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The use of ionic liquids as efficient extraction medium in the reactive separation of cycloolefins from cyclohexane[☆]

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ABSTRACT

In this study the selective extraction of cycloolefins from their mixtures with cyclohexane by chemical complexation with silver ions in ionic liquid solutions has been performed. The solubilities of cyclopentadiene (CP) and dicyclopentadiene (DCP) in the reactive medium, silver tetrafluoroborate dissolved in 1-butyl-3-methylimidazolium tetrafluoroborate, were investigated. Experimental results were obtained working at different concentrations of cycloolefins (100–1000 ppm) in the organic phase and at a temperature range between 283 K and 323 K. The solubility of the olefins is substantially determined by the concentration of the silver ions, an increase in the metal content of the solutions being associated with a strong increase in solubility. Experimental results show that this process allows purification of cyclohexane reducing also the content of cycloolefins down to few parts per million (ppm). Furthermore, the use of BMImBF4 as extraction media involves important advantages due the regeneration capacity.

1. Introduction

Cyclohexane (*CH*) is used as a solvent and reaction medium in the manufacturing of different types of synthetic rubbers. In the manufacturing of styrene-based synthetic rubber by anionic polymerization, *n*-butyl lithium is used as an initiator. The presence of certain impurities (e.g., water, cyclopentadiene (CP), etc.) in the raw materials or in the solvent used in polymerization may have a poisonous effect on the catalyst. After reaction, cyclohexane is separated from the polymer by steam-stripping, recovered and pumped to a distillation purification column for water removal. In the manufacturing of hydrogenated synthetic rubber, during the hydrogenation process (after the anionic polymerization) small quantities of CP are formed by degradation of the titanocene compounds, which are used as hydrogenation homogeneous catalyst [1]. Additionally, cyclopentadiene easily dimerizes at room temperature to form dicyclopentadiene (DCP) that must be also removed. In order to recycle cyclohexane to the reaction process, the cyclopentadiene and dicyclopentadiene contents must be reduced to less than several parts per million (ppm). Because of the low CP and DCP concentrations in the cyclohexane stream, separation based on conventional distillation is difficult and energy intensive [2].

The separation of condensed olefins from corresponding paraffins has been investigated widely in literature [3–6]; the most promising alternative appears to be π-complexation with silver ions. Separation by π-complexation is a subgroup of chemical complexation reaction where the mixture is contacted with the second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those formed by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bounded. At the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.

Recently, considerable attention has been drawn to room temperature ionic liquids (RTIL) as green alternative to common organic solvents. RTIL are organic salts with melting points at or below room temperature. They have substantial potential as diluents in separations and their application is an important step in the design of environmentally safe separation processes, because ionic liquids are considered to be non-flammable, non-volatile and thermally stable [7,8]. In general, ionic liquids have higher density than organic liquids and water. Therefore, many ionic liquids exist as a separate phase when in contact with organic and aqueous phases. These features make it possible to readily recycle the ionic liquids for multiple extractions without additional environmental concern. Recently, our group reported on the selective absorption of propylene from their mixtures with propane by chemical complexation with silver ions in ionic liquid solutions [9].

Reliable data on the solubility of the olefins in a compatible solvent are required for the proper design of extraction systems. In

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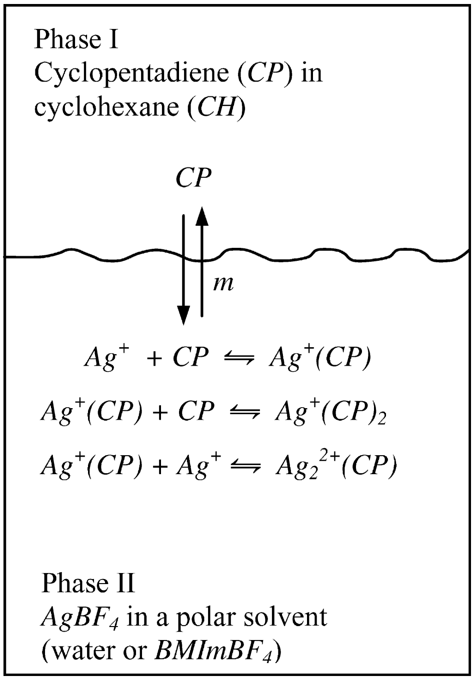

