

Ternary mixtures of phosphonium ionic liquids + organic solvents + water*

Shahana A. Chowdhury^{1,†}, Janet L. Scott¹, and
Douglas R. MacFarlane^{2,‡}

¹ARC Special Research Centre for Green Chemistry, Monash University, Clayton, Victoria 3800, Australia; ²School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

Abstract: Ionic liquids (ILs) and water are both potentially green solvents that are useful in a variety of extraction processes. This report presents the ternary phase diagrams and tie-line data of trihexyl(tetradecyl)phosphonium dicyanamide [P_{6,6,6,14}][DCA], phosphonium bis(2,4,4-trimethylpentyl)phosphinate [P_{6,6,6,14}][((CH₃)₃C₅H₈)₂PO₂], and 1-ethyl-3-methylimidazolium ethylsulfate [emim][C₂H₅SO₄] ILs in organic solvents (ethanol, acetonitrile, toluene) and water. [P_{6,6,6,14}][DCA] and [P_{6,6,6,14}][((CH₃)₃C₅H₈)₂PO₂] tended to yield emulsions when combined with water and ethanol, while [emim][C₂H₅SO₄] combined with toluene and water provided two clear phases of reasonable viscosity. The compositions of the ternary mixtures were determined to obtain the tie-lines. A noticeable difference was observed for the tie-lines of the same IL (e.g., [P_{6,6,6,14}][DCA]) with different organic solvents (ethanol and acetonitrile) and water mixtures. In all cases, the addition of ethanol eventually produced a single phase.

Keywords: green chemistry; ionic liquids; phosphonium-based ionic liquids; ternary phase diagrams; tie-lines.

INTRODUCTION

With the growing challenge of environmentally benign chemical processing, room-temperature ionic liquids (RTILs) have emerged as useful alternative solvents during the past decade. ILs are in general defined as liquids composed entirely of ions—a class of novel solvents with very interesting properties [1]. These unique compounds are organic salts that are liquid over a wide range of temperatures near room temperature (<100 °C); they often have low vapor pressure, high thermal stability, and with low flammability [2]. ILs have thus gained increasing interest in recent years as “green” alternatives to volatile organic compounds (VOCs), for application in electrochemical, synthetic, catalytic, separation, and extraction processes. The ability to tune the cation/anion combination to alter diverse characteristics such as hydrophobicity/hydrophilicity, acidity/basicity, and dissolvability to many organic and inorganic materials is also a major advantage of these materials [3,4]. The possibility of synthetic variations has led to ILs being described as “designer solvents” [5]. Potential applications using ILs in separation processes include metal extraction, refining, and recovery of materials in the nuclear industry,

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‡Corresponding author: E-mail: douglas.macfarlane@sci.monash.edu.au

†E-mail: shahana.chowdhury@sci.monsh.edu.au

and in the preparation of selective liquid membranes and sensors [6]. One of the goals of green chemistry in this respect is to have a mechanism to transport a chemical from one phase to another with the least processing effort or energy cost, and without cross-contamination of phases [7].

In the context of separation processes, it is of importance to understand the liquid–liquid phase behavior of various ILs in contact with other solvents. Prior work reports either liquid–liquid equilibria (LLE) for binary systems, solubility curves for ternary systems, or distribution ratios of different solutes in mixtures of two immiscible solvents, one of them being the IL [8–10]. In the case of three liquid components, when two of the components are only sparingly miscible, the addition of the third may cause either an increase or decrease in the mutual solubility of these components. An increase in the mutual solubility is generally found when the third component dissolves readily in each of the other two [11–13].

