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Shedding Light on Thermodynamics and Physical Properties of Deep Eutectic Solvents for Separating Toluene-Heptane Mixtures Using COSMO-RS

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A total of 150 deep eutectic solvents (DESs) with varying salt, hydrogen bond donor, and molar ratios were studied to develop a screening tool for separating toluene-heptane mixtures. The activity coefficient at infinite dilution (γ^∞) of each DES was predicted using COSMO-RS, and selectivity (S^∞), capacity (C^∞), and performance index (PI) were calculated. Key DES properties, including density, viscosity, melting/freezing point, surface tension, and conductivity, were compiled from the literature to create a DES property library. A comprehensive screening tool with four evaluation criteria was developed, which identified ethyl triphenylphosphonium bromide:$ZnCl_2$ (1:4) as the optimal solvent for toluene-heptane separation. Tetrabutyl-based DESs exhibited higher S^∞, while phenyl phosphonium-based DESs showed higher C^∞. DESs with Cl^- anions provided higher selectivity, whereas those with Br^- anions had higher capacity. Generally, DESs with high S^∞ also showed high PI, indicating superior separation performance.

1. Introduction

In aromatic compounds, carbons are linked together to form a ring structure, whereas in aliphatic compounds, they are linked with each other to form a straight chain. These two types of compounds exist as mixtures in the petrochemical industry. Thus, separating aromatic compounds, such as benzene, toluene, and xylene (BTX), from aliphatic mixtures is a crucial step in this industry. In naphtha steam cracking, aromatic hydrocarbons must be removed to obtain a high-purity product at a low operating cost. However, separating this mixture is challenging, since these hydrocarbons have similar boiling points [1]. The separation of aromatics from aliphatic compounds requires specialized processes. According to Spargo [2], several methods can be used to separate aromatic–aliphatic liquid mixtures, such as azeotropic distillation, extractive distillation, liquid–liquid extraction (LLE), crystallization by freezing, and adsorption on solids.

In this study, we focus on LLE as the separation technique, as it enables the extraction of aromatics even at high concentrations. LLE is also more economical and energy-efficient than other processes, since it is carried out at ambient temperature. In industry, it is commonly used to separate and purify mixtures due to its simplicity and mild operating conditions [3]. However, conventional organic solvents commonly used in LLE, such as sulfolane, glycol, and N-methyl pyrrolidone, are highly volatile, toxic, and flammable [4]. Thus, it is of particular interest to find alternative solvents that can overcome these limitations.

Ionic liquids (ILs) have gained significant interest as a new class of safe solvents to replace conventional organic solvents, since they have negligible vapor pressure. They consist of organic cations paired with either organic or inorganic anions that coexist in the liquid state at ambient temperature [5]. However, due to their complex synthesis, ILs are expensive and unsuitable for large-scale applications. To address these limitations, Abbott et al. [6] introduced deep eutectic solvents (DESs) as an alternative class of eutectic solvents with unique physicochemical properties. Specifically, their components exhibit enthalpic-driven negative deviations from thermodynamic ideality [7,8]. DESs share many interesting properties with ILs, such as nonflammability, water compatibility, low vapor pressure, and a wide liquid range. Additionally, DESs can be prepared more easily and economically than ILs, allowing them to be used to mitigate the limitations of conventional organic solvents and the high synthesis cost of ILs.

There are a huge number of potential DESs, since altering the hydrogen bond acceptor (HBA)/hydrogen bond donor (HBD) combination and the molar ratio results in new DESs exhibiting different properties. Thus, experiments to screen potential DESs for different applications are not practical or time-efficient [9]. Although the properties of particular DESs have been the subject of many tests, systematic collection of the abundant data is lacking, and no specialized library of DESs has been developed to catalog this information. It is therefore difficult to compare the suitability of existing DESs for particular operations.

The Conductor-like Screening Model for Real Solvents (COSMO-RS) is the main screening instrument used for DESs. This tool screens DESs according to their capacity, selectivity, and performance index (PI) to predict their activity coefficients at infinite dilution. However, factors including cost, toxicity, and transport qualities must also be considered when selecting a solvent. Therefore, it is essential to overcome the aforementioned difficulties to fully realize the potential of DESs.

The objectives of this study were to determine the most suitable DESs for facilitating toluene–heptane separation and to investigate the influence of the salt cation and anion, as well as the salt:HBD molar ratio, on the performance of DESs. Additionally, we aimed to establish a comprehensive database that includes the PIs and physical characteristics of different DESs. Another goal was to compare the predicted physical properties of DESs with those measured experimentally. Furthermore, we sought to develop a screening instrument that integrates both chemical affinity variables and physical characteristics of solutes and solvents to offer a comprehensive method of screening DESs.

