Liquid–liquid equilibrium for binary and ternary systems containing *di*-isopropyl ether (DIPE) and an imidazolium-based ionic liquid at different temperatures

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ABSTRACT

Liquid–liquid equilibrium (LLE) data were determined for two binary systems {*di*-isopropyl ether (DIPE) + 1-ethyl-3-methylimidazolium-ethylsulfate (EMISE)} and {DIPE + 1-butyl-3-methylimidazolium-tetrafluoroborate([Bmim][BF$_4$])}at temperatures between 293.15 K and 313.15 K. LLE data for six ternary systems {DIPE + water + EMISE} and {DIPE + water + [Bmim][BF$_4$]} at 293.15 K, 303.15 K, and 313.15 K were also reported. Experiments were carried out at atmospheric pressure using stirred and thermo-regulated cells. The experimental data were correlated with the well-known NRTL and UNIQUAC activity coefficient models. In addition, distribution coefficients and selectivities of the ionic liquids EMISE and [Bmim][BF$_4$] for water in the DIPE phase were measured.

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1. Introduction

Oxygenates raise gasoline combustion temperatures and can improve overall engine efficiencies. They also lower the levels of carbon monoxide and unburned hydrocarbons in auto exhaust. Methyl *tert*-butyl ether (MTBE) by far dominates the market for fuel oxygenates. However, heavier ethers have received increased interest due to an insufficient supply of MBTE and the concern over groundwater contamination. *Di*-isopropyl ether (DIPE), ethyl *tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME) could all be suitable gasoline additives [1].

Phase equilibriums and mixture properties must be examined to design an effective DIPE synthesis and separation process and properly analyze DIPE as a fuel additive. Thus, we have systematically reported the phase equilibriums and mixture properties for oxygenated ether compounds inclusive DIPE [2,3]. DIPE is gained by a reaction of propylene with isopropyl alcohol, which is initially produced by hydration of propylene. The ether purification involves extraction of alcohol with water. Arce et al. reported therefore ternary phase equilibria for DIPE with alcohol and water [4,5].

Ionic liquids are an unusual class of nonvolatile chemical compounds with interesting properties. They are therefore studied in several fields. Ionic liquids possess high ionic conductivity, electro-

chemical stability, and variable physical and chemical properties. They typically contain large organic cations and smaller inorganic or organic anions. The lattice energy of their crystal structure is therefore generally reduced and results in a lower melting point. This is the reason why ionic liquids usually remain liquid at room temperature. Unlike molecular liquids, ionic liquids have negligible vapor pressures at room temperature and high solvating capacity for organic, inorganic, and organometallic compounds. Thus, they can effectively be used as environmentally friendly solvents in liquid–liquid extractions and can be designed for particular applications [6,7]. However, the solubility between ionic liquids and a second liquid phase is still unknown. Thus, new data concerning phase equilibrium and mixture properties would be of great use to the field of ionic liquids.

In this paper, we present data concerning the liquid–liquid equilibriums (LLE) of two binary systems {*di*-isopropyl ether (DIPE) + 1-ethyl-3-methylimidazolium-ethylsulfate (EMISE)} and {DIPE + 1-butyl-3-methylimidazolium-tetrafluoroborate ([Bmim][BF$_4$])} and six ternary systems {DIPE + water + EMISE} and {DIPE + water + [Bmim][BF$_4$]} at several temperatures: 293.15 K, 303.15 K and 313.15 K. These data were determined at atmospheric pressure using stirred and thermo-regulated cells. Data for the binary and ternary systems were correlated using two activity coefficient models: NRTL and UNIQUAC. In addition, the extraction properties (distribution coefficients and selectivity) of the ionic liquids EMISE and [Bmim][BF$_4$] for water in a DIPE phase were measured.

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Table 1
Purity and UNIQUAC parameters of chemicals used in this work.

Chemical	GC analysis (wt%)	Water content (wt%)	ρ/g cm^3 at 298.15 K		UNIQUAC volume and area parameters[a]	
			This work	Lit. value	r	q
DIPE	>99.9	0.01	0.71874	0.71870[a]	4.7421	4.0880
Water	>99.9	–	0.99711	0.99700[a]	0.9200	1.4000
EMISE	–	0.07	1.23633	1.23720[b]	7.9400	7.2100
[Bmim][BF$_4$]	–	0.05	1.20278	1.20410[b]	10.0570	6.3680

[a] Ref. [11].
[b] Ref. [12].

