Journal of Material and Process Technologies

JMPT

Separation of benzene and cyclohexane azeotrope mixture using 1-ethyl-3-methylimidazolium ethyl sulfate ionic liquid using extractive distillation

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Abstract

Most of the cyclohexane used for various industrial applications is largely produced through catalytic hydrogenation of benzene and the separation of cyclohexane from the unreacted benzene is industrially significant. However, it is tough to separate cyclohexane from benzene by conventional distillation processes since these components have close boiling points and form an azeotrope mixture. Currently, extractive distillation is commercially used for the separation of cyclohexane from benzene using conventional solvents (entrainers) such as sulfolane, dimethyl sulfoxide, N-formylmorpholine, and N-methylpyrrolidone. However, separating benzene and cyclohexane with extractive distillation with these solvents makes the process complex and consumes high energy. On the other hand, ionic liquids are considered green and potentially environmentally friendly, hence have been attracting attention in replacing conventional solvents (entrainers) in extractive distillation because of their unique properties. In this work, 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO$_4$]) was used for the separation of cyclohexane from benzene using extractive distillation. The performance of [EMIM][EtSO$_4$] was evaluated by measuring the isothermal vapour-liquid equilibrium (VLE) for benzene, cyclohexane, and [EMIM][EtSO$_4$] ternary mixture at 353.15 K. The isothermal VLE was measured using Head Space Gas Chromatography (HS-GC). Moreover, the VLE data was also predicted using COSMO-RS and compared with the experimental values. The addition of [EMIM][EtSO$_4$] eliminated the azeotrope and increased the relative volatilities of benzene and cyclohexane resulting in their separation. The performance of [EMIM][EtSO$_4$] on the benzene and cyclohexane system was compared with dimethyl sulfoxide. The current ionic liquid shows higher relative volatility compared to dimethyl sulfoxide showing this ionic liquid can be used for the separation of benzene and cyclohexane using extractive distillation.

1. Introduction

Cyclohexane is used for the production of various chemicals such as adipic acid and ε-caprolactam, which are used as feedstocks for the production of Nylon 6 and Nylon 6,6 [1, 2]. Moreover, cyclohexane is used as a solvent in several industries, including the paint, varnish, and plastic industries [1, 3]. Further, it is widely used as a solvent in extracting essential oils from various sources. Previously, cyclohexane had been obtained by direct fractionation of crude oil. However, cyclohexane demand was continuously increasing and this could not be met by cyclohexane naturally in crude oil [4]. Moreover, the cyclohexane obtained from crude oil direct distillation has low purity [1, 3]. Hence, currently, more than 85% of the cyclohexane used worldwide is produced through hydrogenation of benzene [5]. In this process, benzene is hydrogenated catalytically to cyclohexane in the presence of hydrogen and catalyst. Unreacted gaseous hydrogen may easily be purged from the product stream leaving an azeotropic mixture of liquid benzene and cyclohexane. The removal of the cyclohexane from unreacted

benzene from the outlet stream of the hydrogenation reactor is a very crucial [1, 6]. However, due to their close boiling temperatures and the formation of an azeotropic mixture, the separation of benzene and cyclohexane mixtures is one of the most challenging operations in the petrochemical sector. [1, 7]. Conventional separation processes such as distillation cannot separate the two components.

Special distillation such as extractive distillation is the main separation technology presently available to separate benzene and cyclohexane mixture [1]. Common solvents (entrainers) such as sulfolane [8-10], N-formylmorpholine [11], N-methylpyrrolidone [12], and dimethyl-sulfoxide [12] have been used to break the azeotrope and enhance the relative volatility of cyclohexane to benzene. However, these entrainers (solvents) require complicated processes and consume high energy [5]. Recently, ionic liquids (ILs) have attracted attention in replacing these conventional solvents in separation processes. Due to their unique properties and potential environmental benefits ionic liquids (ILs) have attracted attention

as an alternative to traditional solvents for separating cyclohexane from benzene through extractive distillation [3, 4, 12, 13]. Ionic liquids have garnered significant attention due to their notable properties, including negligible vapor pressure and flammability, high thermal, chemical, and electrochemical stability, high ionic and electrical conductivity, and distinct solubility characteristics [14, 15].

Ionic liquids derived from imidazolium and pyridinium cations demonstrate high solubility for benzene and low solubility for cyclohexane. This means these ILs have a high affinity toward benzene compared to cyclohexane which helps separation of benzene and cyclohexane using extractive distillation or liquid extraction processes [16]. However, in liquid extraction processes involving benzene and cyclohexane, the benzene/cyclohexane selectivities reported for the tested ionic liquids were below 30, which is considered the benchmark value of selectivity needed to ensure the feasibility of a liquid-liquid extraction process for aromatic hydrocarbons [17]. As a result, extractive distillation using ILs has recently been proposed as an alternative method for separating benzene and cyclohexane. Extractive distillation involves the use of a non-volatile separating agent with a high boiling point, commonly referred to as a solvent or entrainer. This agent is added to the azeotropic mixture to modify the relative volatility of the components, facilitating their separation.

