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Precipitation behaviour of bicarbonate salts in carbon capture solvents

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Abstract

Solvent-based chemical absorption using aqueous amines, is currently the most mature carbon capture technology. Many amine-based capture solvents form both carbamate and bicarbonate species upon reaction with carbon dioxide (CO₂). The formation of bicarbonate, rather than carbamate, is preferable due to its reaction stoichiometry, requiring a 1:1 ratio of amine to CO₂, compared to 2:1 required for carbamate. Additionally, bicarbonates are also less thermally stable than carbamates, reducing the cost of solvent regeneration. It is therefore beneficial to have a capture solvent which only produces bicarbonate as the product of the reaction with CO₂. Such solvents which have this property include hindered amines, carbonate- and carboxylate-based solvents. Upon reaction of CO₂ with these types of solvent, and subsequent formation of bicarbonate species in solution, it is possible for solid bicarbonate to precipitate from solution. The precipitation of bicarbonate from such solutions could provide advantages for their operation by increasing the CO₂ absorption capacity of the solvent as the precipitation of bicarbonate shifts the reaction equilibrium to favour the products.(1)

Understanding the formation of solids within these types of carbon capture solvents, particularly the influence of the other additives on precipitation will be essential for large-scale implementation. The precipitation of bicarbonate in carbonate solutions has already been studied in the literature (1-3), and differences in key crystallisation parameters such as metastable zone widths (MSZWs) and crystallisation onset temperatures were observed with different carbonate concentrations and apparent CO₂ loading. The addition of glycine to concentrated potassium carbonate solvents was also studied whereby the addition of glycine to the carbonate system was shown to widen the MSZW, resulting in faster nucleation kinetics of bicarbonate than in its absence. Different crystal structures were also observed by SEM at medium cooling rates (35 °C/h).(2)

This work applies similar experimental procedures and analysis to study the influence of carboxylate species and organic solvents on the precipitation of potassium bicarbonate (KHCO₃) in particular. Carboxylate-based capture solvents use organic solvents to modify the reactivity of the carboxylates so they can react with CO₂.(4) Polythermal cooling crystallisation techniques, with turbidity monitoring, have been used to investigate the influence of potassium acetate and potassium isobutyrate on the dissolution temperature (T-dissolution), crystallisation onset

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temperature (T-crystallisation), and the MSZW of KHCO_3 crystallisation in aqueous solutions. Subsequently, the nucleation kinetics were evaluated using a variety of methods, including Nývlt, Self-Nývlt relation and CNT theory.

Solubility curves of KHCO_3 , KHCO_3 with 10 mol% potassium acetate and potassium isobutyrate were constructed which showed that the solubility of KHCO_3 decreased with the addition of the carboxylate salt to the system, with increased T-dissolution values for all concentrations when carboxylate salt was added. Polythermal crystallisation measurements of 5.0 M KHCO_3 with 10 mol% of potassium acetate or potassium isobutyrate, were completed at various cooling rates, between (18 and 60 °C/hr), and the crystallisation onset temperatures and equilibrium solubility measurements used to calculate the MSZW at each of these cooling rates (Figure 1). Values of T-crystallisation increased for both carboxylate salts, with a higher value for potassium isobutyrate. The MSZW for KHCO_3 cooling crystallisation with the carboxylate additive systems was narrower than in the aqueous-only solution and there was a general trend of decreasing MSZW with increasing cooling rate, up to 45 °C/h for all systems. At higher cooling rates, the trends did not hold; this may be due to crystallisation at higher cooling rates being more stochastic. However, similar results were seen for the addition of glycine to the carbonate system, similar behaviour was seen at high concentrations of glycine for cooling rates above 35 °C/h, so this may be a real effect for bicarbonate precipitation in the presence of additives. It was found that in the presence of carboxylate, at cooling rates <45 °C/h, the nucleation kinetics of KHCO_3 were slower but the energetic barrier to nucleation was reduced.

