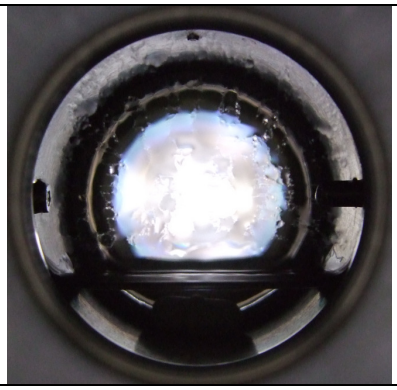
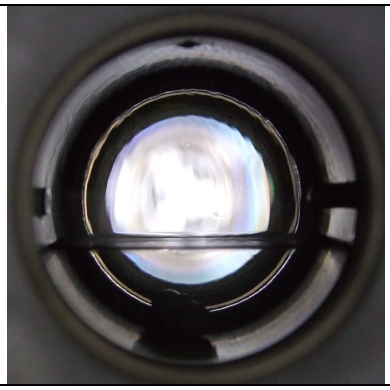
Phase Exploration of Propionaldehyde

3.87 g of propionaldehyde was added to a variable volume view cell set to 24.90 mL.[1] This was then heated to an external temperature of 90 °C and CO_2 was then pumped in with a PU-1580-CO_2 HPLC pump to gradually increase the pressure. The ratio of organic to CO_2 is higher than that found in the continuous flow system to aid visualisation (approximately 5 times higher at 100 bar) and the measurements were used as an estimate of the solubility of the organic in CO_2.

i) 26.2 °C, 1.0 bar



ii) 82.8 °C, 3.6 bar



iii) 85.2 °C, 78.8 bar

iv) 85.6 °C, 89.0 bar

v) 87.9 °C, 99.6 bar

vi) 88.0 °C, 109.6 bar

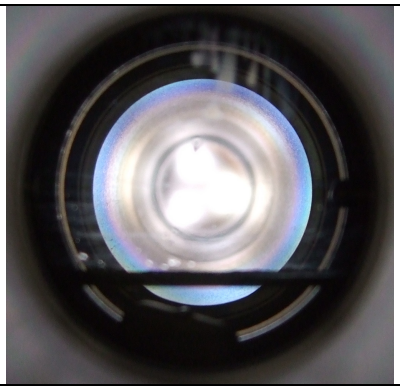
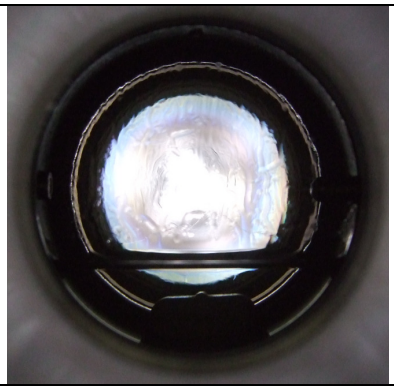
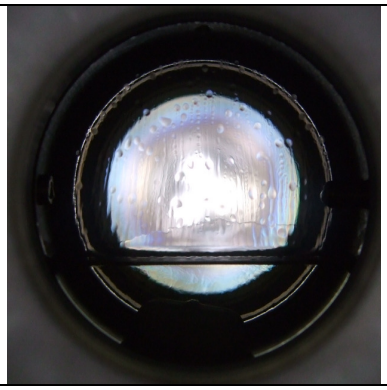
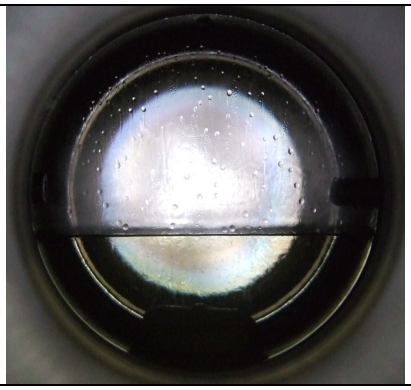
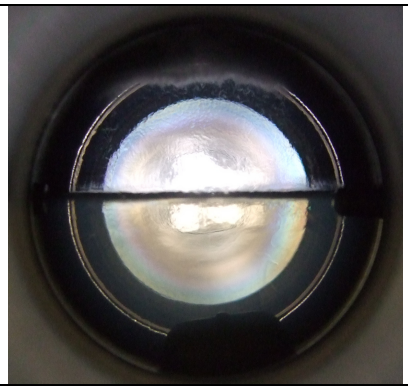
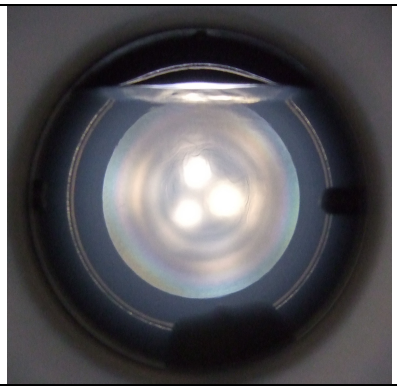
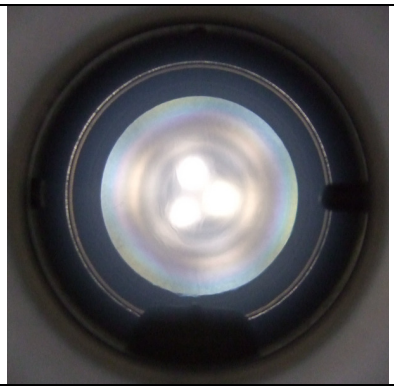
vii) 88.4 °C, 117.2 bar

viii) 88.7 °C, 140.4 bar

From ii) to iii) we can see that there is already a rapid expansion in the volume of the lower phase indicating that at even at 80 bar propionaldehyde has been expanded by CO_2 and the CO_2 phase is also likely to be very organic rich. By 120 bar (image vii) the system has become single phase.

Phase Exploration of 2-Methylpentenal

2.01 g of 2-methylpentenal was added to a variable volume view cell set to 7.90 mL. This was then heated to an external temperature of 90 °C and CO_2 was then pumped in with a PU-1580-CO_2 HPLC pump to gradually increase the pressure. The ratio of organic to CO_2 is approximately 5 times higher to aid visualisation than that found in the continuous flow system and the measurements were used as an estimate of the solubility of the organic in CO_2.

		
i) 22.2 °C, 1.0 bar	ii) 83.7 °C, 1.7 bar	iii) 85.2 °C, 78.6 bar
		
iv) 85.1 °C, 97.2 bar	v) 84.8 °C, 116.3 bar	vi) 85.0 °C, 136.3 bar
		
vii) 85.2 °C, 135.0 bar	viii) 85.6 °C, 162.0 bar	ix) 86.0 °C, 183.2 bar

As the pressure is initially increased to 79 bar we can see that the organic layer begins to become expanded by the CO_2 (image iii), this continues until the system becomes single phase at 180 bar.

The product clearly is less soluble in CO_2 than the propionaldehyde starting material. At the lower concentrations of material in the continuous flow apparatus we would expect both materials to be more efficiently solvated. The intermediate product is thought to be significantly less soluble in CO_2 than the product due to its higher polarity, however, it could not be isolated in sufficient yield to explore its solubility.

References

1. P. Licence, M. P. Dellar, R. G. M. Wilson, P. A. Fields, D. Litchfield, H. M. Woods, M. Poliakoff and S. M. Howdle, *Review of Scientific Instruments*, 2004, **75**, 3233-3236.