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Experimental determination of the LLE data of systems consisting of \{hexane + benzene + deep eutectic solvent\} and prediction using the Conductor-like Screening Model for Real Solvents

Nerea R. Rodríguez\textsuperscript{a}, Thomas Gerlach\textsuperscript{b}, Daniëlle Scheepers\textsuperscript{a}, Maaike C. Kroon\textsuperscript{c}, Irina Smirnova\textsuperscript{b}

\textsuperscript{a} *Eindhoven University of Technology. Department of Chemical Engineering and Chemistry. Separation Technology Group. STO1.22, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

\textsuperscript{b} Hamburg University of Technology, Institute of Thermal Separation Processes, Eissendorfer Strasse 38, 21073 Hamburg, Germany.

\textsuperscript{c} The Petroleum Institute, Chemical Engineering Department, P.O. Box 2533, Abu Dhabi, United Arab Emirates.

*Corresponding Author: n.rodriguez@tue.nl; Phone: +31 40-247 8234; Fax: +31-40-2463966

**Keywords:** Aliphatic; Aromatic; Deep eutectic Solvents; COSMO-RS; Liquid-liquid extraction
Abstract

Recently, deep eutectic solvents (DESs) have proven to be excellent extracting agents in the separation of aromatic components from their mixtures with aliphatic compounds. The tunable properties of the DESs allow to tailor-make optimal solvents for this application. In this work Type III DESs, based on chloride quaternary ammonium salts (tetramethylammonium chloride, tetraethylammonium chloride, tetrabutylammonium chloride and tetrahexylammonium chloride) as hydrogen bond acceptor molecules and polyols (ethylene glycol and glycerol) as hydrogen bond donor molecules were used. The liquid-liquid equilibrium (LLE) data of the system {hexane + benzene + DES} was measured at room temperature and atmospheric pressure. The solute distribution ratio and the selectivities were calculated and compared. The highest solute distribution ratios were obtained for salts with long alkyl chain length as hydrogen bond acceptor molecules and for ethylene glycol as hydrogen bond donor molecules.

COSMO-RS was used for the prediction of the LLE data of the studied systems. It was found that both the LLE data and the solute distribution ratio of the ternary systems containing DESs can be qualitatively well predicted using this model. Moreover, the LLE data was quantitatively predicted within a root mean square error of 10 wt% without the need of any experimental data. This implies that COSMO-RS is an effective screening tool for the optimization of the separation process of aromatic components from {aliphatic + aromatic} mixtures using DESs as extracting agents.
1. Introduction

The recovery of aromatic components from naphtha streams is of great importance for the petrochemical industry. Aromatic components have a high economic value as raw material in several processes. Moreover, recent modifications in the legislation demand new requirements in the aromatic content of petroleum products. However, the separation of aromatic components from naphtha streams is a process that still can be further improved. The main difficulty in this separation is the presence of close boiling point and azeotropic mixtures.

Several separation processes could be used for this separation, but the concentration of aromatic compounds in the feed stream plays a very important role in the economic feasibility of the process. For example, azeotropic distillation is only advisable for concentrations of aromatic compounds in the feed stream higher than 95 wt%. Extractive distillation is only convenient for concentrations of aromatic compounds between 65-90 wt%. Liquid-liquid extraction can be efficiently used for concentrations of aromatic compounds between 20-65 wt%. Unfortunately, there is not any efficient process for the separation of aromatic compounds from mixtures with an aromatic concentration lower than 20 wt%.

Generally, the separation via liquid-liquid extraction is industrially performed with the sulfolane process, which necessitates a distillation column for the solvent recovery step. This process is not efficient for aromatic contents lower than 20 wt% because of the high energy investment needed for the sulfolane recovery. This limitation implies that the separation of aromatic compounds from aliphatic compounds has to be done after the naphtha cracking, because the aromatic concentration is higher. However, the development of a liquid-liquid extraction process with an easy solvent recovery will permit the extraction before the naphtha cracking and will reduce the energy requirements because of the decrease of the flows to be heated in the cracking columns. Moreover, sulfolane, as well as other organic solvents currently used for this extraction, are volatile, toxic, and flammable, which are undesirable properties in regard of the need for save and environmentally friendly processes.

In the last decades, several research groups studied the applicability of ionic liquids (ILs) for this specific separation problem. Several review articles dealing with the applicability of ILs for the separation of different aromatics compounds from different {aliphatic + aromatic} mixtures have been published. In all of them, the main conclusion is that ILs are promising alternative solvents, because the experimental LLE data show that the aromatic distribution ratio and the selectivities are comparable to those of sulfolane. The negligible vapor pressure of ILs resolves the solvent recovery problem that is found using sulfolane as extracting agent. For example, ILs could be easily recovered after the extraction by flash distillation. Besides, the ILs show tunable properties, which allow the design of the IL for a specific application by modifying the type of anion and cation. For the {aliphatic + aromatic} separation it has been stated that imidazolium- and pyridinium-based cations with long alkyl chain lengths are preferable. The effect of the anion of the IL on the extraction efficiency was found to be less important compared to the effect of the cation. However, in order to obtain high aromatic distribution ratios and selectivities, the anion of an IL should be
non-coordinating and small-sized. The temperature was found to have a very limited effect on the extraction efficiency. Unfortunately, ILs show disadvantages when considered for large scale application, mainly associated with their high price due to a complicated synthesis and purification requirements.

