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Ionic liquids as separating agents in extractive rectification

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ABSTRACT

This article presents extractive rectification of binary mixtures. The choice of extractive agents was made from a set of well-known separating agents with ionic liquids. Gas–liquid chromatography was used to estimate the separating agent selectivity. Vapour–liquid equilibrium mathematical modelling was used to predict the quality of the product. The applicability of ionic liquids in extractive rectification of different binary azeotropic mixtures (both positive and negative azeotropes) was proved by laboratory experiments and computer simulations. Experimental conditions, parameters of rectification column and the separation results are presented.

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1. Introduction

The study of separation processes of mono- and biazotropic mixtures in the presence of additional substances is still required.

Ionic liquids (ILs) can be used successfully in extractive rectification (ER) as separating agents (SAs), because of their physical and chemical properties (e.g. very low vapour pressure, low melting point and large temperature range of existence in a liquid state) (Beste et al., 2005; Seiler et al., 2004; Lei et al., 2006). There is also a possibility of directional formation of properties of ILs into SAs due to different concentrations of cations and anions. This plays an important role in the separation of mixtures of a specific nature (Domanska et al., 2007).

The use of reference information to determine the properties of ILs and their mixtures (with different components) is necessary for the preliminary selection of ILs as SAs. Generally, such information is systematically available in data banks. For

example, one of these data banks, developed in Lomonosov Moscow State Academy of Fine Chemical Technology (MITHT) (Reshetov et al., 2009a, 2011), includes reference and original information on liquid–vapour, liquid–liquid, liquid–gas and liquid–solid-phase equilibrium. This bank also has other data on the properties of pure ILs, such as critical properties, density, dynamic viscosity and boiling, melting and decomposition temperatures. The benefits of using a data bank are that it allows for the following: (1) collecting, processing and storing information; (2) sorting of the data to identify specific groups of properties; and (3) performing a hierarchical search of necessary information on any number of characteristics in a dialog mode. In this study, the data bank was used to evaluate the influence of some structural properties of ILs on the homogeneous and heterogeneous properties of their mixtures with water and organic compounds (Reshetov et al., 2009b; Reshetov and Frolkova, 2010). The selection of a number of ILs, which can be used as potential SAs in the ER process, was made.

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Nomenclature

T	temperature (K)
$t_{R1(2)}$	retention time of component 1(2)
S	selectivity
x	mole fraction of component in liquid phase

Greek letters

A	parameter of NRTL equation
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Subscript

B_{ij} B_{ji}	parameters of NRTL equation
D	distillate product
F	feed
W	bottom product
1,2	components in a system (or mixture)

Superscript

∞	infinite dilution
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The selection of SAs resulted from gas–liquid chromatography (GLC) separation, vapour–liquid equilibrium (VLE) modelling (Kato and Gmehling, 2005) and experimental work in a laboratory-size rectification column.

The evaluation of the potential selectivity of the SAs by GLC allows for the formation of a plurality of agents for the first stage of ER. This problem was solved only by using unreal conditions (e.g. infinite dilution by an SA). Therefore, it was necessary to confirm this prediction by experimentation.

2. Results and discussion

The ER of mixtures acetone–chloroform(I), chloroform–ethanol(II) and benzene–perfluorobenzene(III) was studied. These mixtures were characterised as negative, positive and azeotropic, respectively. The uniqueness of the system III is the presence of two azeotropes. The variations of temperature with composition of the binary systems at 101.325 kPa are depicted in Fig. 1.

The SAs used were 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) for mixtures I–III and triethylammonium trifluoromethylsulphonate ([HEt₃A][triflate]) for mixture I. The choice was made from a number of potential SAs, including traditional solvents such as dimethylsulphoxide, dimethylformamide, ethylene glycol, N-methylpyrrolidone and different ILs.

Table 1 shows a preliminary list of agents used, which includes ILs such as [HEt₃A][triflate]–triethylammonium

trifluoromethylsulphonate, [bmim][PF₆]-1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][BF₄]-1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][Cl]-1-butyl-3-methylimidazolium chloride and [emim][Cl]-1-ethyl-3-methylimidazolium chloride.

Selectivity was determined by GLC as a ratio of the retention times (t) of the original components at infinite dilution by an SA–IL, which is a stationary liquid phase:

$$S_{1,2(SA)}^{\infty} = \frac{t_{R2}}{t_{R1}} \quad (1)$$

[Bmim][Cl] and [emim][Cl] were found to be the best SAs among the investigated ILs. These SAs were able to distil acetone as a product in the ER of acetone–chloroform and ethanol, and as a distillate product in the ER of ethanol–chloroform.

The selection of 1-butyl-3-methylimidazolium chloride as an extractive agent in the ER of the bi-azeotropic mixture benzene/perfluorobenzene was evaluated. It was shown that perfluorobenzene was in the distillate.

The IL [bmim][Cl] as an SA for the ER of all mixtures is preferred due to its high selectivity, relative affordability and availability. The choice of the IL [HEt₃A][triflate] for the ER of chloroform–acetone is uncertain because, according to GLC, its selectivity is close to unity and therefore requires additional study.

SA selectivity estimation by GLC differs from the process conditions in an ER column. Therefore, it is necessary to validate the selection of SA from GLC data with rectification experiments.

2.1. The study of extractive properties of [bmim][Cl]

The experiment was conducted in a laboratory rectification column with a height of 2 m. The internal diameter of the column was 12 mm. The nozzle was made of nichrome, and had spiral-prismatic dimensions of 2.5 × 2 × 2 mm. The column consisted of 10–12 theoretical plates. It was operated continuously at atmospheric pressure. The feed mixture from the container was fed using a plunger pump. IL [bmim][Cl] is a solid under normal conditions. Therefore, it had to be melted by heating using heated burettes, before being fed into the column using gravity.

Because the GLC analysis of the bottom liquid containing the IL is difficult to perform, only the initial samples of mixtures (F) and the distillate products (D) were collected and analysed. The composition of the bottom product (W) was determined by material balance. The consumption of SA, which was provided at a predetermined separation, was determined for each of the original mixtures. The conditions, parameters and results are shown in Table 2.

Table 1 – Selectivity of ionic liquids for pairs of components at infinite dilution at 90 °C.

No.	Ionic liquid	Selectivity values	
1	[HEt ₃ A][triflate]	Chloroform (R ₁)–acetone (R ₂) 1.03	Ethanol (R ₁)–chloroform (R ₂) 1.83
2	[bmim][PF ₆]	Acetone (R ₁)–chloroform (R ₂) 1.68	Ethanol (R ₁)–chloroform (R ₂) 1.93
3	[bmim][BF ₄]	Acetone (R ₁)–chloroform (R ₂) 1.04	Ethanol (R ₁)–chloroform (R ₂) 1.47
4	[bmim][Cl]	Chloroform (R ₁)–acetone (R ₂) 11.36	Ethanol (R ₁)–chloroform (R ₂) 1.91
5	[emim][Cl]	Chloroform (R ₁)–acetone (R ₂) 10.0	Ethanol (R ₁)–chloroform (R ₂) 2.24

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