

# **A Novel and Environmentally Benign Approach to Combine Reactions and Separations Using Ionic Liquids and Supercritical Carbon Dioxide**

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## **Abstract**

A novel and environmentally benign approach is described to combine reactions and separations, using simultaneously ionic liquids (ILs) and supercritical carbon dioxide (SC-CO<sub>2</sub>). The novel approach is based on the phenomenon that two (partially) immiscible liquid phases upon pressurization with CO<sub>2</sub> is able to force to form one homogeneous fluid phase. The homogeneous phase allows reactions to be carried out at high rates without the need for an additional co-solvent to enhance solubility. However, pressure reduction will restore the presence of two liquid phases. This behavior is called “miscibility switch”. Since the light liquid phase is free of IL, SC-CO<sub>2</sub> is used to extract the product from the reaction mixture, i.e., contamination of the product by the IL is not possible. To investigate the applicability of the miscibility switch, the asymmetric hydrogenation of methyl-(Z)- $\alpha$ -acetamido cinnamate (MAC), yielding methyl-(Z)- $\alpha$ -acetamido hydrocinnamate (MAHC), catalysed by a Rh-catalyst, is chosen as a model reaction. It is possible to bring the IL, the reactant and the product into a homogeneous phase by applying CO<sub>2</sub> pressure.

## **1. Introduction**

The chemical industry is under considerable pressure to design new and environmentally benign processes, which minimize adverse effects on safety, health and environment. These processes should minimize or preferably eliminate the formation of waste, avoid the use of toxic and/or hazardous reagents and solvents and being energy-efficient.

The production of waste can be reduced significantly by replacing traditional stoichiometric syntheses by atom-efficient catalytic alternatives. Of course, efficient recycling of the catalyst is a prerequisite for economically and environmentally attractive processes. It is possible to perform atom-efficient reactions catalytically in ILs as reaction media, because they are able to dissolve a wide range of catalysts [1,2]. In case of hydrogenations, hydroformylations and carbonylations, atom-efficiencies as high as 100% can be achieved, i.e., no waste is produced at all! Moreover, the use of ILs as reaction media may lead to enhancement of reaction rates and the improvement of chemo- and regio-selectivities in comparison to conventional reaction media [3,4].

Solvent losses can be minimized using alternative ‘green’ solvents. For instance, ILs have the potential to be used as green solvents for reactions. ILs don’t have any measurable vapour pressure, so they don’t evaporate and they cannot pollute the atmosphere [1,4]. Furthermore, it is possible to extract organic compounds from ILs with SC-CO<sub>2</sub>. Because ILs don’t dissolve in CO<sub>2</sub> and depressurisation completely removes CO<sub>2</sub> from the IL-phase, it is possible to recover pure products without any IL contamination and minimal environmental pollution [5,6].

In this paper, for a selected reaction a novel and environmentally benign way to combine the reaction and the separation is described, using an IL and SC-CO<sub>2</sub>. The novel approach is based on the miscibility switch phenomenon: two immiscible phases can be forced to form one homogeneous phase in presence of compressed CO<sub>2</sub> [7,8]. With this two-phase/single-phase transformation, it is possible to carry out the reaction in a homogeneous system with high reaction rates without the need of an additional co-solvent to lower the viscosity or to enhance solubility. After completion of the reaction, the product formed can be extracted by using SC-CO<sub>2</sub>. The extraction process will not cause contamination of the product by the IL, since it has no solubility in SC-CO<sub>2</sub> and the IL/catalyst phase can be easily reused.

## 2. Miscibility switch phenomenon

For ternary fluid multiphase systems of near-critical CO<sub>2</sub> and certain organic solutes, the miscibility switch phenomenon was first described by Peters and Gauter [7] and Gauter et al. [8], although at that time the various liquid-liquid immiscibility phenomena observed in ternary CO<sub>2</sub> systems were mentioned immiscibility windows and holes, respectively. The miscibility switch phenomenon turned out to be a very general phenomenon. For instance, it was established also to hold for systems with an IL, an organic solute, and SC-CO<sub>2</sub> [9].

