Development of a Comprehensive Screening Method of Deep Eutectic Solvents for the Separation of Toluene-Heptane Mixtures

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Outline

Introduction

Solvent Screening & Selection

Toluene-heptane as the case study for DES solvent screening

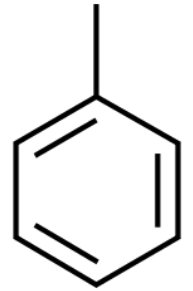
Results and Discussion

Recommendations

Introduction

Context and motivations

- Aromatics are important chemicals in the petrochemical and chemical industries as building blocks for chemical processes
- Challenges related to the separation of aromatics and aliphatics
  - ✓ No feasible methods when the aromatics content is below 20 wt%
  - ✓ Substantial amounts of solvent are present in the raffinate
  - ✓ Degradation of solvents by vacuum distillation at elevated T
  - ✓ High energy consumption and corrosion of the equipment



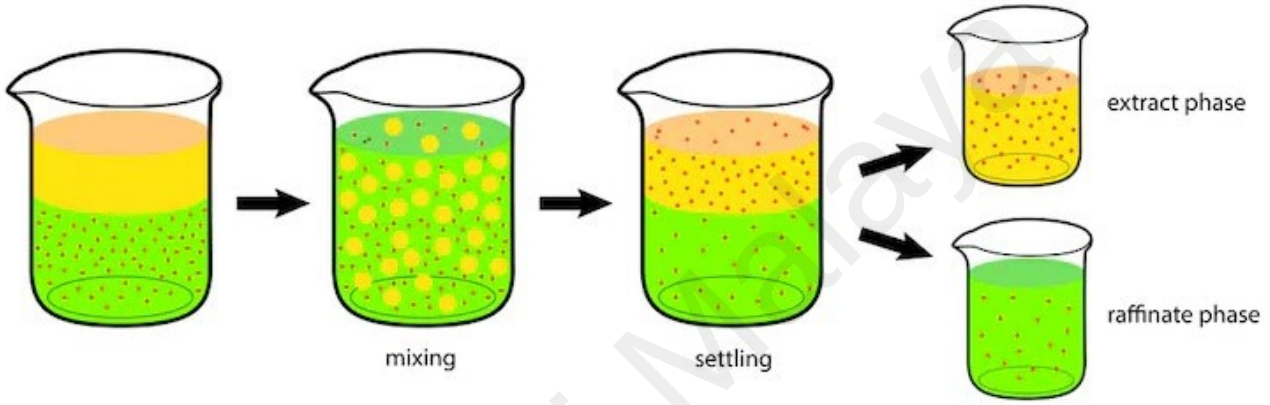
Toluene

Heptane

Research objective

- Finding new green solvents based on multiple criteria such that the solvents are not only highly selective but also have favorable properties for use on a larger scale.

Liquid-liquid Extraction



https://chemicalengineeringworld.com/liquid-liquid-extraction/

Pros

- **Mild operating conditions**
- **Not energy intensive**
- **Simple operation**

Cons

- **Solvent & product recovery**
- **Time-consuming**
- **Highly dependent on solvent selection**

Solvent Selection

Conventional Solvents

- ✓ Widely used
- ✗ Highly volatile
- ✗ Toxic
- ✗ Flammable
- ✗ Solvent loss

Ionic Liquids

- ✓ Negligible vapor pressure
- ✓ Tunable
- ✗ Expensive
- ✗ Effects not widely studied

DES

- ✓ Negligible vapor pressure
- ✓ Tunable
- ✓ Cheaper alternatives to ILs
- ✗ Effects not widely studied

Properties of the ideal solvent

Selectivity

The solvent should be more selective towards the solute than the carrier

Distribution ratio

Higher value means lesser quantity of solvent is required

Recoverability

Ease of product recovery and reuse of solvent. Factors include avoiding the formation of azeotrope, having favourable properties for recovery method e.g. low vapor pressure or low heat of vaporization

Density

A larger difference in density between the extract and raffinate phase will facilitate the separation of the two phases

Interfacial tension

Determine which phase is dispersed and which is continuous

Inertness / Reactivity

Solvents should not be reactive with the mixture to be separated

Other properties

Vapor pressure, viscosity. toxicity, flammability, cost, availability, freezing point, etc.

