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Separation of 1-hexene and *n*-hexane with ionic liquids

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Abstract

This work deals with the separation of 1-hexene and *n*-hexane as the representation of olefins and paraffins with ionic liquids, as well as *N*-methyl-2-pyrrolidone (NMP) screened by computer-aided molecular design (CAMD). On the basis of conformation analysis of solvents and ionic liquids, the conductor-like screening model for real solvents (COSMO-RS) was used to make a priori prediction for suitable ionic liquids. It was found that the suitable ionic liquids should have small molecular volume, unbranched group and sterical shielding effect around anion charge center. Headspace-gas chromatography (HSGC) experiments were done at 313.15 and 333.15 K. It was verified that the anion with sterical shielding effect around anion charge center is favorable for increasing the selectivity, and $[C_8Chin]^+[BTA]^-$ is the best among all the ionic liquids investigated. The separation mechanism of olefins and paraffins with ionic liquids can be explained by the theory of Prausnitz and Anderson's solution thermodynamics. This work also can be extended to the separation of other hydrocarbons with ionic liquids since the separation mechanism between *n*-hexane/1-hexene and other hydrocarbons is consistent.

Keywords: 1-Hexene/*n*-hexane; Ionic liquids; Extractive distillation; COSMO-RS model; Separation; Prausnitz and Anderson's solution thermodynamics

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1. Introduction

Separation of olefins and paraffins is a specific problem in the field of hydrocarbon processing. Since the boiling points of olefins and paraffins lie within narrow temperature ranges, it is difficult and expensive to separate them by conventional distillation. There are five methods put forward for this purpose: extraction with high pressure CO_2 [1], adsorption [2,3], liquid–liquid extraction [4], membrane/extraction hybrid [5,6] and extractive distillation [7]. Among them, the extractive distillation process is simple and can deal with large amount of feedstock. But it requires the addition of a third component, entrainer that modifies the relative volatilities of paraffins to olefins. So it is evident that selection of a suitable solvent is very important to ensure an effective and economical design of extractive distillation.

Up to date, there are four kinds of entrainers used in extractive distillation, i.e. solid salts, liquid solvents, the mixture of liquid solvents and solid salts, and ionic liquids [8–15]. Organic high boiling liquids and dissolved salts are suitable entrainers. But extractive distillation with a single liquid entrainer is more widely used in industry. However, ionic liquids as the entrainers comprise advantages of both liquid solvents and solid salts [15]. So it is interesting for us to study extractive distillation with ionic liquids.

The conductor-like screening model for real solvents (COSMO-RS) can be used for evaluating the ionic liquids as the entrainers in extractive distillation. It is a novel and efficient method for the priori prediction of thermophysical data of liquids, and has been developed since 1994. The details about the COSMO-RS model are described in Refs. [16–20].

In this work, 1-hexene and *n*-hexane are taken on as the representation of olefins and paraffins, respectively, because the separation mechanism is consistent and 1-hexene is a high value-added product in industry. Ionic liquids, as well as the liquid solvents (except ionic liquids) screened by computer-aided molecular design (CAMD), are used as the entrainers for this system. The aim is to find the best entrainer. The experimental results at finite dilution are compared with the calculated results at infinite dilution by the COSMO-RS model in order to qualitatively verify the reliability of calculation.

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The theory of Prausnitz and Anderson's solution thermodynamics can be used to explain why ionic liquids are effective for separating olefins and paraffins and which ionic liquid is more favorable for this separation [21]. In terms of this theory, the mechanism for separating olefins and paraffins by extractive distillation is based on the different mobility of the electron cloud of C–C (no double bond), C=C (double bond) and thus different interaction between solvent and the component to be separated. The greater the mobility is, the easier the group is to be polarized by polar solvent. The mobility of electron cloud of C=C bond is larger than that of C–C bond so that *n*-hexane is brought out as a light component and 1-hexene as a heavy component (although the boiling point of *n*-hexane (341.9 K) is a little higher than that of 1-hexene (336.6 K)). That is, *n*-hexane would be obtained as the overhead product in extractive distillation column, 1-hexene and the solvent being the bottom product. This theory is always emphasized in our previous publications. The work of Prof. J.M. Prausnitz affects our research in the field of separation processes until now.

