ADSORPTION OF NITROGEN ON THE SURFACE OF LIQUID HYDROCARBON BODIES ON TITAN

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Introduction: Besides earth, Saturn's giant moon Titan is the only other planetary body in our solar system that has stable and accessible liquid on its surface, an active hydrologic cycle similar to Earth, and a dense atmosphere with a pressure of about 1.5 times that of Earth [1–3]. Early interest in a methane cycle on Titan [4, 5] was motivated by Voyager 1's discovery of a thick, nitrogen-based atmosphere with a significant methane abundance. Ethane clouds in the Stratosphere were later identified by the Cassini at high northern latitudes [6, 7]. Cassini mission to Saturn has further revealed many features of this moon including the existence of large liquid hydrocarbon lakes and seas composed primarily of methane and ethane in different ratios [8]. With the low surface-temperature of about 90K and the pressure about 1.5 atm, both methane and ethane condense out of the atmosphere and exist in the stable liquid phases on the surface in dynamic equilibrium with its atmosphere [2].

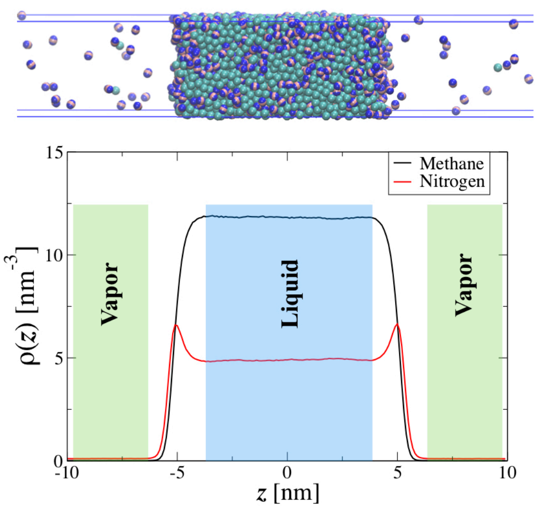

Figure 1 A snapshot of the nitrogen-methane binary mixture at T = 90K (Top). Average number density profile, ρ(z), for ethane and nitrogen along the z-direction (Bottom). The blue shaded region represents the liquid phase and the green shaded region represents the vapor phase.

While thermodynamic models have been developed and experiments have been performed, a microscopic picture of the dissolution of nitrogen in liquid hydrocarbon bodies on the surface of Titan is still lacking.

We have performed molecular dynamics vapor-liquid-equilibrium (VLE) simulations [9-10] of binary mixtures of methane and nitrogen, and ethane and nitrogen to investigate the solubility and surface adsorption of nitrogen in methane and ethane at Titan-like conditions. The simulations were performed in a range of temperature between 90K and 110K and at a pressure of 1.5 atm. The trappe-UA force field [11] was used to model methane, and ethane was modeled using an improved parameterization of ethane, trappe-UA2 [12]. Trappe-small parameterization was used to model nitrogen. All the simulations were performed in Gromacs 4.6.5 [13]. The equations of motion are integrated with a time step of 2 fs and velocity rescaling is used to attain constant temperature and anisotropic Berendsen barostat for constant pressure. A typical configuration of the nitrogen-methane binary system is shown in Figure 1. The dimension of the final simulation box was Lx = Ly = 5.0nm<< Lz. In such a box, the liquid-vapor interface is stable and forms along the smallest surface area in the xy-plane, perpendicular to the long-axis.

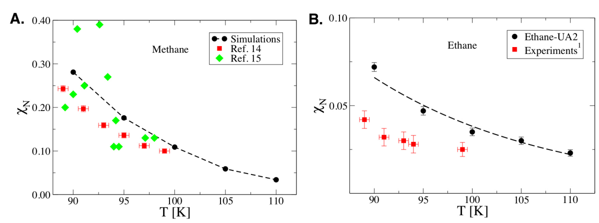

Figure 2 (A) Mole-fraction, χ_N, of the nitrogen in methane as a function of temperature. To compare with experiments, we also show the data from Refs. [14, 15]. Simulation results are in reasonable agreement with the experimental data with a slight overestimation of solubility at low temperatures. (B) Nitrogen in ethane exhibits a decrease of solubility with temperature and is in quantitative agreement with experimental values in Ref. [14].

