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Vegetable oil-based ionic liquid microemulsions and their potential as alternative renewable biolubricant basestocks

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ABSTRACT

This paper reports the successful formulation of microemulsions with vegetable oil as the continuous phase, room-temperature ionic liquid (IL) 1-butyl-3-methyl-imidazolium tetrafluoroborate as the polar phase, TritonX-100 as the surfactant, and 1-butanol as the cosurfactant. A pseudo-ternary phase diagram, dynamic light scattering data, UV–vis spectra, and kinematic viscosity measurements were employed to characterize and analyze the phase behavior and microstructure of the vegetable oil-based IL microemulsions. The tribological properties of the designed microemulsions were evaluated using a four-ball tester. The results confirmed the formation of an IL microemulsion containing vegetable oil. The designed petroleum-free microemulsions exhibit excellent viscosity-temperature characteristics and friction–reduction proprieties, indicating the tremendous potential of IL microemulsions as renewable biolubricant basestocks.

1. Introduction

The ongoing research on alternative and renewable biolubricants is vital in addressing the worsening energy crisis and increasing environmental awareness. Vegetable oils, which are renewable and biodegradable, have been widely considered as alternative lubricant sources (Fox and Stachowiak, 2007; Padmaja et al., 2012). Moreover, the environmental acceptability vegetable oils have attracted interest as replacement for petroleum-based ingredients in conventional microemulsions (Naksuk et al., 2009). Alander and Warnheim (1989) prepared model microemulsions with vegetable oil and concluded that triglyceride-based microemulsions have a smaller stability region than microemulsions containing hydrocarbons or fatty acid esters.

Room-temperature ionic liquids (RTILs) continue to attract public interest as a result of their unique properties, such as low volatility, non-flammability, negligible vapor pressure, and excellent chemical and thermal stability (Marsh et al., 2004; Minami, 2009). Ye et al. (2001) introduced a new field of application for ILs as high-performance lubricants. Their report showed that certain kinds of imidazolium-based ILs are promising versatile lubricants for the contact of steel/steel, steel/copper, steel/SiO_2, and so on. These ILs possess excellent lubricating properties, such as friction reduction, antiwear performance, and high-carrying capacity. These promising results attracted considerable attention in this field, and numerous articles focusing on fundamental tribological research into ILs have been published since then (Liu et al., 2002; Minami, 2009; Morales et al., 2012; Stolte et al., 2012). Despite these features, the solubility limitations of ILs in non-polar solutes, such as fatty hydrocarbons or vegetable oils, limit their widespread use.

Recently, IL microemulsions have shown tremendous potential in overcoming the immiscibility between ILs and non-polar solutes. The use of RTIL to replace either the non-polar phase or polar phase in conventional microemulsions has been widely researched since Han et al. (Gao et al., 2004) first reported on 1-butyl-3-methyl-imidazolium tetrafluoroborate ([BMIM][BF_4])/TritonX-100 (TX-100)/cyclohexane microemulsions (Harrar et al., 2011; Pramanik et al., 2010).

In the present study, we show that vegetable oil can replace conventional petroleum-based ingredients as the continuous phase in microemulsions containing RTIL. The designed microemulsions have tremendous potential as alternative renewable biolubricant basestocks because they can significantly improve the viscosity–temperature characteristics and viscosity index (VI) of castor oil. To our knowledge, reports on the formulation, friction, and wear properties of vegetable oil-based IL microemulsions have been few. The current study highlights an efficient method of formulating environmentally compatible vegetable oil-based IL microemulsions, and the potential for new applications for these ILs as biolubricant basestocks is explored as well.

2. Experimental

2.1. Materials

The [BMIM][BF_4] (>99 wt%) was provided by the Centre of Green Chemistry and Catalysis at the Lanzhou Institute of

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Chemical Physics in China. The TX-100 (>99 wt%), 1-butanol (>99 wt%), and castor oil (>99 wt%) were obtained from Tianjin Kermel Chemical Reagent Science and Technology Co. Ltd. in China. Prior to the experiment, both the TX-100 and castor oil were vacuum dried at 70 °C for 6 h to remove excess water. The lubricant base oil 400SN was provided by Guangzhou Mechanical Engineering Research Institute Co. Ltd. Methyl orange (MO; >99 wt%) was provided by Sigma–Aldrich.

2.2. Methods

The phase diagram of the microemulsions consisting of the IL [BMIM][BF_4], the surfactant TX-100, the cosurfactant 1-butanol, and castor oil was determined by direct observation of phase behavior. The temperature was controlled by a thermostat water bath. In a typical experiment, different proportions of the surfactant–cosurfactant (mass ratio 4:1) mixture to castor oil were prepared in 10% steps between 0 wt% and 100 wt% of the castor oil. The [BMIM][BF_4] was then added dropwise under gentle agitation. The phase transitions from transparency to turbidity were observed by the unaided eye. The weight fraction of [BMIM][BF_4] at which the transparency-to-turbidity transition occurred was derived from precise weight measurements, and the corresponding composition of the solution was then calculated from the masses of castor oil, [BMIM][BF_4], TX-100, and 1-butanol.

