Precipitation behaviour of bicarbonate salts in carbon capture solvents

Rose E. McCarthy[1], Christopher M. Rayner[1], Fiona Meldrum[1], Nikil Kapur[2] cmrem@leeds.ac.uk
1. School of Chemistry, University of Leeds, 2. School of Mechanical Engineering, University of Leeds

1. Carbon Capture using Carboxylate-Based Solvents

- Carbon capture and storage (CCS) is **essential** for achieving global atmospheric temperature targets[1]
- Traditional amine solvents used for CCS have issues with undesirable degradation products and high energy penalties

Lean carboxylate capture solvent

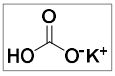
CO_2 loaded carboxylate capture solvent with **bicarbonate solid precipitate**

- Carboxylate salt-based solvents are a new class of solvents which have benefits over amine solvents, i.e. lower toxicity and degradation[2]
- They produce **bicarbonate salts** as the product of the **reaction** with carbon dioxide (**CO_2**) and, the bicarbonate may **precipitate** during the reaction
- Precipitating systems have scale-up challenges e.g. blockages, flow and, unwanted secondary crystallisation processes

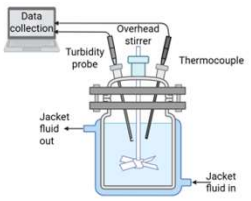
Project Aim: Investigate the influence of **bicarbonate concentration** and **carboxylate salt additives** on the crystallisation of potassium bicarbonate

2. Experimental Methods for Crystallisation

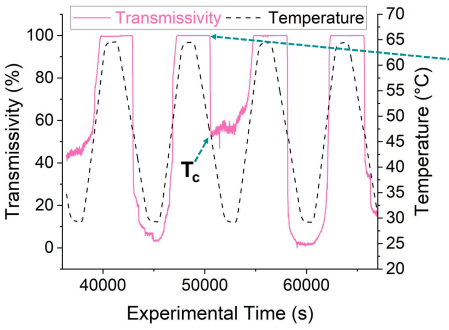
- **Cooling crystallisations** of potassium bicarbonate (**$KHCO_3$**) were completed in a stirred jacketed reactor with **transmissivity** and **temperature** monitoring
- The **onset of crystallisation** upon cooling is detected by the turbidity probe when the **transmissivity** of the solution **drops** suddenly



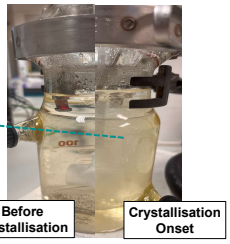
Potassium bicarbonate



Experimental set-up for crystallisations



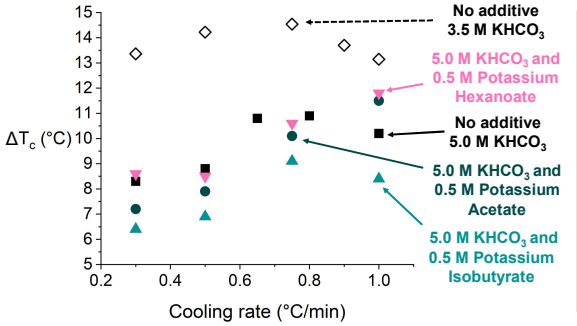
Temperature and transmissivity trace for cooling crystallisation

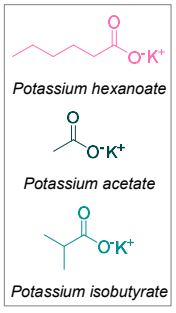


- Multiple heating and cooling cycles were done at various cooling rates
- **Crystallisation onset temperature (T_c)** was recorded for each cycle

3. Metastable Zone Widths of $KHCO_3$ Solutions

- **T_c** was measured for 2 $KHCO_3$ **concentrations** (3.5 and 5.0 M) and 3 **carboxylate salts** (at additive concentration of 0.5 M) in aqueous solution
- The **metastable zone width (ΔT_c),** the difference between equilibrium saturation and when crystals form from solution, was calculated from **T_c** and equilibrium solubility data at different cooling rates for kinetics evaluation





- Narrower **ΔT_c** = easier crystallisation – **isobutyrate** gives the narrowest **ΔT_c**
- General **ΔT_c** increase with cooling rate up to 0.7-0.8 °C/min where **no additive** and **potassium isobutyrate** systems deviate and start to decrease

4. Evaluation of Crystallisation Nucleation

- Several models utilise **ΔT_c** crystallisation data collected at different cooling rates to understand crystal **nucleation behaviour and kinetics**
- Most models assume an **increase in the metastable zone width** with **increasing cooling rate**, therefore, only data collected between cooling rates of 0.3-0.8 °C/min were used for this analysis
- KBHR theory[3] uses a **ln-ln plot of cooling rate** vs **critical undercooling (u_c)** to determine whether crystal nucleation is **progressive** (slope > 3) or **instantaneous** (slope < 3)
- Critical undercooling is calculated from ΔT_c and equilibrium solubility (T_e)

