Solubility measurements of piperazine

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Introduction

The interest towards precipitating systems has increased in the recent years due to Alstom's chilled ammonia process and the suggestion of precipitating amino acid salt systems. In precipitating systems solid precipitates are produced as the CO_2 loading exceeds a certain value making it theoretically possible to reach high rich loadings. Additionally since high loadings can be reached, the amount of solvent needed will decrease and this can lead to reduced energy required for regeneration.

Piperazine is a carbamate forming diamine which has a high capacity to bind CO_2. Unlike many other amines, piperazine has a limited solubility in water, possibly making it attractive for precipitating CO_2 capture systems. It also has other advantages since it is known to have fast kinetics[1,2], and energy consumption for concentrated piperazine based CO_2 capture system is estimated to be lower compared to 30 wt % MEA[2]. Moreover piperazine is stable against oxidative and thermal degradation.[2,3] However piperazine does not biodegrade and it has been reported to form nitrosamines when in contact with NO_x.[4,5]

In this work the solubility of piperazine in the piperazine-water-CO_2 system was measured by dissolution and crystallization sequences.

Experimental

In this work solid liquid solubility of piperazine was studied over a range of piperazine concentrations and CO_2 loadings using the Lab-Max system equipped with probes for in-situ focused beam reflectance measurements (FBRM) and particle vision microscope (PVM) , supplied by Mettler Toledo. The set-up includes a mechanically agitated (stirring speed?), jacketed glass reactor of 1 L volume suitable for operation at temperatures up to 200 ^{o}C and pressures up to 5 bar. The FBRM technique measures the light reflected by particles that pass close to the probe window, and reports the chord length distributions giving information about the onset of crystallization and the size of the particles. The emerging crystals was visualized by PVM. Prepared solutions were subjected to a series of cooling/heating sequences and the temperature at the onset of crystallization (by cooling) or completion of dissolution (at heating) was recorded. These in-situ laser techniques make it is possible to observe the dissolution of the crystals to determine the solubility in a solvent system without liquid sampling and to get information about the size and shape of the piperazine crystals.

Results and discussion

Dissolution temperatures were measured in this work for unloaded piperazine solutions in the concentration range from 17.2 to 61.5 wt%. Results are compared to literature data[1,3,6,7] in Figure 1. The data from literature show a eutectic point around 60 wt% (61.5 wt% according to DOW Chemicals). It was observed in this work that the crystals formed in 61.5 wt% piperazine solution have different morphology when compared to crystals formed at lower

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concentrations (supersaturations) and that the crystallization was slower. This probably explains the lower temperature of dissolution at this concentration shown in Figure 1. An example of the PVM picture taken within the minute after onset of crystallization is shown in Figure 2.

Effect of CO_2 loading on solubility of piperazine solutions was studied for 40, 50 and 61.5 wt% piperazine solutions at CO_2 loading up to 0.65 mol-CO_2/mol-amine. In these experiments the solutions were heated/cooled after some amount of CO_2 was added to the solution. Results from this work agree very well with the data from Freemen et al.[2,3]

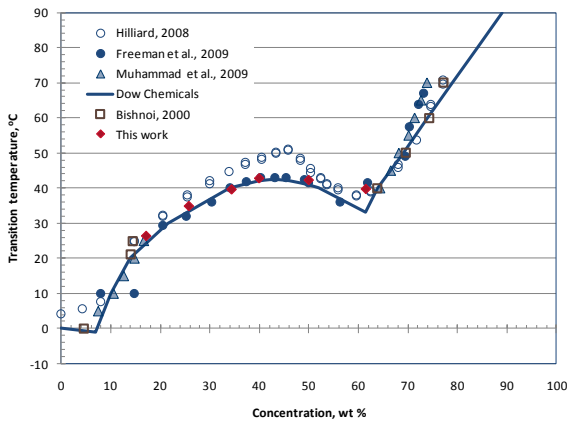

Figure 1. Piperazine dissolution temperatures for unloaded solution. The literature data can be found from [1,2,*]

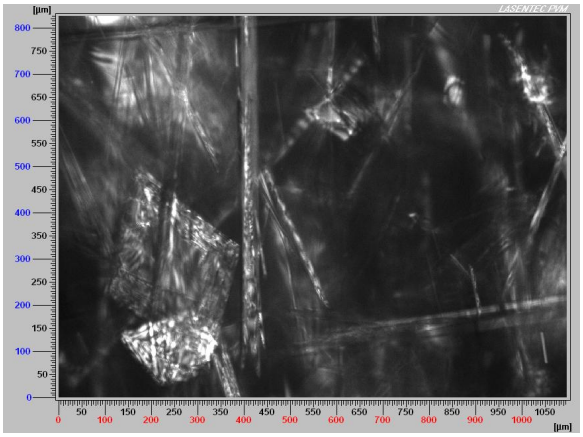

Figure 2.PVM pictures of crystals in 61.5 wt% Piperazine solutions (unloaded).

Conclusions

In this work the solubility of piperazine in the piperazine-water-CO_2 system was measured in crystallization and dissolution sequences using the Lab-Max reactor system. The crystallization was monitored insitu by PVM and FBRM to follow crystal nucleation and particle size and morphology development without liquid sampling. The solubility results agree well with literature data. This work has shown the benefit of the reactor system and the online methods for studying precipitating CO_2 capture systems, pointing to the potential use of the same method in future for other solvent systems.

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