Experimental report

15/02/2023

Proposal: **6-03-444** **Council:** 10/2018

Title: The dynamic behaviour of CH4-H2O solutions

Research area: Physics

This proposal is a new proposal

Main proposer: **Katherine BROWN**

Experimental team:
Stefan KLOTZ
Ciprian PRUTEANU
Katherine BROWN
John S. LOVEDAY

Local contacts: Jean-Marc ZANOTTI

Samples:
Methane hydrate (deuterated water)
Methane hydrate (deuterated methane)

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	4	4	15/07/2019	19/07/2019

Abstract:

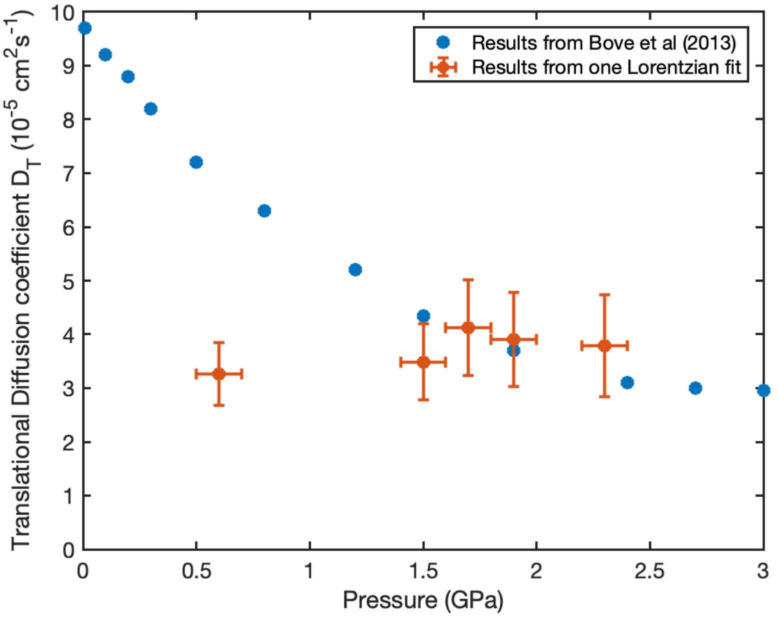
In the proposed experiment both the rotational and transitional dynamics of the molecules in CH4- H2O mixtures will be studied. This will be achieved by selectively deuterating the mixture, such that the CH4 and H2O dynamics may be studied separately. Measurements will be carried out at multiple pressures, both above and below the proposed change in hydrophobicity at 1.5 GPa. Our results will be compared to existing QENS studies of CH4 and H2O [7, 8], in order to establish if there are any effects due to mixing on the individual components. We will track the diffusive behaviour with pressure, with the aim of determining any links between the molecular motions and the CH4 solubility.

Report on Experiment , 6-03-444 QENs studies of methane dissolved in water at high pressure

We have shown that between the pressures of 1.3 and 2.0 GPa the maximum solubility of methane in water changes rapidly and increases from less than 1 mole% to 41(3) mole% [1]. Following this unexpected discovery, we have embarked on a series of experiments to understand the properties of methane-water solutions and to explore the causes of pressure induced solubility enhancement. We have shown that the water network remains H-bonded and that there is evidence of increased polarisation of the methane molecules [2]. Given this, we decided to explore the diffusive properties of the water component of the mixture using QENS and IN6.

To produce a sample with known methane concentration the sample was loaded cryogenically into a Paris-Edinburgh cell in the form of crystalline methane clathrate hydrate. This compound has a known composition of 16.6 mole% methane. The sample was produced in Edinburgh using deuterated methane and hydrogenous water so that the experiment was sensitive only to hydrogen atoms bonded to water. After loading the sample was warmed to K (where both methane and water are fluid) and data were collected at pressures of 0.6, 1.5, 1.7, 1.9 and 2.3 GPa (estimated from the load applied to the pressure cell). Based on the measured solubility [1] and the known sample composition, it would be expected that the sample would transform from a two-phase mixture of fluid methane and water to a single-phase solution of methane in water at ~1.5 GPa.

Figure 1 shows the values of translational diffusion coefficient D_T obtained from the QENS as a function of pressure along with those determined for water by Bove et al [3]. As can be seen, there is a clear change between 1.5 and 1.7 GPa which appears to be associated with the solvation of the methane. At lower pressures the diffusion coefficient deviates from that of pure water whereas above 1.5 GPa it is similar. This behaviour is constituent with the presence of bubbles of methane in the unmixed sample.



References

[1] C.G.Pruteanu *et al*, Sci. Adv. **3**, 8 (2017).
[2]C.G.Pruteanu *et al*, J. Phys. Chem. Lett., **11**, 4826-4833 (2020).
[3] L.E.Bove*et al*, Phys. Rev. Lett., **111**, 185901 (2013).