Extractive denitrogenation of diesel fuel using ammonium- and phosphonium-based deep eutectic solvents

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A B S T R A C T

Recently, we published the results of screening the performance of 94 deep eutectic solvents (DESs) by COSMO-RS for potential use in the extractive denitrogenation of diesel. In this work and based on our previous predictions, tetrabutylammonium bromide + ethylene glycol and tetrabutylphosphonium bromide + ethylene glycol DESs at molar ratio 1:2 were explored experimentally for the removal of pyrrole, pyridine, indoline and quinoline from a model diesel compound, *n*-hexadecane. Ternary (liquid + liquid) equilibrium experiments were conducted at room temperature with nitrogen concentrations in the feed ranging from (5 to 50) wt%. ^{1}H NMR spectroscopy was used for compositional analysis of the extract and raffinate phases. No amount of the solvent in the raffinate phases was detected; indicating minimal cross contamination. Also, it was found that all systems exhibit Type I phase behavior with positive slopes which indicate that small amount of solvents is required to remove the nitrogen compounds. Moreover, the distribution ratio and selectivity values are all greater than unity with higher values reported for non-basic nitrogen compounds. COSMO-RS predictions of the ternary tie lines were in good agreement with experimental data with average RMSD value of 2.51%. The experimental data were also well correlated with NRTL model with average RMSD value of 0.60%.

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1. Introduction

In recent years, a new generation of solvents namely deep eutectic solvents (DES) has gained increasing attention as a low-cost alternative to ionic liquids (ILs). By definition, a DES is a salt combined with a hydrogen bond donor (HBD) or a complexing agent (CA). The salt normally used to create a DES consists of a large quaternary ammonium or phosphonium cation, combined with a halide anion. When the salt is combined with a HBD or a CA at a certain ratio, the HBD or CA will form a complex with the halide anion, thus lowering the freezing point of the produced eutectic mixture far from its individual constituent [1]. DESs are characterized by a very large depression of their freezing point and are liquid at temperatures below 150 °C. The first DES was described by Abbot *et al.* for a mixture of choline chloride (ChCl) and urea with a molar ratio of 1:2 [2]. The physico-chemical properties of DESs are very similar to those of common ILs including their density, viscosity, surface tension, conductivity and chemical inertness. Like ILs, DESs are chemically tailorable solvents because they can be designed by appropriate combination of various salts

with different HBDs and at different ratios. Nevertheless, DESs are considered as potential candidates to replace ILs due to the following advantages: (1) simplicity of synthesis, (2) the low cost of their raw materials and (3) better bio-compatibility [3,4]. However, although DESs are prevalently described as IL analogues or an alternative to ILs for some applications, they cannot be considered as ILs due to the following reasons: (i) DESs are not composed entirely by ionic species and (ii) DESs can also be obtained from non-ionic species.

Till date, applications of DESs for (liquid + liquid) separation have not been widely reported in the literature like it has been for ILs. The applications of DESs for this purpose can be summarized into separation of aromatic/aliphatic mixtures, azeotropic mixture and desulfurization of fuels as shown in table 1. In this table, the DESs were annotated to indicate the salt/HBD with salt:HBD molar ratio in parentheses. Table 2 shows the full name and abbreviations of each salt and HBD used in table 1. Kareem *et al.* were the first group to report the use of DES for (liquid + liquid) separations particularly in the petrochemical processing field, where they used the DES methyltriphenylphosphonium bromide (MTPPBr) with ethylene glycol (EG) at salt:HBD molar ratios of 1:4, 1:6 and 1:8 to separate benzene from *n*-hexane [5]. The DESs used provided superior result compared to sulfolane and

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TABLE 1
DESs used in (liquid + liquid) extraction process reported in the literature.

Application	Feed mixture	DES	References
Aromatic/aliphatic separation	Benzene + *n*-hexane	MTPPBr:EG (1:4), (1:6), (1:8)	[5]
	Toluene + *n*-heptane	TBPB:EG (1:2), (1:4), (1:6), (1:8)	[6]
		TBPB:Sul (1:2), (1:4), (1:6), (1:8)	
	Toluene + *n*-heptane	ETPPI:EG (1:6), (1:8), (1:10)	[7]
		ETPPI:Sul (1:4), (1:6), (1:8)	
	Benzene + *n*-octane		
	Toluene + *n*-octane		
	Ethylbenzene + *n*-octane	TBAB:Sul (1:4)	[8]
	m-Xylene + *n*-octane		
	Ethylbenzene + *n*-octane	TBAB/EG (1:8), TBAB/Py (1:4)	[9]
		TBAB/Py/EG (1:4:4), (1:4:6), (1:6:4)	
Azeotropic mixture	Ethanol + *n*-heptane	ChCl:Gly (1:2), ChCl:LA (1:2), ChCl:EG (1:2)	[10]
Desulfurization	Benzothiophene + *n*-octane	TBAC/Pr (1:2), TBAC/PEG (1:2)	
		ChCl/Pr (1:2), ChCl/MA (1:2),	
		ChCl/Gly (1:2), ChCl/EG (1:2)	
		TMAC/EG (1:2), TMAC/PA (1:2)	[11]
		TBAC/MA (1:2), TBAC/Gly (1:2)	
		TBAC/EG (1:2), TBAC/PA (1:2)	
		TBAC/CA (1:2), TBAC/AA (1:2)	

TABLE 2
Full names and abbreviation of the salts and HBDs mentioned in table 1.