2. Experimental

2.1. Materials

Commercial grade of *di*-isopropyl ether (DIPE, $C_6H_{14}O$, $M = 102.18$ g mol^{-1}, CAS-RN 108-20-3) was obtained from Aldrich, 1-ethyl-3-methylimidazolium-ethylsulfate (EMISE, $C_8H_{16}N_2O_4S$, $M = 236.29$ g mol^{-1}, CAS-RN 342573-75) was obtained from Fluka Co. and 1-Butyl-3-methylimidazolium-tetrafluoroborate ([Bmim][BF$_4$], $C_8H_{15}BF_4N_2$, $M = 226.02$ g mol^{-1}, CAS-RN 174501-65-6) was supplied from CTRI Chemical Co. (Korea). Water was distilled twice in our laboratory. EMISE and [Bmim][BF$_4$] were dried using molecular sieves with a pore diameter of 0.3 nm and purchased from Fluka. Other chemicals were dried using sieves having a pore diameter of 0.4 nm. The water content of the chemicals, which was determined using a Karl-Fischer titrator (Metrohm 684 KF-Coulometer), was less than 7×10^{-5} g/g. The purity of the chemicals was determined by gas chromatography and by comparing the density with values reported in the literature. The water contents, purities, and densities of the chemicals are listed in Table 1. The values reported in the literature are also listed.

2.2. Apparatus and procedure

The system designed in our laboratory to measure the liquid–liquid equilibrium is similar to that reported by Correa et al. [8]. It consists of three parts: an equilibrium glass vessel jacket, a thermostat (Lauda MD 20 with DLK15 cooler) with a system that precisely measures the temperature (AΣA F250), and a Corning PC-320 magnetic stirrer. The sample temperature of the equilibrium vessel was regulated by the thermostat within an accuracy of ± 0.02 K. The mixture was then allowed to settle for about 8 h at constant temperature. Sampling was then carefully carried out

Table 2
Experimental liquid–liquid equilibrium data for the binary systems {DIPE + EMISE} and {DIPE + [Bmim][BF$_4$]}.

T/K	DIPE-rich phase x_1	Ionic liquid-rich phase x_1
{DIPE (1) + EMISE (2)}		
293.15	0.999	0.001
298.15	0.998	0.004
303.15	0.998	0.008
308.15	0.998	0.010
313.15	0.998	0.013
{DIPE (1) + [Bmim][BF$_4$] (2)}		
293.15	0.999	0.044
298.15	0.999	0.053
303.15	0.999	0.059
308.15	0.998	0.061
313.15	0.998	0.065

from the upper liquid phase and from the lower liquid phase without cross-contamination of the two phases. Ionic liquids were not detectable by gas chromatography. Both samples (approximately 0.5 ml each) were therefore taken separately in glass vials. Their weight was determined with a precision of $\pm 1 \times 10^{-5}$ g using a microbalance (A&D, HA202). The samples were then dried until DIPE and water were completely evaporated, i.e., after 20 h at 353.15 K. The mole fraction of ionic liquids in both phases was calculated for each sample using the mass difference resulting from the drying process. This analysis method was previously carefully checked. We estimated the uncertainty of the calculated mole fractions to be less than 2×10^{-3}. For accurate measurements, more than two samplings were performed for each phase, and each sampling was analyzed more than three times. The compositions of DIPE and water in both phases were analyzed using a gas chromatography (HP 5890N) having an HP-FFAP (Polyethylene Glycol TPA, 25 m × 0.20 mm × 0.30 mm) capillary column and a thermal
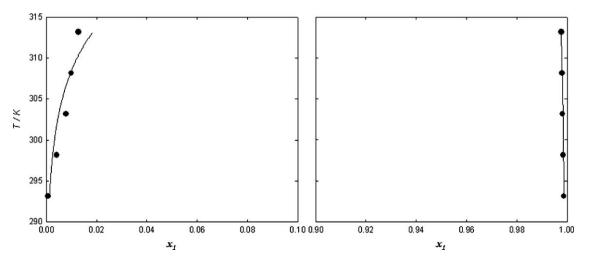

Fig. 1. Solubility diagram for the binary system {DIPE (1) + EMISE (2)}: (●) experimental value. Solid curves were calculated from the NRTL equation.