2. Experimental

The toluene-heptane mixture was used as the liquid-liquid system. The separation of this mixture is useful for the production of aromatic-lean motor fuels [10]. A DES could be used as the solvent in the separation. The LLE system was used in this study. Therefore, the screening tool that we developed was based on the selection of a DES as a solvent to extract toluene from heptane.

2.1 Collection of data from literature

To support property-based filtering, one of the features of the screening tool, the physical properties of DESs were collected from literature sources, web resources, and database programs [11-18]. These properties included the melting point, density, viscosity, surface tension, and conductivity of the DESs. Activity coefficients at infinite dilution of the solvent in toluene and heptane were also obtained for benchmarking. The collected data were used for COSMO-RS benchmarking. Finally, the available data were compared with the predicted results to determine the reliability of the COSMO-RS predictions.

2.2 Prediction of properties by COSMO-RS

For DESs with no reported data on their physical properties or their activity coefficient at infinite dilution (γ^{∞}), predictions can be made using COSMOtherm software. COSMO-RS is a useful tool for predicting the thermophysical and chemical properties of compounds [19]. As it can only predict the density and activity coefficient, other properties were obtained from the collected data.

2.2.1 Molecular geometry optimization

Some compounds may not be available in COSMObase, the TmoleX program package used for the geometric optimization of all species in this study. The Hartree-Fock level and 6-31G* basis set [20] were used to geometrically optimize the molecules. The COSMO file was then generated through a single-point calculation using density functional theory and the triple-ζ valence potential basis set. Finally, the COSMO files were exported to COSMOthermX.

2.2.2 DES representation in COSMOthermX

The approach used for ILs was applied to represent DESs, as they are composed of more than one molecule. Three approaches can be chosen: (i) the metafile approach, (ii) the ion-pair approach, and (iii) the electroneutral approach. Typically, the electroneutral approach is adopted, as it most closely represents the actual nature of ILs, whereby ions are treated as two different compounds in an equimolar mixture. This approach was used in this study to represent DESs according to their molar composition of the salt anion and cation and the HBD.

2.2.3 Selectivity, capacity, and performance index

γ^{∞} can be used to evaluate the maximum capacity and selectivity of a DES. Its value represents the interaction between a solute and a solvent at an infinitesimal solute concentration. Since γ^{∞} only considers the solvent-solute interaction and does not directly reflect the exact extraction ability, it can be used to calculate the selectivity (S^{∞}) and capacity (C^{∞}) of a DES at infinite dilution, as given by eq. (1).

S^{∞} is defined as the ability of a DES to interact more with one compound than with another. In this study, it is expressed as the ratio of the activity coefficients of heptane and toluene. This suggests that a DES with high selectivity toward toluene has a high value of γ_H^{∞} (low interaction with heptane) and a low value of γ_T^∞ (high interaction with toluene).

$$S_{T,H}^\infty = \frac{\gamma_H^\infty}{\gamma_T^\infty} \tag{1}$$

Additionally, C^∞ is used to determine the amount of a DES required for the extraction process. C_T^∞ indicates the maximum amount of toluene that can be dissolved in a DES, which can be calculated as:

$$C_T^\infty = \frac{1}{\gamma_T^\infty} \tag{2}$$

The final parameter used to evaluate the solvent in this extraction process is PI, which is used to estimate the overall performance of a DES:

$$PI = S_{T,H}^\infty \times C_T^\infty \tag{3}$$

2.2.4 COSMO-RS benchmarking

The experimental data collected from the literature and the COSMO-RS-predicted values were compared using the root mean square deviation (RMSD). The predicted data were considered reliable if the RMSD was less than 10%. If it exceeded 10%, the predicted data were corrected until the RMSD was below 10%.

2.3 Construction of DES library

A DES library incorporating both collected and predicted data was constructed. This library included the physical properties of DESs, such as melting and freezing points, density, viscosity, surface tension, and conductivity. It provided the capacity and selectivity of DESs, supporting analysis of the factors influencing separation performance. One hundred and fifty DESs were used in this study, as listed in Table S1.

2.4 Development of comprehensive screening tool

A scoring method was used to develop a comprehensive tool for screening the most suitable DESs for separating toluene-heptane liquid mixtures. Four crucial criteria were selected for scoring, covering both the performance (selectivity and capacity at infinite dilution) and transport properties (density and viscosity) of DESs. DESs with high selectivity toward toluene are desirable, as they require fewer stages in the extraction, thereby lowering capital costs. A DES with high capacity is also advantageous, since it lowers the solvent-to-feed ratio and the column diameter, also lowering capital costs. A DES should also be denser than toluene and heptane to facilitate solvent recovery. Finally, a DES with low viscosity is preferable, as such DESs have a higher mass transfer rate and are easier to transport.

