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IONIC LIQUID SELECTION AND PERFORMANCE EVALUATION FOR THE SEPARATION OF METHYLCYCLOHEXANE/TOLUENE BY EXTRACTIVE DISTILLATION

Juan Pablo Gutierrez, Wytze Meindersma and André B. de Haan
Eindhoven University of Technology, Den Dolech 2, Eindhoven 5600, Netherlands, j.p.gutierrez-hernandez@tue.nl

Abstract
The effectiveness of an extractive distillation process relies on the choice of the extractive solvent. The conventional methodology to select solvents is based on Group Contribution Methods. Ionic liquids have shown several advantages over conventional solvents used in extractive distillation and liquid-liquid extraction processes. However, there is no existing methodology to select ILs as solvents for ED processes due to the lack of experimental data, their low capacity and unavailability of group contribution parameters for most IL systems. The objective of this work is to establish a systematic solvent selection methodology for ED processes for the separation of aromatics/non-aromatics mixtures employing ionic liquids.

Keywords: Extractive distillation, ionic liquids, solvent, screening, COSMO-RS

1. Introduction

Extractive distillation (ED) is a common separation technology used in the petrochemical industry. This technology is used to separate mixtures which cannot be separated by conventional distillation because this process could be economically unfeasible. ED uses a low-volatile solvent which is added to modify the relative volatility of the components. The industrial separation of aromatics from non-aromatics by this technology is done with several solvents. The two more industrially used are N-methyl-2-pyrrolidone (NMP) and sulfolane. Among them, NMP shows a major advantage which is the non-formation of two liquid phases inside the distillation column. In this work, methylcyclohexane (MCH) and toluene were chosen as representative components for the aromatic/non-aromatic mixture obtained in the pyrolysis gasoline process. The term Ionic Liquid (IL) is used for a chemical composed entirely of ions with a melting temperature below 100°C. Suitable cations and anions can be chosen to obtain ILs with the desired properties for specific applications and, like other liquid solvents, they can be mixed to improve their behavior. Therefore, it is possible to design an IL for a particular application by combining a cation with an organic or inorganic anion to obtain the desired melting point, viscosity, density, hydrophobicity, miscibility, etc.

Selection of the conventional solvents used in extractive distillation is done on basis of their selectivity and capacity, normally taken at infinite dilution in the solvent. The selectivity is defined as the ability of the solvent to modify the relative volatility of the components to be separated. The capacity is a measure of the concentration in one of the liquid phases when the compound to be separated is immiscible in the solvent. Both, selectivity and capacity are shown in the equation 1 and 2, respectively.

$$S_{ij}^{\infty} = \left(\frac{\gamma_i^{\infty}}{\gamma_j^{\infty}} \right)_S \tag{1}$$

$$C_i^{\infty} = \frac{1}{\gamma_i^{\infty}} \tag{2}$$

Although many heuristic methods and rules of thumb have been developed in order to assist in the choice and ranking of solvents, these are mostly qualitative. Experimental screening methods of solvent yields good results, but they are time consuming and expensive. A more effective, but less accurate, method to select solvents is Computer-Aided Molecular Design (CAMD). In these methods the required properties of a solvent are specified and its structure is then calculated through the use of e.g. group contribution methods (GCM). CAMD is essentially the inverse of property prediction by group contribution methods. Group contribution methods (GCM), such as UNIFAC, are the most reliable and widely accepted way to predict and calculate activity coefficients and other thermodynamic properties in liquid (multi-component) mixtures. However, the necessary interaction parameters of ILs and substances are not always available. The conductor like screening model for real solvents (COSMO-RS) is a promising, although relatively new, CAMD method to predict the activity coefficients and other thermophysical properties based on unimolecular quantum chemical calculations. It has the advantage of being applicable to molecules where GCMs fail or some parameters are missing.

The objective of this work is to establish a systematic solvent selection methodology for ED processes employing ionic liquids as extractive solvents taking into account the property requirements that the ILs should have in comparison with the conventional solvents.