In Figure 1 the phase diagram of a system consisting of an IL, an organic reactant, and SC-CO<sub>2</sub> is shown. When the organic reactant and the ionic liquid are completely miscible at ambient conditions, indicated by the lowest position of the arrow in Figure 1 (liquid + vapour), it is possible to induce the formation of a second liquid phase by applying CO<sub>2</sub>-pressure upon the mixture at fixed temperature, i.e., the three-phase region liquid + liquid + vapour is entered. The denser liquid phase is rich in IL, the newly formed liquid phase is rich in reactant and the vapour phase is almost pure CO<sub>2</sub>. The applied CO<sub>2</sub> pressure at which the second liquid phase appears depends on temperature and concentrations.

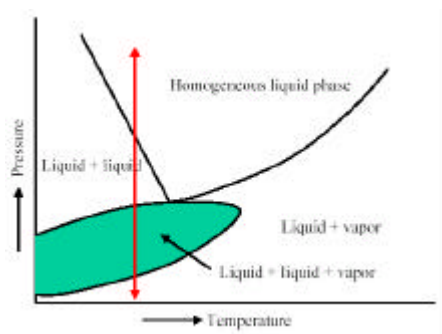


Figure 1: Phase diagram of IL/organic reactant/ CO<sub>2</sub> system

The formation of a second liquid phase is caused by the fact that with increasing concentration of CO<sub>2</sub> in the liquid phase (IL + reactant), CO<sub>2</sub> starts to act as an anti-solvent for the reactant. A further increase of the pressure eventually will cause the disappearance of the vapour phase and, as a consequence, the two-phase region liquid + liquid is entered (see Figure 1). The upper liquid phase is a gaseous like fluid phase in which the IL does not show any measurable solubility [9], i.e., from this phase the last traces of IL are expelled, resulting in a CO<sub>2</sub>/reactant phase, free of IL. Pressurizing the liquid-liquid two-phase system eventually will lead to a homogeneous fluid phase. Since this phase behaviour is reversible, it is called ‘miscibility switch’.

This phenomenon offers both a homogeneous region, which is attractive for performing the reaction, and a two-phase region, which is suitable to separate the product without contamination by the IL.

### 3. Application of the miscibility switch phenomenon

#### a. Model reaction

To investigate the applicability of the miscibility switch, the asymmetric hydrogenation of MAC, yielding MAHC was chosen. This reaction is catalyzed by (-)-1,2-bis((2R,5R)-2,5-dimethylphospholano)benzene-(cyclooctadiene)rhodium(I) tetrafluoroborate (Rh-catalyst). The reaction and catalyst are shown in Figures 2 and 3.

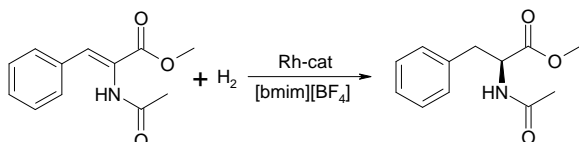


Figure 2: The model reaction

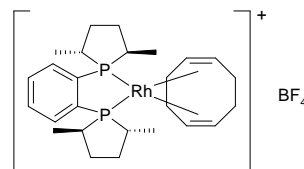


Figure 3: Rh-catalyst

The asymmetric hydrogenation of MAC using an IL, has been carried out before by Berger et al. [10]. They used [bmim][BF<sub>4</sub>] as the IL-phase. However also *iso*-propanol was needed to lower the viscosity of the IL-phase and to increase the solubility of hydrogen in the IL-phase. It was apparent that the conversion and enantioselectivity increased when the solubility of hydrogen increased in the liquid phase [10,11]. This is also valid for other asymmetric hydrogenation reactions in ILs, such as the asymmetric hydrogenation of 2-arylacrylic acids [12] and tiglic acid [13].