The values of these four criteria were obtained either by COSMO-RS prediction or by collecting data from the literature. Room temperature (25 °C) values of C^∞, S^∞, and density for each DES were predicted by COSMO-RS, whereas the viscosity was obtained from the literature. However, some viscosity data were missing or measured above room temperature. As viscosity decreases with increasing temperature [21-23], values obtained at different temperatures should not be compared. Accordingly, scoring tables were separated into two types: (i) with viscosity data obtained at 25 °C and (ii) with viscosity data obtained above 25 °C.

Each criterion was scored from 1 to 5 based on the scoring sheet in Table S2. The scoring sheet was developed by considering the range of available data, since no definitive rule exists for deciding optimum values. The maximum score was 20 for the table including viscosity at 25 °C, whereas it was 15 for the other table, as viscosity was not considered.

3. Results and Discussion

3.1 Benchmarking: predicted infinite dilution activity coefficients and DES densities

Venkatraman *et al.* [24] and Nkosi *et al.* [25-28] reported experimental values of γ^{∞} for several organic solutes in various DESs at different temperatures. We compared the reported data with the predicted values to validate the computational method. The solvents, solutes, and temperatures used in the benchmarking are listed in Table S3. As shown in Figure 1(a), the correspondence between the experimental data and the values predicted by COSMO-RS was generally high, since most plotted points follow a linear trend. However, certain DESs, such as ChCl:Gly (1:1) and ChCl:Gly (1:2), exhibit significant deviations. This discrepancy may stem from inaccuracies in the molecular geometry representation within COSMO-RS. Additionally, because COSMO-RS does not explicitly account for the complex hydrogen-bonding networks characteristic of DESs, some deviations may persist. Despite these deviations, the overall trend suggests that COSMO-RS is a reliable tool for predicting γ^{∞}, as its results generally align well with the experimental data. Further refinement of the molecular geometry representation and the incorporation of hybrid solvation models could enhance predictive accuracy.

The predicted and experimental values of density for the studied DESs were benchmarked against the available data. Similarly, to benchmark the activity coefficient, experimental density values were plotted against predicted values (Figure 1(b)). The plotted points follow a linear trend, indicating that the predictions were accurate. The calculated RMSD was 0.58%, which is very low considering that COSMO-RS does not use experimental data in its prediction correlation. Thus, density predictions by COSMO-RS were concluded to be reliable. Furthermore, to assess the effect of the molecular conformation on COSMO-RS predictions, four conformers of ChCh:Gly (1:2) were examined (Table 4S). Key thermodynamic properties of the DES conformers, including solubility capacity, activity coefficients, and chemical potentials of toluene, showed minimal variation, while the density (1.17 g/mL) closely matched the literature value (1.18 g/mL) [29,30]. These results suggest that conformational differences have a minimal impact on prediction reliability.

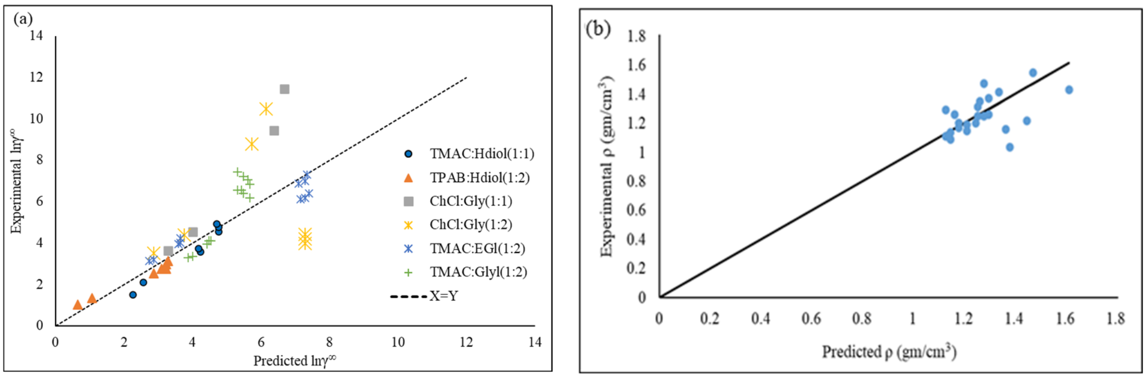

Figure 1. Comparison of (a) experimental and predicted $\ln\gamma^{\infty}$ and (b) experimental and predicted density.

