



Measurement and correlation of ternary phase equilibrium of (hexane + ethyl acetate) with four ILs



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ABSTRACT

The ternary liquid-liquid phase equilibria (LLE) for four systems including {hexane + ethyl acetate + 1-hexyl-3-methylimidazolium tetrafluoroborate ([Hmim][BF₄])}, {1-octyl-3-methylimidazolium tetrafluoroborate ([Omim][BF₄])}, {1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([Hmim][OTf])}, and {1-octyl-3-methylimidazolium trifluoromethanesulfonate ([Omim][OTf])} were determined at 298.15 K and atmospheric pressure. All the investigated systems exhibited Treybal type I behaviour. The solute distribution ratio (β) and the selectivity (S) were calculated for each system to estimate the efficiency of the separation of a hexane + ethyl acetate mixture using ionic liquids as the solvent. The influence of the anion and substituent group of the cation imidazolium rings of the ionic liquid on the LLE was revealed. Two models, NRTL and UNIQUAC, were used to correlate the experimental LLE results for which the binary interaction parameters were obtained. The UNIFAC model was used to predict the LLE data of the ternary systems, and the results were compared with experimental data.

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1. Introduction

Polyolefin is a commonly used plastic owing to its large output, wide application and low cost, but its crystallinity and nonpolar properties limit its use in some cases. Graft modification can confer some special properties and new functions on polyolefin and therefore broaden their application fields. The two components of hexane and ethyl acetate were mixed in the grafted polyolefins purifying process [1]. Hexane is an important organic compound which is widely used in several processes including petroleum catalytic reforming, crude oil leaching in the food manufacturing industry, and recycling of propylene in plastics manufacturing. Ethyl acetate is a fatty acid ester that has a wide range of applications as a solvent, perfume material and adhesive. Ethyl acetate and hexane are in heavy demand as organic solvents in the chemical industry. Therefore, the separation of hexane and ethyl acetate from their azeotropic mixture is of great economic and environmental importance.

Due to the formation of a minimum azeotropic mixture, it is unrealistic and not economically feasible to separate the hexane + ethyl acetate mixture using conventional distillation. Typically, azeotropic mixtures are separated by different separation techniques such as pressure swing distillation and extractive distilla-

tion [2,3]. However, the high energy consumption for these methods cannot be ignored. Liquid-liquid extraction is an environmental-friendly and energy-saving process that can be an alternative method, for which the paramount problem for achieving the best extraction effect is the selection of a suitable solvent [4].

Ionic liquids (ILs) have been widely considered as good solvents because of their many excellent characteristics, including low melting point, non-volatility, stable thermodynamic properties, and favorable solubility for many inorganic salts and organic compounds [5,6]. Additionally, because ILs are easy to recover, they are considered to be “green solvents” and ideal alternatives to conventional organic solvents. Thus, the use of ILs as solvents in the separation process has great potential.

Many papers concerning the application of ILs in liquid-liquid extraction have been published. Many scholars have studied the separation of hexane from its mixtures [7–9]. Hu et al. tested the ternary phase equilibrium of ILs with ethyl acetate mixtures [10], and they determined the tie-line composition by measuring the densities to compare with the standard curves. The ability of ILs to act as solvents to separate azeotropic mixtures has also been demonstrated. The separation performance of ILs towards organics in their aqueous solution has been widely investigated [11–14]. Saïen et al. studied the LLE of acetone + water + [Hmim][PF₆] by putting the mixture inside a shaking water bath to ensure the complete contact of the two phases [15]. Domínguez et al. applied sev-

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eral ILs to separate the alkane + aromatic compounds mixture, for which the composition of the IL-rich phase was calculated by a polynomial expression of density vs. composition [16]. The influence of temperature on the extraction process has been studied by some scholars [17–19], and the effects of cations and anions in ionic liquids on extraction have been investigated in great detail [20,21]. However, there has been only one published paper that focused on the separation of the hexane + ethyl acetate mixture [22] in which two ILs of 1-hexyl-3-methylimidazoliumhexafluorophosphate ([Hmim][PF₆]) and 1-octyl-3-methylimidazolium hexafluorophosphate ([Omim][PF₆]) were used.

In this study, the liquid-liquid phase equilibrium of four ternary systems of hexane + ethyl acetate + [Hmim][BF₄]/[Omim][BF₄]/[Hmim][OTf]/[Omim][OTf] was measured at 298.15 K and atmospheric pressure. The values of β and S were calculated from the experimental liquid-liquid data to estimate the separation efficiency of ILs in separating the mixture. Additionally, the NRTL and UNIQUAC models were used to correlate the experimental LLE data, the fitted interaction parameters were determined, and the *rmsd* (root-mean-square deviation) between the experimental data and the calculated data were obtained. The UNIFAC model was used to predict the LLE equilibria using Aspen plus V8.4.

