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Liquid-liquid separation of azeotropic mixtures of ethanol/alkanes using deep eutectic solvents: COSMO-RS prediction and experimental validation

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ABSTRACT

Separation of azeotropic mixtures is a topic of great industrial interest. In this work, liquid-liquid extraction using deep eutectic solvents (DESs) is explored to separate binary azeotropic mixtures of ethanol and *n*-hexane, *n*-heptane or *n*-octane. Ten DESs were screened using the COSMO-RS approach by predicting the activity coefficient at infinite dilution, γ^{∞} of ethanol and *n*-alkanes in each DES. Then, three DESs were selected for experimental validation where Tetrabutylammonium bromide/Levulinic acid (TBAB/LA) with a molar ratio (1:2) gave the best extractive performance for all systems. Ternary liquid-liquid extraction experiments were conducted at room temperature with this DES. It was found that the tie-lines of all systems have positive slopes, indicating that a small amount of solvent is required to extract ethanol. Moreover, the distribution ratio and selectivity values are all greater than unity and the DES was not detected in the raffinate phase which indicate minimal cross-contamination between extract and raffinate phases. Finally, COSMO-RS predictions of the ternary tie-lines were in excellent agreement with experimental data, with an average RMSD value of 1.65%. The experimental data were also successfully correlated with NRTL model with an average RMSD value of 1.50%.

1. Introduction

The demand for alternative fuels and renewable energy greatly increased during the last few decades due to environmental concerns accompanied by the increase in standards of living and the decrease of fossil fuel reserve. Ethanol is considered as a renewable bio-based alternative fuel. Alkanols and alkanes can be used in the industry to produce oxygenated additives for gasoline, and in the last few decades, alkanols have commonly been employed to replace lead in petrol [1]. However, in many areas of industry, it is necessary to separate the azeotropic mixture of ethanol and alkane into pure components so that they can be reused. The separation of such mixtures is impossible to achieve through ordinary distillation processes due to their close boiling points and azeotrope formation [2,3].

As such, several potential techniques such as pervaporation, azeotropic distillation, liquid-liquid extraction (LLE) and extractive distillation have been employed to separate one of the components selectively from the azeotropic mixture [4]. Most of these processes require a significant amount of energy and, involve volatile compounds, high temperature or high pressure to obtain a one fluid phase system. The mixtures of alcohols/alkanes exist in various petrochemical processes due to the production of oxygen additives which are added to gasoline to reduce lead in fuels [5]. Until now, the most common technique used for the separation of such azeotropic compounds is extractive distillation that requires a large amount of energy, high pressure and the use of volatile organic solvents [6]. However, the LLE process, which is based on the immiscibility of two liquid phases is used as an environmentally friendly substitute to the azeotropic distillation since it does not require a high amount of energy or expensive equipment and can be carried out under ambient conditions [7]. In LLE processes, a third component (extraction agent) is introduced into the azeotropic mixture to perform the separation process. The extraction

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solvent preferentially dissolves one of the elements in the azeotropic mixture and separates it from the initial liquid state. The typical industrial solvents used for the extraction are organic solvents such as, tetraethylene glycol, propylene carbonate and sulfolane [8]. However, these solvents are toxic, volatile and flammable, and require further treatments for purification and energy recovery. To this end, the selection of a suitable solvent is essential to ensure a commercial operation. LLE data can be very useful at finding the suitable solvent to achieve the separation goal. Moreover, the information related to the design of the extraction process can also be obtained from LLE data.

Ionic liquids (ILs) are molten salts that have been viewed as an appealing replacement for conventional industrial solvents, due to their notable properties such as non-flammability, an outstanding dissolving strength, and an extremely low vapor pressure, which, in turn, enhances their recovery and reusability in separation processes [9]. Furthermore, ILs have already been recognized for their high separation efficiency in breaking azeotropic mixtures such as ethanol + alkane. Seoane et al. [10] calculated the LLE data of the ternary system (ILs + ethanol + heptane) to evaluate the efficiency of four different alkyl-imidazolium ILs, all with the same anion, bis(trifluoromethylsulfonyl)imide [NTf_2]. They reported that an increase in the alkyl chain length of the cation leads to a decrease of the selectivity (S) values. They achieved best results with 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMim][NTf_2] in terms of S. Corderi et al. [11] and [2] investigated the ternary LLE system of different ILs with ethanol and hexane. The ILs 1-butyl-3-methylpyridinium trifluoromethanesulfonate, [BMpy][TfO] and I-hexyl-3-methylimidazolium dicyanamide, [HMim][$N(CN)_2$] were found to be the promising solvents in separation efficiency compared with the other ILs used in their work. Aranda and Gonzalez [12] studied the cation effect of two ammonium imide based ILs for the extraction of alcohols from alcohol-alkane azeotropic mixtures. In view of the results obtained, the best S values were achieved when heptane was used as the diluent for the extraction of ethanol. Butyltrimethylammoniumbis(trifluoromethylsulfonyl), [BTMA][NTf_2] was found to be more efficient and selective in those systems where methanol was used in ethanol extraction. However, regardless of the clear advantages of ILs, they are more difficult and more costly to synthesize than organic solvents used in the LLE for large scale applications. Also, ILs are not universally green [13–16], and so searching for a cheap and environment-friendly extracting solvent for the extraction of ethanol from its azeotropic mixtures is essential.