In the novel approach all the components will be forced into one (low-viscous) homogeneous phase in the presence of CO<sub>2</sub>. Consequently, higher reaction rates can be reached and no additional co-solvent will be needed. The product will be subsequently extracted from the reaction mixture by SC-CO<sub>2</sub>. The IL-phase 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) was chosen, because the solubility of hydrogen in this IL is relatively high [11,14] and other properties of this IL are already known [15,16].

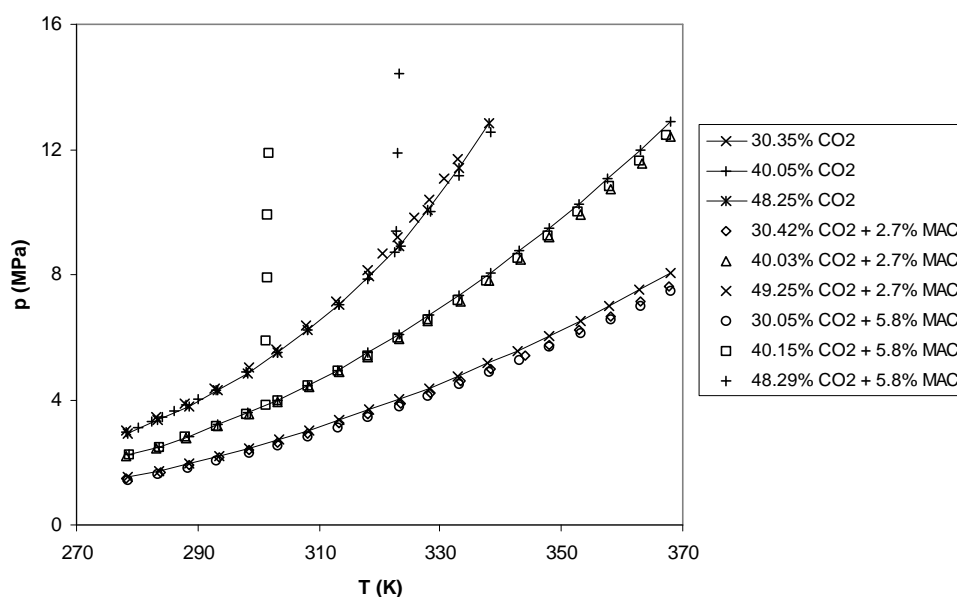


Figure 4: Phase diagram of the system [bmim][BF<sub>4</sub>]/MAC/ CO<sub>2</sub>

### b. Experimental

The effects of MAC (reactant), MAHC (product) and Rh-catalyst on the phase behaviour of the system  $\text{CO}_2$  + [bmim][ $\text{BF}_4$ ] were investigated. The phase behaviour of the system  $\text{H}_2$  + [bmim][ $\text{BF}_4$ ] was also studied experimentally. The phase diagrams were measured using a Cailletet apparatus for  $\text{CO}_2$  systems and using an autoclave apparatus for  $\text{H}_2$  systems. For a detailed description of these facilities and methods of measurement we refer to Shariati and Peters [17].

### c. Results and discussion

Both MAC and MAHC have reducing effects on the equilibrium pressure of the IL/  $\text{CO}_2$  system (see Figure 4 and 5). This is the result of co-solvency effects. The co-solvency effects are dependent on concentrations. A concentration of 5.8 mol% reactant in IL has a smaller influence on the equilibrium pressure than a concentration of 2.7 mol% in IL: an optimum in co-solvency effects exists. Also for  $\text{CO}_2$  concentrations an optimum exists: at lower  $\text{CO}_2$  concentrations this substance acts as a co-solvent, while at higher concentrations  $\text{CO}_2$  becomes an anti-solvent for dissolved solutes in ILs, i.e., the solute precipitates from the IL, see Figure 4.

