Computer-aided design and process evaluation of ionic liquids for *n*-hexane-methylcyclopentane extractive distillation

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ABSTRACT

Ionic liquids (ILs) are highly attractive entrainers for separating close-boiling alkane-cycloalkane mixtures in extractive distillation processes while studies on this particular topic are still scarce. This work employs computer-aided molecular design (CAMD) and process simulation to identify suitable ILs for the extractive distillation of *n*-hexane-methylcyclopentane, a representative alkane-cycloalkane mixture. A large number of experimental data on the infinite dilution activity coefficient of methylcyclopentane and vapor-liquid equilibria of relevant systems are collected from literature to validate the reliability of the employed UNIFAC-IL model, which is the basis of CAMD and process simulation. Combining the UNIFAC-IL model and two group contribution models of IL physical properties, a mixed integer nonlinear programming (MINLP) problem is then formulated for the CAMD of ILs. The top IL candidates pre-identified from MINLP-CAMD are further introduced into Aspen Plus for process simulation and evaluation. By comparing their process performances with the benchmark solvent *N*-methyl-2-pyrrolidinone, 1-nonyl-imidazolium thiocyanate ([C$_9$Im][SCN]) is consequently identified as the optimal entrainer.

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1. Introduction

n-Hexane as a broad-spectrum petrochemical product is widely used in the chemical, pharmaceutical, and food industry. Generally, it is produced from raffinate oils composed of C6 alkane mixtures (*e.g.*, 6# solvent oil), where the separation of *n*-hexane (boiling point 341.88 K) and methylcyclopentane (boiling point 344.96 K) represents one of the most challenging tasks. Currently, the *n*-hexane-methylcyclopentane separation is mainly achieved by distillation, molecular sieve adsorption or extractive distillation. However, due to their very close boiling points, distillation is very energy- and cost-intensive, and even unrealistic to obtain high purity products. Molecular sieve adsorption suffers from poor capacity and difficulties in regeneration of adsorbent. Compared to the above methods, extractive distillation is an energy- and cost-efficient option because of the enhanced relative volatility of *n*-hexane to methylcyclopentane in the presence of an additional solvent (namely entrainer or separating agent) [1–4]. Moreover, the product purity can be adjusted through different solvent to feed ratios. Therefore, extractive distillation is widely regarded as the most promising technique for the separation of *n*-hexane-

methylcyclopentane mixture and other close-boiling hydrocarbon mixtures in petrochemical engineering.

The technical and economic feasibility of a specific extractive distillation process strongly relies on the selection of a suitable entrainer. So far, several conventional organic solvents, *e.g.*, dibutylphthalate (DBP), *N*-methyl-2-pyrrolidinone (NMP) and *N*,*N*-dimethylformamide (DMF) have been tested as the entrainer for *n*-hexane-methylcyclopentane separation. However, for such extractive distillation processes, several disadvantages still exist as follows: (a) These organic solvents may bring about consequent safety and environmental problems because of their toxicity, flammability, and volatility. (b) Poor capacity and selectivity lead to either a large number of column stages or high solvent demand. (c) Due to the presence of entrainer at the top and/or bottom of the extraction column, complex regeneration units are also required in these processes. Taking into account of all these disadvantages, the selection of more effective and environmental-friendly alternatives to these organic solvents are highly desirable.

In the past decade, ionic liquids (ILs) have attracted significant attention of chemical engineering community due to their unique physical and chemical properties, such as non-volatility, non-flammability, high thermal/chemical stability, wide liquid range, and so on [5,6]. More importantly, the properties of ILs can be fine-tuned by judicious combination of cation, anion, and substitution groups, which make them particularly promising entrain-

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ers for extractive distillation. In the early 2000s, Lei et al. proposed the technology of extractive distillation with ILs and reported the VLE data of ternary systems (cyclohexane + toluene + [BMIm][BF$_4$], ([BMIm][PF$_6$], and [BMIm][AlCl$_4$]) for the first time [1]. Since then, numerous studies on IL-based extractive distillation for polar-polar (e.g., alcohol-water, alcohol-ester), polar-nonpolar (e.g., alcohol-aliphatic hydrocarbon) and nonpolar-nonpolar systems (e.g., alkane-alkene, aliphatic-aromatic hydrocarbon) have been carried out [7–12]. However, reports on the separation of alkane-cycloalkane, such as the highlighted n-hexane-methylcyclopentane, using extractive distillation, are rarely available by far.

For IL-based extractive distillation, the separation performance of ILs largely depends on their cation and anion structures [13–15]. Moreover, suitable IL entrainers also vary greatly from system to system. That is to say, it is very crucial to select proper ILs according to the characteristics of different systems. Most studies of IL selection strongly depend on laboratory experiments. However, considering the huge number of possible cation-anion combinations, such experimental approach is time-consuming, expensive, and in most cases unrealistic to obtain the optimal solvent. Therefore, in this respect, efficient and reliable theoretical methods for IL screening or design are of great significance [16].

