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The equilibrium conditions, hydrate formation and dissociation rate and storage capacity of ethylene hydrate in presence of 1,4-dioxane

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HIGHLIGHTS

- The equilibrium data of hydrate formation for ethylene + 1,4-dioxane have been obtained.
- 1,4-Dioxane enhances the storage capacity of ethylene hydrate remarkably.
- The addition of 1,4-Dioxane results in an increase in the hydrate formation pressure.
- 1,4-Dioxane accelerates the hydrate growth rate.
- 1,4-Dioxane decreases dissociation percentage of ethylene hydrate.

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ABSTRACT

The effect of 1,4-dioxane on ethylene hydrate was investigated at three additive molar concentrations of 2.78%, 5.56% and 8.34%. The equilibrium conditions for hydrate dissociation were obtained by step heating method. The results showed that addition of 1,4-dioxane concentration increases the pressure of hydrate dissociation. Diagram of $Ln(P_{eq})$ vs. T_{eq} demonstrated that system of 1,4-dioxane + ethylene + water form ethylene hydrate with structure I. In fact 1,4-dioxane cannot participate in hydrate structure because ethylene molecules are not a good help gas for occupation of S-cages in structure II. So, in this condition only ethylene hydrate with structure I could be formed. The experimental results on hydrate formation indicted that 1,4-dioxane accelerates the hydrate growth rate by increasing the solubility of ethylene in water and a maximum storage capacity of $(V_{STP}/V_H) = 146$ is obtained in a critical dioxane concentration of 5.56% by mole. Also hydrate dissociation experiments revealed that maximum dissociation percentage is related to pure water (48%) and 1,4-dioxane decreases dissociation percentage of ethylene hydrate.

1. Introduction

Produced ethylene in petrochemical plant is normally mixed with various kinds of refinery and cracking gases such as CO_2 and methane. For obtaining of pure ethylene, a separation step is necessary. Cryogenic distillation is a widely practiced process for separation of low boiling systems, but energy consumption of this process is so much.

Recently gas hydrates have received attention for separation of low boiling systems and/or close-boiling systems [1,2]. Clathrate hydrates are formed when small gas molecules such as methane, CO_2, ethane, and ethylene are trapped inside a cage-like structure is formed by hydrogen-bonded water molecules at high pressures and low temperatures. There are many researches for enhancement of rate of hydrate formation [3] and investigation of effect additives on gas hydrates [4].

It is well known that there are three structures of gas hydrate: structure-I, structure-II, and structure-H. Small molecules such as CO_2, methane, and Ethylene form structure-I which has two small cages (S-cages, 5^{12}) and six large cages (L-cages, $5^{12}6^2$). Cyclic ether compounds such as THF and 1,4-dioxane affect hydrate formation conditions. These chemical additives construct structure-II which consists of 16 small cages (S-cages, 5^{12}) and 8 large cages (L-cages, $5^{12}6^4$) [5]. They occupy large cages of structure II and this structure will not stabilize without the presence of a help gas. The help gas stabilize the hydrate structure by occupation of small cages [5].

Jager et al. [6] showed that for the methane + water + 1,4-dioxane system the equilibrium pressure of hydrate formation at a specific temperature decreases with the addition of 1,4-dioxane up to a concentration of 6 mol%. Seo and Kang [7] measured hydrate phase equilibria for carbon dioxide + cyclic ethers + water. The

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