Deep Eutectic Solvent (DES)

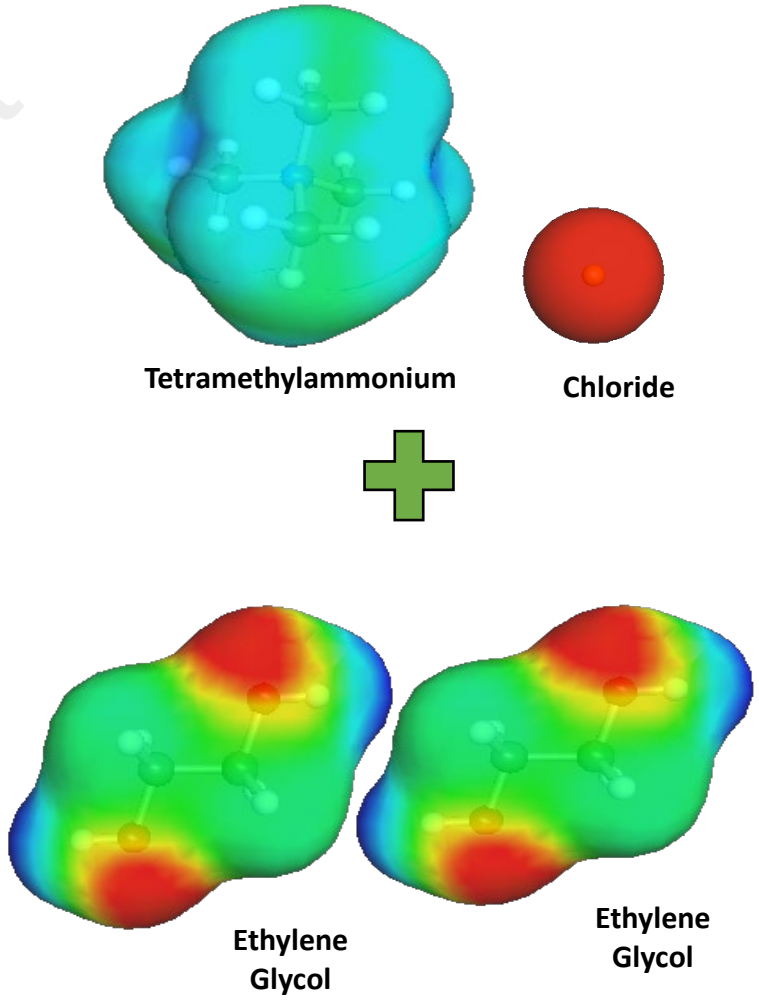
- Combination of a hydrogen bond acceptor (typically salt) and hydrogen bond donor (HBD)

- When salt & HBD are combined, they form a liquid homogeneous mixture with a lower melting point (eutectic)
  - Similar properties with ILs: negligible vapor pressure, tunable to specific application
  - Advantages: Cheaper raw material & Simpler synthesis route

- Different combinations will result in different DESs and properties
  - Cation/anion combination
  - HBD choice
  - Salt:HBD ratio

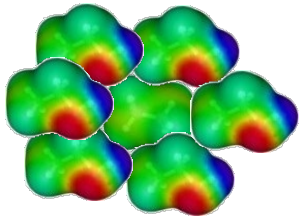
- Recent applications in liquid-liquid extraction:
  - Separation of aromatic/aliphatic mixtures
  - Separation of azeotropic mixture (ethanol/heptane)
  - Removal of benzothiophene from model oils

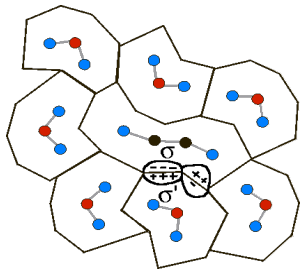
- **But how to screen DES systematically?**

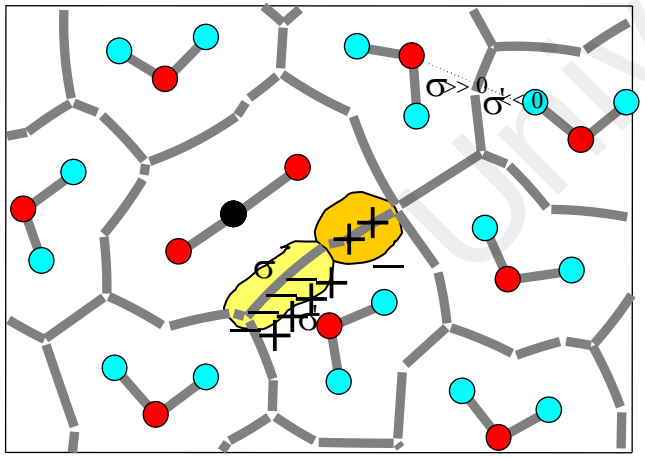


COSMO-RS Method for Solvent Screening

COSMO-RS: **CO**nductor-like **S**creening **MO**del for **R**eal **S**olvents, developed by Klamt et. al in 1999