Two ILs with the same organic cation, i.e., trihexyl(tetradecyl)phosphonium ($[P_{6,6,6,14}]^+$), and different anions, i.e., dicyanamide ($[DCA]^-$) and bis(2,4,4-trimethylpentyl)phosphinate ($[((CH_3)_3C_5H_8)_2PO_2]^-$) have been studied here. The purpose of this study is to develop ternary phase systems for phosphonium-based ILs and to determine the tie-lines in the $[P_{6,6,6,14}][DCA]$ + water + ethanol (EtOH) or acetonitrile (ACN), $[P_{6,6,6,14}][((CH_3)_3C_5H_8)_2PO_2]$ + water + ethanol, and $[emim][C_2H_5SO_4]$ + water + toluene systems. This allows us to analyze the effect of two different solvents on the tie-lines of the $[P_{6,6,6,14}][DCA]$ IL. The structures of the ILs investigated in this work are shown in Fig. 1. The density and viscosity of the IL- and water-rich phases were also measured for each of the ternary systems.

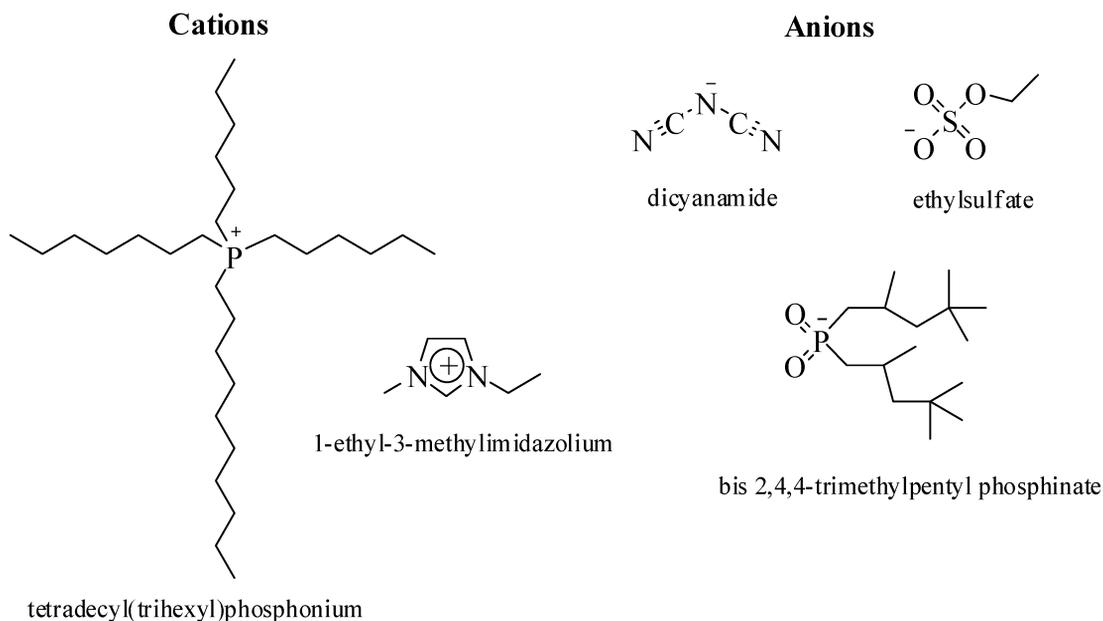


Fig. 1 Cations and anions of ILs investigated.

EXPERIMENTAL SECTION

Materials

Toluene and 1,4-dioxane were purchased from BHD Chemicals, England, and absolute ethanol, acetonitrile, chloroform-D1 ($CDCl_3$) and deuterium oxide (D_2O) were purchased from Merck Chemical Company, Germany. Acetone-D6 was purchased from Cambridge Isotope Laboratories, Inc. (USA). All

solvents were ≥ 99.8 mass % pure. ILs, phosphonium dicyanamide (CYPHOS IL 105), and phosphonium bis(2,4,4-trimethylpentyl)phosphinate (CYPHOS IL 104) were obtained from Cytec, Canada; and 1-ethyl-3-methylimidazolium ethylsulfate (ECOENG 212) was obtained from Solvent Innovation, Germany, respectively. Distilled water was used to prepare the sample mixtures.

