Clathrate hydrate formation in ternary system of methane, water and ethylene carbonate

Vladimir I. Medvedev, Pavel A. Gushchin, Vladimir S. Yakushev, Anton P. Semenov

Gubkin Russian State University of Oil and Gas
Department of Physical and Colloid Chemistry

Introduction

Gas hydrates are ice-like crystalline molecular complexes that are composed of water and suitably sized guest molecules like methane. Gas hydrates have drawn much attention in various fields. Formation of gas hydrate plugs may cause serious problems for oil and gas transportation in pipelines. On the other hand, gas hydrates are also used for other applications such as natural gas storage and transportation. Extensive researches on the screening of appropriate additives with inhibition and promotion effects in gas hydrate systems have been presented in literature. It was demonstrated [1] that cyclopentanone C_5H_8O (CP) additive has a promotion effect on the formation of methane hydrate and shifts hydrate phase boundaries to lower pressure and higher temperature. Ethylene carbonate $C_3H_4O_3$ (EC) is the structure analogue of more hydrophobic CP.

Aim

Aim of this study is to investigate hydrate formation in ternary system of methane, water and ethylene carbonate and to measure phase equilibrium conditions for this system.

Materials & Methods

The following materials were used:
1. distilled water;
2. methane (Moscow's Gas Refinery Plant, >99.99 % pure);
3. Ethylene Carbonate (Sigma Aldrich, >99 % pure).

We used the Gas Hydrate Autoclave GHA350 to prepare the gas hydrates and to measure their dissociation conditions. Three-phase equilibrium conditions L_w-V-H (liquid water solution-vapor-hydrate) were determined by the isochoric method. New experimental results are reported for pressures ranging from 4 to 22 MPa and for mass fraction of ethylene carbonate ranging from 0.05 to 0.25 (0.011 to 0.064 for mole fraction).

Results & Discussion

The experimental results show that the addition of ethylene carbonate in the system shifts hydrate phase boundaries to higher pressure and lower temperature in contrast to more hydrophobic cyclopentanone.

With the concentration of 0.240 mass fraction (0.061 mole fraction) of the ethylene carbonate additive in an aqueous system, the most significant decrease of the equilibrium temperature is about 3 K at a given pressure, in comparison to that of methane + water system without additive.

Employing the Clausius-Clapeyron equation, the structures of methane hydrates with additive of ethylene carbonate are determined. Obtained data suggest that at a pressure more than 8 MPa, apparently, there is a structure sII hydrate formation, while at lower pressures - structure sI hydrate formation.

Conclusions

We measured the three phase equilibrium conditions in the methane, water and ethylene carbonate system. Ethylene carbonate shifts hydrate phase boundaries to higher pressure and lower temperature. Despite the similarity of cycle dimensions and chemical structure, these compounds behave in the opposite way. CP is a thermodynamic hydrate promoter whereas EC acts as thermodynamic hydrate inhibitor.

Acknowledgement

This work was supported by the Ministry of Education and Science of the Russian Federation (Target funding, project 13.1926.2014/K).

References

1. Yu-Wan Juan et al. Fluid Phase Equilibria. 386, 162–167 (2015).

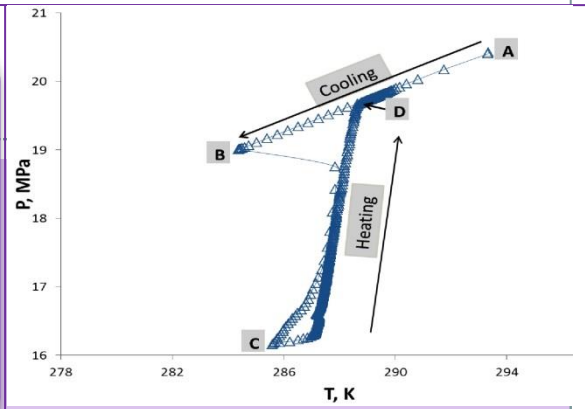

Figure 1 –Schematic illustration of experimental procedure

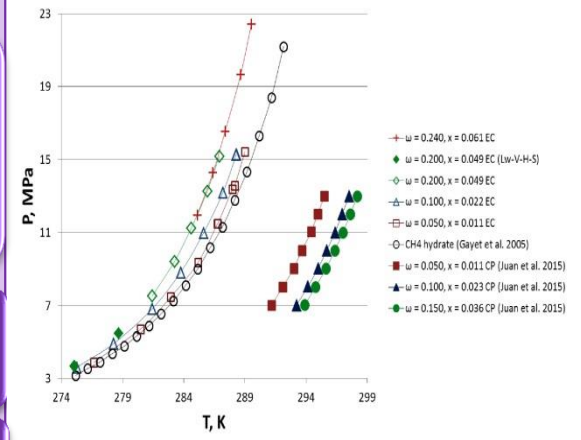

Figure 2 –Comparison of equilibrium conditions for gas hydrates in CH4+H2O+EC and CH4+H2O+CP systems