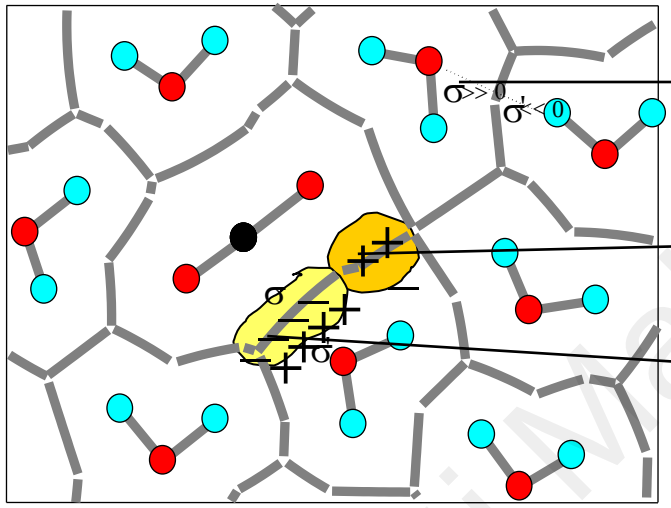


1) Molecules are put in a virtual conductor state

2) The ensemble is compressed to approximate density

3) The virtual conductor is removed and energetic cost from this removal is calculated in terms of σ and σ'.

Molecular Interaction in COSMO-RS



Hydrogen Bonding Interaction

Misfit Energy Interaction

Ideal Electrostatic Contact

Electrostatic Misfit Interaction Energy: $E_{misfit}(\sigma,\sigma') = a_{eff}\frac{\alpha'}{2}(\sigma+\sigma')^2$

Misfit constant

Effective contact surface area

Hydrogen Bonding Interaction Energy: $E_{hb}(\sigma,\sigma') = a_{eff}c_{hb}min(0,\sigma\sigma' + \sigma_{hb}^{\ 2})$

Hydrogen bonding coefficient

Threshold σ for hydrogen bonding

$a_{eff} = 6.25\text{Å}^{-2}$
$\alpha' = 5950\ \text{kJ mol}^{-1}\text{Å}^{-2}$
$c_{hb} = 36.7\ \text{kJ mol}^{-1}\text{Å}^{-2}$
$\sigma_{hb} = 0.0085\text{kJ mol}^{-1}\text{Å}^{-2}$

Statistical Thermodynamic in COSMO-RS

Activity Coefficient of a Segment

$$\ln \gamma_S(\sigma) = -\ln\left[\int d\sigma' p_S(\sigma') \times \exp\left\{\frac{-a_{eff}E(\sigma,\sigma')}{RT}\right\}\right]$$

Where $E(\sigma,\sigma') = \frac{\alpha'}{2}(\sigma + \sigma'^2) + c_{hb}\min\{0, \min(0, \sigma_{don} + \sigma_{hb})\max(0, \sigma_{acc} - \sigma_{hb})\}$

Activity Coefficient of Component *i* in Mixture Ensemble *S*

$$\ln \gamma_{i/S} = n_i \sum_{\sigma} p_i(\sigma)[\ln \gamma_S(\sigma) - \gamma_i(\sigma)] + \ln \gamma^{SG}{}_{i/S}$$

Where $n_i = \frac{A_i}{a_{eff}}$; i.e. the contribution of molecule *i* towards the effective contact surface area

Selectivity, Capacity & Performance Index

- Selectivity is defined as the ratio of distribution coefficient of solute in the extract phase (DES) to that of in the raffinate phase (heptane)

$$S_{12,\max} = S_{12}^{\infty} = \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)_{\text{DES phase}} \left(\frac{\gamma_1^{\infty}}{\gamma_2^{\infty}}\right)_{\text{heptane phase}} \approx \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)_{\text{DES phase}}$$

- Capacity can be estimated as the inverse of activity coefficient at infinite dilution of the solute in the solvent phase (DES)