Apparatus

Densities were measured using a U-shaped tube densimeter (Anton Paar, model DMA 512). For viscosity measurements, an Anton Paar AMVn automated micro viscometer was used. Viscosities were recorded using a 1.8-mm-diameter capillary and 1.5-mm-diameter ball. Karl–Fisher titration analysis (831 KF Coulometer from Metrohm) was used to determine water contents for the two phases of the different compositions of IL + organic solvent + water systems. The ^1H NMR spectra were recorded on a Bruker Avance DRX 300 series NMR spectrometer at 300 MHz, using D_2O for phosphonium IL systems and CDCl_3 for emim ethyl sulfate system.

Procedure

The points on the phase boundary curves were determined by the formation of a cloudy mixture on shaking after the addition of increasing known masses of one component to a mixture of known masses of the other two components [10]; each curve is constructed from many such points. For the tie-line composition determination, known masses of the three materials (IL, organic solvent, water) were added to a sealed glass vessel containing a magnetic stirrer connected to a temperature-controlled circulating bath for 8–10 h, then the two liquid phases were allowed to settle until no droplets were visible in either phase. Two samples of the two phases were withdrawn for analysis by glass syringes equipped with stainless steel hypodermic needles and then stored in closed glass vials. The upper liquid phase was IL-rich, and the lower phase was water-rich for the three phosphonium ILs ternary systems except for the $[\text{emim}][\text{C}_2\text{H}_5\text{SO}_4]$ IL system, where the lower phase was IL-rich.

Analysis

Water content in the IL-rich phase was determined by Karl–Fisher titration. The mass percent of the IL present in the IL-rich phase was determined from the residual mass of the sample after evaporation under vacuum at 90–100 °C overnight to remove the volatiles. Organic solvent mass % was then calculated from these two experimental results. Compositions of the water-rich phase were determined by ^1H NMR for the content of organic solvent and Karl–Fisher titration for water content. Integrated areas of suitably resolved signals in ^1H NMR spectra were measured to calculate the mass % of the organic solvent using 1,4-dioxane (9.85×10^{-6} M) as an internal standard. For each sample, a minimum of three analyses (for the $[\text{P}_{6,6,6,14}][\text{DCA}] + \text{water} + \text{ethanol}$ and $[\text{P}_{6,6,6,14}][((\text{CH}_3)_3\text{C}_5\text{H}_8)_2\text{PO}_2] + \text{water} + \text{ethanol}$ systems, four to six) were performed to obtain an average value and a measure of the reproducibility of the data.

RESULTS AND DISCUSSION

$[\text{P}_{6,6,6,14}][\text{DCA}] + \text{water} + \text{acetonitrile}$ ternary

Phosphonium dicyanamide + acetonitrile, and water + acetonitrile, are miscible with each other in all proportions, but water and this IL are only partly miscible. When the IL was shaken with a larger amount of water it dissolved partly, and two layers were formed, consisting of a saturated solution of water in the IL and the other of a saturated solution of IL in water. ACN distributes itself between the two liquid layers, and Table 1 presents the (% w/w) compositions of each of the components present in

each phase of four mixtures prepared. Tie-lines and phase boundaries for this system are presented in Fig. 2.

Table 1 Compositions of the phases present in the trihexyl(tetradecyl)phosphonium DCA (IL) + ACN + H₂O system.

IL (20 %): ACN (50 %): H ₂ O (30 %)	H ₂ O content (%)	ACN content (%)	IL content (%)
IL-rich phase	15.8 ± 1.3	[14.3 ± 0.7]	70.0 ± 0.5
H ₂ O-rich phase	68.5 ± 1.5	27.5 ± 0.5	[4 ± 1]
IL (30 %): ACN (40 %): H ₂ O (30 %)			
IL-rich phase	19.5 ± 1.5	[23 ± 2]	57.5 ± 0.5
H ₂ O-rich phase	70.5 ± 1.5	22.3 ± 1.5	[7.3 ± 3]
IL (35 %): ACN (50 %): H ₂ O (15 %)			
IL-rich phase	8.0 ± 1.0	[40.0 ± 1.5]	52.0 ± 0.5
H ₂ O-rich phase	67.5 ± 1.0	25.8 ± 0.7	[6.8 ± 1.7]
IL (35 %): ACN (30 %): H ₂ O (35 %)			
IL-rich phase	9.8 ± 0.2	[50.2 ± 0.8]	40.0 ± 0.5
H ₂ O-rich phase	75 ± 1	18.5 ± 1.0	[6.5 ± 2.0]

[] = values calculated from the other two compositions.

