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Effective selection of green organics and natural deep eutectic solvents as advanced entrainers by COSMO-RS and group contributions methods for enhanced design of extractive distillation

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Abstract

Green organic entrainers and natural deep eutectic solvents (NADESs) possessing high boiling points and decomposition temperatures, exhibit considerable potential as advanced materials for green entrainers in extractive distillation. However, there is a wide range of solvents to choose from and their properties are only rarely available for use in process design and simulation. The present study aims to assess the selection parameters and examine the performance of and select green organic entrainers and NADESs for the separation of the close boiling mixture methylcyclohexane-toluene. The evaluation carried out was based on selectivity and relative volatility values obtained by using predictive models. COSMO-RS (a unimolecular quantum chemical calculation) was employed to predict the selectivity at infinite dilution, while group contribution methods such as UNIFAC and modified UNIFAC (Dortmund) were used to predict the relative volatility. According to the calculated results, the selectivity appeared a more important selection parameter than the performance index. The relative volatility prediction using the UNIFAC and UNIFAC Dortmund methods exhibits comparable trends to the selectivity results derived from COSMO-RS. However, the use of UNIFAC and modified UNIFAC (Dortmund) in predicting the relative volatility of NADES containing mixtures is limited due to the absence of functional group parameters. This CAPE study reveals that, based on the calculated selectivity (using COSMO-RS) and relative volatility (using UNIFAC, and modified UNIFAC (Dortmund)), most of the proposed green organic entrainers and NADESs exhibit a higher or comparable selectivity and relative volatility as the benchmark entrainers. This confirms the potential of the evaluated green entrainers with higher selectivity and relative volatility to enhance the design of extractive distillation. Therefore, the cost, energy and water consumption, as well as CO₂ emissions in the methylcyclohexane and toluene separation can be reduced.

Keywords: COSMO-RS, group contribution method, green organic entrainers, natural deep eutectic solvents, extractive distillation.

1. Introduction

Distillation is the predominant separation method in the chemical industry due to its numerous advantages (Rico-Ramírez and Diwekar, 2000). However, conventional distillation technology requires high energy consumption, consumes cooling water, incurs considerable costs, and generates significant amounts of CO₂ emissions, particularly when employed for the separation of close-boiling or azeotropic mixtures. Therefore, the utilization of extractive distillation (ED) along with the incorporation of entrainers is frequently employed to overcome the difficulty of the separation. Entrainers can provide interaction with a certain component, hence increasing its relative volatility and thereby facilitating separation. As a result, entrainers can decrease the energy, cost, and water consumption, as well as the emissions of CO₂ in the process. The selection of an entrainer has become a crucial stage in determining the most viable entrainer for the extractive distillation process because the performance of the entrainer determines the design and effectiveness of the extractive distillation process. The most common entrainers used are called conventional organic entrainers such as *n*-methyl pyrrolidone (NMP) and sulfolane. Nevertheless, these entrainers possess several disadvantages, including volatility, toxicity, lack of environmental friendliness, unsustainability, non-biodegradability, high energy consumption, and prohibition under regulations (George Wypych, 2019). Thus, the search for alternative entrainers that possess more environmentally friendly characteristics has acquired significant interest in recent years. Greener entrainers must exhibit additional features such as sustainability, low or non-toxicity, biodegradability, eco-friendliness, and/or derivatives from bio-based materials (Yilmaz and Soylak, 2020). Some of greener entrainers such as ionic liquids, and bio-based entrainers such as Cyrene and glycerol have been studied (Ayuso et al., 2022; Brouwer & Schuur, 2021; and Hartanto et al., 2021). However, industrial-scale utilization of ionic liquids is constrained by their excessive cost, hazardous proclivity, and its limited biodegradability (Costa et al., 2017). In addition, some of bio-based entrainers have limitations due to their low boiling points and/or low decomposition temperatures. In this work, green organic entrainers and NADESs with a high boiling point, a high decomposition temperature, and green characteristic(s) are studied as improved and intensified entrainers. Selection parameters such as selectivity, capacity, and performance index are evaluated. The performance of each entrainers in methylcyclohexane-toluene mixture is examined using selectivity and relative volatility calculated by predictive models. COSMO-RS as a unimolecular quantum chemical calculation, is used to predict the activity coefficient at infinite dilution, while group contributions method such as UNIFAC and modified UNIFAC (Dortmund) is employed to calculate the relative volatility at finite dilution.