The reactant MAC has a larger influence on the equilibrium pressure of the IL/ $\text{CO}_2$  system than the product MAHC. The reason is that the reactant and  $\text{CO}_2$  are chemically more different than the product and  $\text{CO}_2$ . The reactant is insoluble in hexane (it can be crystallized

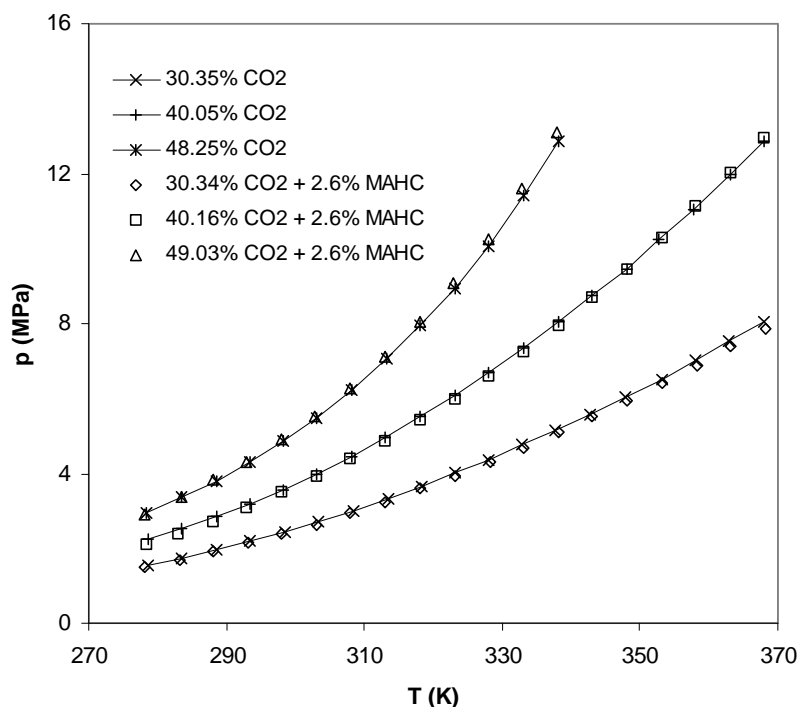


Figure 5: Phase diagram of the system [bmim][ $\text{BF}_4$ ]/MAHC/  $\text{CO}_2$

from hexane), whereas the product is soluble in hexane. Because the polarity of hexane and SC- $\text{CO}_2$  are equal and ‘like dissolves like’, it is expected that  $\text{CO}_2$  and reactant are chemically more different than  $\text{CO}_2$  and product, resulting in stronger co-solvency effects.

Figure 6 compares the p-x diagrams of the systems IL/Rh-catalyst/ $\text{CO}_2$  and IL/ $\text{CO}_2$  at 320 K. As shown in Figure 6, the presence of the catalyst does not have any significant effects on the

equilibrium pressure. Figure 7 shows the phase diagram of the system  $\text{H}_2 + [\text{bmim}][\text{BF}_4]$ . This system has elevated equilibrium pressures. In the near future, we will study, if  $\text{CO}_2$  is able to increase the equilibrium concentrations of  $\text{H}_2$  in the system  $\text{IL}/\text{H}_2/\text{CO}_2$  by expanding the IL solution and lowering the viscosity of the system.