3.2 Calculated selectivity, capacity, and performance index at infinite dilution

3.2.1 Ranking of DESs from C^{∞}, S^{∞}, and PI

Next, the results of DES screening by COSMO-RS are presented in terms of the selectivity of DESs toward toluene, their capacity, and the PI at infinite dilution. The parameters are depicted in Figures S1(a-f). The DESs are classified into six categories according to their salt cations: (i) phenylphosphonium-based DESs, in which the salt cations are allyl triphenylphosphonium (ATP), benzyl triphenylphosphonium (PTP), ethyl triphenylphosphonium (ETP), and methyl triphenylphosphonium (MTP) with bromide or chloride anions; (ii) ethylammonium- or methylammonium-based DESs, in which the salt cations are benzyl triethylammonium, benzyl trimethylammonium, and ethylammonium with a chloride anion; (iii) tetrabutyl-based DESs, in which the salt cations are tetrabutylammonium and tetrabutylphosphonium with both chloride and bromide anions; (iv) choline-based DESs, in which the salt anions are acetate, chloride, nitrate, and tetrafluoroborate; (v) ethanolammonium-based DESs, in which the salt cation is diethyl ethanolammonium with a chloride anion; (vi) zinc-based DESs, in which the salt cation is zinc and the anion is chloride. In the solvent selection process, the capacity at infinite dilution, C^{∞}, is considered the decisive parameter due to its greater influence than solvent selectivity on economic evaluations [31].

ATPB:TrEG (1:10) and EAC:Ur (1:1.5) had the highest and lowest capacities, respectively. Only six DESs had a capacity greater than 1, ranked as ATPB:TrEG (1:10) > BEAC:TSA (3:7) > BTPC:TSA (3:7) > TBAB:Imi (3:7) > MTPB:TrEG (1:5) > BTPC:DG (1:7). Most DESs exhibited an S^{∞} value of less than 100, with the lowest value of 5.107 observed for MTPB:TFA (1:8). The five DESs with the highest selectivity contained a zinc chloride HBD and are ranked as ETPB:ZnCl (1:5) > ChCl:ZnCl (1:4) > TBPB:ZnCl (1:5) > DEAC:ZnCl (1:4) > ETPB:ZnCl (1:4). Generally, DESs with high C^{∞} and S^{∞} values had high PI values, as PI is the product of the two parameters [32]. Only five DESs had a PI higher than 10, ranked as BEAC:TSA (3:7) > ATPB:TrEG (1:10) > BTPC:TrEG (1:8) > TBAB:Imi (3:7) > ChCl:MDA (1:8). EAC:Ur (1:1.5) exhibited the lowest PI due to its low C^{∞}. The maximum and minimum values of C^{∞}, S^{∞}, and PI are summarized in Table 1.

Table 1. Maximum and minimum values of C^{∞}, S^{∞}, and PI among the DESs.

Value	C^{∞}	DES	S^{∞}	DES	PI	DES
Min	0.001496	EAC:Ur (1:1.5)	5.107	MTPB:TFA (1:8)	0.07388	EAC:Ur (1:1.5)
Max	2.3225	ATPB:TrEG (1:10)	250.0	ETPB:ZnCl (1:5)	16.57	BEAC:TSA (3:7)

3.2.2 Effect of anion choice

In this section, we discuss the influence of the anion in the salt component of the DES. We examined the effects of chloride (Cl^-), bromide (Br^-), acetate ($C_2H_3O_2^-$), nitrate (NO_3^-), and tetrafluoroborate (BF_4^-) anions on the performance of DESs in the tetrabutyl- and choline-based groups. These salts were combined with HBDs, such as diethanolamine and urea, at a molar ratio of 1:2. Generally, for tetrabutyl-based DESs, TBA with the Br^- anion exhibited a higher C^{∞} value than TBA with the Cl^- anion. For the same anion, the capacity increased with the molar ratio. In contrast, the TBA salt with the Cl^- anion exhibited a higher S^{∞} value than that with the Br^- anion. The selectivity decreased with increasing molar ratio for the same anion, as shown in Figure 2(a).

Regarding the effect of the halide anion on selectivity and capacity, the difference in S^∞ is greater than that in C^∞. In other words, the halide anion influences selectivity more than it influences the capacity at infinite dilution. Consistently, DESs with Cl^- anions exhibit higher values of selectivity and, consequently, higher PI values. Cl^- is a stronger hydrogen bond acceptor than Br^- and has greater affinity with HBDs, as indicated by the sigma potentials reported by Hizaddin *et al.* [32]. Thus, toluene-heptane mixtures interact more favorably with DESs containing Cl^- anions than with those containing Br^-.