Over the last few years, ILs analogs named deep eutectic solvents (DESs) have emerged as promising substitutes to conventional solvents and ILs [17,18]. DESs generally consist of two or three components which combine via hydrogen bond interactions to form eutectic mixtures characterized by a melting point lower than that of each individual component [19,20]. DESs have several advantages over ILs because they are green solvents [19,21,22] with most of them being biocompatible, biodegradable, and non-toxic, and their synthesis is very simple and cheap. ILs require costly starting materials and several purification steps for the synthesis, while the purity of a DES is only reliant on the purity of the individual components (starting materials) [17,23]. Moreover, DESs also exhibit tunable properties like ILs. The physiochemical properties of DESs can be modified by changing the nature of the hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) and the molar ratio between them [24,25].

Rodriguez et al. [4] investigated two different low transition temperature mixtures, including lactic acid: choline chloride (ChCl) (2:1) and glycolic acid (GA): ChCl (1:1) for the extraction of ethanol from two different azeotropic mixtures, hexane + ethanol and heptane + ethanol. They reported that the solvent S and solute distribution ratio (D) values of the two DESs used were higher compared with the previous used ILs. Oliveira et al. [1] investigated three ChCl based DESs, as a solvent for the extraction of ethanol from the azeotropic mixture (ethanol + heptane) at 25 °C. They achieved good efficiency and a reduction in energy consumption of the overall process by using the DESs. DESs were also recovered by evaporation of heptane and ethanol after the extractions.

Besides the application of DESs for separation of ethanol from its azeotropic mixtures, DESs have also been reportedly used for a number of LLE processes. Kareem et al. used the DES methyltriphenylphosphonium bromide (MTPPB) with ethylene glycol (EG) at salt:HBD molar ratios of 1:4, 1:6 and 1:8 to separate benzene from *n*-hexane [26]. The DESs used provided superior result compared to the widely used conventional solvents for aromatic/aliphatic mixture separation, sulfolane and N-formylmorpholine. The same group also reported the use of DESs tetrabutylphosphonium bromide (TBPB) with either EG or sulfolane at various salt:HBD/complexing agent (CA) molar ratios to extract toluene from *n*-heptane [27] and the use of a combination of ethyltriphenylphosphonium iodide with either EG or sulfolane at various molar ratios to separate toluene from *n*-heptane [28].

Later on, our group reported the use of DES tetrabutylammonium bromide (TBAB) with sulfolane at molar ratio 1:4 to separate BTEX aromatic compounds (benzene, toluene, ethylbenzene, and *m*-xylene) from *n*-octane [29] and also a novel approach in the synthesis of DESs based on the combination of salt with both HBD and CA to separate ethylbenzene from *n*-octane; where the salt TBAB was combined with either EG (HBD), or pyridine (CA), or both at various molar ratios [30]. These reports also include the use of Conductor-like Screening Model for Real Solvents (COSMO-RS) for the prediction of ternary LLE tie line composition for systems containing DESs for the first time, using the electroneutral approach in the description of DESs in the COSMO-RS calculations.

Separately, sixteen different DESs were experimentally screened to extract benzothiophene from *n*-octane for use in desulfurization of liquid fuels by Li et al. [31] where the DES ChCl with propionate at 1:2 ratio, tetrabutylammonium chloride (TBAC) and propionate at 1:2 ratio and TBAC with polyethylene glycol at 1:2 ratio were reported to have the highest extraction efficiency. Our group was also the first to report the use of COSMO-RS model to evaluate the performance of 94 DESs in removing aromatic nitrogen compounds from simulated diesel fuel based on the prediction of activity coefficient at infinite dilution of the nitrogen compounds in the DESs and in simulated diesel to estimate the S and capacity at infinite dilution [32]. It was found that quaternary ammonium- and phosphonium-based DESs are potential solvents for extractive denitrogenation and that the values of estimated S and capacity at infinite dilution depends on factors of i) nitrogen heterocyclic structure, ii) cation choice, iii) anion choice, iv) HBD choice, and v) salt:HBD molar ratio. It was based on this screening result that our group reported the experimental work using the DESs tetrabutylammonium bromide with ethylene glycol at 1:2 ratio and tetrabutylphosphonium bromide with ethylene glycol at 1:2 ratio for the removal of aromatic nitrogen compounds from model diesel compound. The liquid-liquid extraction data reported favorable values of both distribution ratio and selectivity towards the aromatic nitrogen compounds, especially for the non-basic nitrogen compounds. Prediction of ternary tie-lines composition using the COSMO-RS model was also reported where the predicted values agree well with experimentally obtained composition [33].

Table 1 displays the values of S and D for different ILs, DESs and organic solvents that have been reported for the extraction of ethanol at 298.15 K and under atmospheric pressure [1,2,7,10–12,34–37]. Comprehending the lack of experimental LLE data on the use of DESs to extract ethanol from its azeotropic