The effectiveness of ILs in separating benzene from cyclohexane is influenced not only by the type of cations but also by the nature of the anions that combine to form ILs. Additionally, when selecting ILs for certain applications, other factors such as environmental impact and cost must also be considered. In this work, we investigated 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]) for the separation of benzene and cyclohexane using extractive distillations. ILs with alkyl sulfate such as ethyl sulfate anions can be easily synthesized in a halide-free way [18]. Chlorides are often corrosive and can produce harmful by-products, which may require additional treatment or disposal measures. Previously, 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]) was investigated for the breaking azeotropic mixtures. Oliveira et al. [19] used ([EMIM][EtSO₄] for breaking of n-heptane and ethanol azeotropic mixture. Graczová and Steltenpohl [20] utilized this ionic liquid for the recovery of ethanol from water through extractive distillation. In the current work, [EMIM][EtSO₄] was used as an entrainer for the recovery of benzene from cyclohexane using extractive distillation. Isothermal vapour-liquid equilibrium (VLE) of benzene and cyclohexane was generated using headspace gas chromatography (HS-GC) and their relative volatilities were obtained from the VLE data. The performance of [EMIM][EtSO₄] for the separation of cyclohexane from benzene was also compared with that of a conventional solvent. Dimethyl sulfoxide (DMSO) was selected for comparison which is one of the conventional solvents used for the separation of aromatics from aliphatic hydrocarbons [21]. Moreover, the VLE data and relative volatility were also predicted using the COSMO-Rs model. COSMO-RS is widely used for the prediction of thermodynamic properties of pure and mixture of components including ionic liquids [14, 15, 22-28].

2. Materials and methods

2.1. Chemicals

The chemicals used in the present research work are benzene (>99.5%), cyclohexane (>99%), dimethyl sulfoxide (99.9%), and 1-ethyl-3-methylimidazolium ethyl sulfate were obtained from Merck GmbH. Before

usage, benzene, and cyclohexane were dried using a molecular sieve (3A, 8-12 mesh). 1-ethyl-3-methylimidazolium ethyl sulfate was dried in a vacuum oven for 24 h. The water contents of 1-ethyl-3-methylimidazolium ethyl sulfate were determined by Karl Fischer titrator (DL39) and found to be less than 100 ppm.

2.2. Vapour-liquid equilibrium

Isothermal vapour-liquid equilibrium (VLE) data for binary (benzene + cyclohexane) and ternary systems, that is, benzene + cyclohexane + [EMIM][EtSO₄] and benzene + cyclohexane + DMSO) were obtained at a temperature of 353.15 K using headspace gas chromatography (HS-GC) (Trace GC-2000) using the method previously reported [4]. Headspace gas chromatography is an effective technique in determining vapour-liquid equilibrium volatile components in ionic liquids [2, 4, 5]. HS-GC comprises a headspace sampler containing 20 vial trays and gas chromatography. Using a Mettler Toledo balance (ML104), feed mixtures (10 mL) with predetermined compositions were prepared gravimetrically with a precision of ± 105 g. The prepared samples were added to the 20 mL headspace vials and then closed tightly with the cap and septum. For ternary systems, 50 mol% [EMIM][EtSO4] or DMSO was added to the mixture of benzene and cyclohexane. The vials were tempered in the HS-sampler oven at 353.15 K until the vapour liquid equilibrium was attained. When the equilibrium between the liquid and the vapour phase was attained; the vapour phase of the vials was then analysed using gas chromatography. The equilibration time was established experimentally and found to be 50 min. The compositions of the vapour phase were determined using a flame ionization detector (FID) and the peaks were analysed. BP20 (polyethylene glycol of 30 m × 0.25 mm × 0.25 μm) capillary column was used for the separation of benzene and cyclohexane in the gas chromatography. A total vaporization technique was applied to calibrate the HS-GC [13, 29]. Both [EMIM][EtSO₄] and DMSO have insignificant vapour pressure at 353.15 K, hence, only two peaks are shown in the vapour phase. The effect of the entrainers on the phase behaviour of the binary system of benzene (1) + cyclohexane (2) is given by the relative volatility. The relative volatility was calculated using Eq (1).

$$\alpha_{12} = \frac{\gamma_{1i}}{\gamma_2}\frac{P_1^s}{P_2^s} = \frac{y_{i1}/x_1}{y_2/x_2} \qquad (1)$$

where, subscripts 1 and 2 refer to cyclohexane and benzene; x and y are the mole fractions of the components in the liquid and vapour phases, respectively; γ is the activity coefficient and Ps is the saturated vapour pressure.