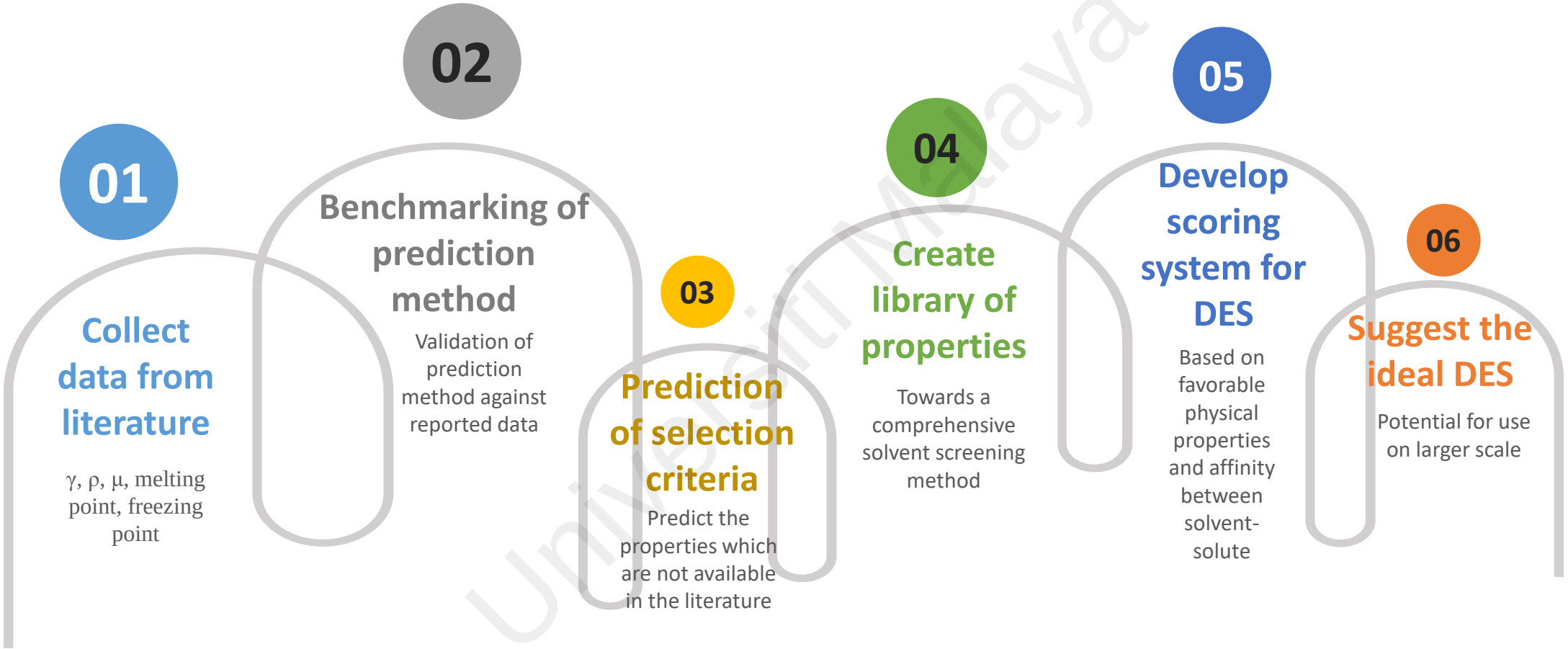
$$C_1^{\infty} = \left(\frac{1}{\gamma_1^{\infty}}\right)_{\text{DES phase}}$$

- Performance Index (PI) is defined as the product of maximum selectivity and maximum capacity

$$\begin{aligned} PI &= S_{12,\max} \times C_{12}^{\infty} \\ &= \left(\frac{\gamma_2^{\infty}}{\gamma_1^{\infty}}\right)_{\text{DES phase}} \times \left(\frac{1}{\gamma_1^{\infty}}\right)_{\text{DES phase}} \\ &= \left(\frac{\gamma_2^{\infty}}{(\gamma_1^{\infty})^2}\right)_{\text{DES phase}} \end{aligned}$$

