Coupling the capabilities of different complexing agents into deep eutectic solvents to enhance the separation of aromatics from aliphatics

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ABSTRACT

(Liquid + liquid) extraction of ethylbenzene from n-octane by using tetrabutylammonium bromide-based deep eutectic solvents (DESs) containing pyridine, ethylene glycol, or a mixture of both complexing agents was investigated at 25 °C and atmospheric pressure. The performance of each DES was determined from the distribution ratio and selectivity values calculated using experimental (liquid + liquid) equilibrium data of the ternary systems ethylbenzene + n-octane + DESs. The DES with only ethylene glycol had a high selectivity but a low distribution ratio, whereas the DES with only pyridine had a high distribution ratio but a low selectivity. For the other DESs, adding pyridine increased the distribution ratio, and increasing the molar ratio of ethylene glycol increased the selectivity. Generally, whenever the selectivity increased, the distribution ratio decreased, and vice versa. The nonrandom two-liquid model was used to correlate the experimental data, and the average root mean square deviation (RMSD) between correlated and experimental tie lines was 1.4%. Moreover, the Conductor-like Screening Model for Real Solvents was successfully used to predict the ternary tie lines for the studied systems with an average RMSD of 3.7%.

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1. Introduction

Aromatics are essential chemicals for the petrochemical processing industry because they are the major raw materials for the production of plastic and polymer products. However, separating aromatics with high purity from petroleum streams is challenging because of the formation of azeotropic mixtures and the close boiling range of the mixture constituents. Removing low-concentration aromatics is desirable in many industrial processes because it increases the product purity, reduces fouling, and increases the energy efficiency, which eventually lead to lower operating cost. In the naphtha steam cracking process, for example, the cracker feed contains (10 to 25)% aromatics [1]. However, even at this low concentration, aromatic compounds occupy a large portion of the furnace capacity because they are not converted to olefins during the cracking process. This imposes an unnecessary burden on the separation section and causes inefficient conversion of thermal energy because of the fouling of the radiation sections and transfer line exchangers.

Commercial separation methods used for removing aromatics include the conventional (liquid + liquid) extraction process that is applicable to a mixture with (20 to 65) wt% aromatics, extractive distillation for aromatic concentrations (65 to 90) wt%, and azeotropic distillation for even higher aromatic content (i.e., greater than 90 wt%). To date, there has been no feasible commercialized separation process for aromatic concentrations less than 20 wt% [2]. However, on a research scale, it has been reported that (liquid + liquid) separation processes that involve using an ionic liquid (IL) or a deep eutectic solvent (DES) can extract aromatics from aliphatics even at aromatic concentrations lower than 10 wt% [3,4].

ILs have attracted increasing interest in the last decade because of their unique properties such as a negligible vapor pressure, high thermal and chemical stability, and a wide electrochemical window. Many applications of liquid separation processes, such as the separation of azeotropic mixtures, separation of aliphatic/aromatic mixtures [5], desulfurization [6], and denitrification [7], involve using ILs as the extraction solvent. The main advantage of using ILs is that they are nonvolatile because of their negligible vapor pressure, compared to conventional extraction solvents such as sulfolane and glycols. In addition, using the appropriate ILs helps achieve a high selectivity and distribution ratio in the extraction process. However, the high density and viscosity of ILs makes it challenging to commercialize their use as extraction solvents, apart from their being uneconomical for use on a large scale because of their complicated synthesis process. In addition, many ILs have

also been proven to be toxic when released into the environment [8].

Another class of solvents has also been attracting increasing interest in recent years. DESs may be considered as an alternative to ILs in some cases. A typical DES comprises a combination of quaternary ammonium or phosphonium salt with a hydrogen bond donor (HBD) or a complexing agent (CA). The mixture of these two constituents at a certain molar ratio will produce a liquid mixture that has a melting point lower than that of the individual constituents (thus, the term eutectic). DESs have properties similar to those of ILs, particularly a negligible vapor pressure, which makes them nonvolatile. However, DESs have the advantage of being cheaper alternatives to most of the ILs available because of the abundance of raw materials and a simpler synthesis process. DESs can be synthesized with high purity through simple mixing. Furthermore, DESs are expected to have lower toxicity than ILs because of the biocompatibility of their constituents, particularly those involving choline chloride and urea. However, the subject of the toxicity of DESs requires further investigation before DESs can be declared nontoxic [9].

Applying DESs in separating aromatics from aliphatics was reported by Kareem et al. who used phosphonium-based DESs for separating toluene from n-heptane [10] and for separating benzene from hexane [11]. Later, the same group reported using a different phosphonium-based DES for separating toluene from n-heptane [4]. Kareem et al. reported that the performance of the DESs was comparable with or even superior to conventional organic solvents and ILs. Various ammonium-based DESs were used by Li et al. [12] for extractive desulphurization, and they reported that the applied DESs demonstrated extremely high efficiency in removing benzothiophene from a model oil. Mulyono et al. [13] recently reported using ammonium-based DESs to separate benzene, toluene, ethylbenzene, and xylene (BTEX) compounds from heptane. To date, these are the only reports on the use of DESs for extracting aromatics from aliphatics.