2. Thermodynamic analysis in extractive distillation

Phase splitting due to thermodynamic instability of liquid mixtures plays an important role in simulation and processes design. The formation of two liquid phases due to the addition of the solvent is undesirable in ED. The NRTL method introduced by Renon and Prausnitz is one of the most frequently employed tools in correlating phase equilibrium data. Regression of experimental data is necessary to obtain a good prediction with this model. However, if some simplifications are done to the model, this can be only dependent of one set of parameters (b_{ij}). In this way, for a binary system there are just two parameters (b_{12} and b_{21}) to be obtained with experimental data. Theoretically, just two experimental points are necessary to determine those parameters. The accuracy of the model increases with the number of experimental data points used. However, in this work the experimental activity coefficients at infinite dilution are going to be used, i.e. γ^{∞} of the component *i* in the solvent (*S*) and γ^{∞} of *S* in *i* ($\gamma_{i,S}^{\infty}$ and $\gamma_{S,i}^{\infty}$, respectively). The activity coefficients at infinite dilution for a binary mixture in accordance to the NRTL model are expressed by the following equations:

$$\begin{aligned} ln\,(\gamma_{i,S}^{\infty}) &= \tau_{S,i} + \tau_{i,S} e^{-0.3\tau_{i,S}} \\ ln\,(\gamma_{S,i}^{\infty}) &= \tau_{i,S} + \tau_{S,i} e^{-0.3\tau_{S,i}} \end{aligned} \tag{3}$$

Thus, there are two equations to solve with two unknown variables ($\tau_{i,j}$). With these parameters the entire equilibrium of the binary mixture can be obtained and the formation of two liquid phases can be predicted with the analysis of the Gibbs energy of mixing.

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2}\right)_{T,P} < 0 \tag{4}$$

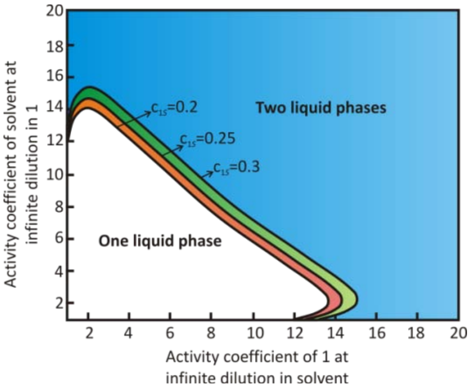


Figure 1. Phase stability analysis for a binary mixture

Therefore, depending on the activity coefficients at infinite dilution, the parameters of the NRTL model change and also the phase behavior of the mixture. In that way, it is interesting to know the combination of parameters (or activity coefficients at infinite dilution) that gives the formation of two liquid phases. Applying the above criteria (4), the Figure 1 was obtained. As can be seen in this figure, there is a triangular region where only one liquid phase exists. A good solvent for extractive distillation should be located inside that area. Therefore, the solvent selection should be based in the analysis of the activity coefficients of the components in the solvent (as with the conventional solvent selection methodology) and the solvent in the components. In section 3 it is shown that the interaction between the solvent and the components are weaker when ILs are used, which makes this parameter very important for these new solvents.

3. COSMOtherm solvent screening

A new model called COSMO-RS, the conductor-like screening model for real solvents, is based on unimolecular quantum chemical calculations of the individual species in the system (pure components). This model is especially suitable for property calculations of some substances if reliable experimental data is missing or not available. COSMOtherm is a software package for the quantitative calculation using the COSMO-RS theory. The software (version C2.1 release 01.08) is used in this work to obtain the thermodynamic properties of some pure components and mixtures. COSMOtherm has a large database; however, the amount of ILs present is limited. Thus, they have to be created and stored in the database (the fundamentals and procedure are not shown in this work). The screening of 2262 ILs was carried out. The cations studied in this work were: imidazolium, ammonium, piperidinium, pyrrolidonium, pyridinium, phosphonium, sulfonium and quinolinium-based. The effect of the variation of alkyl chain length and the degree of branching on the activity coefficients at infinite dilution and the selectivity was analyzed and some results are presented below.