Subscripts 1 and 2 refer to toluene and heptane, respectively

But selectivity and capacity are not good enough …



Results and Discussion

BENCHMARKING COSMO-RS PREDICTION

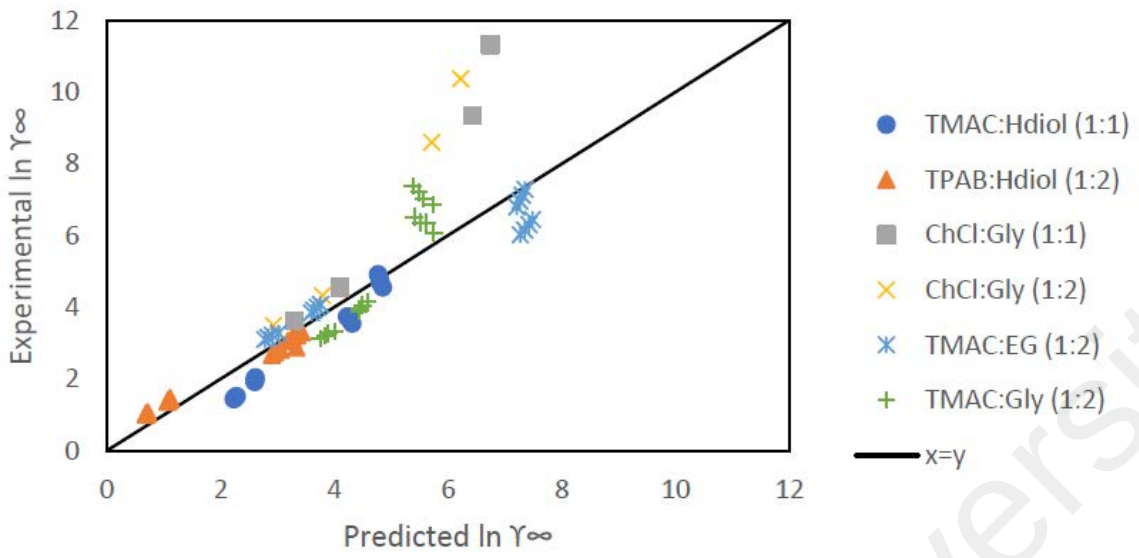


Figure 1: Comparison between experimental $ln\,\gamma^{\infty}$ and predicted $ln\,\gamma^{\infty}$

