**Separation of methycyclohexane – toluene mixture in the presence of ionic liquids**

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**1. Introduction**

Modern chemical research is focused on the use of alternative, green, solvents as the traditional ones show numerous adverse properties including human health risk, volatility and flammability. Moreover, stringent legal requirements adopted recently oblige chemical and pharmaceutical companies to re-evaluate and adapt existing processes.

Since the 90th, there is an enormous increase in the number of studies regarding application of ionic liquids (ILs). ILs are a new type of solvents, often denoted as green solvents. They possess outstanding physical-chemical properties; they are liquid in a large region of temperatures, non-flammable, chemically and thermally stable. They act as liquid salts and due to their negligible vapor pressure, ILs are environment friendly and relatively easy to be regenerated [1].

Elevated polarity of ILs influences the properties of mixtures to be separated; in homogeneous systems it affects relative volatility of components of the original mixture, in case of heterogeneous systems, ILs polarity influences the components solubility and selectivity towards the extracted component. Hence, there is potential of ILs use in the separation of azeotropic and close boiling point mixtures, e.g. in extraction distillation and liquid phase extraction [2].

ILs are considered substitutes for traditional organic solvents in extraction of aromatics from their mixtures with aliphatic hydrocarbons. Thanks to their high selectivity, ILs can be used to separate aromatics by liquid extraction from mixtures containing less than 20 mass % of aromatics [1].

**2. Methods**

Aim of this work was to propose the process of **separation for** **methylcyclohexane─toluene model mixture in the presence of ionic liquid** (IL). Production line was composed of a counter-current liquid-phase extraction column coupled with single effect evaporator for extraction solvent regeneration and distillation column used to purify toluene. Mathematical models of individual devices were based on material and enthalpy balances taking into account phase equilibrium, too. Organic part of the equipment model simulation was energetic analysis of this complex systems including heat integration. Calculations were carried out partly in ASPEN+ simulation software and partly employing proprietary programs elaborated in Matlab.

**3. Results and discussion**

In the work, three ionic liquids (1-ethyl-3-methylimidazolium bis trifluoromethylsulfonyl imide ([Emim][NTf2]); 1-hexyl-3-methylimidazolium tetracyanoborate ([Hmim][TCB]) and 1-butyl-3-methylimidazolium tetracyanoborate ([Bmim][TCB])) were used.

Based on experimental and calculated LLE data [3, and our experiment], capacities and selectivities of individual solvents were evaluated. Selectivities of [Bmim][TCB] and [Hmim][TCB] ILs were comparable, both ILs reached high capacity value (*kB* > 1,2). [Emim][NTf2] exhibited the lowest selectivity and capacity values amongst the ILs studied.

The input parameters of the extractor design calculations were the composition of the feed (methylcyclohexane–toluene mixture containing 10 mole % of toluene) and the extraction solvent composition (containing 99 % of IL). The required purity of the raffinate was maximum 0,5 mole % of toluene in the raffinate. The desired purity of toluene in the bottom product of the distillation column was 99,8 %.

The yield of methylcyclohexane in raffinate (99,98 %) was reached regardless the IL used. Assuming yield of toluene in the bottom product of distillation column, the values ranged from 95,50 % (for [Emim][NTf2]) to 95,92 % (in case of [Hmim][TCB].

Solvent-to-produced methylcyclohexane mass ratio values were as follows: the lowest value (2,54 kg/kg) was obtained when [Hmim][TCB] was used as extraction solvent. In case of [Bmim][TCB] the value was somehow higher (2.69 kg/kg) and the highest value (9,38 kg/kg), i.e. the largest amount of solvent necessary for the model mixture separation was obtained in case of [Emim][NTf2].

The energetic analysis of the process has shown that the largest heat demand was associated with evaporator operation, where almost 10 times more heat was consumed compared to that in the distillation column reboiler. The highest cooling demand was observed in cooler of the recirculated ionic liquid.

Total energy consumption for heating and cooling of the individual devices was comparable for simulations assuming [Bmim][TCB] and [Hmim][TCB] as extraction solvents (1,01 MJ and 1,05 MJ per kg of methylcyclohexane produced). Use of [Emim][NTf2] ionic liquid for this purpose was connected with more than two-times higher heat and cooling demand.

The last part of the design was the thermal integration of the process. It was found that proper heat integration allows up to 72 % reduction of the overall energy demand.

**4. Conclusions**

Energetic analysis has clearly shown suitability of both [Bmim][TCB] and [Hmim][TCB] ionic liquids for their use in methylcyclohexane–toluene mixture separation.

**References [Calibri 10]**

1. G.W. Meindersma, A.B. de Haan, Chem. Engineering research and design 86 (2008) 745–752.
2. J.P. Gutiérrez, G.W Meindersma,., A.B & de Haan, Industrial & Engineering Chemistry Research 51, (2012) 1518–11529.
3. J.P. Gutierrez, W. Meindersma, A.B. de Haan, J. Chem. Thermodynamics 43 (2011) 1672–1677.

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