Figure 2(b) shows a comparison between C^∞ and S^∞ for choline-based DESs with the same HBD and molar ratio but different anions: acetate, Cl^-, NO_3^-, and BF_4^-. The choline salt with Cl^- exhibited a markedly different C^∞ from the other three DESs, which had C^∞ values very close to zero. It also exhibited the lowest S^∞ value, with the other three DESs having S^∞ values above 30, ranked as ChAc:Ur (1:2) > ChN:Ur (1:2) > ChCL:TFB (1:2) > ChCl:Ur (1:2).

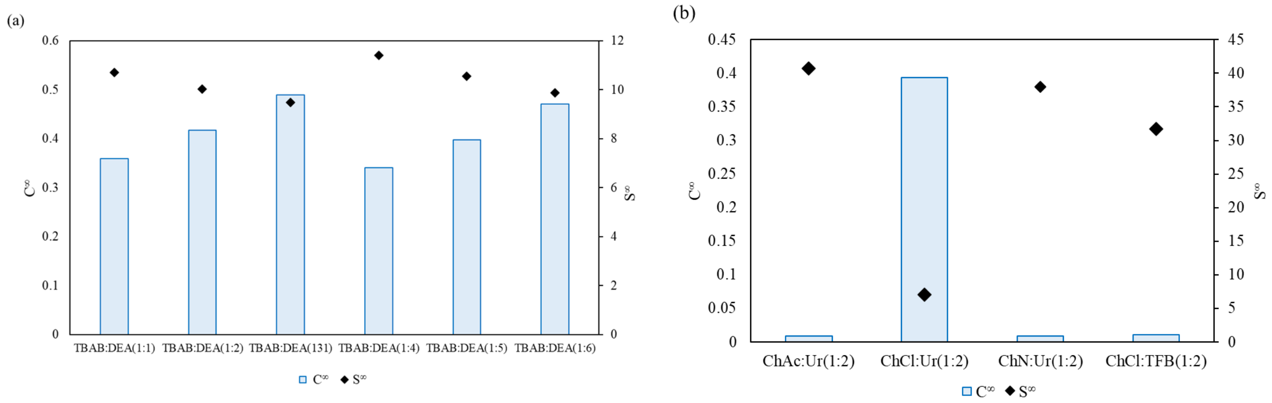

Figure 2. Selectivity and capacity of (a) tetrabutyl-based DESs and (b) choline-based DESs used to compare the effect of the anion.

3.2.3 Effect of hydrogen bond donor

In this section, the influence of the HBD of DESs on S^∞ toward toluene compounds is discussed, along with their C^∞ and PI values. The DESs were divided into different categories: (i) phenylphosphonium-based, (ii) ethylammonium-based, (iii) tetrabutyl-based, (iv) ethanolammonium-based, and (v) choline-based. For each category, the HBA was chosen from the same compound. For the phenylphosphonium-based DESs, the amount of salt and molar ratio were kept constant, similar to the MTPB-based DESs. As shown in Figure 3(a), there is a significant difference between the capacity of the DES with TrEG as the HBD, which is close to 1, and the other three, which are below 0.30. The value of S^∞ for the DESs decreases in the order MTPB:EG (1:4) > MTPB:MEA (1:5) > MTPB:Gly (1:4) > MTPB:TrEG (1:4).

Figure 3(b) shows the capacity and selectivity of the ethylammonium-based DESs. The effect of the HBD was explored for the salt EAC and a constant salt-to-HBD molar ratio of 1:1.5. The DESs paired with an amide-based HBD (TFA and Ace) have much higher capacities than those paired with urea. In contrast, EAC paired with urea has the highest S^∞, followed by EAC paired with Ace and TFA. TBAB was selected as the salt to study the effect of the HBD on S^∞, C^∞, and PI of tetrabutyl-based DESs at a 1:3 salt-to-HBD molar ratio. As shown in Figure 3(c), TBAB:DEA (1:3) exhibits the highest C^∞, followed by the DESs paired with

MEA, EG, and Gly. Figure 3(c) shows that the HBDs from the amine-alcohol group (MEA, DEA) have higher capacities but lower selectivities than the HBDs from the alcohol group (EG, Gly).