Fig. 1. Cyclopentadiene solubility at equilibrium in a reactive solvent.

this work, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) has been selected for experiments because it is essentially immiscible with cyclohexane and it is able to dissolve a suitable silver salt ($AgBF_4$), allowing to absorb both CP and DCP due to reversible complexation of silver ions with unsaturated olefinic double bonds. Foco et al. [10] reported activity coefficients at infinite dilution of alkanes in several ionic liquids. The value reported by these authors for cyclohexane in $BMImBF_4$ at 303 K is $\gamma_i^\infty = 45$.

In this work, experimental results were obtained working at different concentrations (100–1000 ppm) of both dienes in the organic phase. The influence of temperature and silver concentration on the solubility of the dienes in the $BMImBF_4 - Ag^+$ solution was assessed and the enthalpy (ΔH°) for the complex formation reaction was estimated. Also, experimental results with aqueous silver solutions are included as reference.

2. Modeling cyclopentadiene solubility in reactive solvents

The aim of this section is to present a simple equilibrium model that can adequately describe the cyclopentadiene solubility in a solvent containing reactive metal–ligand complexes.

Following the work of Wentink et al. [6], a schematic representation of the distribution of CP between a hydrocarbon phase (cyclohexane, phase I) and a reactive solvent ($AgBF_4$ in aqueous or RTIL solution, phase II) is shown in Fig. 1. In π-complexation systems, various complexes of different stoichiometry can exist simultaneously. Factors influencing the reaction stoichiometry are the temperature, the silver concentration and the concentration and structure of the olefin [6]. Here, equations are derived for the cyclopentadiene solubility as a function of the silver tetrafluoroborate concentration in phase II and the cyclopentadiene concentration in phase I.

This model is derived under the assumption that the reaction complexation constants can be expressed in equilibrium concentrations instead of activities. Furthermore, it is assumed that $AgBF_4$ has a negligible influence on the physical solubility of the CP in water or in $BMImBF_4$. In addition, it is assumed that the complexation reactions only take place in phase II because the silver ions and formed complexes always remain in the polar phase.

The physical partitioning of the CP between both liquid phases is described with the physical distribution constant (m_{CP}):

$$m_{CP} = \frac{[CP]_{II}}{[CP]_{I}} \tag{1}$$

The complexation reaction between CP and Ag^+ ions can be described as:

$$\alpha CP^{(II)} + \beta Ag^+ \Leftrightarrow CP_\alpha(Ag^+)_\beta \tag{2}$$

The equilibrium constant is defined as:

$$K_{CP} = \frac{[CP_\alpha(Ag^+)_\beta]_{II}}{[CP]_{II}^{\alpha} \times [Ag^+]_{II}^{\beta}} = \frac{[CP_\alpha(Ag^+)_\beta]_{II}}{[[CP]_I \times m_{CP}]^{\alpha} \times \left[[Ag^+]_{II}^{Total} - \beta \times [CP_\alpha(Ag^+)_\beta]_{II}\right]^{\beta}} \tag{3}$$

For practical applications, the activities of the liquid phase species are assumed to be proportional to the concentration of the species, with the constant of proportionality (the nonidealities) taken up in the equilibrium constant [11]. The total CP solubility in the polar phase (phase II) is the sum of the physical dissolved CP concentration $[CP]_{II}$ and the complexed CP concentration $[CP_\alpha(Ag^+)_\beta]_{II}$.

