CRYSTALLISATION OF SOLUTES IN THE IONIC LIQUID [AMIm]Cl ASSISTED BY SC-CO_2

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Abstract

Our study concerns the crystallisation by antisolvent effect of the solute in binary solvent mixture of ionic liquid and supercritical CO_2 (SC-CO_2). The aim is to combine for this process, the advantages of ionic liquid and supercritical CO_2: a non-volatile and non-toxic solvent [1] in which SC-CO_2 improves the transport and transfer properties. As the first part, this paper presents some tests of feasibility, for which we choose cyclodextrins and cellulose as solutes.

The experimental solubility measurements of these organic compounds in ionic liquids at different temperatures (70°C, 80°C and 100°C) lead to choose [BMIm]Cl and [AMIm]Cl. They are hydrophilic ionic liquids and the average mass solubility is 3% for the cellulose and more than 30% for cyclodextrins at 70°C.

We also studied the effect of water and SC-CO_2 on the solubility of the compounds in [AMIm]Cl. The results showed that the water had an anti-solvent effect. However, it seems that SC-CO_2 has no effect on solubility. So, it allowed conceiving crystallisation or gelation of these compounds in ionic liquid using water as antisolvent. The use of SC-CO_2 decreases the viscosity of the mixture, improves the kinetic of dissolution and permits an easy spraying for particles generation.

Hence, a process of cellulose particles production assisted by supercritical SC-CO_2 has been tested.

1. Introduction

The ionic liquids form a “not so old” class of solvents that have interesting properties such as good polarity, high thermal stability and negligible vapour pressure. Most of them are non-flammable, liquid over a large range of temperature including room temperature. These advantages balance the poor solubility of inorganic and organic compounds in these liquids.

Their non-volatility property makes them potential candidates to replace hazardous volatile organic solvents in a lot of applications including: liquids separation, extraction, crystallization, electrochemical uses, chromatography, and chemical and biochemical reactions [2, 3].

The ionic liquid is an organic salt made up of an organic cation (ammonium, imidazolium, pyridinium…) and an anion (halides, PF_6^-, BF_4^-, NO_3^-…). Combining different kinds of anions with different cations we can obtain a lot of ionic liquids. Depending on the cation and the anion nature the physical and chemical properties may be significantly affected (density, viscosity, polarity, hydrophilic character…) [4, 5, 6]. Thus, it’s possible to choose the ionic liquid suitable for the desired application. In our work we test the replacement of traditional solvents in crystallization process by a combination of ionic liquids and supercritical CO_2.

The ionic liquids absorb a large amount of SC-CO_2 without an important volumetric expansion whereas the ionic liquid is not soluble in CO_2 rich phase [7, 8, 9]. Therefore, it is very easy to separate the CO_2 from the ionic liquid. Thus, the recycling of the ionic liquid is possible.

In a previous study, an analytical set-up was designed to measure the thermodynamic and physical properties of the binary ionic liquid/CO_2 such as viscosity, interfacial tension, density and solubility of CO_2 in ionic liquid [9]. This current study on a ternary mixture ionic liquid-CO_2-solute is aimed to choose the suitable combination in order to set up a green crystallization process.

Three solutes (cellulose and cyclodextrins) have been tested in ionic liquids and cellulose was the chosen solute. Cellulose is the most abundant biopolymer in the world. Principal constituent of the plant cell, it is used in many applications (industrial, agriculture and medical….). However, it has a rigid structure that makes it insoluble in water or in the conventional organic solvents. Its solubility in ionic liquids has arisen more and more interest in the last years [10, 11, 12].
Hence, a study of crystallization by anti-solvent effect of water on mixture ionic liquid/cellulose assisted by supercritical CO_2 is in progress. This paper presents the preliminary results obtained with the [AMIm]Cl (Allyl Methyl Imidazolium Chloride).