A new generation of solvents called deep eutectic solvents (DESs) was reported for the first time in 2003. DESs show physicochemical properties similar to ILs, for example, low vapor pressure, wide liquid range, water compatibility and non-flammability. DESs are mixtures of one or more hydrogen bond acceptor molecules (HBA) and one or more hydrogen bond donor molecules (HBD) that, when mixed together in the proper molar ratio, show a large decrease in the melting point compared to the initial compounds. Similar to the ILs, the DESs also show tunable properties, they can be specifically designed for an application by modifying the HBD and the HBA, but also the HBD:HBA molar ratio. Moreover, the DESs can be easily and cheaply prepared by mixing the individual components and applying heat (the so-called heating method).

DESs were found to be alternative solvents in several separation processes, such as CO2 capture, biomass treatment and azeotrope breaking via extractive distillation and liquid-liquid extraction. They have already been successfully applied to the separation of aromatic components from aliphatic + aromatic mixtures. The separation of hexane + benzene mixture was studied using quaternary phosphonium and ammonium salts as HBA. Other aliphatic + aromatic mixtures (for example heptane + toluene) were also studied. Although the results are promising, there is a lack of information regarding the effect of the characteristics of both the HBD and the HBA on the extraction process. The effect of the temperature on the extraction using DESs was already studied for several systems and it was found to have little effect on the efficiency of the process.

The first objective of this work is to evaluate the effect of the HBA alkyl chain length and the effect of the HBD on the extraction of aromatic components from aliphatic + aromatic mixtures. DESs were classified by Abbott, Barron, Ryder & Wilson in three different groups. The DESs type III, formed by a quaternary ammonium salt and a HBD were selected for this study because of their successful performance in previous works. The selected quaternary ammonium salts were tetramethylammonium chloride, tetraethyl ammonium chloride, tetrabutylammonium and tetrahexylammonium chloride; and the selected HBDs were polyols (ethylene glycol and glycerol). The LLE data of the binary and ternary systems hexane + DES, benzene + DES and hexane + benzene + DES were measured at room temperature and atmospheric pressure. The distribution ratio of both aromatic and aliphatic compounds, and the selectivities were calculated. The comparison of the calculated distribution ratio and the selectivities allows the evaluation of the performance of the different DESs.

The second objective of this work is the evaluation of the predictive thermodynamic model COSMO-RS (Conductor-like Screening Model for Real Solvents) for the prediction of the tie-line compositions in the systems investigated. COSMO-RS is a model which allows the prediction of thermodynamic properties of liquid mixtures using a combination of statistical
thermodynamics and properties derived from quantum chemical calculations. COSMO-RS has been successfully applied to the prediction of different thermodynamic data of systems containing ILs. Specifically, activity coefficients at infinite dilution, gas solubilities and Henry’s law constants, LLE data and vapor-liquid equilibrium data have been successfully predicted. In all cases, COSMO-RS was found to show good qualitative predictions. The LLE data of ternary systems {aliphatic + aromatic + IL} was predicted using COSMO-RS in several works.

In recent years, COSMO-RS was also used for the prediction of the LLE of {aliphatic + aromatic + DES} systems. In these works DESs composed of tetrabutylammonium bromide:sulfolane and tetrabutylammonium bromide:ethylene glycol/pyridine were used. It was found that the root mean square deviation of the prediction was not higher than 10 mol% in almost all cases. Nevertheless, the aromatic distribution ratio was underestimated in one publication and overestimated in the other, although in both cases the influence of the molar ratio of hydrogen bond donor and acceptor was qualitatively well predicted. However, it was never evaluated if COSMO-RS could qualitatively predict the effect of both the HBA alkyl chain length and the type of the HBD (glycerol vs ethylene glycol) on the extraction performance. This is of great importance, because the validation of this thermodynamic model for the prediction of the effect of the tunable variables on the extraction efficiency may allow the researchers to significantly reduce the need of experimental time and effort.
2. Experimental procedure

2.1. Preparation of the DESs
The source of the chemicals used in this work, and purity as stated by the suppliers are shown in Table 1. All the chemicals were used without further purification.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Purity (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>VWR</td>
<td>≥ 99.9</td>
</tr>
<tr>
<td>Hexane</td>
<td>Sigma-Aldrich</td>
<td>≥ 99</td>
</tr>
<tr>
<td>Tetramethylammonium chloride</td>
<td>Fluka</td>
<td>≥ 98</td>
</tr>
<tr>
<td>Tetraethylammonium chloride</td>
<td>Sigma-Aldrich</td>
<td>≥ 98</td>
</tr>
<tr>
<td>Tetrabutylammonium chloride</td>
<td>Sigma-Aldrich</td>
<td>≥ 97</td>
</tr>
<tr>
<td>Tetrahexylammonium chloride</td>
<td>Sigma-Aldrich</td>
<td>≥ 96</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Merck KGaA</td>
<td>≥ 99</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Merck KGaA</td>
<td>≥ 99</td>
</tr>
<tr>
<td>Ethanol</td>
<td>TechniSolv</td>
<td>≥ 99.5</td>
</tr>
</tbody>
</table>

There are three different ways for preparing DESs: heating method, grinding method\(^{23}\) and freeze-drying method\(^{44}\). In this work, the DESs were prepared applying the heating method. According to this method, proper amounts of HBD and HBA are weighed in a balance, placed in a sealed flask, and heated at a certain temperature while stirring until a clear liquid is formed. A balance Mettler AX205 with an uncertainty in the measurement of ±0.2·10\(^{-4}\) g was used. The mixture was heated at 333.2 K in a thermostatic bath (IKA RCT basic) with temperature controller (IKA ETS-D5) with an uncertainty in the measurement of ±0.1 K. The water content was measured after the DESs preparation using the Karl Fischer titration method (type Metrohm 795) and it was found to be lower than 1 wt% in all cases.

