

Experimental Study and Thermodynamic Modeling of Xenon Clathrate Hydrate Equilibria

Ali Rasoolzadeh

Natural Gas Engineering, Shiraz University, Shiraz, Shiraz, NA, Iran

Louwrens Aaldijk

Delft University of Technology, Delft, Netherlands, Chemical Engineering, Delft, NA, Netherlands

Sona Raeissi and Alireza Shariati

Natural Gas Engineering, Shiraz University, Shiraz, Shiraz, NA, Iran

Muhammad Naveed Khan

Chemical Engineering, UOHB, Hafr AL Batin, Saudi Arabia

Cornelis J Peters^{C, S}

Chemical Engineering, Colorado School of Mines, Golden, Colorado, U.S.A.

cjpeters2003@yahoo.com

Xenon is a good candidate to replace methane in making sl hydrates, because similar to methane, xenon can form sl hydrates but at milder conditions. For example, at a temperature of 303.15 K, the xenon hydrate equilibrium pressure is only about 3.5 MPa, much lower than the corresponding methane hydrate equilibrium pressure. The xenon hydrate can thus be considered for industrial applications, for example, in biotechnology, where xenon hydrates have been investigated as storage media that can maintain the enzymatic activity of model proteins. This is because xenon is a non-reactive and non-toxic noble gas which is not harmful to humans. While the number of investigations on xenon hydrate in the literature is not small, investigations on xenon hydrate equilibria are not significant, with only seven data points available for xenon (I-H-V) equilibria. In this work, the equilibrium conditions of xenon hydrates have been measured within wide pressure and temperature ranges. Various experimental equipment has been used for this purpose, namely the tensimeter, the Cailletet apparatus, and a high-pressure autoclave. For the pressure range of (0.05 to 0.40) MPa, which covers the experimental (I-H-V) data, and several (L_w-H-V) data, a tensimeter was utilized, which consists of a measuring vessel, a gas storage tank, and a mercury pressure gauge. The heart of the measuring vessel is a stainless steel cylinder which is sealed on top with an O-ring Teflon disc. The temperature is digitally read with the aid of a quartz thermometer with an accuracy of ± 0.01 K. The experimental tests in the pressure range of (0.30 to 10.13) MPa were conducted with the aid of the Cailletet apparatus, which works according to the synthetic method. With this apparatus, equilibrium data points can be measured in the temperature range of (250 to 450) K and pressure up to 15 MPa. A platinum resistance thermometer measures the temperature with a maximum error of ± 0.02 K. The pressure is determined by a dead-weight pressure gauge with an accuracy of 0.03% of the reading. Mercury is used as a pressure transmitting and sealing fluid in the Cailletet apparatus. Xenon hydrates may be formed by reducing the solution temperature at constant pressure. Then, by increasing the temperature at a slow rate ($0.1 \text{ K}\cdot\text{h}^{-1}$) at constant pressure, the hydrate crystals are decomposed. The hydrate formation step is involved with meta-stabilities; therefore, the temperature is increased very slowly until the ice completely melts. Further increase in temperature results in the beginning of hydrate dissociation. The temperature at which the hydrate crystals disappear is taken as the hydrate equilibrium temperature. Since the xenon hydrate is denser than the ice and water phases, it can visually be recognized from the other phases. A microscope placed in front of the equilibrium cell, together with an adjustable light source, both assist in providing higher visual clarity. For the pressure range of (10.13 to 405.30) MPa, a high-pressure autoclave apparatus was used to perform the xenon hydrate stability experiments. The autoclave is equipped with sapphire windows, and the contents are mixed using a magnetic stirrer. A platinum-resistant thermometer records

temperatures with an accuracy of ± 0.01 K. Measurement and control of the pressure is done using a pressure gauge with an accuracy of 1% of the reading. A number of three-phase equilibrium data points were measured for liquid water-hydrate-vapor (L_w-H-V) and the ice-hydrate-vapor (I-H-V). It was concluded that there is good consistency between the experimental data points measured in this work and those obtained by the other groups in the literature. A modified van der Waals-Platteeuw (vdW-P) model was used to predict the xenon hydrate stability conditions. The basis of the vdW-P model is the equality of the chemical potential of water in the hydrate, aqueous liquid/ice, and the vapor phases. The Kihara spherical-core potential function was used to represent the intermolecular forces between the water molecules and the xenon molecules in the cavities. The fugacity of xenon in the vapor/gas phase was computed using the Peng-Robinson (PR) EoS. The solubility of xenon in the liquid phase was calculated through the Krichevsky-Kasarnovsky equation. The investigated model had the ability to predict the xenon hydrate equilibria with good accuracy within wide ranges of pressures and temperatures, resulting in an average absolute deviation (AAD) of about 0.61 K for (L_w-H-V) and 0.42 K for (I-H-V) equilibrium temperatures.