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Selection of entrainers in the 1-hexene/*n*-hexane system with a limited solubility

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Abstract

Vapor-liquid equilibria (VLE) have been measured for five 1-hexene/*n*-hexane/ionic liquid systems and 1-hexene/*n*-hexane/NMP (*N*-methyl-2-pyrrolidone) system with a headspace-gas chromatography (HSGC) apparatus at 333.15 K. The ionic liquids investigated were 1,3-dimethylimidazolium tetrafluoroborate $[C_2MIM]^+[BF_4]^-$, 1-butyl-3-methylimidazolium tetrafluoroborate $[C_4MIM]^+[BF_4]^-$, 1-methyl-3-octylimidazolium tetrafluoroborate $[C_8MIM]^+[BF_4]^-$, 1,3-dimethylimidazolium dicyanamide $[C_2MIM]^+[N(CN)_2]^-$ and 1-octylquinolinium bis(trifluoromethylsulfonyl)amide $[C_8Chin]^+[BTA]^-$. It was found that at low feeding concentration of 1-hexene and *n*-hexane, the separation ability of ionic liquids is in the order of $[C_2MIM]^+[BF_4]^- > [C_4MIM]^+[BF_4]^- \approx [C_2MIM]^+[N(CN)_2]^- > [C_8MIM]^+[BF_4]^- > [C_8Chin]^+[BTA]^-$, which is consistent with the priori prediction of the COSMO-RS (conductor-like screening model for real solvents) model. But at high feeding concentration, the separation ability of ionic liquids is in the order of $[C_2MIM]^+[BF_4]^- < [C_4MIM]^+[BF_4]^- \approx [C_2MIM]^+[N(CN)_2]^- < [C_8MIM]^+[BF_4]^- < [C_8Chin]^+[BTA]^-$. The liquid demixing effect should be taken into account. The activity coefficients of 1-hexene and *n*-hexane at infinite dilution calculated with the COSMO-RS model were correlated using the NRTL, Wilson and UNIQUAC model. In this work the predictive results from the COSMO-RS model and UNIFAC model for the 1-hexene/*n*-hexane and 1-hexene/*n*-hexane/NMP systems were compared. The UNIFAC model is one of the most important academic contributions by Prof. Jürgen Gmehling.
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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. In this work, 1-hexene and *n*-hexane are taken to represent olefins and paraffins, respectively, because the separation mechanism is consistent and 1-hexene is a high value-added product in industry. Ionic liquids are used as the entrainers for this system. 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 [7,16]. Among them, the extractive distillation process is simple consisting of a main column and a regeneration unit, and can deal with a large amount of feedstock. But this process requires the addition of a third component, the entrainer that modifies the relative volatilities of paraffins to olefins. The entrainer does not need to be vaporized in the extractive distillation process. 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 [8–16]. 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 both advantages of liquid solvents and solid salts

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[15–20]. So it is wise to use extractive distillation with ionic liquids as the entrainers for the separation of 1-hexene and *n*-hexane.

In the process simulation of extractive distillation the VLE model is the key in order to solve the traditional equilibrium stage model (MESH equation) of the distillation column. For a better understanding of their thermodynamic behavior and for the development of thermodynamic models, reliable experimental phase equilibrium data are required. Therefore, this work presents results of a part of our research work in the field of ionic liquids. In our previous paper [16], the selectivity of *n*-hexane to 1-hexene using 39 kinds of ionic liquids at finite dilution where $x_{entrainer} = 0.3$ at 313.15 and 333.15 K was reported. However, the influence of concentration on selectivity was not investigated, and a suitable thermodynamic model in which the parameters can be directly input into some commercial process simulation softwares (e.g. ASPEN Plus and PROII) was not established.

For this purpose, the selectivity at different feeding concentrations was measured for five 1-hexene/*n*-hexane/ionic liquid systems with a headspace-gas chromatography (HSGC) apparatus at 333.15 K. The activity coefficients of 1-hexene and *n*-hexane at infinite dilution obtained from the COSMO-RS model were correlated using the NRTL, Wilson and UNIQUAC models [7,21]. In addition, the 1-hexene/*n*-hexane/NMP (*N*-methyl-2-pyrrolidone) system was also investigated because NMP is a liquid solvent commonly used in the separation of hydrocarbon mixtures.