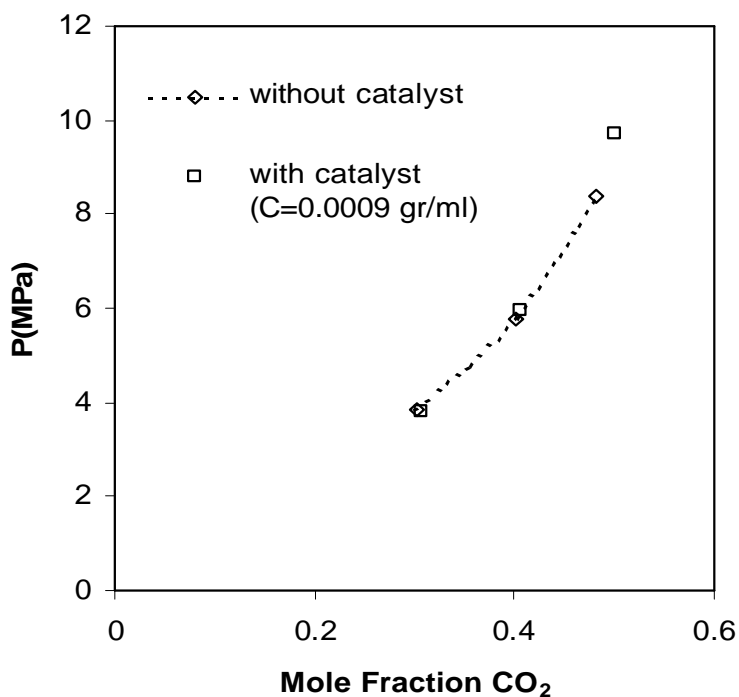


Figure 6. Phase diagram of the system  $[\text{bmim}][\text{BF}_4]/\text{Rh-catalyst}/\text{CO}_2$  at 320 K

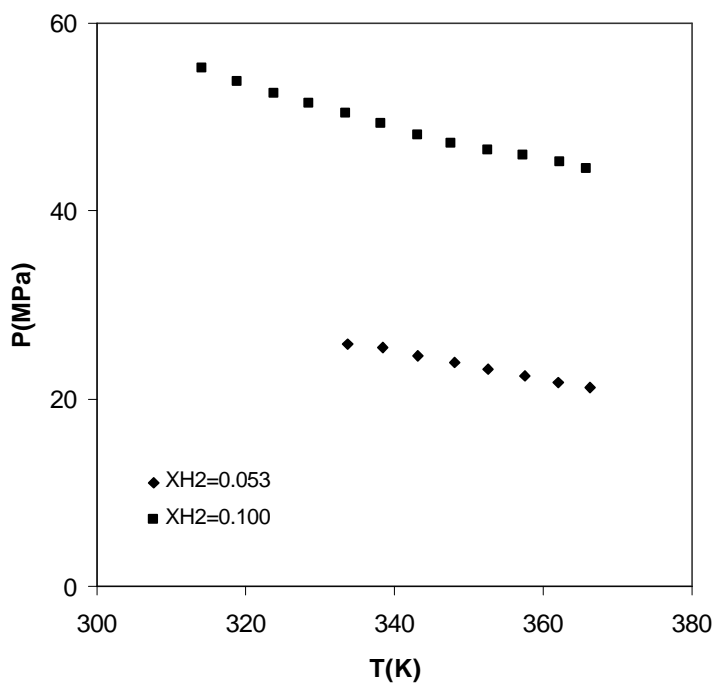


Figure 7. Phase diagram of the system  $\text{H}_2 + [\text{bmim}][\text{BF}_4]$

#### 4. Conclusions

The miscibility switch phenomenon can be used to combine reactions and separations. The reaction can be carried out in the homogeneous system under SC-CO<sub>2</sub> pressure and the SC-CO<sub>2</sub> can be used to extract the product simultaneously from the reaction mixture.

To investigate the applicability of the miscibility switch, the asymmetric hydrogenation of MAC, yielding MAHC, catalysed by a Rh-catalyst, is chosen as model reaction. It is possible to bring IL, reactant and product in a homogeneous phase under CO<sub>2</sub> pressure. Both reactant and product have a reducing effect on the equilibrium pressure of the IL/ CO<sub>2</sub> system as a result of co-solvency effects, but the effect of reactant is larger. The co-solvency effects are dependent on concentrations. However, high concentrations of CO<sub>2</sub> can have an anti-solvent effect on dissolved solutes in ILs.

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