2.2. LLE data determination.
The LLE data of both binary and ternary mixtures \{hexane + DES\}, \{benzene + DES\} and \{hexane + benzene + DES\} were experimentally determined at 298.2 K using the equilibrium cell method. That is, certain amounts of DES, benzene and/or hexane were placed in 20 mL headspace vials. The mixtures were stirred for 2 h at 500 rpm in a temperature controlled shaker (IKA KS 4000 i-control with temperature stability of ±0.1 K) kept at 298.2 K. Thereafter, the mixtures were left to settle overnight in a heating block. The heating block was kept at 298.2 K in a hot plate (IKA RCT basic) with temperature controller (IKA ETS-D5). After reaching equilibrium, both the top and the bottom phase were sampled using needled syringes in order to analyze their composition.

The analysis of the composition was performed using a Varian 430 gas chromatograph (GC) equipped with a flame ionization detector (FID). The GC method can be described as follows: 
(i) column: Varian CP-SIL 5CB (25 m x 0.25 mm x 1.25 μm); (ii) column oven temperature: 313.2 K for 2 min; (iii) temperature ramp: 373.2 K (rate = 40 K/min) for 2.75 min; (iv) carrier
gas: helium; (v) flow rate: 3 mL/min; (vi) injector temperature: 548.2 K; and (vii) detector temperature: 473.2 K. Injection was done with a split ratio of 200 and the injection volume was 1 µL. Ethanol was used as dilution agent. Within this method the composition of hexane and benzene can be measured; the DES concentration is determined via mass balance calculation. We validated the method with samples of known composition before the experiments. In order to avoid column contamination during the analysis, empty injector liners in which the DES is retained due to its low volatility were used. The samples were measured at least three times and the relative standard deviation was found to be smaller than 5%. The absence of DES in the top phase was confirmed via ¹H-NMR.

3. Computational Methods
For each COSMO-RS computation first a quantum chemical calculation has to be performed to determine the screening charge density on the surface of the molecular cavities in the reference state of the perfect conductor. As these screening charge densities not only depend on the type of the molecule but also on the molecular conformation, these quantum chemical calculations have to be done once for each molecular conformer being considered. COSMO-RS is based on a model of pairwise independently interacting surface segments from the surfaces of the molecular cavities of the molecules that constitute a liquid mixture. By using the screening charge densities from the quantum chemical calculations to describe the molecular interactions with few, general interaction energy expressions, the model can be applied to various mixtures without the need for component or mixture specific parameters. Due to the reduction of the problem of molecular interactions to the interactions of surface segments, the solution of the relevant equations can be obtained fast on a personal computer. More detailed descriptions of the COSMO-RS model are given by Eckert and Klamt⁴⁵ and Klamt⁴⁶.

The conformer search has been performed using COSMOconf 3.0 in this work⁴⁷. Quantum chemical calculations were done with Turbomole 6.6 using density functional theory with the B-P functional and the TZVP basis set⁴⁸. COSMOtherm was used with the BP_TZVP_C30_1501 parameterization for all COSMO-RS calculations⁴⁹.
4. Results and discussion

4.1. Preparation of the DESs

The DESs prepared in this work (expressed in molar ratio) were: (i) tetramethylammonium chloride: glycerol (1:2) (TMACl:Gly(1:2)), (ii) tetramethylammonium chloride: ethylene glycol (1:2) (TMACl:EtGly(1:2)), (iii) tetraethylammonium chloride: glycerol (2:1) (TEACl:Gly(1:2)), (iv) tetraethylammonium chloride: ethylene glycol (1:2) (TEACl:EtGly(1:2)), (v) tetrabutylammonium chloride: glycerol (1:2) (TBACl:Gly(1:2)), (vi) tetrabutylammonium bromide: ethylene glycol (1:2) (TBACl:EtGly(1:2)), (vii) tetrahexylammonium chloride: glycerol (1:2) (THACl:Gly(1:2)), and (viii) tetrahexylammonium chloride: ethylene glycol (1:2) (THACl:EtGly(1:2)).

From the prepared HBD:HBA mixtures, all of them became a clear liquid except for the mixture formed by tetramethylammonium chloride: ethylene glycol (1:2), in which solids remained undissolved in the liquid at temperatures up to 373.2 K. Therefore, this mixture was not considered for further experiments.

The mixture formed by TBACl:Gly(1:2) formed a clear liquid; however, it was observed that a precipitate formed at high hexane concentrations but not in presence of benzene. In the supporting information, the reader can find a picture (Figure S1) that illustrates this behavior. Considering the precipitation in presence of hexane, the LLE data of this mixture was also not measured.

The physicochemical properties of the DESs are highly influenced by the impurities, especially the water content. Therefore, prior to the measurement of the LLE data, the water content of the DESs was also measured. The obtained values can be found in Table 2.