Instantaneous Nucleation
All nuclei form at start of crystallisation and then grow

Progressive Nucleation
Nuclei are constantly forming throughout crystallisation

Equation for critical undercooling

$$u_c = \frac{\Delta T_c}{T_e}$$

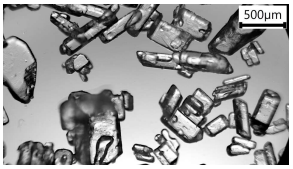
System	KBHR Analysis Results	
	KBHR Slope	Nucleation Type
3.5 M $KHCO_3$	10	Progressive
5.0 M $KHCO_3$	2.8	Instantaneous
5.0 M $KHCO_3$ with 0.5 M Potassium Acetate	2.5	Instantaneous
5.0 M $KHCO_3$ with 0.5 M Potassium Isobutyrate	2.3	Instantaneous
5.0 M $KHCO_3$ with 0.5 M Potassium Hexanoate	3.2	Progressive

- Nucleation is **progressive** for 3.5 M $KHCO_3$ compared to **instantaneous** for 5.0 M $KHCO_3$, indicating nucleation is **more difficult at lower concentration**
- KBHR slope value for 5.0 M $KHCO_3$ **decreases** upon addition of **potassium acetate** and **potassium isobutyrate** and remains **instantaneous,** indicating addition of these molecules **promotes** crystallisation of $KHCO_3$
- However, addition of **potassium hexanoate** increases the slope value and type changes to **progressive** indicating this additive **inhibits** crystallisation

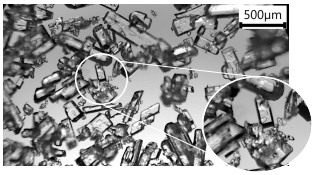
5. Microscopy of $KHCO_3$ Crystals

- Crystals from all experiments are exclusively **$KHCO_3$** and the examples shown are from 0.5 °C/min cooling experiments

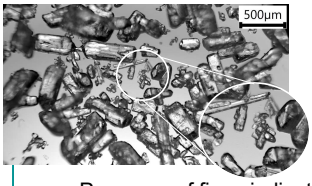
5.0 M $KHCO_3$



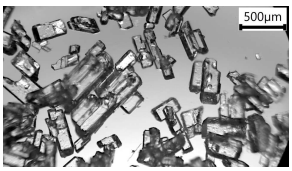
5.0 M $KHCO_3$ + 0.5 M Potassium Acetate



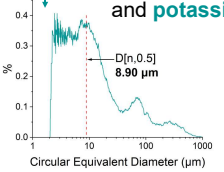
5.0 M $KHCO_3$ + 0.5 M Potassium Isobutyrate



5.0 M $KHCO_3$ + 0.5 M Potassium Hexanoate

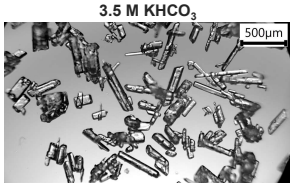


- Presence of fines indicates secondary nucleation at the 0.5 °C/min cooling rate for crystallisation of $KHCO_3$ with **potassium acetate** and **potassium isobutyrate** additives



PSD for $KHCO_3$ product with Potassium Isobutyrate Additive

3.5 M $KHCO_3$



Crystals from 3.5 M $KHCO_3$ cooling crystallisation have a higher aspect ratio than 5.0 M $KHCO_3$

6. Conclusions and Future Work

- The addition of carboxylate salts impacts the crystallisation behaviour and the final crystal product of $KHCO_3$
- Different carboxylate salts influence crystallisation parameters to different extents. **Potassium acetate** and **isobutyrate** may promote crystallisation and **hexanoate** may inhibit it

Future work: study wider concentration ranges and a variety of carboxylate additives and, measure growth rates of $KHCO_3$ under different conditions

References and Acknowledgements

1. Intergovernmental Panel on Climate Change. *Global Warming of 1.5°C: IPCC Special Report. Cambridge:* Cambridge University Press, 2022.
2. Barnes, D., Schoolderman, C., Jakab, G., Lawlor, D., Holdsworth, D., Nesti, K., Osterstrom, K., McCarthy, R., Bilal, F., Mackay, J., Rela, G., Wheatley, J. and Rayner, C. Transformational Low Energy, Amine-Free Solvents for CO_2 Capture. In: *IEAGHG 5th Post Combustion Capture Conference*, September 2019.
3. Kashchiev, D., Borissova, A., Hammond, R.B. and Roberts, K.J. *Journal of Crystal Growth.* 2010, **312**(5), pp.698-704

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