The unknown free silver concentration at equilibrium $[Ag^+]_{II}$ is deducted from a total silver balance which is equal to the total dissolved silver concentration $[Ag^+]_{II}^{Total}$ minus the complexed silver concentration $\beta \times [CP_\alpha(Ag^+)_\beta]_{II}$.

The partition coefficient m_{CP} has been computed by UNIQUAC method for partition equilibrium of CP between cyclohexane and water, and it has been experimentally measured in the case of partition of CP and DCP between cyclohexane and $BMImBF_4$.

Complexation reactions are exothermic and consequently the equilibrium constants will decrease with increasing temperature. We use the van't Hoff equation (Eq. (4)) to calculate the complexation reaction enthalpy (ΔH°):

$$Ln\frac{K_{(T_2)}}{K_{(T_1)}} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{4}$$

A similar scheme can be used to describe to the complexation of dicyclopentadiene with ions silver.

3. Experimental

3.1. Materials

Dicyclopentadiene was purchased from Sigma–Aldrich. Cyclopentadiene was experimentally obtained by thermal cracking of dicyclopentadiene at 451 K and atmospheric pressure. Silver tetrafluoroborate (analytical grade) was supplied by Merck and silver nitrate (analytical grade) was supplied by Panreac. Cyclohexane with a purity of 99.9% was also supplied by Sigma–Aldrich and used without further purification. The ionic liquid $BMImBF_4$ (CAS number 174501-65-6) was supplied by Solvent Innovation (Germany). The $BMImBF_4$ has a glass-transition (T_g) temperature of about −85 °C [12] and is water miscible. As liquids at room temperature, this compound is thermally stable up to about 300 °C, in the absence of strong acid. Ultrapure water (resistivity >18.0 MΩ cm at 298 K) was used to prepare aqueous solutions.

3.2. Methods

A stirred mini-reactor with a volume of 50 mL was used to determine the extraction equilibrium of cycloolefins in ionic liquid

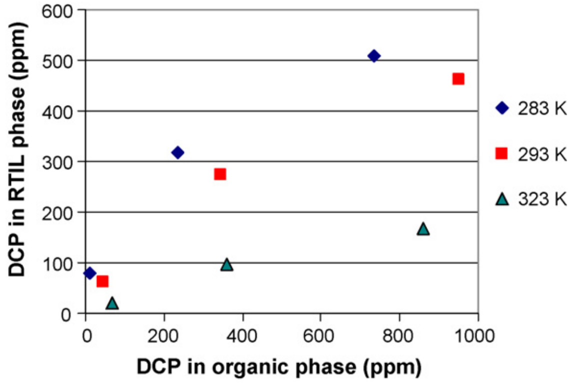

Fig. 2. Partition of dicyclopentadiene between cyclohexane and $BMImBF_4$ phases (cyclohexane – $BMImBF_4$ ratio = 1:1; $[AgBF_4] = 0.02\ mol\ L^{-1}$).

solutions containing the silver salt. The liquids in the mini-reactors were stirred with a flat blade stirrer at 500 rpm. For each experiment the mini-reactor was filled with 10 mL of RTIL solution of silver salt like extractive phase and 10 mL of cyclohexane solution containing the cycloolefins (100–1000 ppm) as organic phase. It has been verified that stirring the absorption vial for 3 h is more than sufficient to establish the equilibrium. After stirring, the two phases were allowed to settle for about 1 h. The organic phase was then removed from the ionic liquid phase for analysis. In the case of experiments using an aqueous phase as extracting solution, the ionic liquid solution was replaced by an aqueous solution of the silver salt ($AgBF_4$ or $AgNO_3$).

The concentration of cycloolefins in the ionic liquid phase was calculated from the concentration of cycloolefins in cyclohexane after extraction. Samples of organic phase were analyzed using a CE Instruments 8130 gas chromatograph equipped with a FID detector and with a semi-capillary column (length 30 m, nominal diameter 0.53 mm, model HP-1). The carrier gas was helium at a flow rate of $4\ mL\ min^{-1}$. The injector operated in the split mode (15/1) at 523 K. The oven temperature was set at 313 K for 7 min, then increased to 423 K at $40\ K\ min^{-1}$ and then it is increased up to 483 K at $10\ K\ min^{-1}$, and finally was held at 483 K for 1 min. For solutions of cycloolefins in the range 100–1000 ppm the analytical error was less than 5%.