2. Experimental section

2.1. Materials

[AMIm]Cl is provided by IOLITEC (Germany). It is more than 98% pure, with a pK_a of 20-25, a melting point of 55°C, and water content less than 1000 ppm. Cotton cellulose is provided by Sigma Aldrich. γ-cyclodextrin comes from Wacker chemie GmbH (Germany). Its molecular weight is M=1297g/mol, solubility in water at 25 °C equal to 233g/l. β-cyclodextrin comes from the same supplier and its molecular weight is M=1135g/mol, solubility in water at 25 °C is equal to 18,5g/l, and its melting point is T_m=260°C.

2.2. Hygroscopic character of [AMIm]Cl

The hygroscopic character is an important feature that influences the physical properties of the different ionic liquids such as density, viscosity and melting temperature [13].
Dynamic Vapour Sorption (DVS) technique was used to test the hygroscopic character of [AMIm]Cl. The experimental results presented in figure 1 shows the sorption and desorption cycle of water vapour onto [AMIm]Cl. The sample mass is recorded in function of time at fixed temperature and relative humidity (RH). The transition to a higher (or lower) RH plateau (with unchanged temperature) is linked to fixed criteria for equilibrium conditions: maximal time for RH level=300mn, equilibrium assumed when |dm/dt|<0,003. For RH>50% the equilibrium is not reached.
At relative humidity RH=90%, the equilibrium level of adsorbed mass is not reached yet, so [AMIm]Cl can absorb more water. Desorption cycle was studied by decreasing relative RH from 90% to 0% and no hysterisis was observed. These results indicate that [AMIm]Cl is very hygroscopic. The ionic liquid, which is solid at room temperature, adsorbs progressively water and the mixture becomes

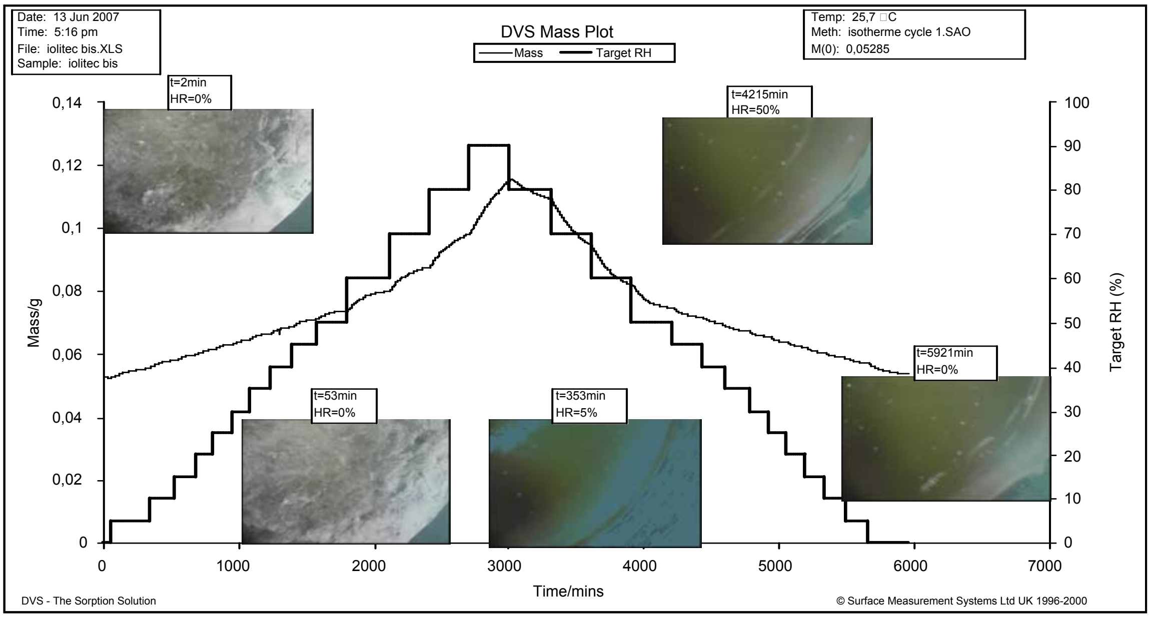

Figure 1. Water uptake of [AMIm]Cl at different RH levels and at fixed temperature.