2. Calculation of CAMD and COSMO-RS model

2.1. CAMD

In order to compare the separation ability between ionic liquids and traditional liquid solvents, computer-aided molecular design is used as a tool to screen the best traditional liquid solvents (except ionic liquids) rapidly. As we know, it is tiresome to choose the best solvent from thousands of different substances for a given system through experiments. CAMD developed in the 1980s may break new ground in this aspect by largely reducing the amount of experimental work. The detailed calculation procedure has been described in our previous publications [22].

The prediction methods for explicit properties [23–25] are given in Table 1. The restrictions for entrainers in CAMD are listed as follows:

Table 1
Explicit properties estimation for screening liquid solvents (except ionic liquids)

Properties	Methods
Relative volatility at infinite dilution	$\alpha_{ij}^{\infty} = \frac{\gamma_i^{\infty} P_i^0}{\gamma_j^{\infty} P_j^0}$
Selectivity at infinite dilution	$S_{ij}^{\infty} = \frac{\gamma_i^{\infty}}{\gamma_j^{\infty}}$
Solubility capacity (the influence of molecular weight considered)	$\mathrm{SP} = \frac{1}{\gamma_1^{\infty}} \frac{\mathrm{MW}_1}{\mathrm{MW}_s}$
Molecular weight	Pure component data bank or by adding group parameters
Normal boiling point	Pure component data bank or by adding group parameters
Critical properties	Pure component data bank or Joback method
Vapor pressure	Antoine equation or Riedel equation
Azeotropic judgement	By drawing the curves of *x* (mole fraction in the liquid phase)–*y* (mole fraction in the vapor phase) to judge

(a) pre-selected group types: CH_3, CH_2, CH_3COO, CH_3CO, COOH, OH, CH_2CN, CH_2NH_2, H_2O, CH_3OH, $(CH_2OH)_2$, acetonitrile (ACN), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), Morpholine (Morph), Furfural;
(b) expected group numbers: 1–6;
(c) maximum molecular weight: 5000;
(d) minimum boiling point: 383.15 K;
(e) maximum boiling point: 503.15;
(f) minimum relative volatility at infinite dilution (refer to Table 1 for definition): 1.40;
(g) minimum solubility capacity (refer to Table 1 for definition): 0.10;
(h) for the additive added to a main entrainer, its concentration 10 wt%.

The calculation was done at temperature of 303.15 K. The design results are obtained by means of CAMD and listed in order of decreasing relative volatility at infinite dilution (see Table 2). It seems that for single solvent, the solvent with molecular structure of CH_3COO-CH_2-CH_2NH_2 (no. 1) produces the largest relative volatility of *n*-hexane to 1-hexene, but it is difficult to be sought in chemical markets. Therefore, the remaining NMP (no. 2) is regarded as the potential solvent. For solvent mixture, the separation ability of the mixture of NMP and water (10 wt%) is higher than pure NMP. However, water forms azeotrope with *n*-hexane and 1-hexene, respectively. From this viewpoint, it is better to use pure NMP.

2.2. COSMO-RS model

COSMO-RS model can be used to evaluate the separation ability of ionic liquids. The calculation procedure of COSMO-RS model is depicted in Fig. 1. It is composed of three steps: conformational analysis, conductor-like screening model (COSMO) calculation and COSMO-RS calculation [26].

The conformational analysis was carried out using the molecular modeling program HyperChem. This program was also used to generate the molecular structures. It was assumed that single molecules and ions were in a vacuum, and their potential energies are calculated with the semi-empirical PM3 methods.

For further considerations in subsequent COSMO-RS model, the screening charges of molecular structures obtained from the conformational analysis have to be available. For this purpose, quantum chemical continuum solvation models (CSM) are applied. Since the dielectric boundary conditions for arbitrary shaped cavities are very complex, the COSMO model employs an ideal conductor as the dielectric medium. This approach results, compared with other CSM, in simplified boundary conditions and therefore highly efficient algorithms. So far the COSMO model is implemented in the programs Turbomole, Gaussian, DMOL3 and MOPAC applying either density functional theory or semi-empirical methods. In this work the calculation of molecular energies was accomplished using the TZVP basis set and BP function. As the result of COSMO calculation, a "COSMO" file is generated. This file delivers all information of the respective molecular or ionic structure that is necessary