

Experimental Study and Thermodynamic Modeling of CCl₄ + O₂ and CCl₄ + N₂ Hydrate Equilibria

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Nitrogen and oxygen are the main components of air. Liquid nitrogen is an alternative to fossil fuels. However, little attention has been paid to this energy resource. Liquid oxygen is not a fuel in itself; however, it can be used as an oxidizer to run vehicles. In this respect, gas hydrate technology can be of interest, as applicable media for nitrogen/oxygen transport or nitrogen/oxygen separation. Both nitrogen and oxygen tend to form hydrates, especially at high pressures, with double occupancy of the large cavities of structure sII. Thermodynamic hydrate promoters (THPs) can facilitate the formation of nitrogen or oxygen hydrates at more moderate equilibrium conditions. For this purpose, CCl₄ can be a potential candidate. In this contribution, hydrate equilibrium conditions for binary mixtures of nitrogen + CCl₄ (50 data points) and oxygen + CCl₄ (41 data points) were experimentally measured. This was done using three experimental equipment: a tensimeter, the Cailletet apparatus, and a high-pressure autoclave. According to the van der Waals-Platteeuw (vdW-P) solid solution theory, a thermodynamic model was then employed to predict the hydrate equilibrium temperatures of the aforementioned mixtures. The fugacities of the components in the mixtures were calculated through the Peng-Robinson (PR) EoS and the classical van der Waals mixing rules. The Kihara potential model was applied to represent guest-host interactions. The results reveal that the model can predict the hydrate equilibrium temperatures with the average absolute deviation (AAD) of 0.32 K. The fractional occupancy calculations indicate that the CCl₄ molecules mostly occupy the large cages and do not enter the small cages of sII hydrates because of their size. At the same time, nitrogen and oxygen have small contributions in filling the large cages of sII.