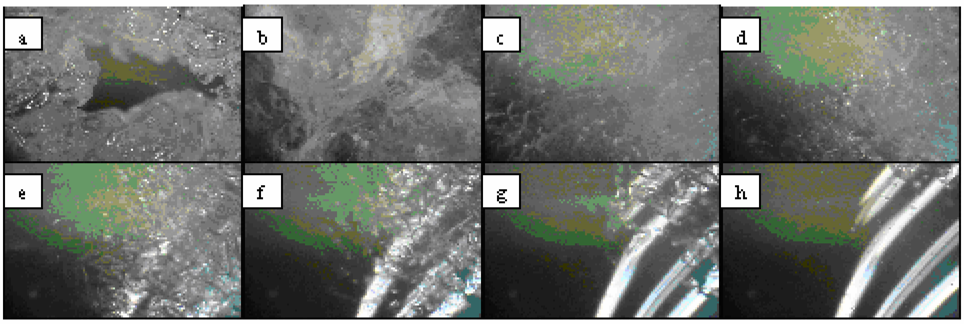

Figure 2. [AMIm]Cl sample visualised in DVS experiments at RH=5% after (a) 0mn, (b) 18mn, (c) 30 mn, (d) 160mn, (e) 280mn, (f) 380mn, (g) 420mn, (h) 460mn.

liquid. The phase transition occurs at 5% RH.
Considering that phase change occurred at RH= 5 % (as it is showed on figure 1). The powder was subjected to a constant RH= 5 % during 10 hours and pictures were taken every 2 minute. Figure 2 presents some of them. It is noticed that the water content of product increased until reaching 7%. Moreover, we noticed a change of appearance progressively with time: the solid powder became very wet in 15 mn, then a liquid drop charged with solid particles was formed and finally a total liquefaction was obtained after 460 mn.
This property is important because the presence of water in the sample affects the solubility of solutes such as cellulose in the ionic liquid [10].

2.3. Solubility of solutes in ionic liquid

First, we tested previously the solubility of different organic compounds (cyclodextrins and cellulose) in ionic liquids: [AMIm]Cl (Allyl Methyl Imidazolium Chloride), [BMIm]Cl (Butyl Methyl Imidazolium Chloride), [BMIm]PF_6 (Butyl Methyl Imidazolium Hexafluorophosphate), [BMIm]BF_4 (Butyl Methyl Imidazolium Tetrafluoroburate) and [BMIm]NTf_2 (Butyl Methyl Imidazolium Bistriflimide) at different temperatures (70°C, 80°C and 100°C).
The solubility has been determined in a vessel of 200 ml equipped with a mechanical stirrer, and connected to a thermostated bath for heating. We preset the temperature and we added progressively a few amount of solute in the ionic liquid until saturation is reached (solid stayed in suspension).
From the results obtained, [BMIm]Cl and [AMIm]Cl have been chosen. They are hydrophilic ionic liquids, non-toxic with a good solvent power for the different substances. In this paper, we present a qualitative study of solubility with [AMIm]Cl at 70 and 80°C (Table 1).
Cyclodextrins are highly soluble in [AMIm]Cl and cellulose is soluble (Table 1). [AMIm]Cl contained free chloride that disturbed and broke hydrogen bonds present in the molecules of cellulose and cyclodextrins and formed a new network [10, 11]. The possible dissolution mechanism of cellulose in [AMIm]Cl is illustrated in the figure 3.

Table 1. Solubility results of organic solutes in [AMIm]Cl.

Solute	Solubility	Effect of CO_2 P=[1-200]bars, T=45°C	Effect of water at atmospheric Pressure
γ-cyclodextrin	=40% (at 70°C)	Co-solvent or modification of dissolution kinetic	No effect
β-cyclodextrin	=30% (at 80°C)	No apparent effect	Anti-solvent
Cellulose	3.5% (at 80°C)	No apparent effect	Anti-solvent

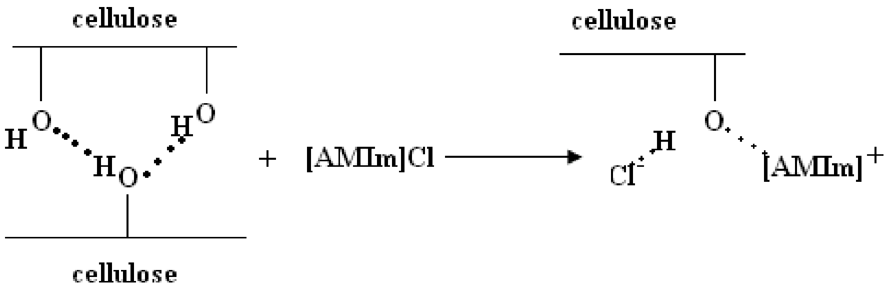

Figure 3. Possible dissolution mechanism of cellulose in [AMIm]Cl [11].