4. Results

Since cyclopentadiene dimerizes easily at room temperature to form dicyclopentadiene [13], first the separation of DCP from cyclohexane using ionic liquid solution containing silver ions has been studied. Once demonstrated the viability of the separation and characterized the partition equilibrium of DCP, the simultaneous extraction of CP and DCP has been studied. Finally the separation of cyclopentadiene from cyclohexane using aqueous silver solutions was studied, with the purpose of to make a comparison with the behavior of ionic liquid solutions like extracting agents.

4.1. Extraction of dicyclopentadiene using ionic liquid solutions

Experimental results were obtained working at different dicyclopentadiene concentrations (100–1000 ppm) in the organic phase, with a silver concentration of $0.02\ mol\ L^{-1}$ in the extracting solution. In Fig. 2, the results of partition of dicyclopentadiene between organic and RTIL phases are given.

The general reaction between dicyclopentadiene and Ag^+ in RTIL solution can be described as:

$$DCP + 2Ag^+ \Leftrightarrow DCPAg_2{}^{2+} \tag{5}$$

$$K_{DCP} = \frac{[DCP(Ag^+)_2]_{II}}{[[DCP]_I \times m_{DCP}] \times [[Ag^+]_{II}^{Total} - 2 \times [DCP(Ag^+)_2]_{II}]^2} \tag{6}$$

In this study we have checked different stoichiometric ratio and we have found that Eq. (5) represents the stoichiometry that better fits the equilibrium experimental data. DCP dissolves from the organic phase into the RTIL phase and subsequently reacts with the dissolved positively charged silver ions to form a 2:1 silver–dicyclopentadiene complex species, that is, one silver ion per double bond; this is a reversible complexation reaction.

Factors influencing the reaction stoichiometry are the temperature, the silver concentration and the concentration and structure of the olefin [3,6,9]. Here, equations are derived for the dicyclopentadiene solubility as a function of the silver tetrafluoroborate concentration in phase II and the dicyclopentadiene concentration in phase I. Kraus and Stern [14] report similar stoichiometric ratio for the complexation reaction of 1,3-butadiene with $AgNO_3$ in aqueous solutions. However, at high pressure of butadiene above the solution they found a tendency for additional butadiene to be dissolved in accordance with a 1:1 stoichiometric ratio. In a previous work [9], we have found that the absorption of propylene by chemical complexation with silver ions in ionic liquid solutions can be described by the formation of complexes with different stoichiometry.

The distribution coefficient (m_{DCP}) of dicyclopentadiene between $BMImBF_4$ and cyclohexane was experimentally measured. Liquid–liquid equilibrium data were collected for mixtures of 100 ppm, 500 ppm and 1000 ppm DCP in cyclohexane with $BMImBF_4$. The distribution coefficient, m_{DCP}, was directly calculated from the ratio of the concentrations in the extract and raffinate phases at equilibrium and a value of 0.025 has been found. The coefficient m_{DCP} was found to be independent of the composition in the experimental range of 0–1000 ppm of DCP in the organic phase.

In this work an increase in the solubility of dicyclopentadiene in the silver RTIL solutions with a decrease in temperature was observed. The influence of the temperature on equilibrium was evaluated by means of experiments carried out over a temperature range between 283 K and 323 K, as shown in Fig. 2. Complexation reactions are exothermic and consequently the equilibrium constants will decrease with increasing temperature.