For the ethanolammonium-based DESs, DEAC was chosen as the salt. Two salt-to-HBD molar ratios, 1:2 and 1:3, were considered, because these DESs have been reported in the literature as liquids at room temperature. Figure 3(d) reveals that DEAC paired with an alcohol-based HBD yields a higher C^{∞} than when paired with ZnCl. In contrast, DEAC:ZnCl (1:2) has the highest value of S^{∞}, exceeding those of DESs with an alcohol-based HBD. Finally, the choline-based DESs were compared while keeping the amount of salt and molar ratio constant to enable a consistent comparison. Choline chloride paired with ZnCl at a 1:2 salt-to-HBD molar ratio gives the highest C^{∞} but the lowest S^{∞}. Mixed trends can be observed for C^{∞} and S^{∞} in Figure 3(e). However, a consistent pattern remains, where DESs with high selectivity tend to have low capacity, and vice versa.

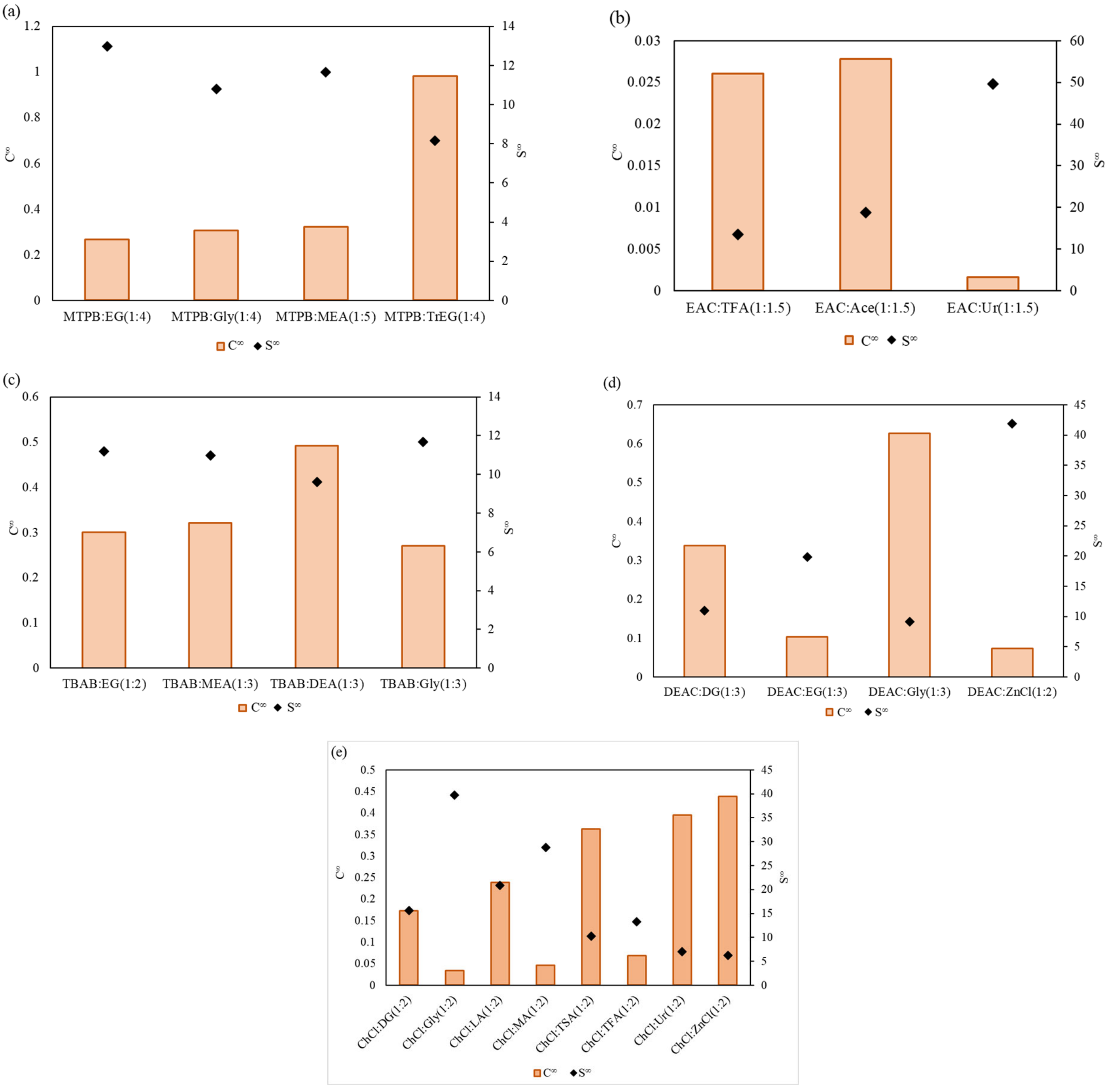

Figure 3. Selectivity and capacity of (a) phenylphosphonium-, (b) ethylammonium-, (c) tetrabutyl-, (d) ethanolammonium-, and (e) choline-based DESs, showing the effect of the HBD choice.

