

Silver assisted separation of n-decane/1-decene using distillable CO₂-derived alkyl carbamate ionic liquids



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ARTICLE INFO

Article history:

Received 27 October 2015

Received in revised form

15 December 2015

Accepted 23 December 2015

Available online 29 December 2015

Keywords:

Distillable ionic liquid

Separation

Olefin

Paraffin

Silver

Carbon dioxide

ABSTRACT

A series of distillable alkyl carbamate ionic liquids (ALKCARB ILs) have been prepared from CO₂ and an amine, and then treated with silver (I) oxide to give the task specific ionic liquids. The synthesized ionic liquids have been used for the separation of 1-decene selectively from the mixture of n-decane/1-decene at room temperature. Presence of CO₂ to form carbamate with alkyl amine in the synthesis of ionic liquids remarkably enhanced the separation of olefin from mixture; however in its absence silver containing amine solvent provided very poor separation under identical conditions.

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1. Introduction

Linear terminal or alpha olefins (LAO) are versatile and highly useful petrochemical products which find large and diverse applications including the manufacture of polymers, as synthetic lubricants, as intermediate for the production of detergents and base oil for synthetic drilling fluids and lubricant additives etc. [1,2]. Although a number of processes are known for the manufacturing of these olefins, most of them produce hydrocarbon streams that are mixture of olefinic and paraffinic hydrocarbons [3,4]. Therefore, the separation of the desired olefinic components from paraffin-rich streams is not only essential but also is one of the most costly processes in the petrochemical industry. The conventional approach for the separation of olefins from olefin/paraffin mixtures involving cryogenic distillation is a costly and highly energy intensive due to the similarity in boiling points between olefins and their corresponding paraffins [5]. Several processes have been proposed and investigated as cost-efficient alternatives including extractive distillation, absorption, adsorption and membranes [6,7]. Among the various known ways, the separation of olefin/paraffin mixtures via reversible π -complexation reactions of unsaturated

hydrocarbons with certain metal ions [e.g., Ag (I), Cu (I)] have been extensively studied [8–11]. Recently, considerable attention has been given to task specific metal ion containing ionic liquids (ILs) as potential alternative to common organic solvents in extraction processes. Owing to their unique features such as higher stability, non-flammability and tunable properties, they have been considered as green extractive media for the separation of organic compounds from various product streams [12,13]. However, expensive nature, tedious synthetic procedures and limited accessibility of ionic liquids make these processes less acceptable from practical viewpoints.

Ionic liquids readily prepared from addition of carbon dioxide and a secondary amine to give N,N-dialkylcarbamates (DIALKCARB), have been appeared to be a new class of solvents and recognized as self-associated “distillable” ionic media [14]. These ionic liquids belong to the class of ionic liquids that can be synthesized at room temperature merely by mixing the reactants. These dialkylcarbamates which undergo dissociation to the respective amine and carbon dioxide at higher temperatures can then be regenerated at room temperature [15]. Such CO₂-derived distillable ionic liquids have previously been used by Kreher et al. as reaction media for Diels–Alder reaction [16]. Later on Vijayaraghavan et al. used these ionic liquids as distillable extractive solvents for natural products [17]. However, to the best of our knowledge these ILs have never been used for the selective

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separation of olefins from the mixtures of olefin/paraffin.

Herein, we report for the first, the use of DIALKCARBS (synthesized from a secondary amine such as diethylamine and CO₂) enriched with silver (I) oxide as the extractive medium for the selective separation of 1-decene from the mixture of n-decane/1-decene. The presence of CO₂ in the formation of carbamate along with the amine leads to a remarkable enhancement in the separation efficiency than the simple silver containing amine as solvent. After selective extraction, olefin was readily recovered from the ionic liquid by distilling off the low boiling carbamate followed by decomposition of Ag-olefin complex in the presence of a hydrocarbon solvent which is miscible to olefin (Fig. 1). The recovered silver oxide was recycled for the separation of n-decane/1-decene in the subsequent runs. The olefin separation cycle via reversible π -complexation with silver ion containing distillable ionic liquid has been schematically shown in Fig. 1.

2. Experimental

2.1. Materials

All the chemicals such as n-decane, 1-decene, diethylamine, dibutylamine, dibenzylamine, silver nitrate, silver tetrafluoroborate, silver triflate and n-heptane used in the present study without further purification are given in Table 1.

