

Why methane and water mix under pressure : the complete story

C.G. Pruteanu^{1*}, V.N. Robinson², C.L. Bull³, D. Marenduzzo⁴, A. Hassanali², S. Scandolo² and J.S. Loveday⁴

¹Department of Physics and Astronomy, University College London, London, United Kingdom

²Abdus Salam International Centre for Theoretical Physics, Trieste, Italy

³ISIS Neutron Spallation Source, Rutherford-Appleton Laboratory, Harwell, United Kingdom

⁴School of Physics and Astronomy, University of Edinburgh, Edinburgh, United Kingdom

Keywords: water, methane, mixtures, neutron scattering, computational methods, hydrophobicity.

*e-mail: cip.pruteanu@ucl.ac.uk

Methane and water are a well-known, textbook example of immiscible chemical species and as such a widely studied model system for hydrophobic interactions[1]. Our understanding of their behaviour underpins much of today's chemical manufacturing technology[2] as well as most of our current planetary models, the two being found in large amount in Neptune, Titan and Uranus[3].

We have recently shown that when subjected to moderately high pressures, the miscibility gap present in methane-water closes, allowing them to form homogeneous mixtures having almost 1:1 methane:water content[4]. As we have presented in previous instances on this conference, there appeared to be 3 distinct pressure-dependent hydration regimes for methane in water: one where solubility is low as commonly expected (in the 2 mole % range) below 1.3 GPa; a second regime where there is a constant increase in the amount of dissolved methane in water with increasing pressure; and a third regime above 2.0 GPa where the solution remains at the same concentration irrespective of further changes in pressure.

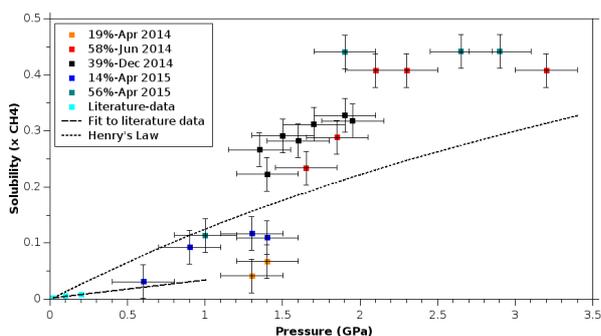


Figure 1: Pressure dependence of the maximally soluble amount of methane in water, as determined using Raman spectroscopy and quantitative image analysis. Two discontinuities can be easily noticed, around 1.3 and 2.0 GPa[4].

Previous attempts aiming to model this increasing in miscibility using classical molecular dynamics have proven fruitless, so we have resorted to performing neutron scattering measurements. These coupled with *ab initio* molecular dynamics allowed us a first glimpse into the atomic level structure and bonding, seemingly exhibiting a H-bond network similar to that of pure water closer to ambient conditions (pressure and temperature).

In this talk I will present new neutron scattering measurements on the mixture at different pressures, showing evidence for different hydration regimes and discuss associated mechanisms and hydrogen-bond network topology. Additionally, I will further elaborate on our progress using *ab initio* methods seeded from configurations obtained by reverse Monte Carlo analysis of the real total scattering fluid data.

This holistic approach both complements and contrasts clearly the weaknesses as well as the strengths of experimental and computational techniques, strengthening the case for them to be used in conjunction and as a direct feedback measure to one another.

Finally, I will tie together all these threads into a coherent and comprehensive picture of the iconic methane-water mixture, and showcase the crucial properties this system showcases both about water and methane separately and about hydrophobic binary mixtures in general.

These results and techniques used in order to attain them are likely to prove valuable for further research efforts in high pressure fluid mixtures and fundamental physics and chemistry as well as for more practical purposes such as material design or planetary modeling.

[1] D. Chandler, *Nature*. **437**, 640–647, 2005.

[2] C. I. Herreras, X. Yao, Z. Li, C. J. Li, *Chem. Rev.* **107**, 2546–2562 (2007).

[3] T. Guillot, *The Interiors of Giant Planets: Models and Outstanding Questions*, 43 (2005).

[4] C. Pruteanu et al, *Science Advances*, **3**(8), p.e1700240.