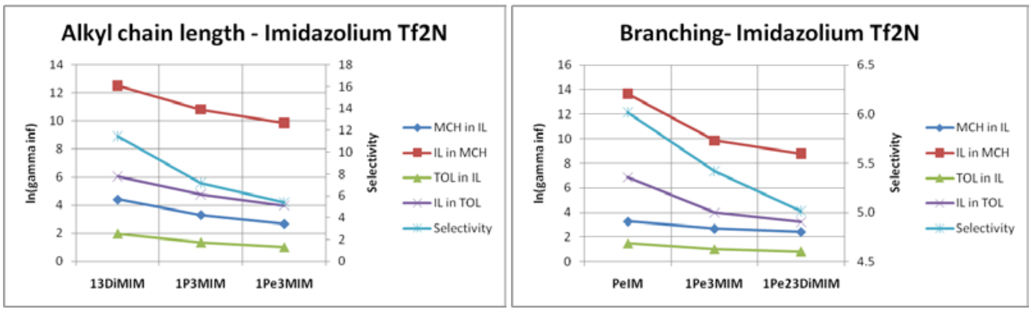


Figure 2. Alkyl chain and degree of branching prediction in COSMOtherm

As can be seen in Figure 2, the alkyl chain length and the degree of branching of imidazolium-based ILs play an important role in the determination of the activity coefficients at infinite dilution. It can be seen that the increase in the alkyl chain length and branching result in a decrease in the activity coefficients and selectivity. The high values of $\gamma_{IL,MCH}^{\infty}$ give a high probability to form two liquid phases, as was shown in section 2. To decrease the value of this property, larger cations should be selected, resulting in a decrease of the selectivity, increase of the molecular weight and viscosity. The same trend was observed for the others kind of cations (not shown in this work).

As can be seen in the Figure 3 (top left), the cation type (for the same alkyl chain length, which is pentyl) influences in the activity coefficients and selectivity, being pyridinium the most selective cation among the ring-structured ILs. The piperidinium-based ILs are the least selective; however they showed the highest solubility. Among the non-ring structure ILs, Figure 3 (top right), the sulfonium and the phosphonium-based ILs are the most and least selective cations, respectively. According to the two liquid phase analysis done in section 2, it is necessary to reduce $\gamma_{IL,i}^{\infty}$. If this is done by changing the alkyl chain length the selectivity of the IL is affected. Nevertheless, the interactions among the solvents and the components can also be changed by the anion. As can be seen in the Figure 3 (bottom), changing the anion from phosphate to BTI or Tf2N (bis((trifluoromethyl)sulfonyl)imide) gives a reduction from 30 to 6 in $\gamma_{IL,MCH}^{\infty}$. According to COSMOtherm results the selectivity is increased from 3.5 to 4.5. As can be seen in the figure, the selectivity does not have a clear tendency when the anion is changed. This may be an advantage because the anion can be selected to increase the solubility and at the same time increase the selectivity.

As can be concluded, the most suitable cations for the separation of aromatics/non-aromatics are those who have long alkyl chain and high degree of branching, even though, it is known that their viscosity and molecular weight are higher. In addition, the ring structured cations seems to be the most suited for this kind of separation. Besides this, the most attractive anions, according to its selectivity and solubility are listed in Table 1.

Table 1. Suitable anions for the separation of MCH/toluene

Abb.	Anion name	MW (g/mol)
TCM	Tricyanomethanide	90.1
PF6	Hexafluorophosphate	145.0
TCB	Tetracyanoborate	114.9
BTI	Bis((trifluoromethyl)sulfonyl)imide	280.2
BPI	Bis((pentafluoroethyl)sulfonyl)imide	380.2
FAP	Tris((pentafluoroethyl)trifluoro)phosphate	445.0