<table>
<thead>
<tr>
<th>DES</th>
<th>Water content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMACl:Gly(1:2)</td>
<td>0.458</td>
</tr>
<tr>
<td>TEACl:Gly(1:2)</td>
<td>0.810</td>
</tr>
<tr>
<td>THACl:Gly(1:2)</td>
<td>0.436</td>
</tr>
<tr>
<td>TEACl:EtGly(1:2)</td>
<td>0.336</td>
</tr>
<tr>
<td>TBACl:EtGly(1:2)</td>
<td>0.480</td>
</tr>
<tr>
<td>THACl:EtGly(1:2)</td>
<td>0.422</td>
</tr>
</tbody>
</table>

The values presented in Table 2 show the water content immediately after the preparation. All the chemicals used for the preparation of the DESs were used as such, without previous drying. Therefore, the water content can be an indication of the hygroscopicity of the individual compounds and the DESs. All the prepared DESs were used as such for all the subsequent experiments.
4.2. Experimental LLE Data

4.2.1 Binary LLE Data

The LLE data of the binary systems \{hexane + DES\} and \{benzene + DES\} were measured at 298.2 K and atmospheric pressure (1.01 bar). The obtained results are shown in Table 3, in which is noticeable that no presence of DES was detected in the top phase, at least up to levels detectable by the measuring technique (see 1H-NMR spectra in the supporting information). For a more visual and easier understanding, the results are also plotted in Figure 1.

<table>
<thead>
<tr>
<th>System</th>
<th>(w_1) top-phase</th>
<th>(w_1) bottom-phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>{hexane + TMACl:Gly(1:2)}</td>
<td>1.000</td>
<td>0.0003</td>
</tr>
<tr>
<td>{hexane + TEACl:Gly (1:2)}</td>
<td>1.000</td>
<td>0.001</td>
</tr>
<tr>
<td>{hexane + THACl_Gly(1:2)}</td>
<td>1.000</td>
<td>0.057</td>
</tr>
<tr>
<td>{hexane + TEACl_EtGly(1:2)}</td>
<td>1.000</td>
<td>0.003</td>
</tr>
<tr>
<td>{hexane + TBACl_EtGly(1:2)}</td>
<td>1.000</td>
<td>0.025</td>
</tr>
<tr>
<td>{hexane + THACl_EtGly (1:2)}</td>
<td>1.000</td>
<td>0.157</td>
</tr>
<tr>
<td>{benzene + TMACl:Gly(1:2)}</td>
<td>1.000</td>
<td>0.024</td>
</tr>
<tr>
<td>{benzene + TEACl:Gly (1:2)}</td>
<td>1.000</td>
<td>0.060</td>
</tr>
<tr>
<td>{benzene + THACl:Gly(1:2)}</td>
<td>1.000</td>
<td>0.460</td>
</tr>
<tr>
<td>{benzene + TEACl:EtGly(1:2)}</td>
<td>1.000</td>
<td>0.170</td>
</tr>
<tr>
<td>benzene + TBACl:EtGly(1:2)</td>
<td>1.000</td>
<td>0.649</td>
</tr>
<tr>
<td>benzene + THACl:EtGly (1:2)</td>
<td></td>
<td>No phase separation</td>
</tr>
</tbody>
</table>

Table 3: LLE data of the studied binary mixtures \{hexane (1) + DES (2)\} and \{benzene (1) + DES (2)\}, measured at 298.2 K and 1.01 bar. All the compositions are presented in mass fractions. No presence of DES was detected in the top phase. The DESs HBA:HBD ratio is expressed as a molar ratio.

\(\triangle\) The uncertainties in the measurements are \(u(p)= 0.02\) bar, \(u(T) = 0.1\) K, \(u(w) = 0.003\)

From Figure 1 three different behaviors can be clearly observed: (i) the solubility of benzene is always higher than the solubility of hexane in all the studied DESs, (ii) the solubility of both benzene and hexane increase with the length of the alkyl chain of the cation, and (iii) both
hexane and benzene are more soluble in the ethylene glycol-based DESs than in the glycerol-based DESs.

The increased solubility of aromatic compounds in contrast to aliphatic compounds in ILs is well known \(^4,5,10,12\) and similar results have also been previously obtained for DESs \(^29,33,36\). For both type of solvents, this trend is commonly explained with the favorable interactions of the ions with the significantly stronger electrostatic field due to the \(\pi\)-system of the aromatic components \(^50–53\). The cations are able to interact with the electron-rich region of the benzene, while the anions orient themselves around the equator of the molecule \(^52\). The aforementioned explanation can be assumed to be also plausible in systems containing DESs.

The increase of the solubility of both hexane and benzene in the DESs with increasing alkyl chain lengths on the cation was similarly observed in systems containing ILs. This behavior was previously explained for IL-containing systems on basis of the increase of the free molar volume \(^8,10,12\). It has been stated that the increase of the free molar volume with increasing alkyl chain lengths of the cation facilitates the accommodation of hexane and benzene. Therefore, the solubilities of both compounds increase. It can be assumed that this explanation is also valid for DES-containing systems.

A different explanation of this behavior is based on the favorable solvation of the aliphatic and aromatic components in the non-polar domain of the ILs \(^50,51\). Therefore, an increase of the cation alkyl chain length leads to an increase of the non-polar domain; thus, increasing the solubility of both aliphatic and aromatic compounds. It can be expected that similar effects also occur in DES-containing systems.

### 4.2.2 Ternary LLE data

The LLE data of the ternary systems \{hexane + benzene + DES\} was measured at 298.2 K and atmospheric pressure. The analysis of these LLE data allows the study of the effect of both the salt alkyl chain lengths of the cation (methyl, ethyl, butyl, and hexyl) and the hydrogen bond donor nature (ethylene glycol, and glycerol) on the extraction performance.