It is found that with increase in the initial concentration of dicyclopentadiene, the percentage of extraction decreases. Fig. 3 shows that by increasing the initial concentration of dicyclopentadiene from 500 ppm to 1000 ppm the percentage of extraction at 293 K decreases by almost 21%. This is due to high dicyclopentadiene concentration, which gets limited Ag^+ for complex formation. While by decreasing initial concentration from 500 ppm to 100 ppm, percentage of extraction at 293 K increases by 20%. This is due to a

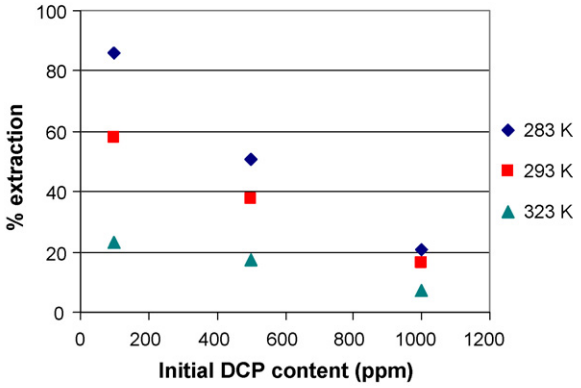

Fig. 3. Effect of initial dicyclopentadiene concentration in feed phase on the percentage of extraction of dicyclopentadiene at different temperatures.

Table 1
Calculated values of the equilibrium constant for complexation of dicyclopentadiene with silver ions ($[AgBF_4] = 0.02\ mol\ L^{-1}$).

Temperature (K)	K_{DCP} ($L^2\ mol^{-2}$)
283.15	19.7×10^4
293.15	11.3×10^4
323.15	2.68×10^4

low dicyclopentadiene concentration compared to a large amount of silver ion to form the Ag^+–π-complex.

Experimental equilibrium data have been fitted to Eqs. (4) and (6) in order to obtain the values of the model parameters (K_{DCP} (at 293 K) and ΔH°) and to check the validity of the proposed model. A non-linear multiparametric regression procedure was performed using the Aspen Custom Modeler (AspenTech) software tool. Calculated values of K_{DCP} were obtained by minimizing the weighted square error between simulated values with the model and experimental data; the best values of the parameter K_{DCP} are listed in Table 1. Fig. 4 compares the experimental values of the equilibrium concentrations with the simulated results using the proposed model together the estimated parameters. The experimental results are in good agreement with the prediction of the model and hence support the main assumptions of the model. Also the enthalpy (ΔH°) for the complex formation reaction was estimated, with a value of $-37.9 \pm 1.4\ kJ\ mol^{-1}$, in agreement with the exothermic character of the complexation reaction.

4.2. Simultaneous extraction of cyclopentadiene and dicyclopentadiene using ionic liquid solutions

By means of successive equilibrium stages with fresh organic phases and the same polar phase, we have determined the partition equilibrium that is shown in Fig. 5. Initial concentrations of CP and DCP in organic phase were about 1000 ppm for both cycloolefins. The results of partition of CP and DCP between organic and ionic liquid phases are given at 293 K; as shown, both solutes are selectively extracted from cyclohexane.

In this case, the evidence obtained implies the formation of a complex between one silver ion and one molecule of cyclopentadiene. This reaction is described by the equilibrium:

$$CP + Ag^+ \leftrightharpoons CPAg^+ \tag{7}$$

$$K_{CP} = \frac{[CP\,Ag^+]_{II}}{[[CP]_I \times m_{CP}] \times \left[[Ag^+]_{II}^{Total} - [CP\,Ag^+]_{II}\right]} \tag{8}$$

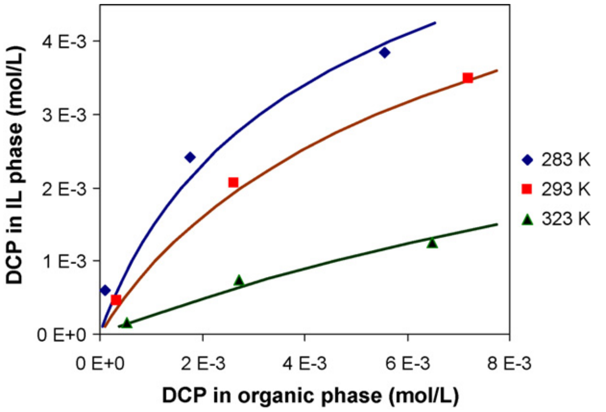

Fig. 4. Distribution of dicyclopentadiene between cyclohexane and $BMImBF_4$ phases. The lines represent the predictions of the model.