2. Methods

2.1. COSMO-RS simulation

The study utilized the COSMOthermX17 program (version C30_1705), which is based on the COSMO-RS concept, to compute the thermophysical properties of individual components and mixtures. Turbomole (version 7.1.1) was employed to optimize new compounds and generate their COSMO files. The COSMO-RS calculation was performed using the BP_TZVP_C30_1701 method with the COMSO density functional theory (DFT) parameterization to estimate the thermophysical properties.

2.2. Group contribution methods (GCMs) simulation

GCMs employ different methodologies for computing molecular interactions compared to COSMO-RS. GCMs are semi-empirical approaches that rely on the optimal binary

interaction parameter of the segments obtained from empirical fitting. This study utilizes the original UNiVersal Quasichemical Functional-group Activity Coefficients (UNIFAC) and the modified UNIFAC (Dortmund).

3. Results and discussion

3.1. Evaluation of selectivity, capacity, and performance index

As selection parameters, selectivity, capacity, and performance index can be utilized to identify the most efficient entrainer. Selectivity (S) stands for the capability of an entrainer to selectively interact with a particular compound over another. Capacity (C) refers to the amount of entrainer required for the extractive distillation process. While Performance Index (PI) is expressed as the combination of selectivity and capacity (Jiang et al., 2019). The infinite dilution (∞) method, which focuses on the solute-solvent interaction towards pure solvent, can be employed to achieve the maximum effect of interaction. It is crucial to assess the effectiveness of each selection parameter prior to identifying the parameter that can be used as a deciding factor. Figure 1 demonstrates a clear inverse relationship between selectivity and capacity for methylcyclohexane-toluene mixture with the addition of green organic entrainers and NADESs. It shows that increased selectivity results in decreased capacity, and conversely. Therefore, the performance index was examined to combine selectivity and capacity.

The performance index in the methylcyclohexane-toluene mixture exhibits an inverse correlation with selectivity but demonstrates a tendency to align with capacity. Thus, the capacity has a greater impact on the performance index compared to selectivity. It can be inferred that the performance index may exhibit a varying profile in relation to selectivity, or that the capacity depends upon the selectivity value. A higher selectivity value will have a greater impact on the performance index. In order to have a more comprehensive understanding of the extractive distillation performance, it is necessary to conduct further evaluations by process design. This should be done instead of solely relying on the performance index as the sole determinant for selecting an entrainer.

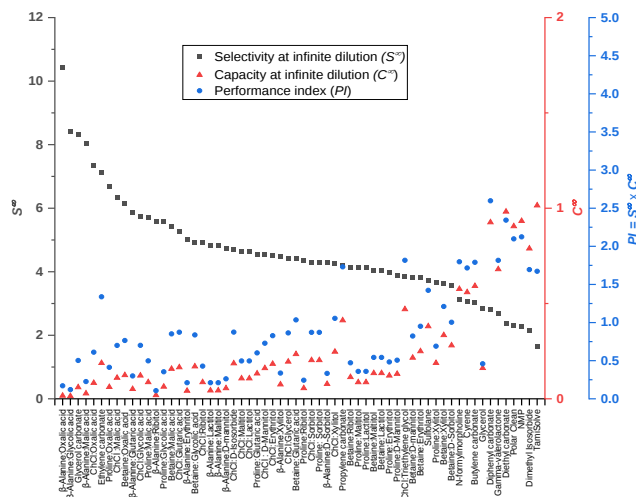


Figure 1. Selectivity, capacity, and performance index prediction of entrainers in methylcyclohexane - toluene mixture at temperature of 400 K.

