



	Experiment title: Hydrate formation at the liquid Xe-water interface studied by high energy x-ray reflectivity measurements	Experiment number: SI- 1787
Beamline: ID15 A	Date of experiment: from: 30.01.2009 to: 03.02.2009	Date of report: 09.03.2010
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Report:

Gas hydrates are structures where guest molecules, e.g. xenon, methane or carbon dioxide, are trapped in a hydrogen bond water cage network, usually stable at high pressures and low temperatures [1]. In this study we investigated the formation of xenon hydrate at the water-xenon liquid-gaseous interface and the formation of xenon-cyclohexane bi-hydrate at the water-cyclohexane liquid-liquid interface with the presence of xenon by means of x-ray reflectivity measurements.

The measurements were carried out at beamline ID15A at a photon energy of $E_{\text{ph}} = 69.9$ keV using the liquid surface setup [2]. Thus we were able to access the buried liquid-liquid interface. In addition the absorption of xenon requires high energies even for the measurement of the liquid-gaseous interface.

For the investigation of the water-xenon interface the cell was filled with approx. 30 ml of water and pressurised with xenon up to a maximum pressure of 9 bar. For the liquid-liquid system the water phase was covered with approx. 30 ml of cyclohexane (C_6H_{12}) forming a sharp meniscus between the two liquid phases, and afterwards pressurised with xenon up to a maximum pressure of 3 bar. X-ray reflectivity measurements were performed to reveal the electron density profile along the normal to the interface, selected data are shown in figure 1. By refining these data we were able to deduce the composition of the interface structure. The best fit to the data of the water-xenon interface was obtained assuming a model with two layers on top of the water surface. The uppermost turns out to be a thin layer of adsorbed xenon, which is common for liquid-gaseous systems [3]. The other layer has a slightly higher electron density compared to water. We assign this to an enrichment of xenon dissolved in the water which accumulates at the interface. Increasing the xenon pressure leads to

increased layer thicknesses. Further increasing of pressure passing the hydrate stability point leads to the formation of xenon hydrate.

For the water-cyclohexane-xenon system a model with one layer between water and cyclohexane fits the data best. Similar to the water-xenon system an increase in layer thickness is observed with increasing xenon pressure. In addition the electron density of the cyclohexane shifts to higher values with rising pressure. This is due to the enrichment of xenon at the interface. A further increase of the xenon pressure above 9 bar at $T = 10^\circ\text{C}$ leads to the formation of gas hydrate.

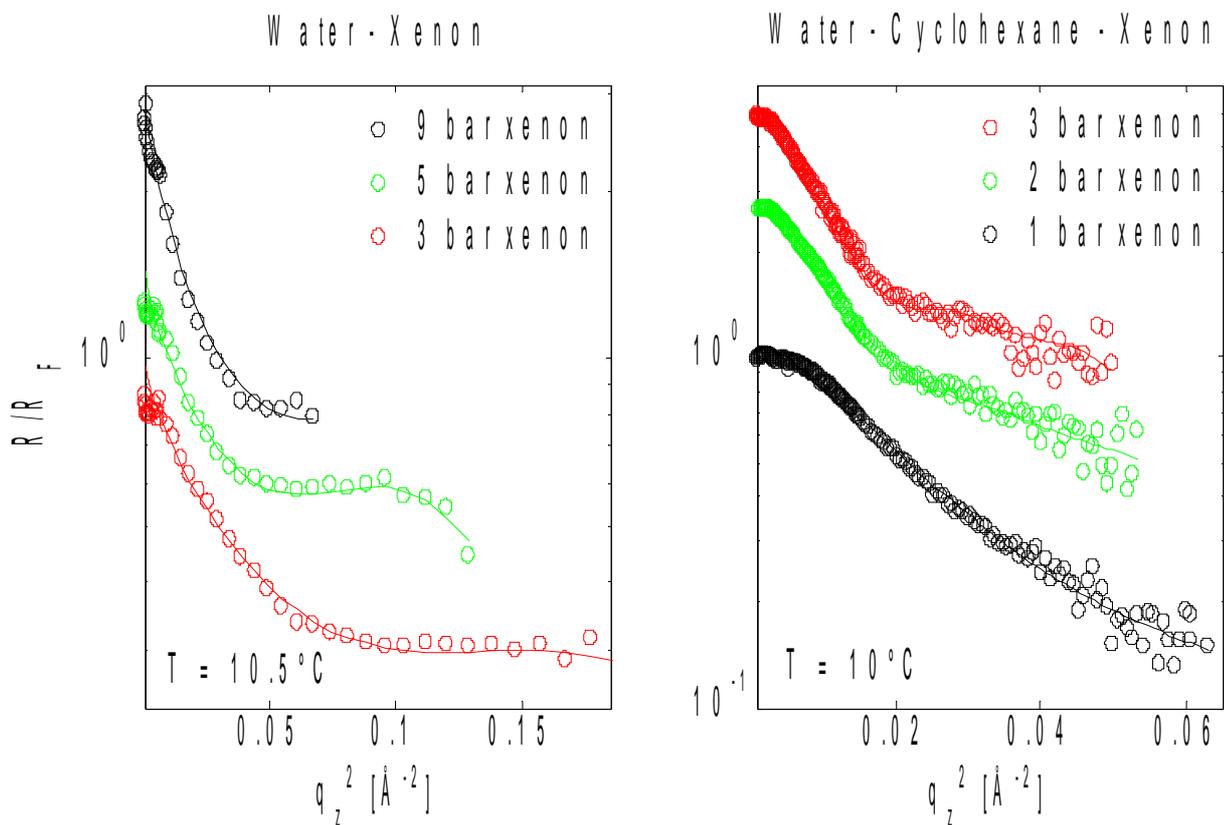


Figure 1: Reflectivity curves of the water-xenon liquid-gaseous interface at $T = 10.5^\circ\text{C}$ and the water-cyclohexane liquid-liquid interface at $T = 10^\circ\text{C}$ and different xenon pressures.

Though the data analysis is still in progress it becomes clear that the enrichment of the hydrate forming gas at the liquid-gaseous and liquid-liquid interface respectively is essential for the gas hydrate formation process. In systems with hydrate forming gases of lower solubility in water than xenon (e.g. propane, carbon dioxide) hydrate formation was not observed at these interfaces [4].

[1] E.D. Sloan and C.A. Koh, Clathrate Hydrate of Natural Gases, Boca Ranton, 2008.

[2] V. Honkimäki *et al.*, J. Synchrotron Rad. **13** (2006) 426.

[3] M. Paulus *et al.*, Phys. Rev. E **72** (2005) 061601.

[4] F. Lehmkuhler *et al.*, J. Am. Chem. Soc. **131** (2009) 585.