Salt		HBD/CA	
MTPPBr	Methyltriphenylphosphonium bromide	EG	Ethylene glycol
TBPB	Tetrabutylphosphonium bromide	Sul	Sulfolane
ETPPI	Ethyltriphenylphosphonium iodide	Py	Pyridine
TBAB	Tetrabutylammonium bromide	Gly	Glycerol
ChCl	Choline chloride	LA	Levulinic acid
TBAC	Tetrabutylammonium chloride	Pr	Propionate
TMAC	Tetramethylammonium chloride	PEG	Polyethylene glycol
		MA	Malonic acid
		PA	Phenylacetic acid
		CA	Caproic acid
		AA	Acetic acid

N-formylmorpholine which are the most widely used conventional solvent for aromatic/aliphatic separation. Furthermore, they found that the DESs used have lower viscosity than sulfolane and that there is no presence of the DES constituents in the raffinate layer. Later on, the same group reported the use of DESs consisting of tetrabutylphosphonium bromide (TBPB) with either EG (as HBD) or sulfolane (as CA) at various salt:HBD/CA molar ratios to extract toluene from *n*-heptane [6]. It should be noted here that sulfolane is not an HBD thus the term complexing agent is used instead of HBD. The separation of toluene from *n*-heptane was also performed again by the same group using a different DES, this time a combination of ethyltriphenylphosphonium iodide (ETPPI) with either EG or sulfolane at various molar ratios [7]. In both reports, the DES mixtures were able to trap EG and sulfolane in the extract layer instead of when EG and sulfolane are used individually, they will be present in the raffinate layer which leads to extra cost and energy consumption for solvent recovery. With the use of DES, solvent recovery is simplified to only the extract layer. Later, the DES tetrabutylammonium bromide (TBAB) with sulfolane at molar ratio 1:4 and the DES was used to separate BTEX aromatic compounds (benzene, toluene, ethylbenzene, and *m*-xylene) from *n*-octane [8]. More recently, a novel approach in the synthesis of DESs based on the combination of salt with both HBD and CA was used 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 [9]. The DESs formed reported moderate values of selectivity and distribution ratio compared to conventional organic

solvents and ILs used for separating similar feed mixtures. However, the advantage of using DESs over conventional solvents remains in the fact that there is no presence of DES constituents in the raffinate phase thus less cost and lower energy consumption for solvent recovery.

DESs were also used for the separation of azeotropic mixture of ethanol and *n*-heptane as reported by Oliveira *et al.* where the DESs were made of ChCl mixed with either glycerol (Gly), levulinic acid (LA), or EG at salt:HBD molar ratio of 1:2 [10]. Oliveira *et al.* reported very high values of distribution ratios and selectivities for all of the DES towards ethanol due to the formation of strong hydrogen bonding between the HBD and ethanol. Among the DESs, ChCl/Gly (1:2) and ChCl/EG (1:2) have lower distribution ratio but high selectivity, compared with ChCl/LA having high distribution ratio and low selectivity. The difference in distribution ratio and selectivity values was attributed to the different structural features of HBDs present in each DES.

Li *et al.* experimentally screened sixteen different DESs to extract benzothiophene from *n*-octane for use in desulfurization of liquid fuels [11]. Among the screened DESs, they reported that the DES ChCl/Pr (1:2), TBAC/Pr (1:2) and TBAC/PEG (1:2) (see table 2 for abbreviations) reported the highest extraction efficiency. From the extraction experiments, it was found that extraction of benzothiophene from *n*-octane can be conducted up to five times without significantly compromising the extraction efficiency. The DESs became saturated after six times of repeated use and lost its extraction capacity. The used DESs can be recycled by simply washing with organic solvent such as diethyl ether and when reused for extraction, the efficiency is comparable to fresh DESs.

Recognizing the importance of denitrogenation of fuel to enhance the efficiency of deep desulfurization process and the potential application of DESs for this purpose, Hizaddin *et al.* reported an approach using the Conductor-like Screening Model for Real Solvents (COSMO-RS) model to evaluate the performance of 94 DESs in removing aromatic nitrogen compounds from simulated diesel fuel based on prediction of activity coefficient at infinite dilution of the nitrogen compounds in the DESs and in simulated diesel to estimate the selectivity and capacity at infinite dilution [12]. They reported that quaternary ammonium- and phosphonium-based DESs are potential solvents for extractive denitrogenation and that the values of estimated selectivity 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. However, up to now,