PHASE EQUILIBRIA AND DISSOCIATION ENTHALPIES OF HYDRATES AND SEMICLATHRATES IN THE CH_4-C_3H_8-H_2S SYSTEM WITH TBAF AND $TBANO_3$

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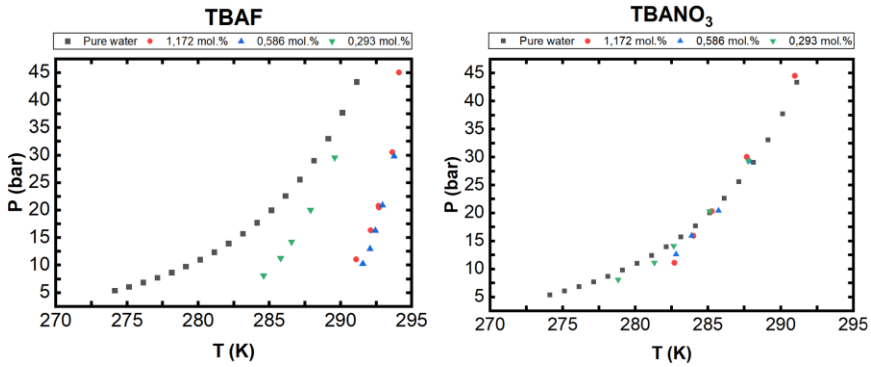
Gas hydrates are solid crystalline compounds in which gas molecules are enclosed in a hollow framework consisting of water molecules. Quaternary ammonium salts such are often used to stimulate the formation of gas hydrates. This is due to the ability of these substances to fill crystal cavities and to participate in the construction of the cavities themselves, forming structures called semiclatrates.

In this work, the conditions of thermodynamic equilibrium of gas hydrates of a mixture of CH_4 (92,74 mol.%) - C_3H_8 (5,36 mol.%) - H_2S (1,90 mol.%) in water and aqueous solutions of TBAF and $TBANO_3$, as well as in each system, the enthalpy of dissociation is calculated using the Clausius-Clapeyron equation. The results of experiments to determine the conditions of phase equilibrium (dissociation of gas hydrates) are shown in the figure below.



Dissociation conditions of CH_4 - C_3H_8 - H_2S
for different concentrations of the aqueous solution

Next, the enthalpies of dissociation were calculated. The addition of vertical ammonium salts to the system led to the fact that there are two inflection points on the P-T curve, meaning two moments of complete destruction of structures. In one case, these are gas hydrates, and in the other, semi-hydrates.

The enthalpies of dissociation were determined for two different thermodynamic equilibrium curves corresponding to gas hydrates (80-93 $kJ \cdot mol^{-1}$) and semi hydrates (170-330 $kJ \cdot mol^{-1}$). Significantly higher values for semi-clathrates reflect the additional energy required to break the hydrogen bonds between the aqueous lattice and salt anions (F- or NO_3-), which confirms their greater structural stability compared to pure gas hydrates.

The research work was supported by the Russian Science Foundation (№ 22-79-10222-ІІ).