In order to compare the efficiency of the different DESs for this specific separation, the solute distribution ratio and the selectivities were calculated using Eq. 1 and Eq. 2, respectively.

\[
\beta_i = \frac{w_{iE}}{w_{iR}} \quad \text{(Eq. 1)}
\]

\[
S = \frac{\beta_i}{\beta_j} \quad \text{(Eq. 2)}
\]

where \(w_i\) refer to the mass fractions of component \(i\); the subscripts \(E\) and \(R\) refers to the extract (DES-rich phase) and the raffinate (aliphatic-rich phase), respectively. The solute (benzene) distribution ratio quantifies the solvent capacity for dissolving the solute; thus, high distribution ratios lead to decreased solvent-to-feed ratios. The selectivity quantifies the affinity of the solvent to the solute in comparison to the carrier. High selectivities will minimize the carrier recovery from the solvent stream. It has to be noted that in different publications the distribution ratio was defined in mole fractions instead of mass.
fractions\textsuperscript{8,18,54,55}. Due to the high molar masses of the DESs the difference in mole fraction based distribution ratios may be large for equal mass based distribution ratios. For the evaluation of the solvent requirements for an extraction process, the mass based distribution ratio is of higher interest.

The experimentally determined LLE data, together with the calculated distribution ratios and selectivities are shown in Table 4. A graphical representation of the experimentally determined data is shown in Figure 2 by means of triangular diagrams. The solute distribution ratio and the selectivities as function of the aromatic concentration in the aliphatic-rich phase are shown in Figure 3 and Figure 4, respectively.

Table 4: Experimental LLE data, measured at 298.2K and 1.01 bar. The compositions (w\textsubscript{1} and w\textsubscript{2}) are expressed in mass fractions, while the DESs HBA:HBD ratio is expressed as a molar ratio. No presence of DES was detected in the top phase. Distribution ratio (\(\beta\)) and selectivities (S) are also included. \textsuperscript{a}

<table>
<thead>
<tr>
<th>Top-phase</th>
<th>Bottom-phase</th>
<th>(\beta)</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>{hexane (1) + benzene (2) + TMACl:Gly(1:2) (3)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.903</td>
<td>0.097</td>
<td>0.0006</td>
<td>0.001</td>
</tr>
<tr>
<td>0.816</td>
<td>0.184</td>
<td>0.0007</td>
<td>0.004</td>
</tr>
<tr>
<td>0.737</td>
<td>0.263</td>
<td>0.0007</td>
<td>0.006</td>
</tr>
<tr>
<td>0.665</td>
<td>0.335</td>
<td>0.0003</td>
<td>0.007</td>
</tr>
<tr>
<td>0.599</td>
<td>0.401</td>
<td>0.0004</td>
<td>0.009</td>
</tr>
<tr>
<td>0.543</td>
<td>0.457</td>
<td>0.0002</td>
<td>0.010</td>
</tr>
<tr>
<td>0.436</td>
<td>0.564</td>
<td>0.0005</td>
<td>0.012</td>
</tr>
<tr>
<td>0.341</td>
<td>0.659</td>
<td>0.0003</td>
<td>0.013</td>
</tr>
<tr>
<td>0.258</td>
<td>0.742</td>
<td>0.0002</td>
<td>0.014</td>
</tr>
<tr>
<td>0.183</td>
<td>0.817</td>
<td>0.0006</td>
<td>0.018</td>
</tr>
<tr>
<td>{hexane (1) + benzene (2) + TEACl:EtGly(1:2) (3)}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.912</td>
<td>0.088</td>
<td>0.0008</td>
<td>0.007</td>
</tr>
<tr>
<td>0.833</td>
<td>0.167</td>
<td>0.0007</td>
<td>0.016</td>
</tr>
<tr>
<td>0.760</td>
<td>0.240</td>
<td>0.0005</td>
<td>0.023</td>
</tr>
<tr>
<td>0.691</td>
<td>0.309</td>
<td>0.0005</td>
<td>0.028</td>
</tr>
<tr>
<td>0.627</td>
<td>0.373</td>
<td>0.0005</td>
<td>0.033</td>
</tr>
<tr>
<td>0.561</td>
<td>0.439</td>
<td>0.0004</td>
<td>0.038</td>
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<td>0.550</td>
<td>0.0004</td>
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<tr>
<td>0.355</td>
<td>0.645</td>
<td>0.0004</td>
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<td>0.190</td>
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<tr>
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<td>0.001</td>
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<td>hexane (1) + benzene (2) + THACl:Gly(1:2) (3)</td>
<td>hexane (1) + benzene (2) + THACl:EtGly(1:2) (3)</td>
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<td>0.731 0.269 0.220 0.219 0.82 2.71</td>
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<td>0.530 0.470 0.213 0.071 0.45 3.39</td>
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<td>0.340 0.660 0.047 0.347 0.53 3.85</td>
<td>0.215 0.785 0.044 0.433 0.55 2.70</td>
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<tr>
<td></td>
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<td>0.302 0.730 0.044 0.433 0.55 2.70</td>
<td></td>
</tr>
</tbody>
</table>

*a Standard uncertainties $u$ are $u(T) = 0.1$ K, $u(p) = 0.02$ bar, $u(w) = 0.003$
Figure 2: (●, solid line) experimentally determined tie-lines for the systems a) {hexane + benzene + tetraethylammonium chloride : ethylene glycol (1:2)}, b) {hexane + benzene + tetrabutylammonium chloride : ethylene glycol (1:2)}, c) {hexane + benzene + tetrahexylammonium chloride : ethylene glycol (1:2)}, d) {hexane + benzene + tetramethylammonium chloride : glycerol (1:2)}, e) {hexane + benzene + tetraethylammonium chloride : glycerol (1:2)}, and f) {hexane + benzene + tetrahexylammonium chloride : glycerol (1:2)}. (●, dashed line) predicted tie-lines using the COSMO-RS model. All six triangular diagrams are expressed in mass fractions.