Oliveira *et al.* [33] used DESs to separate azeotropic mixtures of ethanol and heptane. These HBDs (Gly, EG, LA) differ in their functional groups; LA is an alpha-hydroxy acid (AHA) with a carboxylic group (–COOH) and a carbonyl group (C=O), while EG and Gly are alcohols with an –OH group. The carbonyl and carboxylic groups in LA enhance the polarization of the –OH group in LA compared with in Gly and EG. LA therefore provides a polar environment that enhances solubility [34]. DES exhibits negative μ values in the HBD and HBA regions, indicating their polarity and their ability to interact with both polar and nonpolar compounds [35]. The enhanced dipole strength increases the number and strength of hydrogen-bonding interactions. This finding is analogous to our study of toluene–heptane separation, where the main driving force is also hydrogen-bonding interactions. A similar explanation can be applied to the behavior of DESs with different pairs of HBDs in terms of their selectivity and capacity for toluene. Similar to previous observations, DESs with high selectivity tend to have high PI values, since PI is the product of S^∞ and C^∞.

Overall, it can be deduced that DESs with HBDs consisting of alcohol (EG, Gly, TrEG, 6HDiol) or amide (Ur, TFA, Ace) functional groups yield high S^∞ values but low C^∞ values. In contrast, DESs with HBDs including carboxylic acid (LA, MA, TSA) or amino alcohol (DEA, MEA) functional groups generally have high C^∞ values but low S^∞ values. The observed inverse relationship between C^∞ and S^∞ can be attributed to the interplay of solute-DES interactions and thermodynamic solubility principles. A high capacity suggests that both toluene and heptane interact favorably with DESs, reducing the solubility contrast and consequently lowering selectivity. This trend aligns with fundamental thermodynamic considerations, where activity coefficients influence solute partitioning behavior [32].

3.3 Comprehensive screening tool to select optimum DESs for toluene-heptane extraction

3.3.1 Scoring table with viscosity data at 25 °C

The DESs in the phenylphosphonium group have scores from 25% to 70%, as shown in Figure S2(a). ETPB:ZnCl (1:4) has the highest score, not only within this group but also among all the studied DESs. Ten out of 17 DESs in this group have an overall score of 50% or higher. The average score for the phenylphosphonium-based DESs is 47%. Among the ethylammonium-based DESs, viscosity data were only reported for BEAC:OA (1:1) and BEAC:TSA (3:7). The former, with toluenesulfonic acid as the HBD, has a score of 55%, greater than the 35% score for BEAC with oxalic acid as the HBD. The average score for these two DESs is 45%.

Figure S2(b) shows a comparison of the overall scores for the tetrabutyl-based DESs. TBPB:ZnCl (1:4) has the highest score within the group at 60%, while TBAB:MEA (1:4) and TBAB:MEA (1:5) have the lowest score of 25%. Only four of these 18 DESs have an overall score of 50% or higher. The mean score for this group is 44.4%. A similar comparison for the choline-based DESs is depicted in Figure S2(c). The highest overall score among these 39 DESs is 60% for ChCl:ZnCl (1:2), while the lowest is 25%. This group has an average score of 39.5%; the low score is probably due to the larger amount of data. The seven DESs with scores of 50% or higher are mostly paired with an acid-based HBD.

As shown in Figure S2(d), most DESs in the ethanolammonium group have low overall scores, with the highest score of only 50% for DEAC:ZnCl (1:4). The lowest overall score is 25% for DEAC:DG (1:3). The average score for this group is 40.8%.

Only one DES belonging to the zinc-based group reported viscosity data: ZnCl:Ur (1:3.5), which has an overall score of 40% (Figure S2(d)). Both performance-related criteria, C^∞ and S^∞, received low scores (2 and 1, respectively), indicating that this DES only dissolves a small amount of toluene and has low selectivity toward toluene in the mixture.

The DESs ChCl:EA (1:5), TBAB:Gly (1:4), and ETPB:ZnCl(1:4), which had the highest (70%), average (45%), and lowest (25%) scores, respectively, were compared by spider-web analysis, as shown in Figure S3. All DESs had low C^{∞} values of below 0.5, indicating that a higher solvent flow rate would be required to extract toluene from the mixture, thereby increasing extraction costs. ChCl:MEA (1:5) is not suitable for this separation process since it does not fulfill the required criteria. TBAB:Gly (1:4) has a high viscosity score but low capacity, selectivity, and density scores. The most suitable DES for toluene-heptane separation was found to be ETPB:ZnCl (1:4). Although its capacity score is low, it meets the other criteria, particularly those related to transport properties. In summary, ETPB:ZnCl (1:4) exhibits high overall performance and favorable transport properties.