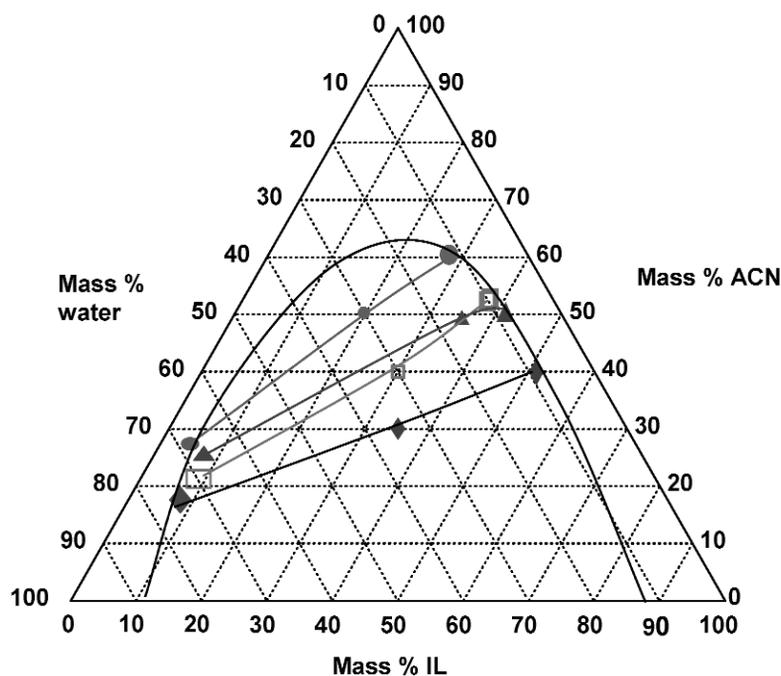


Fig. 2 Two-phase boundary and tie-lines of the [P_{6,6,6,14}][DCA] + H₂O + ACN system: (●) IL (20 %): ACN (50 %): H₂O (30 %); (□) IL (30 %): ACN (40 %): H₂O (30 %); (▲) IL (35 %): ACN (50 %): H₂O (15 %); (◆) IL (35 %): ACN (30 %): H₂O (35 %). The size of the data point in each direction indicates the size of the error in that composition.

Densities and viscosities were measured at a constant temperature (25 °C) for the two phases of each composition (Table 2). The densities and viscosities were found to be vastly reduced compared to the IL itself.

Table 2 Viscosity and density data (at 25 °C) for phosphonium DCA (IL) + ACN + H₂O system.

IL (20 %): ACN (50 %): H ₂ O (30 %)	Viscosity (mPa.s) Mean ± sd	Density (g/mL) Mean ± sd
IL-rich phase	1.446 ± 0.003	0.840 ± 0.001
H ₂ O-rich phase	1.294 ± 0.001	0.914 ± 0.001
IL (30 %): ACN (40 %): H ₂ O (30 %)		
IL-rich phase	2.056 ± 0.003	0.847 ± 0.002
H ₂ O-rich phase	1.323 ± 0.001	0.933 ± 0.001
IL (35 %): ACN (30 %): H ₂ O (35 %)		
IL-rich phase	3.868 ± 0.006	0.860 ± 0.001
H ₂ O-rich phase	1.423 ± 0.002	0.945 ± 0.001

[P_{6,6,14}][DCA] + water + ethanol ternary

Phosphonium dicyanamide + ethanol, and water + ethanol, are miscible with each other in all proportions, but water and this IL are only partly miscible. The compositions of each phase of the four different mixtures prepared are presented in Table 3 and used to obtain the tie-lines presented in Fig. 3.