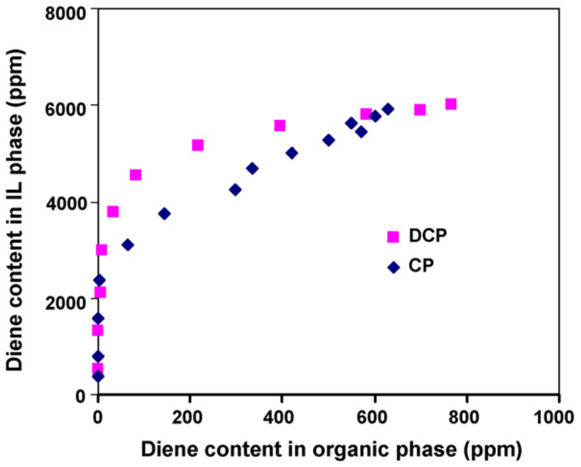

Fig. 5. Partition equilibrium of cyclopentadiene and dicyclopentadiene between organic and ionic liquid phases ($[AgBF_4] = 0.1\ mol\ L^{-1}$ in ionic liquid solution; 293 K).

In this study we have checked different stoichiometric ratio for the cyclopentadiene complexation reaction and we have found that Eq. (7) represents the stoichiometry that better fits the equilibrium experimental data.

The partition coefficient m_{CP} has been experimentally measured in the case of partition of CP between cyclohexane and $BMImBF_4$. A value of $m_{CP} = 0.34$ at 293 K has been found. The coefficient m_{CP} seems to be nearly independent of the composition in the experimental range of 0–1000 ppm of CP in the organic phase.

Experimental equilibrium data have been fitted to Eq. (8) using the Aspen Custom Modeler (AspenTech) software tool, obtaining a value of $K_{CP} = 2050\ L\ mol^{-1}$ at 293 K.

4.3. Extraction of cyclopentadiene using aqueous solutions

Experimental results show that cyclopentadiene is selectively removed to aqueous phase. As shows in Fig. 6 the silver salt concentration have a remarkably influence on the complex cyclopentadiene–Ag^+ formation. The percentage of cyclopentadiene extracted to aqueous phase increase with an increase of the complexation agent concentration (Ag^+).

Previous studies have reported that silver ions form π-complexes with olefins more easily in tetrafluoroborate solutions than in $AgNO_3$ solutions [3,15], and that the difference in concentration effects on molar absorptivity can be explained by the activity

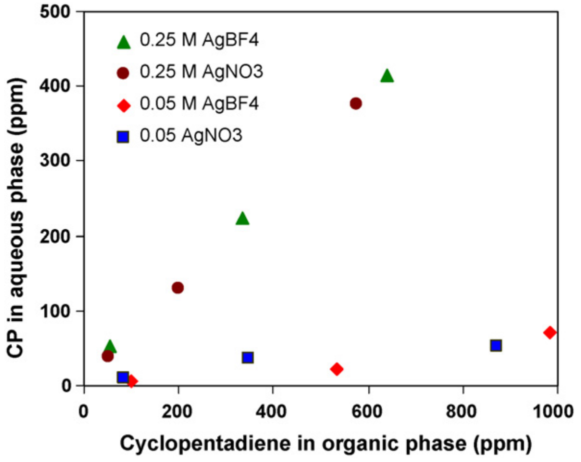

Fig. 6. Extraction of cyclopentadiene to aqueous phases at 283 K using different silver salts.