3.3.2 Scoring table without viscosity data or reported viscosity at above 25 °C

A similar approach was taken to evaluate the DESs without viscosity data or with viscosity data measured above 25 °C. For the phenylphosphonium-based DESs, the highest and lowest overall scores are 73% and 27%, respectively, as shown in Figure S4(a). ETPB:ZnCl (1:5) has the highest score, not only within the group but among all the studied DESs. The mean score of this group is 36%. All scores for the group comprising ethylammonium- and methylammonium-based DESs are below 50% and range from 27% to 33%. All DESs in this group attained 1 mark for both capacity and selectivity, contributing to the low overall scores. BMAC:Gly (1:5) and EAC:Ace (1:1.5) have the lowest overall scores (Figure S4(b)). This group has an average overall score of 31%.

Figure S4(c) shows the overall scores for the tetrabutyl-based DESs. TBPB:ZnCl (1:5) has the highest score of 67%, whereas the other two DESs attained only 27%. The overall mean score of this group is 40%. For the 38 choline-based DESs, the average overall score is 33%. ChCl:ZnCl (1:4) attained the highest score due to its high selectivity and density scores. All DESs in this group have overall scores below 50%. For the ethanolammonium-based DESs, the highest overall score is 40% for DEAC:ZnCl (1:1), and the lowest is 27%. As shown in Figure S4(d), most DESs in this group have low overall scores because they received 1 mark for both capacity and selectivity. The average score for this group is 30%.

Figure S4(e) presents the overall scores for the zinc-based DESs. All have scores of less than 50%, with the highest being only 33% for ZnCl:EG (1:4). All DESs in the group scored 1 mark for both capacity and selectivity, contributing to their low overall scores. The average overall score for this group is 29%.

A similar comparative analysis using a spider-web graph was performed for MTPB:EG (1:3) with an overall score of 27%, ChCl:TFA (1:2) with an overall score of 40%, and ETPB:ZnCl (1:5) with an overall score of 73%. As before, all three DESs scored only 1 mark for capacity. As shown in Figure S5, MTPB:EG (1:3) is not suitable for separating toluene from heptane, as none of the criteria are satisfied. For ChCl:TFA (1:2), the density scored an average value, whereas the other two criteria met only the minimum requirement. ETPB:ZnCl (1:5) had the highest scores for both selectivity and density. However, because viscosity data were unavailable, it cannot be concluded to be the most suitable DES for this separation.

Viscosity data can only be obtained experimentally or through modeling. To our knowledge, only the equation of state can be used to model the viscosity [32,33]. Since this study is limited to predicting properties using COSMO-RS, room-temperature viscosity cannot be predicted. Therefore, incorporating a method for viscosity prediction would improve this study, allowing a broader comparative analysis using the scoring table.

3.4 Compilation of reported physical properties

As discussed in Section 3.3, the physicochemical properties of DESs, such as freezing point, surface tension, and conductivity, play an important role in the solvent selection. However, these three criteria were not evaluated in the scoring table due to a lack of reported data. All the data listed in Table S2 were collected from the literature and pooled to form a library of DES physicochemical properties. The freezing point, melting point, surface tension, and conductivity of DESs have been experimentally studied [20,34-41]. Due to time constraints, DES properties were only predicted using COSMO-RS. Incorporating prediction methods for other physicochemical properties not available in COSMO-RS would improve this study and enable the development of a more accurate and thorough screening tool containing complete information on all DES properties.

4. Conclusion

A total of 150 DESs were analyzed by considering both their performance and their physicochemical properties, such as density, viscosity, and freezing/melting points. A library of these properties was compiled and used to create a comprehensive screening tool for DESs, ranking them by selectivity, capacity, density, and viscosity. As a result, ETPB:ZnCl (1:4) was identified as the optimal solvent for separating a toluene–heptane mixture, based on its high selectivity, suitable density, and low viscosity. However, some data (e.g., surface tension, conductivity) remained incomplete due to limitations in predictive methods, highlighting opportunities for future improvement.

Supporting Information

The Supporting Information is available free of charge at https://doi.org/10.15261/serdj.33.75.

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Declaration

The authors declare that they have no conflicts of interest.

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