The diameters of the IL microemulsions were determined by dynamic light scattering (DLS) using a Malvern Nano ZS instrument. This instrument employed a 4 mW He–Ne laser operating at a wavelength of 633 nm. Measurements were carried out at 25 ± 0.1 °C. The UV–vis spectra were obtained on a computer-controlled UV–vis spectrophotometer. The appropriate amount of MO was added to a reverse microemulsion after uniform mixing and was then placed into a quartz cell. The measurements were performed at 25 °C. All of these measurements were conducted through experiments with the surfactant–cosurfactant to castor oil mass ratio kept constant while increasing the RTIL amount from 6 wt% to 18 wt%. Each set of experiments was repeated three times, and the average of the values obtained was used for data processing and analysis.

An NDJ-5S viscometer with a small sample adapter consisting of a circulating thermostat water bath was fabricated to measure the dynamic viscosity of the IL microemulsions. The friction and wear behaviors of the microemulsion with 6 wt% IL were measured using an MS-10A four-ball tribotester according to SH/T 0762-2005, which is similar to ASTM D5183-95. Friction test was performed at 1450 rpm for 60 min. The balls used in the test were composed of GCr15 steel with an HRC of 61–64. The wear scar diameters were measured using a video camera installed in the four-ball tribotester.

3. Results and discussion

3.1. Pseudo-ternary phase diagram

Phase behavior is essential in the characterization of microemulsions. The pseudo-ternary phase diagram for the results of this study is illustrated in Fig. 1. The calculated data are listed in Table 1. A single homogeneous region, marked “L”, extends from the castor oil corner to the IL corner, whereas the shadow region indicates a multiphase region. The pseudo-ternary phase diagram shows the consistent formation of a continuous stable single phase over the [BMIM][BF_4] or castor oil content range of 0–100 wt%. However, the single-phase region of the castor oil/TX-100/1-butanol/[BMIM][BF_4] microemulsion appears smaller than those of microemulsions with cyclohexane or p-xylene as the continuous phase (Gao et al., 2006; Li et al., 2009). This result may be related to the differences in the molecules of non-polar phase molecules. Small hydrocarbon molecules, e.g., p-xylene and cyclohexane, can penetrate into the surfactant layer and enhance the hydrogen bond between surfactant/hydrocarbon and IL, which is vital in microemulsion formation (Zhou et al., 2001). However, the long carbon chain of each castor oil component confirmed that a higher surfactant–cosurfactant quantity is needed to form reverse micelles.

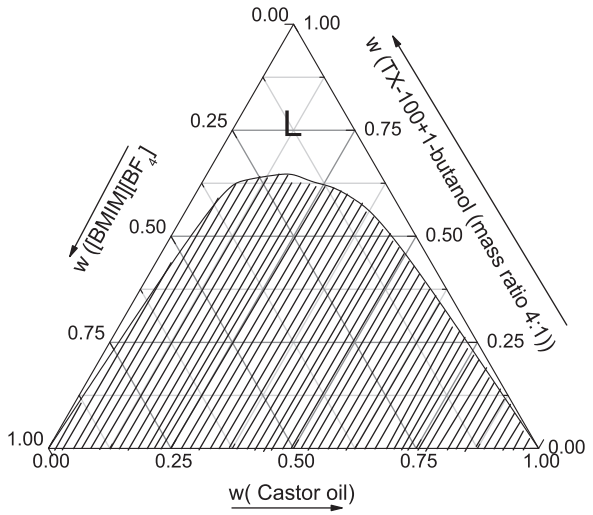

Fig. 1. Pseudo-ternary phase diagram of the castor oil/TX-100/1-butanol/[BMIM][BF_4] microemulsion at 25 °C.

Table 1
Equilibrium compositions of castor oil/TX-100/1-butanol/[BMIM][BF_4] microemulsions at 25 °C.[a]

ω_1	ω_2	ω_3	ω_1	ω_2	ω_3
0.426	0.532	0.042	0.175	0.649	0.176
0.328	0.590	0.082	0.143	0.645	0.212
0.267	0.620	0.113	0.076	0.632	0.292
0.224	0.627	0.149	0.043	0.611	0.346

[a] ω_1 is the mass fraction of oil component, ω_2 is the mass fraction of TX-100 + 1-butanol, and ω_3 is the mass fraction of [BMIM][BF_4].

3.2. DLS measurements

DLS is a powerful measurement technique used to characterize the structural transformation of microemulsions. This method determines whether ILs are encapsulated by surfactant molecules to form microemulsion media (Pramanik et al., 2011). Rao et al. (2012) suggested that if IL was actually encapsulated in the formation of IL-in-oil microemulsions, the size of the droplets must increase regularly as the *R* value (molar ratio of IL to surfactant) increases to a certain level.

A series of reverse microemulsions were prepared for analysis, and the general recipe of these microemulsions is presented in Table 2. Fig. 2 shows the sizes and size distribution of the castor oil/TX-100/1-butanol/[BMIM][BF_4] microemulsions with various

Table 2
General recipe used in the preparation of reverse microemulsions (wt%).

Series	[BMIM][BF_4]	Castor oil	TX-100	1-Butanol	Total[a]
1	0.0	20	64.0	16.0	100
2	6.0	19.0	60.0	15.0	100
3	12.0	17.7	56.2	14.1	100
4	16.0	16.9	53.7	13.4	100
5	18.0	16.4	52.5	13.1	100

[a] Error of ±0.01 in the experimental data.