2.3. Computational details

The vapour liquid equilibrium for the ternary phase was predicted using COSMO-RS mode. COSMOthermX software with BP-TZVP C21_0110 parameterization was used for COSMO-RS calculations [23]. COSMO-RS model calculations were performed using density functional theory (DFT) utilizing the BP functional [30] with resolution of identity (RI) approximation and a triple-ξ valence polarized basis set (TZVP) [31]. The structures of benzene, cyclohexane, DMSO, and [EMIM][EtSO₄] were fully optimized, and the quantum chemical calculations with TmoleX [23]. An electroneutral approach [32] was assumed for VLE data calculations involving [EMIM][EtSO₄]. Hence, the sigma profile of [EMIM][EtSO₄] is a linear addition of the sigma profiles of the cation (1-Ethyl-3-methylimidazolium) and anion (ethyl sulfate).

3. Results and discussion

The experimental isothermal vapour-liquid equilibrium (VLE) of binary system benzene (1) and cyclohexane (2) as well as benzene (1), cyclohexane (2), and [EMIM][EtSO4] (3) and benzene (1), cyclohexane (2) and DMSO (3) ternary systems were obtained at 353.15 K and depicted in Table 1 and 2, respectively. The binary VLE data for cyclohexane and benzene versus mole fraction of benzene in the liquid phase are recalculated on [EMIM][EtSO4] and DMSO-free basis. The binary VLE data of benzene and cyclohexane was compared with the experimental literature data [33] and found in good agreement. As can be seen from Table 1 as well as Figure 1 benzene and cyclohexane form azeotrope and show close boiling points throughout the whole composition range. Benzene and cyclohexane also form azeotrope at about 0.55 volume fraction. Hence, the VLE curve is close to the x–y diagonal and the relative volatility is near to one, indicating that the separation of benzene and cyclohexane is difficult to be carried out by ordinary distillation process. On the other hand, when the entrainer (in this case, DMSO or [EMIM][EtSO4]) is added the azeotrope breaks and the relative volatility (α_{12}) becomes relatively diverge from unity (Figure 2). Moreover, the VLE of benzene (1) and cyclohexane (2) binary system and benzene (1), cyclohexane (2) and [EMIM][EtSO4] (3) and benzene (1), cyclohexane (2) and DMSO (3) ternary system were also predicted by using COSMO-RS and included in Figure 1 and 2. The VLE results obtained by the COSMO-RS model are in good agreement with the experimental results.

Table 1. Isothermal Vapor-liquid equilibrium (VLE) data and relative volatility (α_{12}) for binary system benzene (1) + cyclohexane (2) at 353.15 K.

x_1	y_1	α_{12}
0.09	0.11	1.250
0.15	0.19	1.329
0.23	0.27	1.238
0.31	0.34	1.147
0.41	0.42	1.042
0.47	0.48	1.041
0.54	0.55	1.041
0.62	0.61	0.959
0.70	0.67	0.870
0.75	0.73	0.901
0.82	0.79	0.826
0.89	0.86	0.759
0.95	0.94	0.825

Table 1. Isothermal Vapor-liquid equilibrium (VLE) data for ternary system benzene (1) + cyclohexane (2) DMSO/ [EMIM] [EtSO4] (3) at 353.15 K.

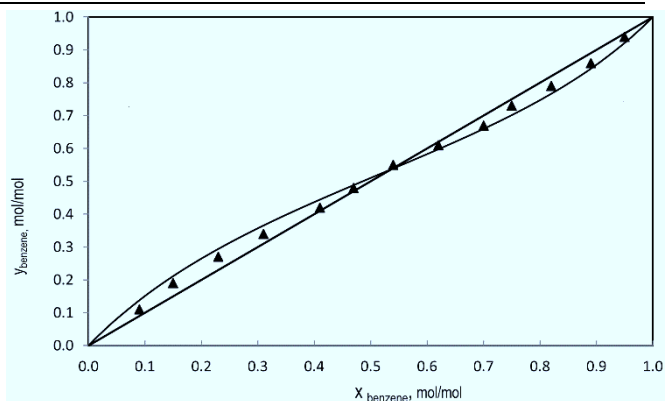| DMSO (50 %)			[EMIM] [EtSO4] (50 %)		
x_1	y_1	α_{12}	x_1	y_1	α_{12}
0.118	0.109	1.09	0.100	0.023	4.80
0.232	0.192	1.27	0.199	0.054	4.37
0.547	0.385	1.94	0.300	0.084	4.66
0.645	0.432	2.36	0.399	0.125	4.63
F0.738	0.566	2.23	0.500	0.182	4.50
0.829	0.676	2.30	0.601	0.266	4.14
			0.700	0.325	4.84
			0.801	0.519	3.73