This paper proposes a novel approach to synthesizing DESs for use in separating aromatics from aliphatics through a (liquid + liquid) extraction process. The DESs were combinations of a salt, HBD, and CA. An HBD demonstrating a high selectivity toward aromatics and a CA exhibiting a high distribution ratio were used. In particular, tetrabutylammonium bromide was used as the salt, ethylene glycol was used as the HBD, and pyridine was used as the CA. Ethylene glycol has been reported to have a high selectivity for extracting aromatics at low temperatures [14]; however, it has a low distribution ratio [15]. Garcia et al. [16] reported that using pyridinium cations in ILs yielded a high distribution ratio for aromatic extraction; therefore, pyridine was used as a CA. Accordingly, we expected to identify a DES that has both higher distribution ratio and selectivity. The importance of this study lies not only in the contribution of a new set of (liquid + liquid) extraction (LLE) data but also in the investigation of the effect of mixing an HBD and a CA in synthesizing DESs on the separation of aromatics from aliphatics. In this study, ethylbenzene and n-octane were used as the model aromatic and aliphatic compounds, respectively. The nonrandom two-liquid (NRTL) model was used to correlate the experimental LLE data, and the Conductor-like Screening Model for Real Solvents (COSMO-RS) was used to predict the LLE data for comparison with the reported experimental data.

Mixing conventional solvents for extracting aromatics is common practice in the industry [17] but mixing ILs for this purpose was a rather new concept suggested by García et al. [18] in 2012. Mixing different HBDs and/or CAs could also enhance specific properties. Dai et al. [16] investigated the formation of natural DESs (NADESs) of mixtures of several abundant primary metabolites from all kinds of organisms. Analysis showed that the formation of DESs is mainly because of hydrogen bonds between the molecules. The authors also reported that the viscosity of the NADESs decreased significantly with the addition of small amounts of water, whereas the characteristics of the NADESs were preserved. They concluded that the nontoxic and environment-friendly nature of NADESs makes them suitable for many applications. In 2014, Liu et al. [19] reported synthesizing a series of novel room-temperature ternary deep eutectic solvents (TDESs) based on imidazolium ILs, zinc halides, and amides. They indicated that the low freezing points, low viscosity, and high conductivity of TDESs make them suitable for promoting polar reactions. Moreover, because of the presence of a Lewis acidic center in TDESs containing zinc halides, the TDESs can be used as both catalyst and solvent in various catalytic reactions. However, based on our research, this is the first time that DESs synthesized by mixing different HBDs and CAs have been suggested to be useful as solvents for the (liquid + liquid) extraction of aromatics.

2. Methodology

2.1. Chemicals

Ethylbenzene and n-octane were purchased from Winlab (England), ethylene glycol and pyridines were purchased from Panreac (Spain), and tetrabutylammonium bromide was purchased from Acros Organics (Belgium). All chemicals were of high purity (>99 wt%) and were used without any further purification. DESs were prepared by mixing salts with ethylene glycol (used as an HBD), pyridine (used as a CA), or both these chemicals. Table 1 presents the synthesized DESs with their abbreviations.

Each DES mixture was heated up to 100 °C and then mixed in an incubator-shaker at a rotational speed of 200 rpm until the formation of a clear liquid was observed [20]. Mixtures of ethylbenzene and n-octane with nine concentrations (5, 10, 15, 20, 30, 40, 50, 60, and 80 wt% of ethylbenzene) were prepared by mixing weighed amounts of pure ethylbenzene and pure n-octane using analytical balance (±0.0001 g). The feed sample was then mixed with the DESs, with a feed to solvent mass ratio of 1:1. Each set of experiments was conducted at 25 °C. The vials were then placed in an incubator-shaker for 6 h with temperature (±0.1 °C) and speed control. This was followed by a settling time of about 12 h to guarantee that the equilibrium state was completely attained. Samples were then taken from the top and bottom layers of the mixture and analyzed using high performance liquid chromatograph (HPLC).

TABLE 1

Compositions and abbreviations of the DESs used in this study.

Component			Molar ratio	Abbreviation
Salt	Component 2	Component 3		
Tetrabutylammonium bromide	Ethylene glycol		1:8	DES1
	Pyridine		1:4	DES2
	Pyridine	Ethylene glycol	1:4:4	DES3
	Pyridine	Ethylene glycol	1:4:6	DES4
	Pyridine	Ethylene glycol	1:6:4	DES5