Liquid−Liquid Equilibria for Benzene + Cyclohexane + 1-Butyl-3-methylimidazolium Hexafluorophosphate

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Experimental liquid−liquid equilibrium data were measured for benzene + cyclohexane + 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim]PF_6) at atmospheric pressure and (298.2, 308.2, and 318.2) K. The selectivity of [C_4mim]PF_6 for benzene is in the range of (20 to 60) when the mass fraction of benzene in the cyclohexane-rich phase is less than 0.08, which increases with a decrease in benzene content. The selectivity is also dependent on the temperature. The highest selectivity is obtained at 308.2 K in this work. Considering the high selectivity for benzene and the negligible solubility in benzene + cyclohexane mixtures, [C_4mim]PF_6 may be used as a potential extracting solvent for the separation of benzene and cyclohexane.

Introduction

Cyclohexane is an important commodity chemical for production of cyclohexanone, cyclohexanol, caprolactam, etc. The main preparation method of cyclohexane is catalytic hydrogenation of benzene. So the product of cyclohexane has a trace of benzene inevitably which needs removal. However, benzene and cyclohexane have extremely close boiling points and can form azeotropes, and a conventional distillation may consume a large amount of energy and can not realize deep separation in practice.[1]

Presently, azeotropic distillation and extraction are commercially used for this separation. The typical entrainers include sulfolane,[2] *N*-methyl-2-pyrrolidone (NMP),[3] *N*,*N*-dimethylacetamide,[4] and cyclodextrin.[5] They suffer from process complexity and high-energy consumption due to their low extractive selectivity, considerable volatility, or high mutual solubility in a benzene + cyclohexane mixture.

Liquid−liquid extraction is another alternative as a widely used industrial separation process for homogeneous liquid mixtures unfit for distillation. A proper extractant should have good selectivity for benzene and low volatility for loss reduction and easy regeneration. In this regard, ionic liquids (ILs) seem superior to the traditional molecular solvents for their unique attributes, e.g., good selectivity for aromatics versus alkanes, negligible solubility in a benzene + cyclohexane mixture, nonvolatility, and thermal stability up to about 200 °C. ILs as extractant have attracted much attention since the 1990s.[6−8] Liquid−liquid equilibria data are important technical information in developing the liquid−liquid extraction process. Letcher et al. studied the performance of 1-octyl-3-methylimidazolium chloride ([C_8mim]Cl), 1-hexyl-3-methylimidazolium tetrafluoroborate, or hexafluorophosphate ([C_6mim]BF_4 or PF_6), on the extraction of benzene from heptane, dodecane, and hexadecane, respectively, at 298.2 K.[9,10] Selvan et al. determined the toluene + heptane + 1-ethyl-3-methylimidazolium triiodide system at 45 °C and the toluene + heptane + 1-butyl-3-methylimidazolium triiodide system at 35 °C.[11] Arce et al. determined the ternary system formed by hexane, benzene, and 1-ethyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}amide ([C_2mim]-[NTf_2]) at (25 and 40) °C.[12] Domańska determined ternary systems containing ethyl(2-hydroxyethyl)dimethylammonium bis{(trifluoromethyl)sulfonyl}imide (C_2NTf_2) at 298.15 K, including hexane + benzene + C_2NTf_2, hexane + *p*-xylene + C_2NTf_2, and hexane, or octane + *m*-xylene + C_2NTf_2.[13] Wang et al. determined liquid−liquid equilibria for benzene + cyclohexane + 1-methyl-3-methylimidazolium dimethylphosphate ([C_1mim][DMP]) or 1-ethyl-3-methylimidazolium eiethylphosphate ([C_2mim][DEP]).[14] All these investigations covering wide composition ranges do not focus on the mixtures containing a trace of aromatics, like those in practical separation processes.

The aim of the present work is to investigate the applicability of 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim]-PF_6) on the extractive separation of benzene + cyclohexane mixtures (with a trace of benzene) in terms of the experimental liquid−liquid equilibria data for the corresponding ternary systems at (298.2, 308.2, and 313.2) K. Besides, the influence of temperature and benzene content on selectivity is discussed.

Experimental Section

Materials. The chemicals used in this study were benzene, cyclohexane, and [C_4mim]PF_6. Benzene and cyclohexane both with a nominal minimum mass fraction of 0.995 were of chromatography grade and used as received from Tianjin Fuchen Chemical Reagent Factory. [C_4mim]PF_6 was provided by Henan Lihua Co., Ltd. The purities of ILs were above 0.980 in mass fraction in terms of NMR. The ILs were subjected to a low-pressure vacuum to remove the residual volatile impurities and stored in desiccators to prevent any absorption of moisture. The water mass fraction was $(2.08 \pm 0.08)\cdot10^{-3}$ as measured by the Karl Fischer method (CA-05). The nominal mass fractions of water for benzene and cyclohexane were both less than $2\cdot10^{-5}$.

Apparatus and Procedures. The liquid−liquid equilibrium measurements for the ternary mixture IL + benzene + cyclohexane were conducted in a jacketed glass cell of about 10 mL.