2.4. Effect of CO_2 on solubility

The effect of CO_2 on the solubility of the compounds in [AMIm]Cl was tested on the high pressure cell (SITEC). We prepared a solution of ionic liquid and solute near saturation at 25%, 35% and 3% (w/wt) for γ-cyclodextrin, β-cyclodextrin and cellulose respectively in the vessel at the conditions of temperatures indicated before (70°C and 80°C). After cooling at ambient temperature for 24h, the dissolution is irreversible. In the SITEC cell at 45°C, we added CO_2 at different pressures (1-200) bars. We followed the appearance of the solution through the sapphire windows and camera during two hours.
In addition, the co-solvent effect was tested in the SITEC cell using suspension (saturated solution + solid in suspension) at 45%, 40% and 4% (w/wt) for γ-cyclodextrin, β-cyclodextrin and cellulose respectively. We preset temperature at 45°C, increased the pressure and waited for the phase modification during two hours for each pressure.
The results (Table 1) showed that CO_2 had no effect on the solubility of cellulose and β-cyclodextrin. It had a slight effect on the solubility of γ-cyclodextrin and played a co-solvent role or affected the dissolution kinetic of cyclodextrin in [AMIm]Cl by decreasing the ionic liquid viscosity . The second case is the most probable effect. So, CO_2 did not influence the interactions between the studied solutes and ionic liquid.

2.5. Effect of water on solubility

The effect of water on the solubility was tested in the same vessel used before to test the solubility. We added water on the solution of ionic liquid and solute under saturation and we observed any modification. The water was an anti-solvent for cellulose and β-cyclodextrin. With the cellulose, we obtained a gel (Figure 3-a). If we injected the solution of cellulose/AMImCl by syringe in the water, we obtained a tub of cellulose (Figure 3-b). With β-cyclodextrin, we obtained solid and powder after drying (Figure 3-c). The water had no effect on the solubility of γ-cyclodextrin, which is hydrophilic compared to β-cyclodextrin.
The gel obtained with cellulose and ionic liquid is yellow. This colour disappeared after washing with distilled water because [AMIm]Cl is a hydrophilic ionic liquid.

(a) (b) (c)

Figure 4. Products obtained after adding water to a mixture solute/ionic liquid for cellulose (a) and (b) and β-cyclodextrin (c).

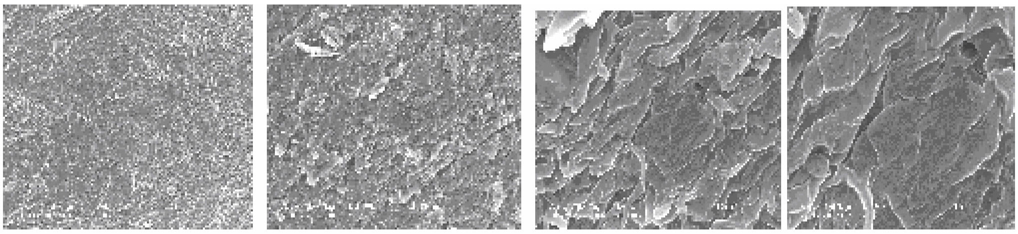

Figure 5. SEM photos of the gel obtained without CO_2.

2.6. Cellulose particles generation process without CO_2

A solution of cellulose 3% (w/wt) was prepared at 80°C. Using water as anti-solvent, we prepared a gel of cellulose at atmospheric pressure without CO_2 and we obtained the same results as before (figure 3-a), that is a thermo reversible gel [11]. After keeping the gel in water for 5 days and changing the water every day, we obtained a transparent gel. This last one was characterized with scanning electronic microscopy (SEM).
The SEM suggests that the gel is composed of some sort of superposed layers inducing the presence of some internal porosity. However this porosity has not been confirmed yet, this gelation model could lead to a new membrane production.