2.2. Synthesis of Ag⁺ containing alkylcarbamate ionic liquids

The synthesis of the alkylcarbamate ionic liquids followed the literature procedure [13]. Typically, the synthesis of diethylcarbamate (DIETHCARB) involves slow addition and stirring of diethylamine (2 mol) with solid carbon dioxide (1 mol) at room temperature (293 K) and atmospheric pressure [18]. In a similar manner, other alkylcarbamates such as dibutylcarbamate and dibenzylcarbamate were also synthesized from their corresponding amines. All the synthesized alkylcarbamates were obtained as liquid at room temperature. The alkylcarbamate ionic liquids were then stirred with freshly prepared silver (I) oxide [19] to give the task specific silver ion containing distillable ionic liquids. The amount of silver (I) oxide was taken in accordance to the olefin to Ag⁺ molar ratio as 1: (0.5–2.0). The silver ion bearing alkylcarbamate ionic liquids were subsequently used for the separation of 1-decene from the mixture of n-decane/1-decene as per the scheme shown in Fig. 1.

2.3. Sample analysis

The raffinate phase and the extracted hydrocarbon were analysed by injecting a specific amount of sample (0.2 μ L) by a syringe

Table 1

Purity of chemicals used in the present study and suppliers.

| Chemical | Supplier | Purity, mass% | Analysis method |
|--------------------------|---------------|---------------|-------------------------|
| n-decane | Sigma–Aldrich | 95 | GC ^a |
| 1-decene | Sigma–Aldrich | 99 | GC |
| Diethylamine | Sigma–Aldrich | 99.5 | GC and NMR ^b |
| Dibenzylamine | Sigma–Aldrich | 97 | GC |
| Dibutylamine | Sigma–Aldrich | 99.5 | GC |
| n-heptane | Sigma–Aldrich | 98% | GC |
| Silver nitrate | Sigma–Aldrich | 99% | Trace metal analysis |
| Silver tetrafluoroborate | Sigma–Aldrich | 98 | Trace metal analysis |
| Silver triflate | Sigma–Aldrich | 99% | Trace metal analysis |

^a Purity checked by gas chromatography.

^b By nuclear magnetic resonance.

graduated in to minimum volume of 0.1 μ L to a gas chromatography (GC) equipped with a PTV injector and a Flame ionization detector. The specification of GC with the column details and oven programme are mentioned below:

GC Model: VARIAN CP-3800

Column: CP-Sil 24 CB-MS -CP5817

Dimension: 30 m \times 0.25 mm \times 0.25 μ m

Injector temperature: 270 $^{\circ}$ C

Injector type: Programmed Temperature Vaporizing injector (PTV)

FID detector temperature: 300 $^{\circ}$ C

Column oven temperature programme:

| Rate ($^{\circ}$ C/min) | Temperature ($^{\circ}$ C) | Hold time (min) | Total time (min) |
|--------------------------|-----------------------------|-------------------|------------------|
| Initial | 40 | 2.0 | 2.0 |
| 5.0 | 120 | 2.0 | 20 |
| 5.0 | 250 | 10 | 56 |
| | | Total time | 56.00 |

The retention time (RT) of components in GC:

| Component | Retention time (min.) |
|-----------|-----------------------|
| n-decane | 13.61–13.72 |
| 1-decene | 13.85–13.88 |

The percentage of component extracted or separated is calculated by:

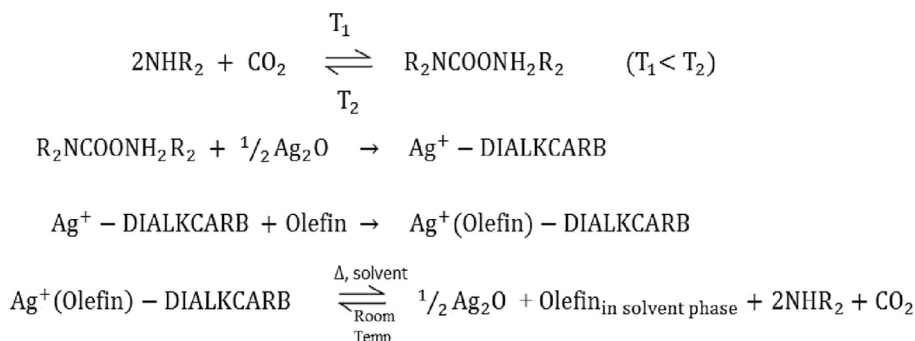


Fig. 1. Scheme for n-decane/1-decene separation by Ag⁺-dialkylcarbamate ionic liquid.

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