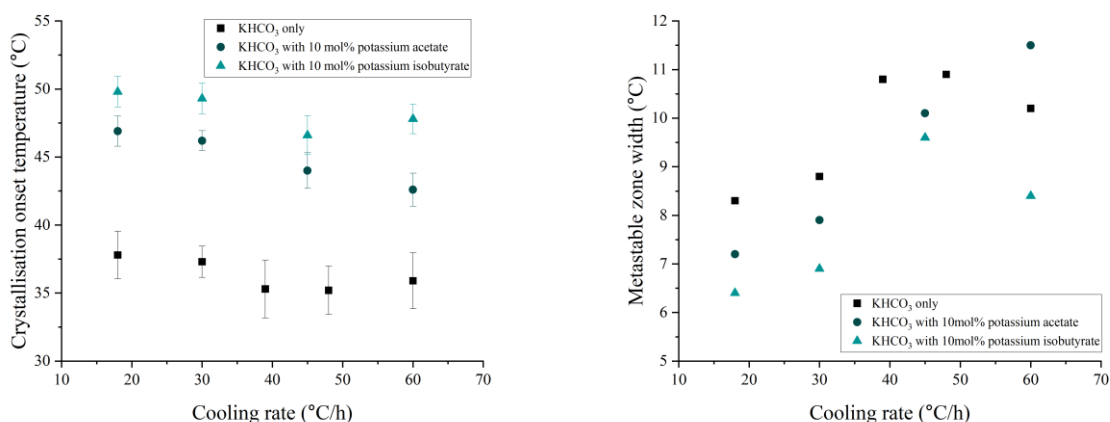


Figure 1 Crystallisation onset temperatures and metastable zone widths for aqueous 5.0 M KHCO_3 and 5.0 M KHCO_3 with 10 mol% of potassium acetate and 10 mol% potassium isobutyrate as additives at various cooling rates

Organic solvents can be used to modify the reactivity of carboxylate-based carbon capture systems. Therefore, a study has also been completed using microscopy and X-ray diffraction techniques to study the influence of organic solvents on the crystal habit and crystal structure of the bicarbonate crystals during batch cooling crystallisation. Interestingly, crystallisation from water and methanol (10 vol%) produced bicarbonate with a flat plate habit, rather than the hexagonal prism habit commonly seen in aqueous solution and the literature (Figure 2). (1, 2, 5) Also, crystallisation with water and glycol ethers produced much larger inter-grown crystals than from purely aqueous solution. The habit of crystals is important for the operability of large-scale continuous processes, therefore this habit modifying behaviour of organic solvents needs to be investigated further to establish how the bicarbonate crystals grow in different capture solvent environments.

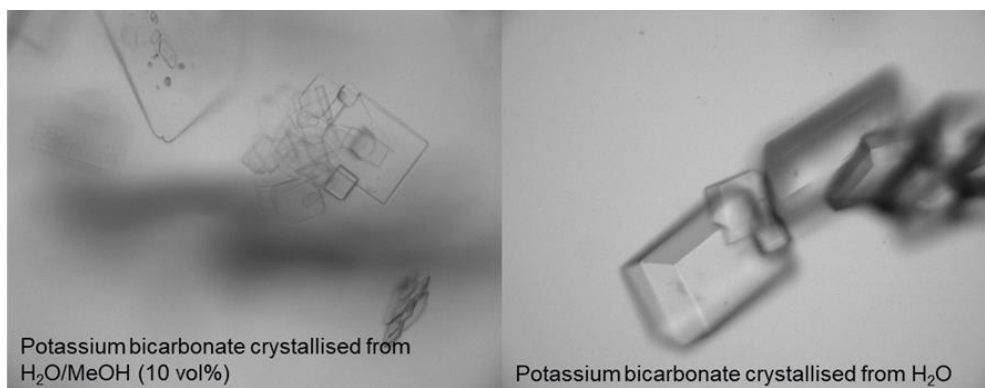


Figure 2 Images of potassium bicarbonate crystal habit obtained during cooling crystallisation in water and water-10 vol% methanol using Mettler Toledo EasyViewer 400 PVM probe

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