However, to simulate the process design for all investigated entrainers will take a lot of time and effort. Therefore, this study recommends using selectivity as entrainer selection parameters as it has the most significant effect on the total annual cost calculation. Entrainers with higher selectivity will consistently yield a lower total annual cost and conversely (Momoh, 1991). Some researchers also confirm that selectivity plays a crucial role in determining the selection of entrainer for extractive distillation (Kyle & Leng, 1965; Krummen et al., 2000; Jiménez & Costa-López, 2003; Gutiérrez et al., 2012; and Sun et al., 2019).

3.2. Selectivity for methylcyclohexane-toluene

Selectivity can be calculated from the ratio of the activity coefficient. The activity coefficient at infinite dilution as a representation of the interaction between the solute and solvent is influenced by temperature, which subsequently impacts the selectivity. This study involved the assessment at two temperatures, specifically 293 K and 400 K, to represent conditions of low and high temperature, respectively. In general, the selectivity profiles for both temperatures are similar, as illustrated in Figure 2. However, increasing the temperature will decrease the molecule's interaction, leading to a decrease in non-ideality and hence a decrease in selectivity. This is consistent with the experimental results, which indicate that the activity coefficient at infinite dilution decreases with increasing temperature (Nkosi et al., 2018). For entrainer selection, the selectivity at 400 K is preferred because it more accurately represents the temperature that occurs during extractive distillation. Figure 2 reveals that the toluene-entrainer activity coefficient at infinite dilution is lower than that for methylcyclohexane-entrainer.

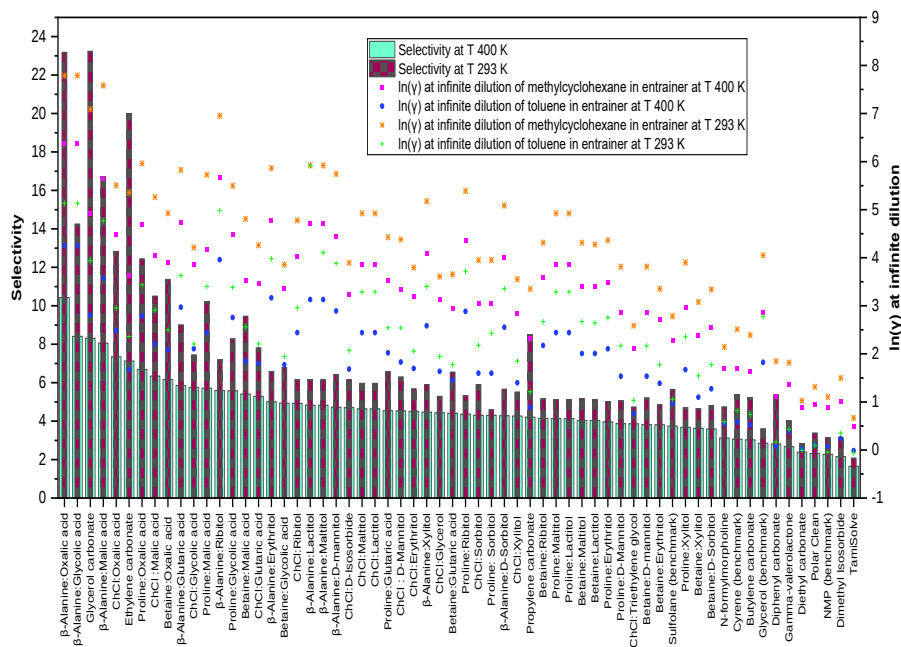


Figure 2. Selectivity prediction of entrainers at different temperatures for methylcyclohexane-toluene mixture and $\ln(\gamma)$ at infinite dilution for methylcyclohexane and toluene in entrainer.