Ab initio methods, the classical activity coefficient models (e.g., NRTL, UNIQUAC) and equation-of-state methods have been used to investigate the thermodynamic properties of IL-involved systems. However, these methods require either expensive computational cost or a number of molecule-specific parameters regressed from experimental data, making them unsuitable for extensive screening of ILs from a large number of potential candidates. The COSMO-RS model developed by Klamt et al. is a novel alternative for calculating thermodynamic properties of pure-component liquids and liquid mixtures, including IL systems [17,18]. It is fully predictive since it only requires the screening charge density distributions (σ-profiles) of involved compounds, which can be obtained by standard quantum chemical calculations. For this reason, the COSMO-RS method has been widely applied to guide IL selection for various separation applications, e.g., separation of aromatic and aliphatic hydrocarbons, extractive desulfurization and CO$_2$ capture, etc. [19–23]. Nevertheless, there still exists large space for development of current σ-profile database and improvement in the quantitative accuracy of the COSMO-RS model [24].

In recent years, several research groups have extended UNIFAC models to IL systems, among which Lei et al. reported the completest one by far (covering 49 IL main groups and 19 conventional main groups) [25–27]. Since the group binary interaction parameters are determined by fitting experimental data, the quantitative prediction performance of the UNIFAC-IL models can always be ensured [28,29]. The group contribution (GC) character of the UNIFAC-IL enables them to be easily incorporated into a computer-aided molecular design (CAMD) framework for IL design [10,29–37]. Moreover, the computation speed of the UNIFAC-IL model is very quick and the model parameters can be readily input into process simulators (e.g., Aspen Plus and PRO-II) for further process design and optimization. Consequently, CAMD of ILs based on UNIFAC-IL is very promising for the accurate identification of suitable ILs for separation tasks. So far, a number of reports on UNIFAC-IL based CAMD of ILs have been published. These studies are mainly restricted to alcohol-water extractive distillation, aromatic-aliphatic extraction and CO$_2$ capture processes. Very few of them have taken the advantages of UNIFAC-IL for process evaluation to directly identify optimal entrainer from process point of view [11,27–29]. To the best of our knowledge, there is still a lack of report on the CAMD of ILs for alkane-cycloalkane separation.

In this contribution, a systematic study integrating CAMD and process evaluation is presented to identify suitable ILs for n-hexane-methylcyclopentane extractive distillation. The whole paper is organized as follows: Section 2 preliminarily validates the employed UNIFAC-IL model for CAMD and process simulation. Section 3 formulates the mixed integer nonlinear programming (MINLP) problem for CAMD and pre-identifies a list of potential IL candidates for n-hexane-methylcyclopentane separation. Section 4 compares the performances of the top IL candidates in n-hexane-methylcyclopentane extractive distillation process to identify the process-based optimal entrainer. Section 5 briefly summarizes this work.

2. UNIFAC-IL model validation

Since UNIFAC-IL model is the basis of the subsequent CAMD and process simulation, its predictive reliability for the studied n-hexane-methylcyclopentane system should be evaluated firstly. As mentioned above, several versions of the original UNIFAC model for ILs that are distinct from one another in the IL group decomposition approach and the model development database, are now available in literature [25–28]. Here, the UNIFAC-IL model extended by our group very recently [29] is selected due to the following two aspects: (a) The database for fitting the group binary interaction parameters in this UNIFAC-IL model is majorly composed of different fuel hydrocarbons including alkanes (n-hexane, n-heptane, n-octane) and cycloalkanes (cyclopentane, cyclohexane, cycloheptane), which matches exactly the characteristic of the studied n-hexane-methylcyclopentane system. (b) ILs are divided into several groups and the cation skeleton as a separate functional group [25–27]. Such an IL group decomposition approach can lead to a larger space and better flexibility for IL design.

In our previous work on extension of UNIFAC-IL model [29], the mean absolute average error (MAPE, as defined in Eq. (1)) between the experimental and correlated infinite dilution activity coefficient (γ^∞) in the model development data set was found to be 10.05%, 26.82% and 32.28% for aromatics, alkanes and cycloalkanes (overall 3248 data points), respectively. The reason that the overall deviation for alkanes/cycloalkanes is almost threefold than that of aromatics may derived from the different ranges of their γ^∞: aromatics (0.43–23.69), alkanes (1.03–1016.00), cycloalkanes (1.17–322.13). The values of MAPEs would be noticeably influenced or biased by outlying data. As well as, according to Paduszyński's very recent research, a similar phenomenon has been found when using the COSMO-RS method to predicted γ^∞ of hydrocarbon in ILs [24].

$$MAPE = \frac{1}{N_d} \sum_i^{N_d} \left| \frac{\gamma_i^{\infty,exp} - \gamma_i^{\infty,cal}}{\gamma_i^{\infty,exp}} \right| \qquad (1)$$

$\gamma_i^{\infty,exp}$ and $\gamma_i^{\infty,cal}$ represent the experimental and calculated γ^∞ of solute i in IL, and N_d is the total number of data points. Moreover, the root mean square deviation (RMSD, as defined in Eq. (2)) between experimental and calculated liquid-liquid equilibria of 131 {IL + aromatic + alkane/cycloalkane} systems in the model validation data set was demonstrated to be in the range of 0.0009–0.0994 with an average of 0.0340.

$$RMSD = \left\{ \sum_i \sum_p \sum_t (x_{ipt}^{exp} - x_{ipt}^{cal})^2 / 6N_t \right\}^{1/2} \qquad (2)$$

Where the subscripts i, p, and t denote the component, the phase and the tie-line, respectively; N_t represents the total number of the tie-lines. These findings generally indicate the very good reliability of the UNIFAC-IL model for the n-hexane-methylcyclopentane system. Nevertheless, the predictive ability of