2.7. Process assisted by supercritical CO_2

Chloride based ionic liquids are viscous and their viscosity increases dissolving cellulose in them. This is a limitation in their use in a particles generation process.
In a previous study [9], it was shown that SC-CO_2 decreased the viscosity of the ionic liquid. Therefore, we add CO_2 in order to improve the process with this less viscous mixture.
So, we have prepared solution with 3% (w/wt) cellulose and [AMIm]Cl at 80°C and SC-CO_2 pressure equal to 11 MPa in mixing cell which is connected with another cell containing water at ambient temperature and SC-CO_2 pressure around 7 MPa (Figure 6).
The ternary mixture [AMIm]Cl/cellulose/CO_2 was sprayed into the second cell through a nozzle. We obtained cloud white-yellow liquid. We filtered the suspension, washed the solid with 500 ml of distilled water until the yellow colour disappeared, dried at 45°C under vacuum for 24 h. Finally, we obtained solid showed in figure 7. This solid seems an entanglement of filament-like particles more porous than the gel without CO_2 as it was shown in figure 8.
In addition, regenerated cellulose seems to have the same X-ray diffraction spectra than the initial one (Figure 9).

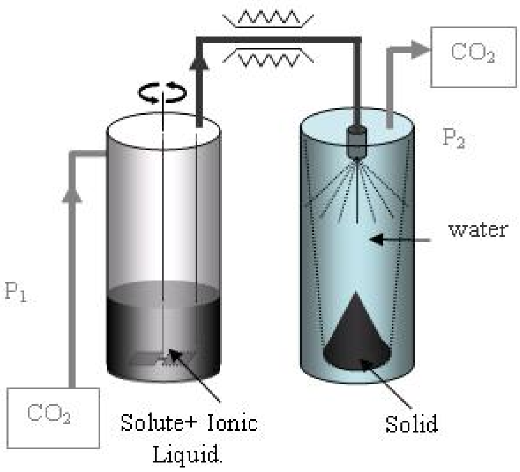

Figure 6. Experimental apparatus

Figure 7. The solid obtained with CO_2

Figure 8. SEM photos of the cellulose obtained with CO_2

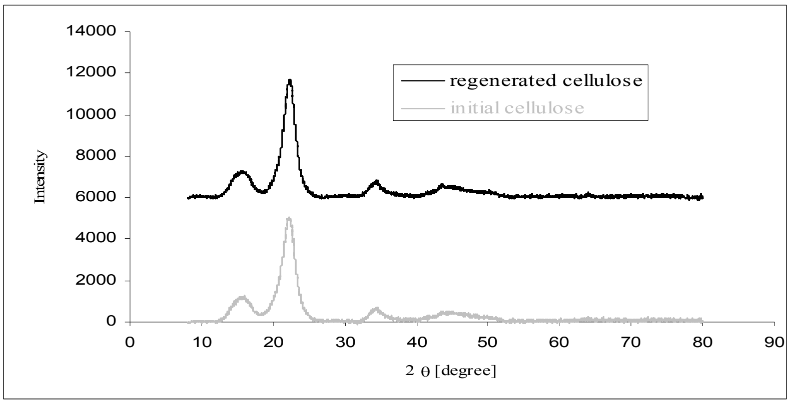

Figure 9. X-Ray diffraction spectra of cotton cellulose

3. Conclusion

Cyclodextrins and cellulose have a sufficient solubility in chloride based ionic liquids for particles generation process by antisolvent effect. Using water as anti-solvent and SC-CO_2 to improve transfer and transport properties of the cellulose in [AMIm]Cl, we are able to achieve crystallization or gelation of cellulose.

So, an environmentally friendly process for cellulose particles generation has been tested. It promises a large success for the future. Further works are to recycle the ionic liquid after washing and to study the influence of different parameters (CO_2 pressure, kind and diameter of the nozzle) on the atomization process.

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