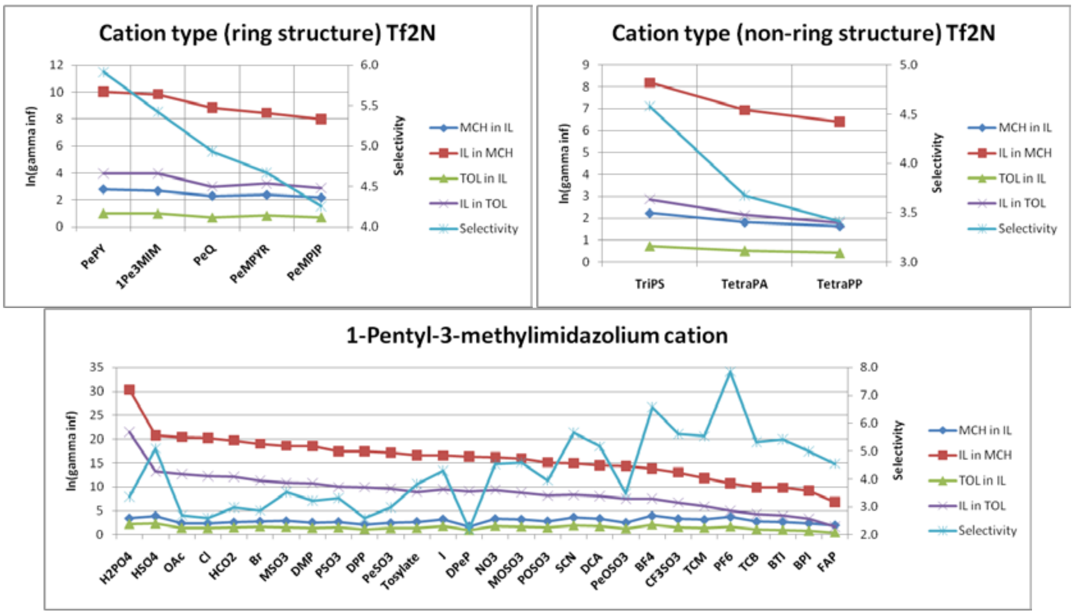


Figure 3. COSMOtherm predictions for the mixture methylcyclohexane/toluene

4. Molecular weight influence

One of the most studied ILs for the separation of organic compounds is HMIM BTI. In this section, the effect of the solvent (NMP or HMIM BTI) in the relative volatility and the purity of a distillation column is studied. To accomplish this, the miscibility gaps among IL-MCH and IL-toluene were neglected and the VLE was described by the simplified NRTL model described in section 2. For the NMP case, the AspenPlus NRTL parameters were used to describe its thermodynamic behaviour. In Table 2, activity coefficients at infinite dilution in those solvents are listed.

Table 2. Actiity coefficients at infinite dilution obtained by COSMOtherm, AspenPlus or experimentally

Solvent	$\gamma_{MCH,S}^{\infty,Exp}$	$\gamma_{Tol,S}^{\infty,Exp}$	$\gamma_{MCH,S}^{\infty,COSMO}$	$\gamma_{Tol,S}^{\infty,COSMO}$	$\gamma_{S,MCH}^{\infty,COSMO}$	$\gamma_{S,Tol}^{\infty,COSMO}$	$S_{MCH,Tol}^{\infty,Exp}$	$S_{MCH,Tol}^{\infty,COSMO}$
NMP	3.830*	0.965*	2.489	0.974	4.319	1.086	3.97	2.56
HMIM BTI	6.060[5]	1.140[5]	8.873	2.542	5464.3	42.7	5.32	3.49

*Values obtained with NRTL parameters from AspenPlus

Table 3. NRTL parameters for the system with HMIM BTI

System (*i-j*)	b_{ij}	System (*i-j*)	b_{ij}
MCH – IL	2558.6	**Toluene – IL**	1348.1
IL – MCH	471.8	**IL – Toluene**	-89.6

As can be seen in Table 2, COSMOtherm over-predicts the activity coefficients of the organic components in HMIM BTI (this behavior was observed for most of the ILs studied in this work, which are not shown). The thermodynamic properties for the system with IL, predicted by the software, were regressed to obtain the NRTL-binary parameters, which are shown in Table 3. The vapor-liquid equilibriums for both solvents are shown in Figure 4 (left). As can be seen in this figure, the use of IL does not improve the relative volatility of the system in comparison with the conventional solvent. Nevertheless, its non-volatile characteristic makes it a good option as a replacement of the conventional solvent. However, it should be noted that the molecular weight of the IL and NMP are 447.4 u and 99.1 u, respectively. As can be concluded from Figure 4 (right), if a purity of 99.6% is desired in an ED column operating with a molar reflux ratio of 2, a solvent to feed molar ratio of 1.9

and 1.6 should be used in the processes utilizing NMP and IL, respectively. This means that it is necessary to use 3.8 times more kilograms of IL than NMP due to its higher molecular weight, besides this, it is shown in section 5.2 that this IL forms two liquid phases at 60°C with both organic components. This makes unfeasible the use of this IL as a solvent.