Solubility of nitrogen in methane and ethane: To compute the solubility, we measure the mole-fraction of nitrogen in the liquid phase of methane/ethane in the nitrogen-methane and nitrogen-ethane binary mixtures at equilibrium. To avoid the interface, we define the liquid phase (or the gas phase) as the region where the z-derivative of the density of methane/ethane and nitrogen is zero (see Fig. 1). In Fig. 2(A), we show the solubility of nitrogen in methane for temperatures T = 90, 95, 100, 105, and 110K respectively. Consistent with the experimental results, we find that the solubility decreases upon increasing temperature. To compare the simulation results with experiments, we also show the data from two different experiments [14, 15]. The solubility values calculated in our simulations are very close to experimental values with small deviations at lower temperatures. In Fig. 2(B), we show the mole-fraction, χ_N, of the nitrogen in ethane as a function of temperature. For a comparison, we also plot the data from Ref. [14]. Nitrogen in ethane exhibits a decrease of solubility with temperature and is in quantitative agreement with experimental values.

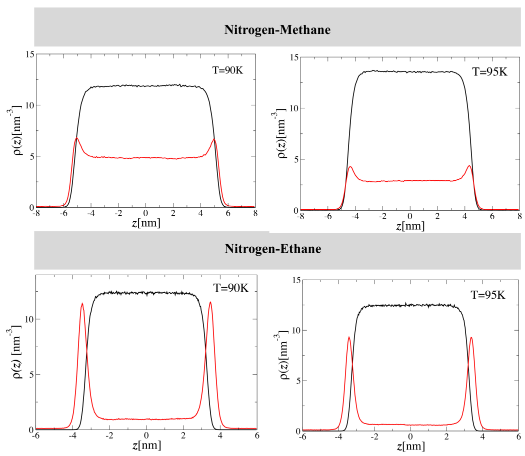

Figure 3 Number density, ρ(z), of nitrogen (solid red curve) and methane/ethane (solid black curve) for the nitrogen-methane and nitrogen-ethane system for two different temperatures T = 90 K and T = 95 K. A strong temperature-dependent surface adsorption of nitrogen is observed in both systems.

Surface Adsorption of Nitrogen: We next investigated the adsorption of nitrogen at the nitrogen-methane and the nitrogen-ethane interface. In Fig. 3, we show the density profile of nitrogen and methane/ethane as a function of temperature for both nitrogen-methane and nitrogen- ethane systems at two different temperatures T = 90K and T = 95K. We find that adsorption of nitrogen at the interface between vapor and liquid phase is very high and increases upon decreasing temperature. Furthermore, the degree of adsorption of nitrogen at the nitrogen-ethane interface is much higher as compared to the nitrogen-methane interface whereas the number density of nitrogen reaches approximately the number density of liquid ethane.

Summary: We have studied the temperature dependence of the solubility of nitrogen in methane, ethane by performing extensive vapor-liquid equilibrium simulations of binary mixtures of nitrogen+methane and nitrogen+ethane for a range of temperatures between 90K and 110K at a pressure of 1.5 atm, thermodynamic conditions that may exist on the Saturn's giant moon, Titan. We find that the solubility of nitrogen in both methane and ethane decreases with increasing temperature. Moreover, solubility of nitrogen in methane is much larger compared to that in ethane at lower temperatures. Furthermore, we find a strong temperature-dependent surface adsorption of nitrogen at the nitrogen-hydrocarbon interface, previously unknown. Such adsorption of nitrogen might affect other processes like dissolution of atmospheric compounds in Titan lakes.

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