This indicates that the entrainer exhibits more interaction with toluene compared to methylcyclohexane. This figure also demonstrates that the selectivity of nearly all NADESs and green organic entrainers is better or comparable with that of benchmark entrainers, indicating that green organic entrainers and NADESs can be potentially applied to extractive distillation to replace conventional organic entrainers.

3.3. Relative volatility of methylcyclohexane-toluene

Relative volatility predictions were conducted to analyze the separation behavior in the methylcyclohexane-toluene mixture when entrainers were added. This was performed using a real solution at finite dilution to simulate an actual condition in the industrial process. Figure 3 shows the relative volatility of methylcyclohexane-toluene mixture with the addition of green organic entrainers, as predicted by UNIFAC and modified UNIFAC (Dortmund). The relative volatility profile predicted by UNIFAC exhibits a comparable behavior to the results calculated by modified UNIFAC (Dortmund). Furthermore, the relative volatility profile exhibits comparable tendencies with selectivity, as predicted by COSMO-RS. It can be observed that all green organic entrainers enhance the relative volatility, hence enabling the separation of methylcyclohexane from toluene. However, both UNIFAC and modified UNIFAC (Dortmund) models have a limitation because these models are unable to estimate the relative volatility of mixtures when NADESs are added since the required functional group parameters are not available.

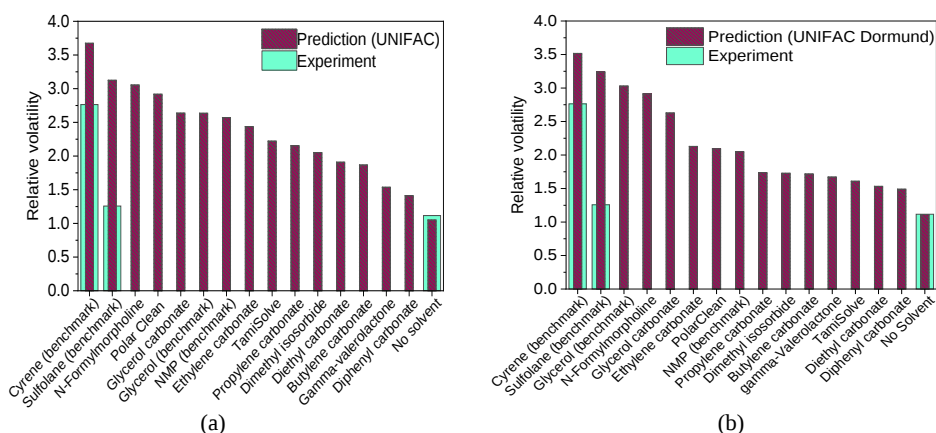


Figure 3. Relative volatility prediction by: (a) UNIFAC and (b) UNIFAC Dortmund for methylcyclohexane (90 mol%) + toluene (10 mol%) mixture with the addition of green organic and benchmark entrainers (Entrainer mass fraction (w_3) = 0.5) at $P = 101$ kPa. Experimental data obtained from Brouwer & Schuur, 2021.

4. Conclusions

This work showed that selectivity can be chosen as a more significant parameter for selecting an entrainer compared to capacity or performance index. Based on calculated selectivity by COSMO-RS and relative volatility by UNIFAC and modified UNIFAC (Dortmund), most green organic entrainers and NADESs exhibit better or equivalent selectivity and relative volatility performance as the benchmark entrainers in the separation of methylcyclohexane and toluene. However, the UNIFAC and modified UNIFAC (Dortmund) property models cannot be used to predict the relative volatility containing NADESs due to the unavailability of the functional group parameters. The

utilization of green organic entrainers and NADESs with higher selectivity and relative volatility can enhance the design of extractive distillation. Hence, it is possible to reduce costs, energy and water consumption, and CO₂ emissions.

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