MODELING OF THE PROPERTIES OF METHANE + ETHANE (PROPANE) BINARY HYDRATES IN DEPENDENCE ON THE GAS PHASE COMPOSITION

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ABSTRACT
This work is concerned with modeling of phase transitions between cubic structures sI and sII of mixed hydrates with account of partial occupation of hydrate cavities by guest molecules. The properties of mixed methane + ethane and methane + propane hydrates of cubic structures sI and sII were theoretically investigated. It was shown that the composition of the formed binary hydrate strongly depends on the presence of a heavier guest in the gas phase. For instance, at low temperature, even at 1% molar ethane concentration in the gas phase, already at low pressure, ethane occupies more than 60% large cavities in the hydrate sII. At temperature higher than ice melting point ethane concentration in the hydrate drops to 30%. In the structure sI, influence of the composition of the gas mixture on hydrate formation is less evident. However, in this case, calculations also have shown that at 1% molar ethane concentration in the gas phase ethane molecules occupy from 8 to 10% large hydrate cavities, depending on the pressure.

For ethane concentrations less than 2% in the gas mixture, structure sII becomes more stable than structure sI. However, as the ethane concentration grows to 20% in the equilibrium ‘ice – gas – hydrate’ and to 40% in the equilibrium ‘water – gas – hydrate’, the structure sI becomes more stable thermodynamically. Results similar to the case of methane + ethane hydrates were obtained for methane + propane system.

Keywords: gas hydrates, double hydrates, divariant equilibrium, monovariant equilibrium.

INTRODUCTION
Clathrate hydrates are crystalline solids consisting of water and gas molecules. The water molecules form a (host) network with pores (voids) in which gas molecules (guests) are placed. Since the middle of the 20th century mixed hydrates have been actively investigated. Special attention was given to studying hydrates of light components of natural gas, such as CH₄, C₂H₆, and C₃H₈. Natural gas mostly consists of methane (55-99%), the content of ethane is about 10%, propane and butane content not more than 10%, also traces of hydrogen, nitrogen, helium, etc. can be found. The main motivation for these investigations is huge deposits of hydrates of natural gas in offshore areas and the problems of gas transportation and conservation. It was shown that even slight changes of the composition of gas mixture

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