Figure 2 shows that increasing the alkyl chain length of the cation significantly increases the solubility of both hexane and benzene in the DES. In other words, it can be observed that the miscibility region increases when the salt alkyl chain length increases.

From Figure 2, the absence of DES in the aliphatic-rich phase is easily noticeable. This behavior was found in other ternary systems composed of {aliphatic + aromatic + DES} \(^{29,33,34,36}\), which is an analogue behavior compared to the systems composed of {aliphatic + aromatic + IL} \(^{8,10,12,56}\). In this work we verified the absence of the DES in the top-phase by analyzing the top-phase samples via \(^1\)H-NMR. Some of the obtained results from the \(^1\)H-NMR measurements are included in the supporting information. From the analysis of Figure S2 to Figure S12 it can be concluded that the top-phases of all the studied systems are DES-free.

The nonappearance of DES in the top-phase is very important from an industrial point of view. This means that no solvent recovery column is needed for the raffinate stream, which will reduce the operational costs of the process. This, together with the low volatility of the DESs, minimizes the solvent loss of the process.
Figure 3: Experimental solute distribution ratio ($\beta$) as function of the benzene mass fraction in the aliphatic-rich phase. (■) [hexane + benzene + tetramethylammonium chloride: glycerol (1:2)], (●) [hexane + benzene + tetraethylammonium chloride: glycerol (1:2)], ( ○) [hexane + benzene + tetrabutylammonium chloride: ethylene glycol (1:2)], (△) [hexane + benzene + tetrahexylammonium chloride: glycerol (1:2)], and (◇) [hexane + benzene + tetrahexylammonium chloride: ethylene glycol (1:2)], all data points were determined at 298.2 K and atmospheric pressure.

Figure 4: Experimental selectivities ($S$) as function of the benzene mass fraction in the aliphatic-rich phase. (■) [hexane + benzene + tetramethylammonium chloride: glycerol (1:2)], (●) [hexane + benzene + tetraethylammonium chloride: glycerol (1:2)], ( ○) [hexane + benzene + tetrabutylammonium chloride: ethylene glycol (1:2)], (△) [hexane + benzene + tetrahexylammonium chloride: glycerol (1:2)], and (◇) [hexane + benzene + tetrahexylammonium chloride: ethylene glycol (1:2)], all data points were determined at 298.2 K and atmospheric pressure.

From Figure 3 and Figure 4, we can analyze and compare the behavior of the selected DESs in the extraction.

A detailed analysis of Figure 3 shows that the benzene distribution ratio increases with the alkyl chain length of the cations for DESs with the same HBD. This behavior was expected based on the binary LLE data, for which it was observed that the solubility of benzene followed the same trend.

Moreover, from Figure 3 it can be observed that the benzene distribution ratio is not highly affected by the concentration of benzene in the raffinate phase. In other words, the benzene
concentration in the system does not significantly affect the extraction efficiency of all the DESs studied.

The hexane distribution ratio as a function of the mass fraction of benzene in the raffinate phase is also shown in Figure 3. Similar to the observations previously made for benzene, the distribution ratio increases with increasing length of the alkyl chains of the cation for the same HBD. The reason for the increase of the hexane distribution ratio at higher benzene concentration in the raffinate phase is that the presence of benzene in the system, and therefore also in the extract phase, promotes the solubility of hexane in the DES-rich phase.

From Figure 3, it is also noticeable that for the same alkyl chain length of the cation, the ethylene glycol-based DESs show always higher benzene and hexane solute distribution ratios. This result was expected considering the results obtained for the binary systems.

Figure 4 shows the selectivities as function of the benzene concentration in the raffinate phase. It can be observed that the DESs with long alkyl chain lengths in the HBA show lower selectivities in comparison to DESs containing cations with shorter alkyl chains. However, for the DESs containing cations with the shortest alkyl chain length a non-expected behavior was found. The DES TMACl:Gly(1:2) was expected to show higher selectivities values than TEACl:Gly(1:2), but this was not the case. Nevertheless, the selectivity is connected with comparatively high experimental uncertainties; therefore, conclusions should be drawn with caution. The selectivity decreases with increasing mass fraction of benzene in the raffinate phase for all the DESs studied. This behavior is explained if we consider that the benzene distribution ratios is almost constant at all concentrations, while the hexane distribution ratios increases with the benzene concentration in the raffinate phase.

From Figure 3, it can be observed that all the DESs show solute distribution ratios smaller than unity. However, the low distribution ratios are compensated by the absence of the DESs in the aliphatic-rich phase and the low volatility of the DESs, which facilitate the solvent recovery after the extraction. From Figure 4, we can observe that in all the studied systems, the obtained selectivities are higher than unity, which is of high importance for the feasibility of an extraction process.

