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Unravelling Anomalous Mass Transport in Miscible Liquids

D. McKechnie[1]*, I. Moreno[1,2], C. Tachtazis[3], A. Nordon[2,4], L. Lue[1], J. Cardona[1,2,3]

[1]Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, U.K.
[2]EPSRC Future Manufacturing Research Hub for Continuous Manufacturing and Advanced Crystallisation (CMAC), Glasgow, UK
[3]Department of Electronic and Electrical Engineering, University of Strathclyde, Glasgow, U.K.
[4]Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, U.K.
*d.mckechnie@strath.ac.uk

The dissolution dynamics between miscible liquids play a key role in many industrial, biological and environmental processes, including solvent-induced phase transformations such as the formation of polymer membranes or antisolvent crystallisation. The "common" current intuition that guides the design of diffusion processes in miscible liquids is rooted in Fick's law. This hypothesis generally holds when the system is close to equilibrium and behaves like an ideal mixture. However, Fickian diffusion has limited applicability far from equilibrium, and many systems display "anomalous" behaviours such as uphill diffusion [1] or the Ouzo effect [2]. Despite the importance of diffusion processes, the mechanisms underlying anomalous mass transfer are still poorly understood [3]. This work provides a direct microscopic view into highly localized anomalous pathways that can occur during the mixing of miscible fluids.

Results will be presented for a model system of glycine-water-ethanol that represents a typical antisolvent crystallisation process where anomalous mass transport can have significant impacts on the critical quality attributes of the resulting crystalline product. We have deployed a novel experimental setup that includes a microfluidic flow cell that is monitored using a confocal Raman microscope, enabling the measurement of spectral maps of the mixing of the solution and antisolvent streams. These maps allow for the evolution of the composition of the multicomponent fluid to be determined as mixing progresses.

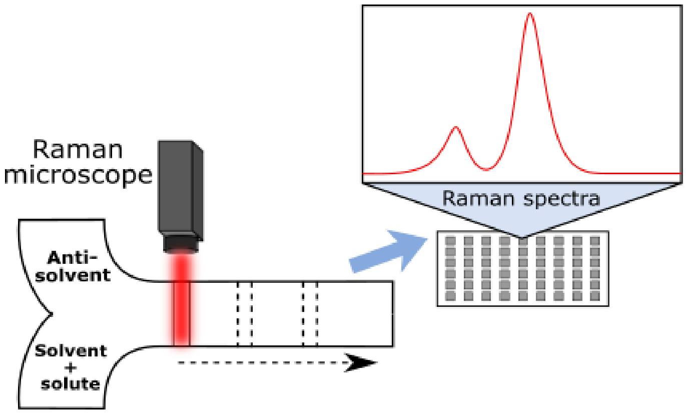

Figure 1: Schematic of the experimental setup.

From the measured spectral maps, the equilibration trajectories of the mixing solution and antisolvent streams can be determined, providing information on what regions of the phase diagrams are accessed during the mixing process, while also revealing the conditions that lead to surprising diffusive behaviours. This work provides new insight into the underlying mechanisms of anomalous mass transport and a better understanding of the equilibration pathways that can occur during antisolvent crystallization.

References

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