Table 3 Compositions of the phases in the trihexyl(tetradecyl)phosphonium DCA (IL) + EtOH + H₂O system.

IL (18.1 %): EtOH (54.3 %): H ₂ O (27.6 %)	H ₂ O content (%)	EtOH content (%)	IL content (%)
IL-rich phase	7.5 ± 0.5	[33.5 ± 1.5]	59 ± 1
H ₂ O-rich phase	32.5 ± 1.0	53 ± 3	[14.5 ± 4.0]
DCA (15.1 %): EtOH (54.8 %): H ₂ O (30.1 %)			
IL-rich phase	7.25 ± 0.25	[33.5 ± 1.3]	59.25 ± 1.00
H ₂ O-rich phase	36 ± 1	48.5 ± 0.5	[15.5 ± 1.5]
DCA (29.9 %): EtOH (50.0%): H ₂ O (20.1 %)			
IL-rich phase	7.5 ± 0.5	[37.5 ± 1.5]	55 ± 1
H ₂ O-rich phase	33 ± 1	56.0 ± 1.5	[11.0 ± 2.5]
DCA (27.3 %): EtOH (54.4 %): H ₂ O (18.3 %)			
IL-rich phase	9.5 ± 0.5	[44 ± 2]	46.5 ± 1.5
H ₂ O-rich phase	26 ± 1	51.5 ± 0.5	[22.5 ± 1.5]

[] = values calculated from the other two compositions.

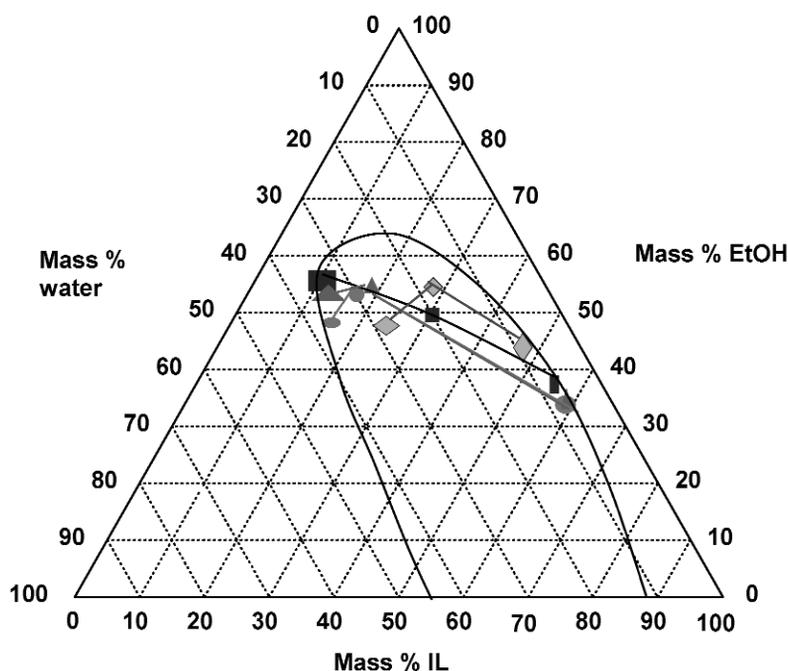


Fig. 3 Two-phase boundary and tie-lines of the $[P_{6,6,6,14}][DCA] + H_2O + EtOH$ system: (●) IL (15 %): EtOH (55 %): H_2O (30 %); (■) IL (30 %): EtOH (50 %): H_2O (20 %); (▲) IL (18 %): EtOH (54.5 %): H_2O (27.5 %); (◆) IL (27.5 %): EtOH (54.5 %): H_2O (18 %). The size of the data point in each direction indicates the size of the error in that composition.

