



Measuring interface induced concentration enhancement in solutions

R. Mackay^{1,2}, K. H. A. Lau³, J. Sefcik^{1,2}

✉ ruairidh.mackay@strath.ac.uk

in linkedin.com/in/ruairidh-mackay-061212140

🐦 @MackayRuairidh

¹EPSRC Future Manufacturing Research Hub in Continuous Manufacturing and Advanced Crystallisation, University of Strathclyde, Glasgow.

²Department of Chemical and Process Engineering, University of Strathclyde, Glasgow.

³Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow.

Introduction

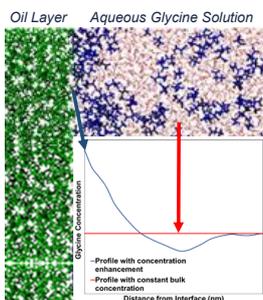


Figure 1: Molecular dynamics screenshot of oil-glycine (307 g/kg) system¹ with accompanying concentration profile inset.

Primary nucleation of crystals from solution typically proceeds heterogeneously at interfaces present in crystallisation processes. Comprehensive understanding of the underlying mechanisms and their control has not yet been achieved.

- Internal collaborators identified that glycine nucleation is rapidly accelerated at a hydrophobic oil-solution interface, which is most likely due to the formation of a concentrated interfacial layer of solution.¹
- Through use of widely available surface measurement techniques, such as surface plasmon resonance (SPR) spectroscopy and optical waveguide spectroscopy (OWG), expected changes in reflectivity, $\theta_{critical}$ and $\theta_{coupling}$ of aqueous glycine solutions can be determined on a variety of different surface substrates.
- "Multi-layer" optics computational analysis of the interface has shown that the predicted interfacial concentration enhancements are within the sensitivity range of SPR and OWG.
- Experiments "close the loop" and facilitate understanding of the underlying drivers of heterogeneous nucleation from solutions by quantifying changes between bulk and interfacial system properties.

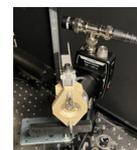
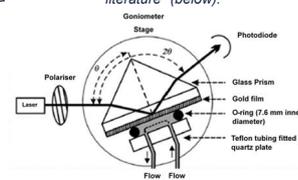


Figure 2: Image depicting current experimental setup (above) and a schematic of the SPR spectrometer setup adapted from literature² (below).



Methods

- Critical angles of aqueous glycine solutions on the surface of a bare prism were compared against simulations, using input parameters obtained from literature.^{1,4}
- Compared experimental SPR scans against simulations of glycine systems with a uniform, bulk concentration profile and glycine systems displaying interfacial concentration enhancement.
- Simulations performed using the "Winspall" program³, which implements a standard transfer-matrix calculation of light propagating through the glass/prism-metal-(waveguide)-glycine-solution "multi-layer".

What Influences the Position of the Critical Angle?

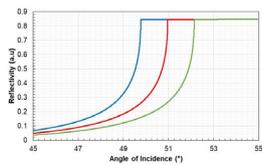


Figure 3: Experimental response when aqueous glycine solution is placed in contact with a prism in the Kretschmann configuration and excited by a 633 nm He/Ne monochromatic light source.

- Wavelength of the incident light source, solution temperature and composition all contribute to the observed responses.
- Small changes in these properties can lead to changes in the position of the critical angle, so corrections for temperature and incident light wavelength need to be implemented.

- Critical angle is observed at the point where the most light is reflected from the prism-solution interface.
- Critical angle depends on bulk solution properties and is directly related to solution concentration.

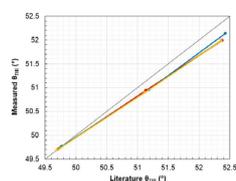


Figure 4: Relationship between experimentally observed critical angles for aqueous glycine solutions (0, 100 & 200 g/kg) and those obtained from literature.⁴

Conclusions

- The position of the critical angle is dependent on the bulk solution properties and is sensitive to temperature and incident light wavelength.
- The optical waveguide reflectivity minimum is sensitive to the interfacial concentration enhancement, and relative changes with respect to overall solution concentration are most promising for detecting interfacial concentration enhancement.
- Cr-Au-OWG sample surface promises greater sensitivity for observing the phenomenon.

Acknowledgements

- EPSRC and the Future Continuous Manufacturing and Advanced Crystallisation Research Hub (Grant Ref: EP/P006965/1) for funding this work.

Measuring Interfacial Concentration Enhancement

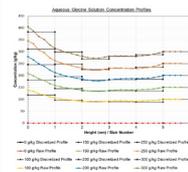


Figure 5: 0-300 g/kg Raw and discretized concentration profiles generated from literature.^{1,4}

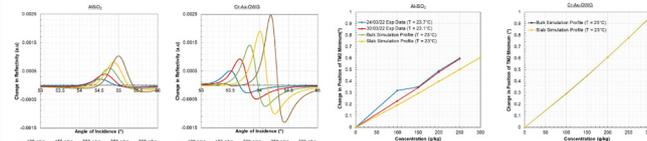


Figure 6: Comparison between Al-SiO₂ and Cr-Au-OWG surfaces and the magnitude of change in reflectivity (Left) and position of angle minima (Right) observed for each respective case.

- Concentration profiles from internal collaborators¹ proportionally scaled to generate profiles spanning 0-300 g/kg concentration range.
- Discretization of profiles generates input parameters to enable simulation of bulk and interfacially enhanced concentration profiles.
- Simulations carried out on two sample substrate surfaces: Al-SiO₂ and Cr-Au-OWG.
- Reflectivity change observed in Cr-Au-OWG sample at higher concentrations is considerably larger than that of Al-SiO₂ (0.25% versus 0.11%).
- Change being observed in both angle position and reflectivity is comparable.

Future Work

- Computational optimisation study to assess which waveguide materials and properties lead to most sensitive detection of concentration enhancement at a solution/surface interface.
- Experimental measurements across range of various solutions and interfaces.

References

1. D. McKechnie, S. Anker, S. Zahid, P. A. Mulheran, J. Sefcik and K. Johnston, Journal of Physical Chemistry Letters, 2020, 11, 2263-2271.
2. K. H. A. Lau, H. Duran and W. Knoll, Journal of Physical Chemistry B, 2009, 113, 3179-3189.
3. R. T. GmbH, Winspall Data Analysis Software, <http://www.res-tec.de/downloads.html>, (accessed March 2022).
4. Soto, A., et al. (1999). "Effect of cation and anion of an electrolyte on apparent molar volume, isentropic compressibility and refractive index of glycine in aqueous solutions." Biophysical Chemistry 76(1): 73-82.

