



	Experiment title: High energy x-ray reflectivity and x-ray diffraction measurements at the liquid-liquid cyclohexane-water interface with the presence of xenon	Experiment number: SI-1877
Beamline: ID15 A	Date of experiment: from: 14/02/2010 to: 22/02/2010	Date of report: 13/09/2010
Shifts: 15	Local contact(s): Dr. D. Pontoni	<i>Received at ESRF:</i>
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Report:

Interfaces between liquids and gases are very common in nature and important for many processes such as gas adsorption and catalysis. In particular, the formation of gas hydrates usually starts at these interfaces. Gas hydrates are cage structures where small guest molecules are enclosed in a hydrogen bond water network [1,2]. Although they reached the focus of a general audience due to their application for gas storage [1,3], little is known about the nucleation process on molecular length scales. Models based on MD simulations predicting the formation of hydrate precursors at the interface were discussed as well as models proposing a spontaneous nucleation [1,4]. On the experimental side, recent x-ray studies on CO₂ hydrate formation at liquid-gas interfaces favored a stochastic and spontaneous formation process [5] while a neutron scattering study suggested the formation of small hydrate precursors at the water-methane interface [6]. Furthermore, a spectroscopic study of the formation of propane hydrate from ice reported on clustering of water molecules in the presence of propane [7]. Altogether, the mentioned results raise the question of a general applicability of the proposed formation models.

We investigated the liquid-gas interface of water and xenon and the liquid-liquid interface of water-cyclohexane with the presence of xenon by x-ray reflectivity measurements. Both interfaces were studied at different temperature and pressure conditions which allow or inhibit the formation of hydrates. Reflectivities were performed at the liquid-liquid water-propane and water-isobutane interfaces. In contrast to the xenon systems, these systems show very long induction times for hydrate formation. Since for experiments at high gas pressures and liquid-liquid interfaces the use of high pressure cells is essential, high x-ray energies are necessary to penetrate both the cell's solid Al windows and the dense gaseous and liquid phases. Thus, the measurements were carried out at beamline ID15 A at a photon energy of $E=69.9$ keV using the set-up for scattering at liquid interfaces [8]. The same sample cell as in experiment SI-1787 was used together with the chiller available at ID15. After the cell was filled with water, it was flushed with helium and a reference measurement of the water surface was performed. Afterwards, either the cell was flushed with the corresponding gas for a few minutes before selecting a certain gas pressure or cyclohexane was filled onto the water surface and the cell

was flushed with xenon. First, a reflectivity measurement was performed at a gas pressure of 1 bar. Then the pressure was raised stepwise. After each reflectivity, the detector was moved to an out-of-plane position to measure the diffusely scattered radiation for background subtraction.

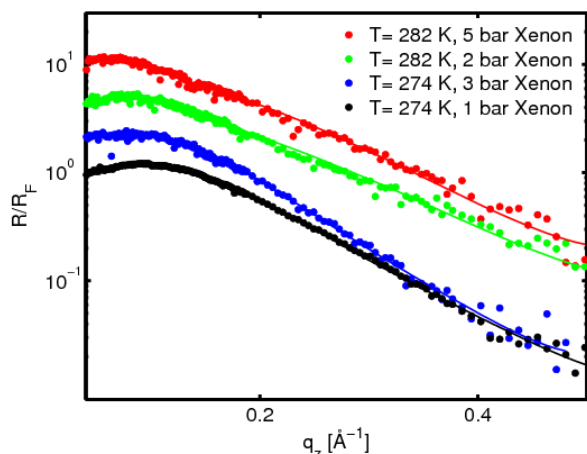


Figure 1: Reflectivities from the Xe-water interface.

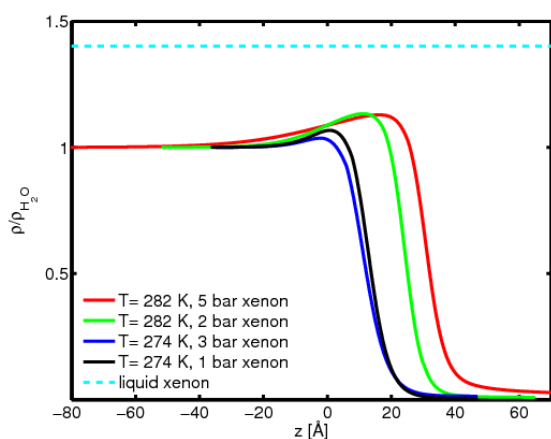


Figure 2: Electron density profiles of the water-Xe interfaces.

liquid water-propane and water-isobutane interface indicate no formation of any layers at the interface. No hydrate formation was found in these systems in agreement with previous experiments on the liquid-gas interface [9].

References:

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Figure 1 shows reflectivities measured at the xenon-water interface. The corresponding electron density profiles are shown in Figure 2. In contrast to the measurements at the water-CO₂ interface [5], we observed the formation of a layer which cannot be explained by pure gas adsorption. Thus, we assume that xenon accumulates at the interface. By comparing the density of this layer with the bulk values of water and xenon, a Xe concentration of approximately 12 ± 4 % is found in the layer at 274 K, similar to the concentration of xenon in Xe hydrate. At this temperature, the formation of Xe hydrate is possible. In every experimental run, the formation of macroscopic amounts of Xe hydrate was found, typically after 1-2 hours, starting from the layer. It has to be noted that such a layer – even more pronounced – is also observable at temperatures where Xe hydrate is not stable (282 K). Hence, it is highly unlikely that the accumulation of Xe represents a formation of hydrate precursors proposed in literature [4]. A similar layer formation was also found at the water-cyclohexane interface (see Figure 3), corresponding to short induction times for hydrate formation. In contrast, the reflectivities performed at the liquid-

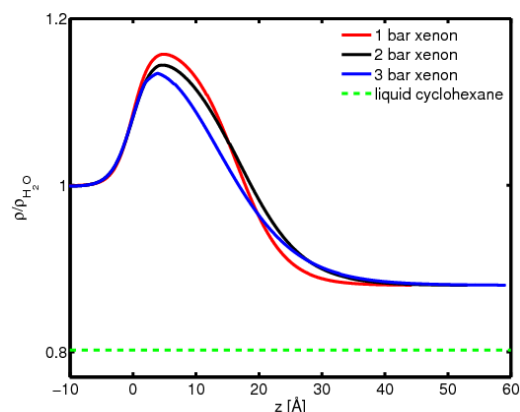


Figure 3: Electron density profiles of the water-cyclohexane interface at different Xe pressures.