Fig. 1. Isothermal VLE of benzene (1) and cyclohexane (2) at 353.15 K. (▲) Experimental data and (–) calculated by COSMO-RS Model.
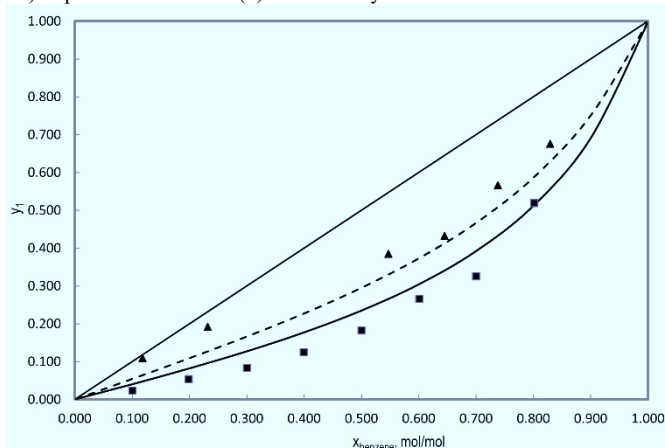

Fig. 2. VLE of benzene (1), cyclohexane (2), [EMIM] [EtSO4] ((■) experimental, (–) COSMO-RS Model) and benzene (1), cyclohexane (2), DMSO ((▲) experimental, (- -) COSMO-RS Model) at 353.15 K.
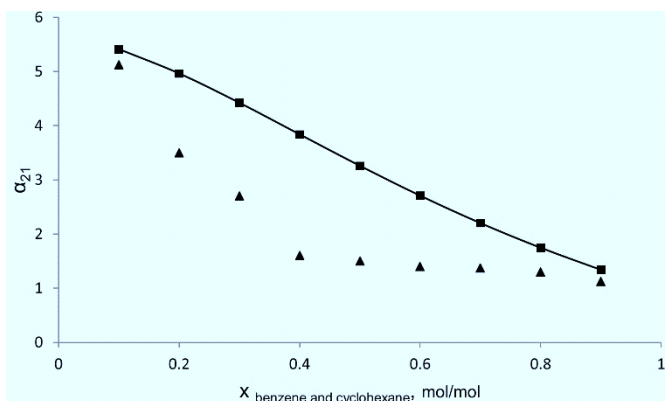

Fig. 3. The relative volatility of cyclohexane to benzene at different feed compositions and T = 353.15 K: (▲) experimental (■) COSMO-RS Model calculation.

As can be seen from Figure 2, the addition [EMIM][EtSO4] and DMSO to the binary mixture of benzene and cyclohexane enhances the relative volatilities of the two components. The addition of [EMIM][EtSO4] leads to a remarkable increase in the molar **vapour** fraction of cyclohexane in the vapour phase and eliminates the azeotrope. This implies the performance of [EMIM][EtSO4] is much better than the conventional solvent, DMSO.

Figure 3 shows the influence of feed composition on the relative volatility of cyclohexane to benzene at 353.15 K. The experimental results were obtained by varying the benzene feed composition from 0.1 to 0.9-mole faction and measuring the vapour and liquid composition at 353.15 K. An increase in benzene mole fraction in the feed reduces the relative volatility of cyclohexane to benzene. On the other hand, the calculated results by the COSMO-RS model under the same concentration and temperature as the experiments show higher relative volatility (Figure 3). The higher calculated relative volatility might be due to the liquid-liquid demixing effect which is not taken into account in the COSMO-RS model.

4. Conclusions

The isothermal VLE data for benzene (1), cyclohexane (2), and [EMIM][EtSO$_4$] (3) were measured at 353.15 K using headspace gas chromatography (HS-GC). The experimental results showed that the ionic liquid [EMIM][EtSO$_4$] can eliminate the azeotrope and increase the relative volatility of the components. The performance of [EMIM][EtSO$_4$] was also better than that of conventional solvent, DMSO. The relative volatility of the system depends on the composition of the ionic liquid in the feed mixture. The isothermal VLE and relative volatility were also predicted using the COSMO-RS model. Both experimental and COSMO-RS calculation shows the relative volatility of cyclohexane to benzene decreases as the concentration of the components increases in the feed. The results show that the current ionic liquid performs better in separating benzene cyclohexane using extractive distillation.

Acknowledgements

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