liquid volumes that caused the solutions to become turbid from clear transparent were noted to determine the phase boundaries. In each plotted phase diagram, the upper part of the phase boundary represented a single-phase region (microemulsion, 1φ), and the lower part was a two-phase region (2φ). Compositions in the phase diagrams were in weight fractions. Corresponding values of the S_{ME} were calculated using AutoCAD software. Each set of experiment was repeated thrice, and the average value obtained was used for data processing and analysis.

3. Results and discussion

3.1. Effect of ionic liquids

Ionic liquids with BF_4^-, PF_6^-, or Tf_2N^- as anions have been previously reported as excellent lubricants [16]. Thus, these ionic liquids were used to investigate ESBO-based ionic liquid microemulsions. [BMIM][PF_6] and [BMIM][Tf_2N] were used as the polar phases of ESBO-based microemulsions, and TX-100 and *n*-butanol, with K_m at 4:1 were used as the surfactant and co-surfactant, respectively. Pseudo-ternary diagrams of ESBO-based microemulsions with different ionic liquid phases at 298 ± 0.5 K are illustrated in Fig. 1a and b. The phase diagram of [BMIM][BF_4]-based microemulsion under the same condition has already been presented in our published work [15]. The S_{ME} values of the above systems are listed in Fig. 2 to illustrate their phase-forming capacities. The phase-forming capacity evidently followed the succeeding sequence: ESBO-based microemulsion containing [BMIM][Tf_2N] > ESBO-based microemulsion containing [BMIM][PF_6] > ESBO-based microemulsion containing [BMIM][BF_4].

In the investigation of the phase formations of ionic liquid microemulsions, the hydrogen bond between the surfactant OEs and imidazolium ring of the ionic liquid was identified as the driving force [17], and the hydrogen bond strength was positively correlated with the electronegativity of the OE units and imidazolium ring [18]. With similar surfactant, the ESBO-based microemulsion containing [BMIM][BF_4] showed the lowest phase-forming capacity because [BMIM][BF_4] has less fluorine atoms