4.3. **Comparison with different systems**

In order to compare the efficiency of the studied solvents with the current available technology, the experimentally determined LLE were compared with the data available in the literature. The experimental data were compared in terms of solute distribution ratios and selectivity with sulfolane, ILs and DESs. The comparison is shown in Figure 5 and in Figure 6 for the distribution ratios of the aromatic species and the selectivities, respectively.
Figure 5: Distribution ratios of the aromatic compounds as function of the benzene mass fraction in the raffinate phase for the \( \text{hexane + benzene + solvent} \) systems. The selected solvents for the comparison are: (■) sulfolane\(^{57}\); different DESs: (●) THACl:EtGly(1:2), (○) THACl:Gly(1:2), (▲) THABr:EtGly(1:2)\(^{29}\), (▲) THABr:Gly(1:2)\(^{29}\); different ILs: (◇)[C\(_3\)Mim][NTF\(_2\)]\(^{18}\), (◇) [C\(_8\)Mim][NTF\(_2\)]\(^{8}\), (◇) [C\(_{10}\)Mim][NTF\(_2\)]\(^{8}\), (◇) [C\(_{12}\)Mim][NTF\(_2\)]\(^{8}\), (◇) [C\(_2\)][NTF\(_2\)]\(^{54}\), and (◀) [EmPy][ESO\(_4\)]\(^{55}\).

Figure 6: Selectivities of the aromatic compounds as function of the benzene mass fraction in the raffinate phase for the \( \text{hexane + benzene + solvent} \) systems. The selected solvents for the comparison are: (■) sulfolane\(^{57}\); different DESs: (●) THACl:EtGly(1:2), (○) THACl:Gly(1:2), (▲) THABr:EtGly(1:2)\(^{29}\), (▲) THABr:Gly(1:2)\(^{29}\); different ILs: (◇)[C\(_3\)Mim][NTF\(_2\)]\(^{18}\), (◇) [C\(_8\)Mim][NTF\(_2\)]\(^{8}\), (◇) [C\(_{10}\)Mim][NTF\(_2\)]\(^{8}\), (◇) [C\(_{12}\)Mim][NTF\(_2\)]\(^{8}\), (◇) [C\(_2\)][NTF\(_2\)]\(^{54}\), and (◀) [EmPy][ESO\(_4\)]\(^{55}\).

From Figure 5 it is possible to compare the values of the aromatic distribution ratios for the separation of aromatic components from \{aliphatic + aromatic\} mixtures applying different extracting agents. It is noticeable that the DES with long alkyl chain lengths of the cations show comparable aromatic distribution ratios compared to sulfolane, as well as ILs with long alkyl chain length.

However, from Figure 5 and Figure 6 it can be observed that the solvents with the highest distribution ratios \([C\(_3\)Mim][NTF\(_2\)]\), \([C\(_{10}\)Mim][NTF\(_2\)]\), \([C\(_{12}\)Mim][NTF\(_2\)]\) \(\text{THACl:EtGly}(1:2)\), \(\text{THACl:Gly}(1:2)\), \(\text{THABr:EtGly}(1:2)\)\(^{29}\), and \(\text{THABr:Gly}(1:2)\)) show lower selectivities in comparison to sulfolane. If the much lower price of sulfolane in comparison to DESs and ILs is taken into account, sulfolane could still be considered a more adequate extracting agent in
terms of economic efficiency. Nonetheless, DESs and ILs are a safer and more environmentally benign alternative than volatile organic solvents. Moreover, the DESs and ILs regeneration process is much cheaper; both in terms of investment (no need for distillation column for the solvent recovery of the raffinate stream) and operational cost (the solvent loss can be expected to be lower). Finally, DESs can be considered tunable solvents, which have not yet been fully optimized for this specific separation.

4.4. COSMO-RS prediction

There are three different ways to describe ILs with COSMO-RS, which may also be applied to the DESs: (1) the meta-file approach, (2) the ion-pair approach, and (3) the electroneutral mixture. All three different approaches and their applications have been extensively explained in the literature. Studies from different groups suggest that the electroneutral mixture approach is the best option for the prediction of LLE data of IL systems. Therefore, this approach was also selected in this work as well as in previous works using COSMO-RS for the prediction of LLE data in systems containing DESs.

In the electroneutral mixture method, the ions, which have been treated separately in the COSMO calculations, are considered as distinct species in the COSMO-RS calculations. For the calculation of the mass fraction of the DES in the subsequent evaluation, the contributions of the individual species of the DES are summed up.

The LLE data of the ternary systems studied in this work were also calculated using COSMO-RS. The root mean square deviation (RSMD) obtained in the prediction of the ternary LLE data was calculated using equation 3, and is shown in Table 5. The tie-lines predicted using COSMO-RS are shown in Figure 2, together with the experimentally determined tie-lines. Moreover, the predicted aromatic distribution ratios together with those calculated from the experimental data are shown in Figure 7.

\[
RMSE(\%) = 100 \sqrt{\frac{\sum_{i=1}^{M} \sum_{j=1}^{N} (w_{ij}^{cal} - w_{ij}^{exp})^2 + (w_{ij}^{I} - w_{ij}^{II})^2}{2MN}}
\]  
(Eq. 3)

Here \( M \) is the number of tie-lines and \( N \) is the number of components (in this case three components). The superscripts I and II represent the aliphatic-rich phase (top-phase) and the DES-rich phase (bottom-phase), respectively.

<table>
<thead>
<tr>
<th>System</th>
<th>RMSD(%)</th>
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</thead>
<tbody>
<tr>
<td>{hexane + benzene + TMACl:Gly(1:2)}</td>
<td>3.55</td>
</tr>
<tr>
<td>{hexane + benzene + TEACl:Gly(1:2)}</td>
<td>5.99</td>
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<tr>
<td>{hexane + benzene + THACl:Gly(1:2)}</td>
<td>2.74</td>
</tr>
<tr>
<td>{hexane + benzene + TEACl:EtGly(1:2)}</td>
<td>8.16</td>
</tr>
<tr>
<td>{hexane + benzene + TBACl:EtGly(1:2)}</td>
<td>4.30</td>
</tr>
<tr>
<td>{hexane + benzene + THACl:EtGly(1:2)}</td>
<td>5.74</td>
</tr>
</tbody>
</table>
The obtained RMSD values are very satisfying considering that the model does not require any experimental or component specific data for the predictions. If the obtained RMSD values are compared to those obtained by other groups studying the LLE of \{aliphatic + aromatic + DES\}, similar deviations can be found\(^{32,36}\).

