CHEMISTRY UNDER SUPERCRITICAL CO_2 CONDITIONS IN A GLASS CHIP

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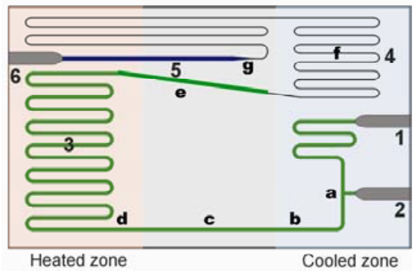
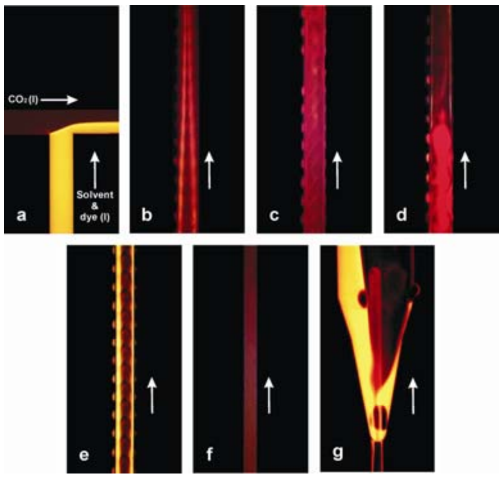
Supercritical (SC) fluids are used as "green" alternatives for organic solvents and they have become attractive media in chemistry due to their unique properties that are different from those of either gases or liquids. SC fluids lead to higher selectivities, better yields and/or orders of magnitude higher reaction rates in synthetic chemistry[1]. Experimental data on the behaviour of these SC fluids is needed to understand and exploit these special properties for supercritical fluid chromatography, extraction and chemistry applications. Here a study by optical microscopy is presented of the flow and phase behaviour of dense fluids in a glass chip. The system is also used for studying the influence of pressure and temperature on chemical synthesis performed under supercritical CO_2 conditions.

Flow and Phase Behavior: Visualization of Phase Transitions

In the microreactor (chip), Fig. 1a, phase transitions in a 50/50 v/v mixture of CO_2 and EtOH with Rh.B as dye, were studied using microscopic visualization. In Fig. 1b the flow patterns at different locations in the chip are shown.



(a)



(b)

Figure 1: Microfluidic chip layout (a) and microscopic visualization of phase transitions (b). Images at different positions in the chip (letters correspond to locations in Figure 1). The flow direction is indicated by arrows. **1** inlet CO_2, **2** inlet alcohol-dye mixture, **3** reaction zone, **4** fluidic resistor, **5** expansion zone, **6** outlet.

During the visualization experiment of Fig. 1b the inlet pressure was maintained at 100 ± 0.5 bar, the temperature of the heated and cooled zone were kept at 60 ºC and 10 ºC, respectively. Image **a** shows the injection of the EtOH+Rh.B solution into the liquid CO_2 stream. The fluids gradually mix in the channel section with a "herringbone" structure, and the initial lamella flow pattern (image **b**) turns into a homogeneous, uniformly coloured mixture (image **c**). When the mixture reaches the required temperature, an abrupt change in the flow pattern occurs: a peculiar red coloured swirling flame structure is observed (image **d**) which represent a transition involving SC CO_2. Downstream, a two-phase system forms with the liquid flowing along the walls, image **e**, and a vapour in the middle of the channel. When the two-phase system enters the fluidic resistor, a uniform coloured liquid mixture is seen again, image **f**. Finally, the liquid mixture enters the expansion zone, where it starts to boil (formation of vapour bubbles - image **g)**.

Flow and Phase Behavior: Phase Diagrams Construction

The visualization events described above were studied over a wider range of temperatures and pressures, for the 50/50 v/v mixtures of EtOH-CO_2 as well as MeOH-CO_2. For pressures up to 140 bars, the temperature was recorded at which the characteristic change in flow pattern occurred at a fixed position in the chip (**d** in fig. 1(a)): these glass microreactors offer the property that phase diagrams can be constructed based on the identification of unique flow patterns. In Fig. 2 the phase diagram for MeOH-CO_2 (50/50 v/v) is presented. The visualized patterns are reproducible and the obtained *p*,*T*-values are in agreement with phase transition data reported in literature for identical mixtures. With these microreactors phase diagrams can be constructed in a time-efficient way.

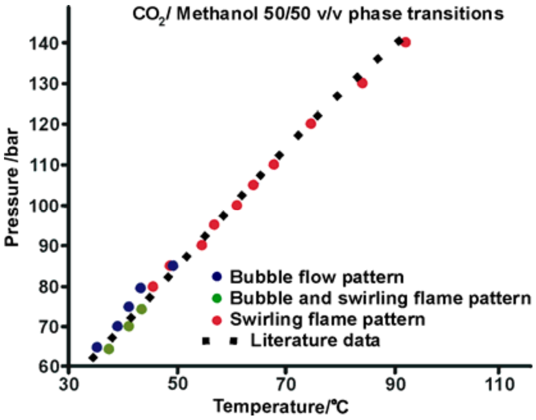
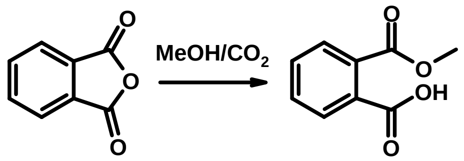


Figure 2: Phase diagram derived from microscopic observation of flow patterns in the chip. The mixture is 50/50 v/v MeOH-CO_2. Dotted line is data from bubble lines reported in literature[2].



Scheme 1: The esterification of phthalic anhydride in methanol at SC CO_2 conditions.

Chemical Synthesis under SC CO_2 Conditions: an Esterification Reaction

The esterification of phthalic anhydride in methanol was performed in the microreactor under SC CO_2 conditions as well at high pressures (reaction time of ~1 second). As can be seen in Fig. 3, substantial improvements in product formation are observed for these conditions, in particular when carried out under SC CO_2 conditions. It is possible to quantify the influence of pressure, temperature and SC conditions on the product formation.

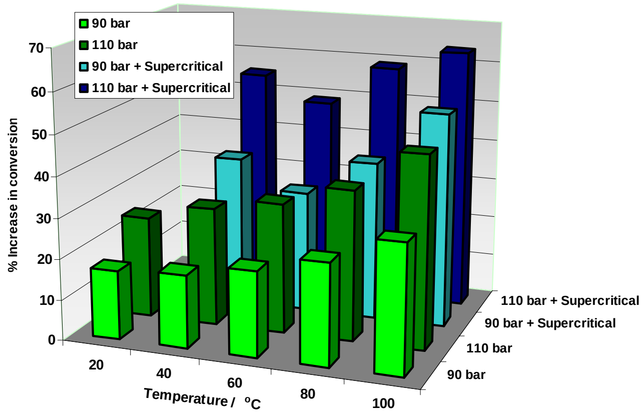


Figure 3: %-product formation in the chip for each experiment with and without SC CO_2 as a co-solvent for the two different pressures are plotted

References

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