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Table 1. Liquid−liquid Equilibrium Data in Mole Fraction for Ternary Systems [C_4mim]PF_6 (1) + Benzene (2) + Cyclohexane (3) at (298.2, 308.2, and 318.2) K and the Selectivity (*S*) of Benzene versus Cyclohexane

	cyclohexane-rich		IL-rich			
T/K	x'_2	x'_3	x''_1	x''_2	x''_3	*S*
298.2	0.0268	0.973	0.833	0.0808	0.0867	33.8
	0.0309	0.969	0.826	0.0902	0.0837	33.8
	0.0388	0.961	0.810	0.108	0.0820	32.6
	0.0490	0.951	0.785	0.129	0.0862	28.9
	0.0661	0.934	0.755	0.160	0.0850	26.6
308.2	0.0117	0.988	0.917	0.0339	0.0490	58.4
	0.0210	0.979	0.884	0.0590	0.0572	48.0
	0.0424	0.958	0.821	0.114	0.0647	40.0
	0.0598	0.940	0.763	0.157	0.0795	31.1
	0.0706	0.929	0.758	0.165	0.0768	28.4
318.2	0.00964	0.990	0.906	0.0274	0.0663	42.5
	0.0134	0.987	0.858	0.0449	0.0966	34.1
	0.0199	0.980	0.859	0.0521	0.0894	28.7
	0.0280	0.972	0.813	0.0789	0.108	25.5
	0.0803	0.920	0.739	0.169	0.0923	20.9

The glass cell was sealed by a silicon rubber cap, and the liquid inside was mixed vigorously with a magnetic stirrer. The equilibrium liquid temperature was maintained by circulating water coming from a superthermostat (SC-15) with temperature fluctuation within 0.1 K.

First, ILs and benzene + cyclohexane mixtures were in turn added into the glass cell. The mixture was stirred with a magnetic stirrer for at least 48 h at specified temperature and then left to stand for 24 h to achieve a clear phase separation. The time used here for equilibrium and phase splitting was fixed according to results from our preliminary tests.

Because IL does not elute from a gas chromatograph, analysis of the IL-rich phase requires NMR (^{1}H NMR, 600 MHz), and the cyclohexane-rich phase requires both NMR and GC analysis. NMR spectra can provide the ratio of three components, thereby giving their mole fraction by normalization. The NMR instrument was operated at a higher temperature than that at which the sample was taken to prevent phase separation during the analysis. The peaks attributed to ILs were not found in the NMR spectra of the samples of the cyclohexane-rich phase. So, it can neglect the content of IL in the cyclohexane-rich phase and following effect on GC instrument and analysis. The gas chromatograph used was an HP 6890 equipped with a flame ionization detector. The analysis conditions include: capillary column, HP-FTAP, 25 m × 0.32 mm × 0.52 μm; oven temperature, 50 °C; injet temperature, 150 °C; detector temperature, 240 °C; external standard method. The uncertainty in temperature was 0.1 K. The uncertainty of mole fraction for IL was considered to be ± 0.010. For each sample, two analyses were performed to obtain an average value. The reproducibility for the compositions was within ± 5 %. The average deviation in the compositions was about 2.5 %.

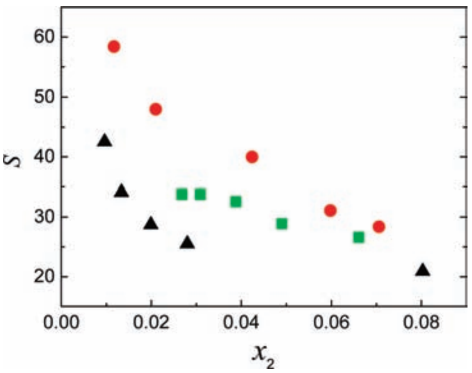

Figure 1. Plot of the selectivity (*S*) against mole fraction of benzene in the cyclohexane-rich layer: ■, 298.15 K; ●, 308.15 K; ▲, 318.15 K. x_2 is the mole fraction of benzene in the cyclohexane-rich phase.

Results and Discussions

LLE data for the ternary system IL (1) + benzene (2) + cyclohexane (3) at (298.2, 308.2, and 318.2) K were obtained experimentally in the mass fraction range of (0 to 0.08) for benzene. The results are listed in Table 1. Selectivity (*S*) is an important parameter in assessing the feasibility of utilizing a solvent in liquid−liquid extraction. With regards to the pseudo-binary mixture of benzene (2) + cyclohexane (3) studied, the feasibility of extracting aromatics from aliphatic is given by eq 1

$$S = \frac{(x'_2/x'_3)}{(x''_2/x''_3)} \tag{1}$$

where x_2 and x_3 refer to the mole fraction of benzene and cyclohexane, respectively, and ′ is the IL-rich phase and ″ is the cyclohexane-rich phase. The selectivity values computed from the tie line data are presented in Table 1 as well. In evidence, [C_4mim]PF_6 has good selectivity, at least in 25 experiments, suggesting that extraction is possible.

Figure 1 is a plot of benzene mole fraction in the cyclohexane-rich layer versus selectivity. Our results are similar to those of Letcher et al.[9] and Selvan et al.[11] in that the selectivity increases with decreasing mole fraction of the aromatic compound in the alkane-rich layer. The results of Selvan et al.[11] increase exponentially, whereas those of Letcher et al. do so linearly. In our experiments, this trend is a linear increase in the higher mass fraction range for benzene and an exponential increase in the lower mass fraction range. Figure 1 also shows the selectivity is dependent on the temperature. In experiments, the highest selectivity was obtained at 308.2 K.

Considering the high selectivity for benzene as well as the negligible solubility in benzene + cyclohexane mixtures at atmosphere and near room temperature, [C_4mim]PF_6 may be used as a potential extracting solvent for the separation of benzene and cyclohexane. In particular, the trend of selectivity versus benzene content provides convenience for deep separation.

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