In this system, the phase separations were complex. Two clear phases were separated and kept in sealed glass vials for 5–6 days during which time water droplets were developed at the bottom of the IL-rich phase; similarly, IL droplets were observed in the water-rich phase vials. When the vials were shaken vigorously, the droplets appeared to redissolve in the contents of the vials and became invisible. Again, when these samples were left for 1–2 days the droplets reappeared. Refractive indices were measured for the IL-rich phase and the water droplets, and these were found to be very close to one another, suggesting that small dispersed droplets may not be easily visible. Pictures of the phenomena are shown in Figs. 4a, b.

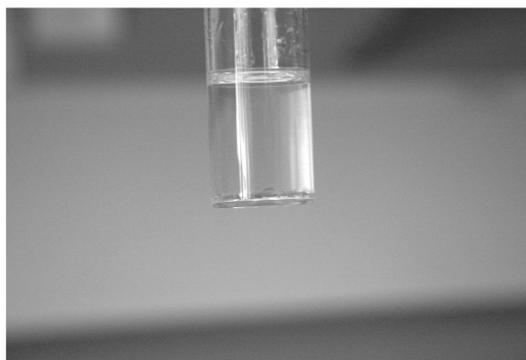


Fig. 4a H_2O droplets formed in the IL-rich phase ($[P_{6,6,6,14}][DCA] + EtOH + H_2O$ system) after 5–6 days.

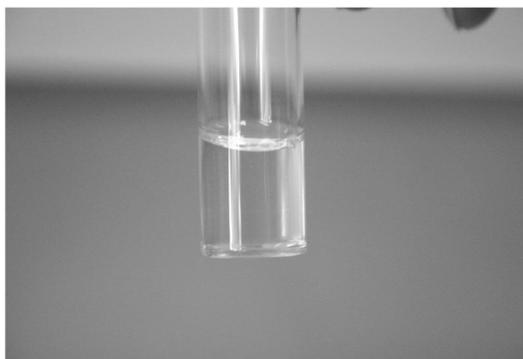


Fig. 4b H₂O-droplets disappeared after mixing the IL-rich phase ([P_{6,6,6,14}][DCA] + EtOH + H₂O system) vigorously forming a clear (no visible water droplets) solution.

[P_{6,6,6,14}][((CH₃)₃C₅H₈)₂PO₂] + water + ethanol ternary

Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate + ethanol, and water + ethanol, are miscible with each other in all proportions, but water and IL are only partly miscible. The compositions of each phase of the four different mixtures prepared are presented in Table 4 and used to obtain the tie-lines of this ternary system. Tie-lines and phase boundaries are presented in Fig. 5.

Table 4 Compositions of the phases in the trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (IL) + EtOH + H₂O system.

IL (34.5 %): EtOH (35 %): H ₂ O (30.5 %)	H ₂ O content (%)	EtOH content (%)	IL content (%)
IL-rich phase	13.5 ± 0.5	[41.5 ± 1]	45.0 ± 0.5
H ₂ O-rich phase	56.0 ± 1.5	36 ± 1	[8.0 ± 2.5]
IL (20 %): EtOH (40 %): H ₂ O (40 %)			
IL-rich phase	14 ± 1	[39.5 ± 1.5]	46.5 ± 0.5
H ₂ O-rich phase	56.5 ± 0.5	35 ± 3	[8.5 ± 3.5]
IL (26 %): EtOH (30 %): H ₂ O (44 %)			
IL-rich phase	12.5 ± 0.5	[48.5 ± 1.5]	39 ± 1
H ₂ O-rich phase	65 ± 2	28.5 ± 0.5	[6.5 ± 2.5]
IL (25 %): EtOH (45 %): H ₂ O (30 %)			
IL-rich phase	16 ± 1	[28.5 ± 1.5]	55.5 ± 0.5
H ₂ O-rich phase	48.5 ± 1.5	40 ± 4	[11.5 ± 5.5]

[] = values calculated from the other two compositions.

