Separation of aromatic and aliphatic hydrocarbons using deep eutectic solvents: A critical review

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A R T I C L E   I N F O

A B S T R A C T

The reported experimental data for the separation of aromatic from aliphatic compounds using green solvents is growing exponentially. This paper surveys the existing data and presents a critical review that helps clarifying the major findings, identifies shortcomings and provides some recommendations. The comparison between deep eutectic solvents (DESs) and both ionic liquids (ILs) and classical organic solvents for this challenging separation is also presented based on experimental selectivity and distribution ratio data. This comparison confirms the capability of DESs to effectively extract aromatic compounds and shows that DESs can compete with ILs and even outclass them in some cases. Moreover, our comprehensive literature survey has revealed that in many cases the use of DESs yields to a minimum cross-contamination between the two phases. This will undeniably facilitate the separation procedure and thus reduce the cost of the separation process. On the other hand, the performance of COSMO-RS to predict ternary liquid-liquid equilibrium diagrams for systems including DESs is also evaluated in this work for all available data. COSMO-RS was able to reproduce the experimental tie-lines with a good accuracy in many cases. Therefore, it represents a cost-effective and time-saving screening tool to evaluate the extraction performance of the unlimited number of possible salt/complexing agents' combinations.

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1. Introduction

The separation and purification of aromatics is a challenging task for chemical engineers due to the sharp differences in the boiling points of the various hydrocarbons and the various combinations of azeotropes that may occur [1]. Commercially three techniques for separation are classified according to solution concentration: (i) at low aromatic concentration within 20—65 wt%, the liquid—liquid extraction is mostly used, (ii) for medium aromatic contents ranging from 65 to 90 wt%, the extractive distillation is typically used and (iii) for very high aromatic substances (>90 wt%) azeotropic distillation is applied. But until now, no practical process exist when the separation aromatic content in the feed mixture is below 20 wt% [2]. However, the liquid extraction process is considered to be the best favorable process for aromatic content of less than 20%. The key advantages of using this process are the low energy consumption and that no change in both physical properties and chemical structure are observed.

Nevertheless, a crucial step in such process is how to select the proper solvent. A perfect solvent should deliver high solute selectivity. Cost-effective solvent should possess great distribution ratio and minimum ratio of feed to solvent. In addition, the physical and thermodynamic characteristics of the solvent such as viscosity, thermal stability, density and surface tension should help its industrial application. Furthermore, the solvent should be environment friendly, easy to regenerate and abundantly available at low cost. Normally organic solvents such as sulfolane, furfuryl alcohol, ethylene glycols, N-methylpyrrolidone (NMP), and N-formylmorpholine (NFM) are used. However, due the high toxicity, flammability, volatile nature and high cost of regeneration of these solvents, researchers are trying to find out alternative solvents with same or better properties.
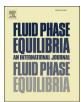
Around one decade ago, for the first time, a newly emerging

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solvents called deep eutectic solvents (DESs) was introduced [3]. DESs, which are much cheaper than ionic liquids (ILs) and easy to prepare, were found to be a promising replacement to conventional carbon-based solvents for the separation of aromatic-aliphatic mixtures. A DES is prepared by mixing various molar ratio of two or more ingredients comprising hydrogen bond donors (HBDs) and hydrogen bond acceptors (HBAs), which results in a eutectic with much lower melting point than that of each individual ingredient [4]. A typical DES is made by mixing urea with choline chloride, as adding 1 mol of choline chloride to 2 mol of urea produces a eutectic mixture [5].