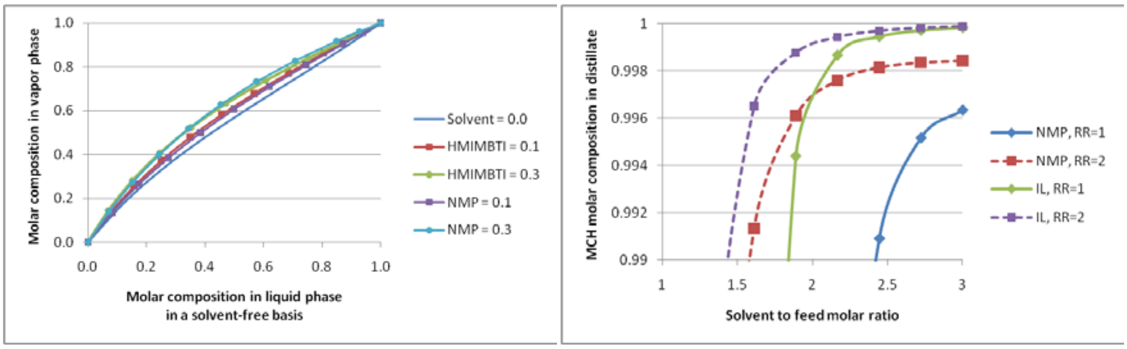


Figure 4: Solvent effect in the thermodynamic equilibrium (left) and purity in the distillate (right)

According to the analysis done in sections 3 and 4, the anions TCB and BTI were selected for further studies due to its “suitability” (which has been shown in several papers), molecular weight and market availability. The ILs selected for further studies are listed below:

- HMIM BTI: 1-Hexyl-3-methylimidazolium Bis((trifluoromethyl)sulfonyl)imide
- HMIM TCB: 1-Hexyl-3-methylimidazolium Tetracyanoborate
- OMIM TCB: 1-Octyl-3-methylimidazolium Tetracyanoborate
- HMPIP BTI: 1-Hexyl-1-methylpiperidinium Bis((trifluoromethyl)sulfonyl)imide
- MtriOcA BTI: Methyl(trioctyl)ammonium Bis((trifluoromethyl)sulfonyl)imide
- TriHtetradecylP BTI: Trihexyl(tetradecyl)phosphonium Bis((trifluoromethyl)sulfonyl)imide
- HPY BTI: 1-Hexylpyridinium Bis((trifluoromethyl)sulfonyl)imide
- HMPYR BTI: 1-Hexyl-1-methylpyrrolidonium Bis((trifluoromethyl)sulfonyl)imide
- HQUI BTI: 1-Hexylquinolinium Bis((trifluoromethyl)sulfonyl)imide

5. Experiments

5.1 Chemicals

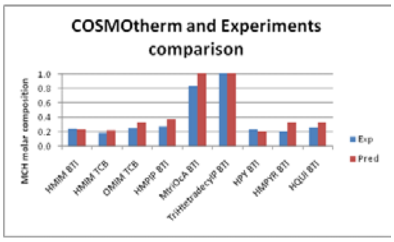
The ILs HMIM TCB and OMIM TCB (>98%) were purchased from Merck. The ILs MtriOcA BTI (>99%), HMIM BTI (>99%), HMPIP BTI (>99%), HPY BTI (>99%), HMPYR BTI (>99%), TriHtetradecylP BTI (>98%) and HQUI BTI (>98%) were purchased from Iolitec. Toluene (99.98%) and methylcyclohexane (99.9%) were purchased from Fluka. After every experiment the ILs were purified under vacuum (<10mbar) at 60°C for minimum 5 hours in a rotary evaporator (Büchi Rotavapor R-200). Ethylbenzene (used as the internal standard in the gas chromatography analysis) was purchased from Fluka with a purity > 99.9%.