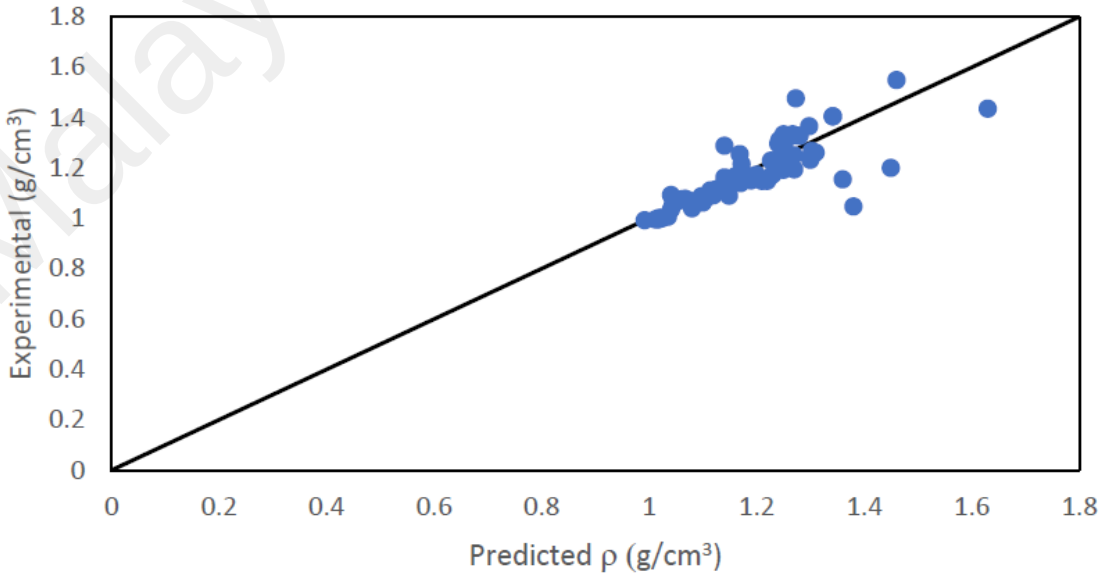


Figure 2: Comparison between experimental and predicted density

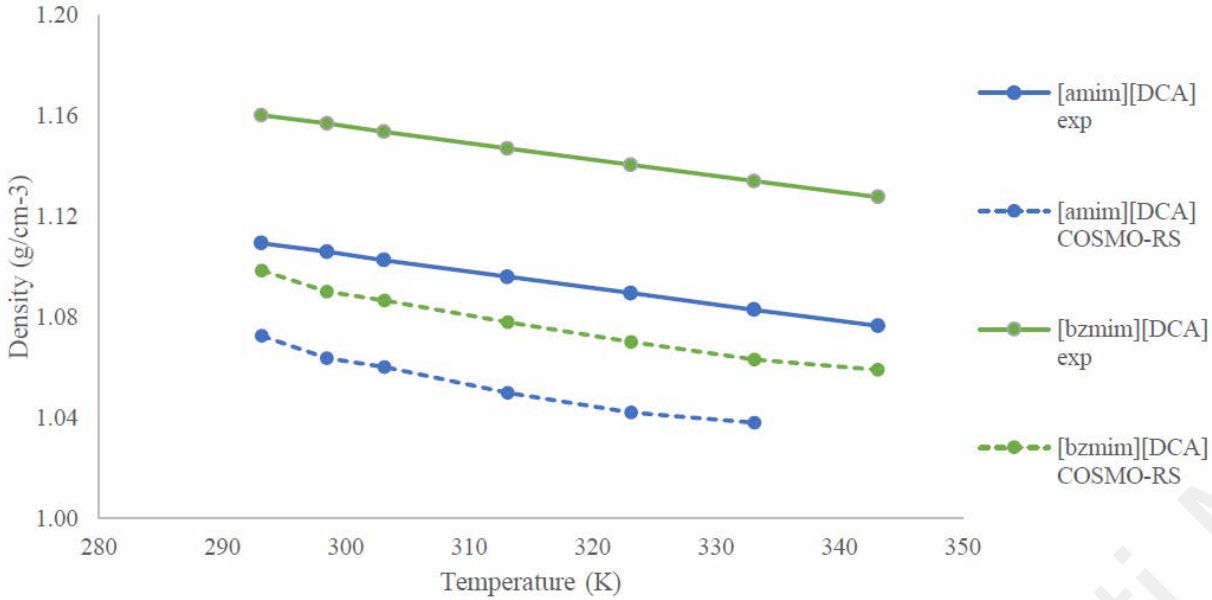


Figure 3: Density as a function of temperature for [amim][DCA] and [bzmim][DCA]