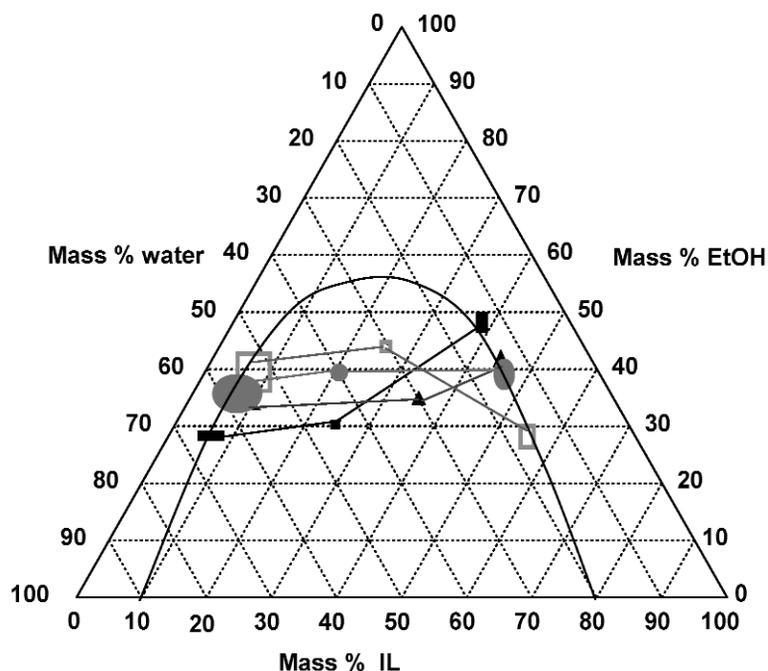


Fig. 5 Two-phase boundary and tie-lines of the $[P_{6,6,6,14}][((CH_3)_3C_5H_8)_2PO_2] + H_2O + EtOH$ system: (●) IL (20 %): EtOH (40 %): H_2O (40 %); (□) IL (25 %): EtOH (45 %): H_2O (30 %); (▲) IL (34.5 %): EtOH (35 %): H_2O (30.5 %); (■) IL (26 %): EtOH (30 %): H_2O (44 %). The size of the data point in each direction indicates the size of the error in that composition.

[emim][C₂H₅SO₄] + water + toluene ternary

1-Ethyl-3-methyl-imidazolium ethylsulfate and water are miscible with each other in all proportions, but water and this IL are immiscible with toluene. When IL and water were mixed, they formed a homogeneous solution, and then addition of toluene produced two separate layers. Tie-line data and diagram are presented in Table 5 and Fig. 6, respectively, for this system. It was observed from these phase compositions that water was partitioned very poorly (1.0–1.5 % (w/w)) with toluene. It appears that this system separates into an IL-water phase and an almost pure toluene phase. The viscosities and densities measured at 21–23 °C for samples of different compositions are listed in Table 6.

Table 5 Compositions of the phases in the 1-ethyl-3-methylimidazolium ethylsulfate (IL) + toluene + H₂O system.

IL (30): H ₂ O (30): toluene (40)	H ₂ O content (%)	Toluene content (%)	IL content (%)
Toluene-rich phase	0.5 ± 0.1	82 ± 1.5	17.5 ± 1.6
IL-rich phase	49 ± 1	0.5 ± 0.1	49.5 ± 0.1
IL (50): H ₂ O (20): toluene (30)			
Toluene-rich phase	0.5 ± 0.1	88 ± 1	11.5 ± 1.1
IL-rich phase	30 ± 1	2.5 ± 0.5	66.5 ± 0.5
IL (20): H ₂ O (40): toluene (40)			
Toluene-rich phase	1.0 ± 0.2	89 ± 1	10 ± 1.2
IL-rich phase	59.5 ± 1.5	3.7 ± 1.8	36.7 ± 0.3
IL (25): H ₂ O (45): toluene (30)			
Toluene-rich phase	1.0 ± 0.2	88.5 ± 1.5	10.5 ± 1.7
IL-rich phase	64 ± 1	2.5 ± 1.5	33.5 ± 0.5

[] = values calculated from the other two compositions.