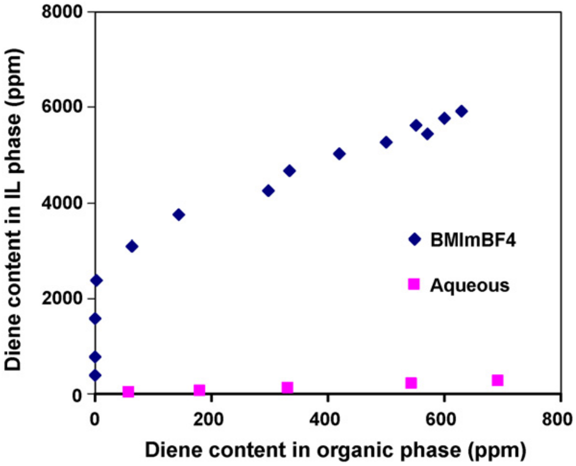

Fig. 7. Comparison of partition equilibria of cyclopentadiene in $BMImBF_4$ and aqueous solution using $AgBF_4$ 0.1 mol L^{-1} as complexing agent (293 K).

of Ag(I) ions in the solutions. Nevertheless, in the present work we have found a similar behavior of both salts in aqueous solution (Fig. 6), possibly due to the relatively low concentrations of salts. When dissolved in water, silver tetrafluoroborate is not completely dissociated into its ions. Especially at low temperatures and in concentrated solutions, this reduced degree of dissociation can have a tremendous effect on the physical properties of the solution and on the equilibrium constants of the reaction between cyclopentadiene and silver ions [15].

As shown, the cyclopentadiene removal can be carried out by extraction with aqueous solution. However, there are a number of disadvantages to this approach. Since water has a significant vapor pressure, some water will go into the olefinic product during the regeneration step. The water must therefore be removed from the olefins product.

The high vapor pressure of water also limits the maximum regeneration temperature that can be used. If sweep gases are used in the regeneration step process, these will further increase the evaporation of water. Also, water lost in the regeneration step must be replaced and the proper balance of water to complexing agent must be maintained.

From the comparison of results shown in Fig. 7 it is evident that the extraction is more efficient when it is carried out in ionic liquid media. Equilibrium experiments using cyclohexane containing about 500 ppm cyclopentadiene demonstrated that this process allowed purification of cyclohexane to a concentration below 0.3 ppm. In contrast to systems comprised of molecular solvents, ionic liquids have two components, a cation and an anion, which do not necessarily play a passive role in extraction, a fact highlighted in the recent literature [16]. Both cation and anion of an ionic liquid can act as a ligand or ligand precursor for a transition metal complex dissolved in the ionic liquid. In this case, the 1-butyl-3-methylimidazolium cation can act as a ligand precursor for the dissolved transition metal, making the silver ions more active in olefin complexation.

5. CONCLUSIONS

Two main conclusions have been obtained from this work, (i) the recovery of the cycloolefins (CP and DCP) via silver complexation has been successfully carried out in ionic liquid media and, (ii) the ionic liquid $BMImBF_4$ containing silver ions showed higher sorption capacity for cycloolefins than the corresponding aqueous solution. It was found that after dissolution of the silver salt ($AgBF_4$) in a RTIL medium, the dissociation of silver ions is more efficient leading to a percentage of extraction for the olefin higher than in aqueous media. The solubility of dienes in extractive mixtures increases with increasing silver concentration, and it decreases at higher temperatures due to a decreasing complexation constant as π-complexation reactions are exothermic.

Experimental results show that this process allows purification of cyclohexane reducing also the content of cycloolefins down to few parts per million. Furthermore, the use of $BMImBF_4$ as extraction media involves important advantages due its regeneration capacity. Negligible vapor pressure of ionic liquid facilitates solvent and olefin recovery by flash distillation after the extraction process.

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