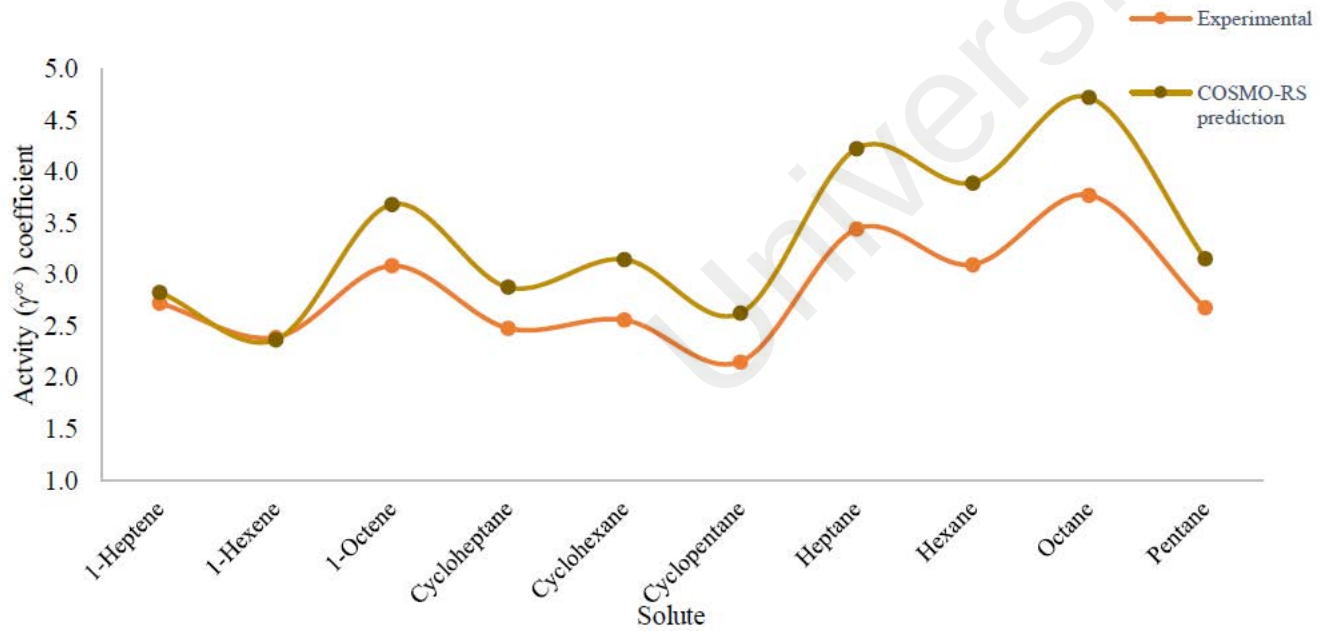


Figure 4: Activity coefficient of various solutes in [HMIM][BF4] at 298.15 K

Calculated S∞, C∞ of Toluene in the DES

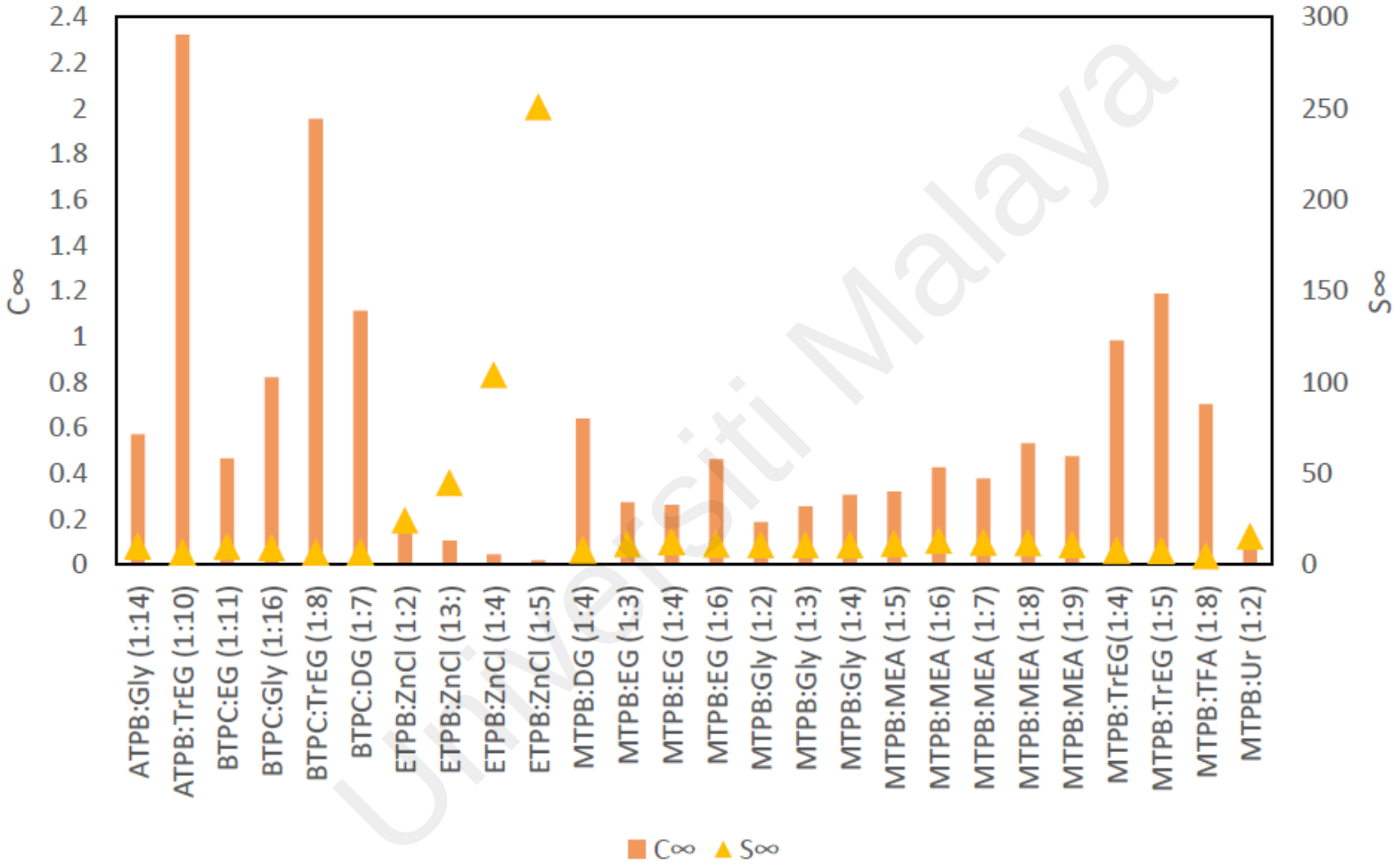


Figure 5: S^{∞} and C^{∞} for phenylphosphonium-based DES

Effect of DES combination towards S^{∞} & C^{∞} of Toluene

Factors	High S^{∞}	High C^{∞}
Salt cation	Tetrabutyl-based	Phenylphosphonium-based
Salt anion	Chloride	Bromide
HBD	Alcohol and amide functional group	Carboxylic acid and amino alcohol
Salt:HBD molar ratio	No significant effect	