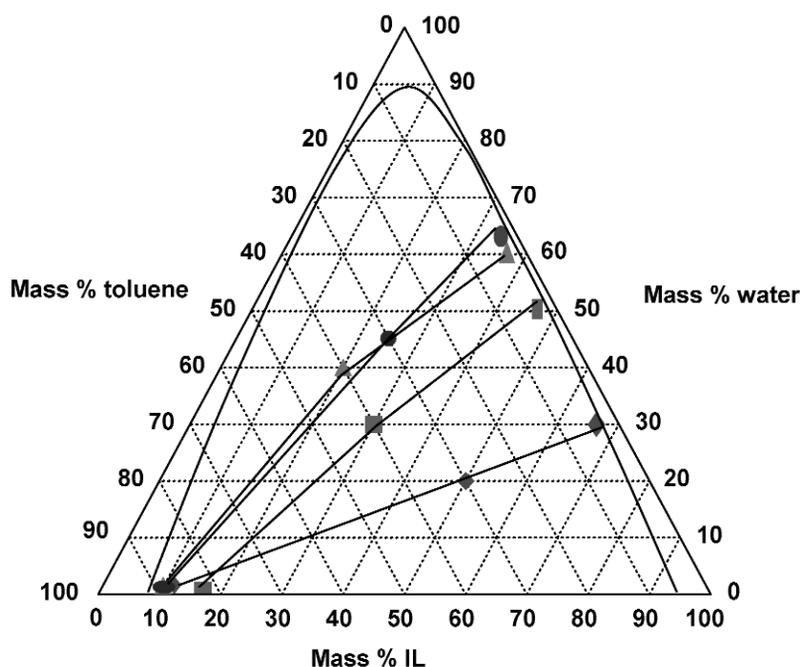


Fig. 6 Two-phase boundary and tie-lines of the [emim][C₂H₅SO₄] + H₂O + toluene system: (●) IL (25 %): toluene (30 %): H₂O (45 %); (◆) IL (50 %): toluene (30 %): H₂O (20 %); (▲) IL (20 %): toluene (40 %): H₂O (40 %); (■) IL (30 %): toluene (40 %): H₂O (30 %). The size of the data point in each direction indicates the size of the error in that composition.

Table 6 Density and viscosity data for the phases in the 1-ethyl-3-methylimidazolium ethylsulfate (IL) + toluene + H₂O system.

IL (30): H ₂ O (30): toluene (40)	Density (g/mL) Mean ± sd	Viscosity (mPa.s) Mean ± sd
Toluene-rich phase (at 21 °C)	0.853 ± 0.001	1.140 ± 0.002
H ₂ O-rich phase (at 22 °C)	1.128 ± 0.001	4.562 ± 0.005
IL (50): H ₂ O (20): toluene (30)		
Toluene-rich phase (at 22.5 °C)	0.865 ± 0.001	1.082 ± 0.004
H ₂ O-rich phase (at 22.5 °C)	1.130 ± 0.001	4.154 ± 0.004
IL (20): H ₂ O (40): toluene (40)		
Toluene-rich phase (at 23 °C)	0.864 ± 0.001	1.029 ± 0.002
H ₂ O-rich phase (at 23 °C)	1.123 ± 0.001	4.022 ± 0.004
IL (25): H ₂ O (45): toluene (30)		
Toluene-rich phase (at 23 °C)	0.841 ± 0.001	1.018 ± 0.002
H ₂ O-rich phase (at 23 °C)	1.128 ± 0.001	4.031 ± 0.004

SUMMARY AND CONCLUSIONS

Three-component systems of IL + organic solvent + water were developed in this work, and their bi-phasic behaviors were observed. For the [P_{6,6,6,14}][DCA] + water + acetonitrile system, simple phase separations were observed and tie-lines were comparatively straight lines, as compared with the [P_{6,6,6,14}][DCA] + water + ethanol and [P_{6,6,6,14}][((CH₃)₃C₅H₈)₂PO₂] + water + ethanol systems. In all cases, the addition of ethanol eventually produced a single phase, a useful observation which could be used to create one or two phase mixtures simply by changing the ethanol content.

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