From Figure 2, it is possible to compare both the predicted miscibility region and tie-lines to the experimentally determined values. It is observed that COSMO-RS overestimates the size of the miscibility regions in all cases except for the THACl:EtGly(1:2) system. Experimentally, it was found that this solvent is fully miscible with benzene, while the prediction shows much lower solubility. Nevertheless, COSMO-RS correctly predicts the higher solubility of the aromatic component in comparison to the aliphatic component.

Furthermore, the model predicts the increase in solubility of the different species with increasing alkyl chain lengths of the cations of the DES. Considering the difference between ethylene glycol- and glycerol-based DESs, the model correctly predicts the higher solubility of benzene and hexane in the ethylene glycol-based DESs. As expected a comparison of the \(\sigma\)-profiles of the two polyols showed high similarities between both components. A factor contributing to the difference between the ethylene glycol and the glycerol-based DESs could be the HBA:HBD mass ratio. In this work, the DESs have a fixed HBA:HBD molar ratio of (1:2). As the molecular mass of ethylene glycol is lower than the molecular mass of glycerol, the mass fraction of the hydrogen bond donor is lower in the ethylene glycol-based DES than in the glycerol-based DES. As the solubility of benzene and hexane is increased with increasing size of the alkyl chains of the cations, the solubility of these components can be expected to be higher with an increase in the mass fraction of the cation in the DES as well.

![Figure 7: Predicted and experimental distribution ratio of the studied systems. In this graph the symbols represent experimental data and the lines represent the calculated data for the systems: (black, dash) \{hexane + benzene + tetramethylammonium chloride: glycerol (1:2)\}, (blue, dot) \{hexane + benzene + tetraethylammonium chloride: glycerol (1:2)\}, (green, dash dot) \{hexane + benzene + tetraethylammonium chloride: ethylene glycol (1:2)\}, (red, dash dot dot) \{hexane + benzene + tetrabutylammonium chloride: ethylene glycol (1:2)\}, (purple, short dash) \{hexane + benzene + tetrahexylammonium chloride: glycerol (1:2)\}, and (orange, short dash dot) \{hexane + benzene + tetrahexylammonium chloride: ethylene glycol (1:2)\}.]
In Figure 7 a comparison of the predicted distribution ratios and the experimentally determined distribution ratio s is shown. It is observable that COSMO-RS overestimates the distribution ratios of the aromatic compounds in all cases, except for the THACl:EtGly(1:2), in which it is underestimated. However, qualitatively the prediction is in most cases correct. This means, the effect of the alkyl chain length and also the effect of the HBD nature are in good agreement with the experimental data, independently from the quantitative value. These very satisfying results indicate that similar to the success of COSMO-RS for predictions of liquid-liquid equilibria of ionic liquid based systems, the model may also be highly valuable as a screening tool for the application of DES systems in extraction processes.
5. Conclusions
In this work, the performance of six different DESs as extracting agents for the removal of aromatic components from {aliphatic + aromatic} mixtures was studied. For this study, we chose type III DESs, formed by chloride quaternary ammonium salts as hydrogen bond acceptor molecules and polyols as hydrogen bond donor molecules. The DESs components were chosen in order to study the effect of the alkyl chain length of the cations as well as the nature of the hydrogen bond donor molecules on the extraction process.

It was found that for the selected DESs, the solubility of the aromatic component is always higher than the solubility of the aliphatic component. This behavior can be explained considering the more favorable electrostatic interactions of the ions with the π-system of the benzene molecule.

It was also found that an increase of the alkyl chain lengths of the cations significantly increases both the solubility of aliphatic and aromatic components. This may be explained with the preferential solvation of these species in the non-polar domains of the DES as was similarly observed for ionic liquids. The increase of the alkyl chain lengths of the cations also leads to an increase of the distribution ratio of benzene; however, the increase of the alkyl chain lengths of the cations concurrently decreases the selectivity.

Regarding the nature of the HBD, we found that using the same mole fraction based HBD:HBA ratio for the different DES the use of ethylene glycol lead to higher solubilities of aliphatics and aromatics, as well as aromatic distribution ratios in comparison to glycerol. Nonetheless, this difference was comparatively small if compared to the effect of the alkyl chain lengths of the cations.

COSMO-RS was used to predict the LLE data of the studied systems. The experimental and calculated data were compared, and we found that COSMO-RS can qualitatively predict the effect of the change in the type of the hydrogen bond donor molecule and the effect of the alkyl chain lengths of the cations. Quantitatively, the experimental data was predicted within a root mean square error of 10 wt%. These results are very satisfying and implicate that COSMO-RS may be highly valuable for DES based systems, allowing to greatly reduce the experimental efforts of finding appropriate DES for specific extraction problems.

6. Acknowledgements
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The authors declare no competing financial interest.
7. Supporting information

In the supporting information the following data can be found: (i) Effect of the hexane on the precipitation of the TBACl:Gly(1:2) deep eutectic solvent, and (ii) The results of the measured $^1$H-NMRs, which show the absence of DES in the aliphatic-rich phase of the studied systems.

This information is available free of charge via the Internet at http://pubs.acs.org/
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