Physical properties of DES

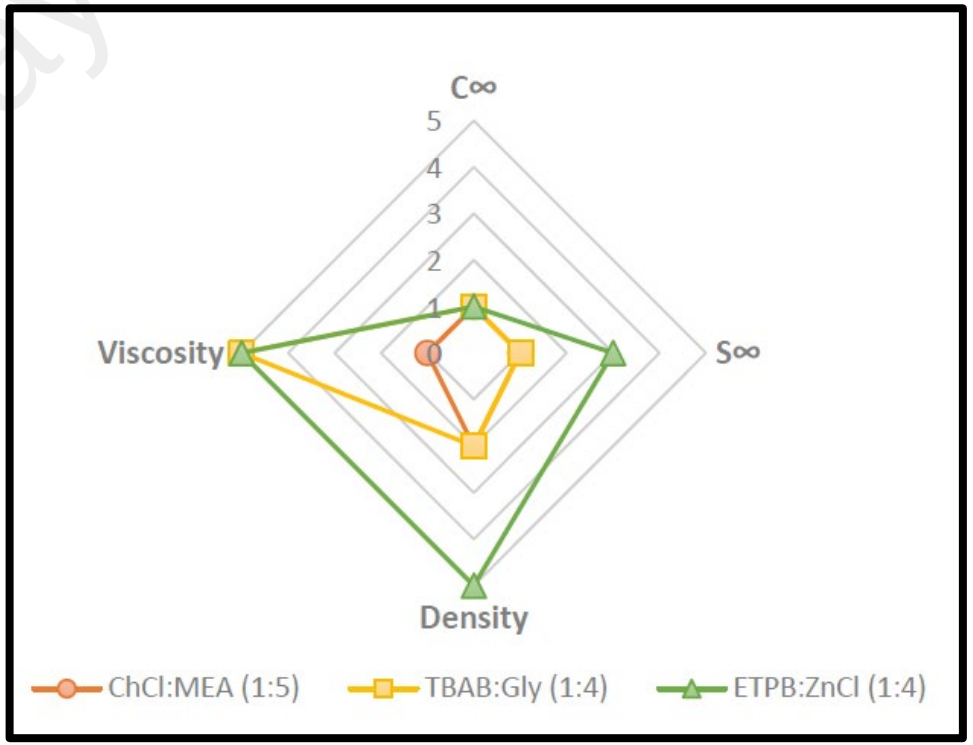
- From the literature, the physical properties of DES reported include density, viscosity, melting point, freezing point, conductivity, and surface tension.
- But not all properties are reported for all DES.
- COSMO-RS can only predict the density of ILs and DES. For viscosity, COSMO-RS can only predict pure compounds (e.g., conventional solvents and pure liquids).
- Viscosity can be predicted but with additional effort, e.g., using sigma as the input for other prediction methods e.g., Multiple Linear Regression (MLR)
- Melting temperature and eutectic temperature need additional calculations e.g., prediction of Gibbs energy of mixing.
- Thus, due to limited resources and time constraints, this work only screens DES based on available physical properties (S, C, density, viscosity).

Scoring sheet for selected criteria

Score	1	2	3	4	5
$C^{\infty}_{toluene}$	0 – 0.50	0.51 – 1.00	1.01 – 1.50	1.51 – 2.00	>2.01
S^{∞}	0 - 50	51 - 100	101 - 150	151 - 200	>200
Density (kg/m3)	0 – 0.60	0.61 – 1.20	1.21 – 1.80	1.81 – 2.40	>2.40
Viscosity (cP)	<100	>10 000	6601 – 10 000	3301 - 6600	101 - 3300

Recommended DES

- A comparative study of selected DESs is done by using spider-web analysis.
- DESs selected are ChCl:MEA (1:5), TBAB:Gly (1:4) and ETPB:ZnCl (1:4) who scored highest (70%), middle (45%) and lowest (25%) scores respectively.
- In terms of C∞, all DESs scored the lowest mark since their values are below 0.5. This depicts a higher solvent flowrate is required to extract toluene from the mixture and will affect the cost proportionally.
- ChCl:MEA (1:5) is not suitable for this separation process since it cannot fulfil the requirements for all criteria.
- For TBAB:Gly (1:4), it attained a high score for viscosity despite low marks are given in terms of capacity, selectivity and density.
- The most preferable DES for toluene-heptane separation process would be ETPB:ZnCl (1:4).
- Although the score for capacity is low, it fulfil the requirements for other criteria especially in terms of transport properties.



Conclusion and Recommendations

- 200 DES have been screened for their selectivity, capacity, density, and viscosity to recommend the ideal solvents for the separation of a toluene-heptane mixture
- It was found that the DES ETPB:ZnCl (1:4) is the most optimum solvent based on the selection criteria in this work.
- Selection of solvents should also include the cost associated with their recovery and regeneration.