2. Experimental

2.1. Materials

Ethyl acetate, hexane and ethanol were purchased from the Tianjin Kermel Chemical Reagent Co., Ltd with claimed purity of ≥ 0.998 , 0.995 and 0.998 (mass fraction), respectively. All ILs used in this study were purchased from the Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences and their purities were claimed to be higher than 0.990 (mass fraction). The substance purities were checked using gas chromatography and all the chemicals were used without further purification. All the chemicals used in the work are listed in Table 1.

2.2. Apparatus and procedure

The experimental facilities and procedures used in this study were described in our previous work [23,24]. Here, we give a brief overview. First, the cloud point method [25] was carried out in the pre-experiment to determine the two-phase region (see Supplementary Material Table S1), and then the content of the three components was determined. The masses of hexane, ethyl acetate and ILs were weighted using FA-1204B electronic scales purchased from Shanghai Tianmei balance instrument co., Ltd. Then, the mixture was placed into the in-house-designed equilibrium cell [13] and the temperature was kept constant at 298.15 K by connecting the jacket to a HX-105 low-temperature thermostat purchased from the Changliu Instrument Factory of Beijing in China, for which the temperature fluctuation was 0.05 K. After 3 h of rigorous stir-

ring in the equilibrium cell by a stir bar, the mixture was settled for 15 h to make sure the two liquid phases were separated completely. The samples of both phases from the lower and upper layers were removed to determine their compositions.

To analyse the composition of ethyl acetate and hexane, a gas chromatograph (GC-2014C, purchased from Shimadzu Corporation) was used, with helium (>99.999% purity) as the carrier gas, and the gas chromatograph was equipped with a TCD (thermal conductivity detector) and a GDX-104 (3 m \times 4 mm) packed column. The pre-column was Porapak Q which prevents the non-volatile matter from contaminating the packed column. Ethanol was the internal standard for the gas chromatography analysis of ethyl acetate and hexane. The detection conditions of the system containing (ethyl acetate + hexane + ILs) were set as follows: the injector temperature was set to 503.15 K, the column oven was maintained at 453.15 K for 2 min with the temperature programmed to (453.15–503.15) K at a rate of 15 K min⁻¹, and then the temperature was maintained at 503.15 K for 5 min. The detector was set to 503.15 K. The composition of the ILs in the samples was determined by the differential subtraction method that calculated the mass difference before and after the vaporization of the solvents, and the vaporization was achieved using a DZF-6020 vacuum drying oven from Shanghai Boxun China. All the measurements in this study were repeated at least three times to confirm the reliability of the results.

3. Result and discussion

3.1. Experimental results

The liquid-liquid equilibrium experiments were carried out at 298.15 K under atmospheric pressure. The experimental tie-line data for the ternary systems {hexane + ethyl acetate + [Hmim][BF₄]}, {hexane + ethyl acetate + [Omim][BF₄]}, {hexane + ethyl acetate + [Hmim][OTf]}, and {hexane + ethyl acetate + [Omim][OTf]} are presented in Table 2. The experimental LLE endpoints and tie-lines of each system and the solubility for hexane and ILs are shown in Figs. 1 to 4 accordingly. The endpoint of {hexane + ethyl acetate + [Omim][OTf]} system seems to be inconsistent with the binodal curve, which could be due to the different methods adopted in the pre-experiment and the final experiment or the measuring error. In Fig. 1, the measured solubility of [Hmim][BF₄] with hexane is not entirely consistent with the measured ternary LLE, which could be due to the experimental error. In Fig. 2 and Fig. 3, the solubility of hexane in ILs measured in this work and in other studies [26,27] shows certain deviations that could be due to the different measuring methods. Alonso et al. [26] determined the experimental data by analysing thiophene and hydrocarbon compositions by using gas chromatography. The ionic liquid composition was calculated by the observed difference. Corderí et al. [27] determined the LLE composition by the density-composition curve for the binary mixture. The values of

Table 1

Sources, CAS number, molar mass, purification, water contents by mass, w_w , and analysis method of the chemicals used in this work.

Chemical	Source	CAS number	Molar mass/ (g·mol ⁻¹)	Mass purity stated by supplier	$w_w/10^{-6}$	Analysis method
ethanol	Tianjin Kermel Chemical Reagent Co., Ltd.	64-17-5	46.07	0.995 ^a		GC
ethyl acetate	Tianjin Kermel Chemical Reagent Co., Ltd.	141-78-6	88.11	0.998 ^a		GC
hexane	Tianjin Kermel Chemical Reagent Co., Ltd.	110-54-3	86.18	0.995 ^a		GC
[Hmim][BF ₄]	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.	244193-50-8	254.08	0.990 ^a	<500 ^a	
[Hmim][OTf]	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.	460345-16-8	316.34	0.990 ^a	<500 ^a	
[Omim][BF ₄]	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.	244193-52-0	282.13	0.990 ^a	<500 ^a	
[Omim][OTf]	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.	403842-84-2	344.40	0.990 ^a	<500 ^a	

^a Analysis by supplier.

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