Many studies have been reported in the literature about utilizing DESs to extract aromatic from aromatic-aliphatic mixture. Sander et al. studied 6 systems of three compounds with choline chloride:urea (ChCl:Ur) and choline chloride:glycerol (ChCl:Gly) at molar ratio of 1:2 [6]. The results proposed that (ChCl:Gly) has better potential as an extracting solvent for the separation of pyridine from its mixture with n-hexane. Recently our group has reported four DESs based on tetrabutylammonium bromide (TBABr) or methyltriphenylphosphonium bromide (MTPPBr) (as typical salts) with ethylene glycol, triethylene glycol or sulfolane (as the HBDs) for the separation of thiophene from a model diesel of n-heptane. The study showed that the sulfolane-based DES (TBABr:-Sulf) (1:7) resulted the best extraction efficiency, 35%, outperforming the other DESs studied. Furthermore, the extraction efficiency could be improved up to 98% after five extraction cycles [7]. The feasibility of two different deep eutectic solvents (DESs) as novel extracting solvents for the separation of benzene from hexane was tested by Rodriguez et al. [1]. They tested two different types of DES i.e. tetrahexylammonium bromide (THABr) with ethylene glycol and glycerol at molar ratio of 1:2. The ternary liquid-liquid equilibrium (LLE) data showed that DESs are the promising extracting agents for the industrial purification of naphtha streams containing diluted aromatic. Kareem et al. studied the extraction of toluene from toluene-heptane mixture using ethyltriphenylphosphonium based DESs [8]. Six DESs were synthesized by mixing ethyltriphenylphosphonium iodide (ETPPI) with either ethylene glycol or sulfolane. The LLE data showed that the DES ETPPI:Sulf (1:4) gave enhanced purification competency at 30 °C. The selectivities observed in the study were higher than those reported for sulfolane in commercial applications. Moreover, Mulyono et al. reported the feasibility of using ammonium-based DESs for the separation of BTEX (benzene, toluene, ethylbenzene and xylenes) from n-octane using DESs [9]. Similarly, Oliveira and co-workers observed remarkably high selectivities and distribution coefficients for chlorine chloride based DESs with three different types of HBD i.e, ethylene glycol, levulinic acid and glycerol which proves them as promising alternatives to ionic liquids ILs in the extraction of ethanol from ethanol-n-heptane mixtures [10]. The same group tested DES based on three different salts, namely choline chloride, benzylcholine chloride and tetrabutylammonium chloride with levulinic acid as HBD (Salt:HBD, 1:2) for the separation of toluene from n-heptane at 298.15 K. Their results showed that the introduction of a more hydrophobic HBA in the DES promotes the improvement of the distribution coefficient, while manipulating the aromaticity of the DES leads to higher selectivity [11]. Some of the equilibrium data from the literature are listed in Table 1.

Per Table 1, the extraction efficiency is evaluated through selectivity and distribution ratio. These measurements are obtained from the measured experimental molar compositions of each component in the extract (DES-rich) and raffinate (aliphatic-rich) phases. For a given DES-aromatic-aliphatic ternary system, we can classify DES, aromatic and aliphatic compounds as the solvent, solute and carrier, respectively. The distribution ratio of solute describes its distribution behavior between the extract and raffinate phase at equilibrium. A similar definition applies to the distribution ratio of carrier. In this particular separation, the distribution ratio of solute is more important because aromatic compounds represent the targeted component to be extracted. Conversely, the selectivity evaluates the ability of solvent to extract aromatic compounds only, rather than extracting aromatic and aliphatic compounds altogether. Equations (1) and (2) reflect the above definitions and are used to calculate the distribution ratio of aromatic compound (D_{Aro}) and the selectivity (S) of each DES.

$$D_{Aro} = \frac{x^1_{Aro}}{x^2_{Aro}} \tag{1}$$

$$S = \frac{x^1_{Aro}}{x^2_{Aro}} \Big/ \frac{x^1_{Ali}}{x^2_{Ali}} \tag{2}$$

where x_{Aro} is the concentration of aromatic compound and x_{Ali} is the concentration of aliphatic compound. The superscripts 1 and 2 represent the extract and raffinate phase, respectively.

2. Comparison between DESs and organic solvents

The results of the DESs and organic solvents used in the extractive separation of aromatic and aliphatic compounds are summarized in Table 2. The information from Table 2 was then extracted into Fig. 1 and Fig. 2 to obtain a clear comparison between DESs and organic solvents used in a specific system. As can be seen in Fig. 1, the highest selectivity for benzene/hexane system was observed with TEACl:EG (1:2) DES, followed by MTPPBr:EG (1:4) and TMACl:Gly (1:2) [12]. However, these selectivity values were traded off in Fig. 2, where the values of distribution ratio were relatively lower than sulfolane, NFM and mixture of both [13]. Similarly, although NFM exhibited the highest value of distribution ratio, it has the lowest selectivity compared to sulfolane and all DESs. In general, this trend is also observable in other aromatic-aliphatic system, where the distribution ratio for all types of solvents (both DESs and organic solvents) were less than unity, but the selectivity of DESs were more superior than the organic solvents. Therefore, it can be concluded that the use of DES will enhance the selectivity, but reduce the distribution ratio. This means the application of DES in the separation of aromatic and aliphatic will give the lower extraction stages than organic solvent, but with higher solvent-to-feed ratio. This finding would make the DESs more favorable because of their negligible vapor pressure and being less hazardous to the environment.

3. Comparison between DESs and ILs

Table 3 shows the summary of ILs that were used in the previous works for the separation of aromatic-aliphatic systems. In order to compare ILs' and DESs' extraction capabilities, we have considered only the systems where both solvents were applied for the same operating conditions. Therefore, in this work, only three systems were examined, namely, benzene-hexane, toluene-heptane and thiophane-n-heptane. The reported experimental results for these combinations are available from different sources at various initial mole fractions. For useful comparison, we limited the analysis on the results obtained when the initial composition of the solute in the mixture is less or equal 20%. This choice represents the most