5.2 Liquid-liquid extractions

The above ILs were tested in several simple liquid-liquid extraction experiments to be sure about the formation of two liquid phases between the binary mixtures formed by MCH-IL, and toluene-IL. Liquid–liquid extraction experiments were carried out in jacketed vessels with a volume of approximately 70 mL. The experimental procedure mentioned in the work of G.W. Meindersma et al[6] was followed. The top of the vessel was closed using a PVC cover, through which a stirrer shaft was passed. Two stainless steel propellers were used with an electronic stirrer control. The vessels were jacketed to circulate water from a water bath in order to maintain the temperature inside the vessels at 60°C (±0.2°C). For each experiment, maximum 50 mL of binary mixture (IL + organic) were placed into the vessels and they were closed. When the desired temperature was reached, the agitation was started. Samples (1 mL) from both phases were taken after two hours. The analysis of the samples was done by a Varian CP-3800 gas chromatograph (GC) with a Varian CP-SIL5CB (50mx0.32mmx0.45mm) column. Because the ionic liquid has no vapor pressure, it cannot be analyzed by GC. The IL was collected in a pre-column in order to do not disrupt the analysis. The IL was determined by mass balance of the measured mole fractions of the hydrocarbons. The results (Table 4) showed that all the ring-structured ILs formed two liquid phases in presence of MCH. The phosphonium-based IL, which has a molecular weight of 764 u, did not form a second liquid phase. However, for this and the ammonium-based IL, it has been shown that their selectivity is rather low. The quinolinium-based IL was solid at 25°C and it was necessary to mix it with the organic compounds and heat the mixture up to form a single liquid phase. This can be a disadvantage for the extractive distillation column.

Table 4. Liquid-liquid extraction experiments for MCH or toluene with several ILs

Solvent	MW IL	Experimental		Prediction	
		x mch	x tol	x mch	x tol
HMIM BTI	447.4204	0.2363	0.8104	0.2260	NA
HMIM TCB	282.1547	0.1842	0.7555	0.2140	NA
OMIM TCB	310.2087	0.2460	0.8082	0.3267	NA
HMPIP BTI	464.4810	0.2759	0.8144	0.3711	NA
MtriOcA BTI	648.8450	0.8259	NA	NA	NA
TriHtetradecylP BTI	764.0000	NA	NA	NA	NA
HPY BTI	444.4070	0.2243	0.8173	0.2015	NA
HMPYR BTI	450.4540	0.2045	0.7952	0.3224	NA
HQUI BTI	494.4670	0.2649	0.8335	0.3233	NA



In Table 4, the third and fourth columns are the molar compositions of MCH and toluene in the IL-rich liquid phase. The other liquid phase was composed by almost pure organic compound (for most of the cases this molar composition was higher than 99.5%). The fifth and sixth columns are the COSMOtherm predictions. In this table NA means that the second liquid phase was not found. Predictions for MCH are in relatively good agreement with the experimental data, which shows the usefulness of COSMOtherm in the solvent selection methodology proposed in this work. As can be seen in Table 4, the ring-structured ILs showed similar behavior in the extraction process (similar molar compositions). However, it is known that the viscosity of the imidazolium-based ILs is lower if they have the same anion. HMIM BTI has been studied in several publications and numerous experimental data exists for it. However, no data for liquid-liquid extraction experiments for this IL and toluene and/or MCH was found. This IL was selected for further experimental studies, especially liquid-liquid extractions. HMPIP BTI, as was discussed in section 2 and shown in table, has higher solubility than the others ring-structure IL. This IL was also selected for further experimental studies, both liquid-liquid and vapor-liquid equilibrium. Finally, due to its low molecular weight, HMIM TCB was also selected. For those ILs it is desirable to know their actual selectivity under operative conditions in extractive distillation columns.

6. Conclusions

According to the figures and tables shown in this work, it can be concluded that for extractive distillation, where the second liquid phase is undesirable, not only the selectivity and activity coefficients at (in)finite dilution of the components in the solvent should be taken into account to make the screening and selection of the solvent (like in the conventional solvent selection methodology) but also the activity coefficients at (in)finite dilution of the solvent in the components. The results from the thermodynamic analysis with the NRTL equation showed that the interactions among the solvent and the methylcyclohexane (and vice versa) should be weak (high activity coefficients) and the interactions among the solvent and the toluene (and vice versa) should be strong (low activity coefficients). In other words, it is desirable to have large values of $\gamma_{1,S}^{\infty}$ and $\gamma_{S,1}^{\infty}$ and small values of $\gamma_{2,S}^{\infty}$ and $\gamma_{S,2}^{\infty}$. The liquid-liquid extractions experiments showed that the ring-structured ILs had approximately the same capacity for both organic components. The Tf_2N (BTI) is a suitable anion to be used in extractive distillation for the separation of methylcyclohexane and toluene due to its market availability and selectivity and TCB anion is suitable due to its low molecular weight and selectivity.

Acknowledgements

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