Both the COSMO-RS model and UNIFAC model can be used for predicting activity coefficients. The UNIFAC model is based on the contributions of the constituent groups in a molecule and relies on experimental data. But group parameters of the ionic liquid cannot be found in the present parameter table of the UNIFAC model. In this case the COSMO-RS model can be used as an alternative to the UNIFAC model. The COSMO-RS model 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 [22–28]. In this work the comparison of the predictive results from the COSMO-RS and UNIFAC models was also made for the 1-hexene/*n*-hexane and 1-hexene/*n*-hexane/NMP systems. In this work the original UNIFAC model was adopted [29–33]. The UNIFAC model is one of the most important academic contributions by Prof. Jürgen Gmehling. His work affects our research in the field of molecular thermodynamics and special distillation processes until now.

2. Experimental

2.1. Materials

The volatile solvents *n*-hexane (purity ≥ 95.0 wt.%, product number: 1.04368.2500, manufactured by Merck AG), 1-hexene (purity ≥ 96.0 wt.%, product number: 52940, manufactured by Fluka Chemie AG) and *N*-methyl-2-pyrrolidone (NMP, purity ≥ 99.0 wt.%, product number: 69118, manufactured by Fluka Chemie AG) were used as received.

Before use, all ionic liquids were dried almost 1 week under vacuum at 323–343 K to remove volatile impurities. The ionic liquids were supplied with a purity of at least 98% by solvent-innovation and BASF AG. The density of ionic liquids was determined with density meter (DMA 5000, Anton Paar) at 298.15 K.

2.2. Experimental apparatus

In this work "headspace - gas chromatography" (HSGC) (GC Clarus 500 and headspace sampler TurboMatrix 40, Perkin-Elmer instruments) was used for measuring the selectivity of *n*-hexane to 1-hexene in five kinds of ionic liquids as well as the liquid solvent NMP for different concentrations at 333.15 K. Samples of different liquids (6 ml) were filled into vials (capacity 15 ml) and sealed with polymer septa. The headspace settings were optimized as follows: equilibration time 60.0 min, injection volume 0.01 ml, injection pressure 200.0 kPa, pressurized time 3 min, GC cycle time 22 min, withdraw time 0.1 min, needle temperature 393.15 K and transfer line temperature 393.15 K. Thus, the compositions in the vapor and liquid phases at constant temperature can be measured. The reproducibility of the experimental results was ensured by means of at least two independent sampling. The details about this apparatus are described in our previous publications [16].

3. Results and discussion

The selectivity provides a useful index for selection of suitable entrainers, which is defined as

$$S_{12} = \frac{\gamma_1}{\gamma_2} = \frac{P_2^0 y_1 x_2}{P_1^0 y_2 x_1} \tag{1}$$

where γ_1 and γ_2 are activity coefficients of *n*-hexane (light component) and 1-hexene (heavy component) in ionic liquids, respectively. So we can deduce the selectivity from the compositions in the vapor and liquid phases.

At infinite dilution, it becomes

$$S_{12}^\infty = \frac{\gamma_1^\infty}{\gamma_2^\infty} \tag{2}$$

which represents the maximum selectivity. The selectivity at infinite dilution is obtained from the calculation using the COSMO-RS model, while the selectivity at finite dilution from the experiment and COSMO-RS model.

But at the same time solvent capacity (SP) is also an important index and should be considered. Solvent capacity at infinite dilution is defined as

$$SP = \frac{1}{r_1^\infty} \tag{3}$$

Firstly, VLE of the 1-hexene (1)/*n*-hexane (2) system at 333.15 K was measured as shown in Fig. 1. The experimental data were compared with the calculated results by the COSMO-RS and UNIFAC models and good agreement was found. It was verified that the experimental data from our HSGC were reliable. Moreover, the VLE curve is close to the *x*–*y* diagonal,