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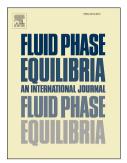
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### **Capillary Effects on Phase Behavior of Liquid and Gaseous Propane and Dynamics of Hydrate Formation and Dissociation in Porous Media**

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#### Abstract

Using a precision adiabatic calorimetry method the phase behavior of liquid and gaseous propane with water in bulk as well as in dry and water saturated porous media have been studied in the temperature range from 240 to 350 K and the pressure range from 0.1 to 12 MPa. Quartz powder with a grain size from 25 to 38 mk as a porous medium was used. Water saturation of the porous medium was about 0.247±0.001 of porous volume. From thermodynamic point of view such water saturation of the porous volume is sufficient to consider the pore water phase practically as a bulk phase. A composite porous medium is formed from the quartz powder grains covered by a water film. In fact, the water film is a mechanical continuation of the quartz powder grains. The water film forms a configuration (a curvature) of the porous space as well predetermines a surface wettability of the composite porous medium. We study capillary effect in composite porous media due to capillary condensation and capillary evaporation of propane, both on a lyophilic surface and on a lyophobic surface of water film. Based on the experimental data of specific heat and temperature derivative of pressure at constant volume, the phase diagrams of propane in bulk and in water saturated and dry quartz powder have been constructed (including the gas hydrate field of phase diagram).

**Keywords:** Adiabatic Calorimetry, Porous Medium, Capillary Condensation, Capillary Evaporation, Phase Transition, Propane, Water, Gas Hydrate, Wettability.

#### Nomenclature

- C Specific heat  $[J \cdot mol^{-1} \cdot K^{-1}]$
- P Pressure [MPa].
- T Temperature [K].

Q<sub>1</sub>, Q<sub>2</sub> – Lower and Upper Quadruple Points of Hydrate.

 $\sigma$  - Surface Tension [J · m<sup>-2</sup>].

 $\xi = \sigma_{hw} \cdot T_m / \rho_h \cdot q_m$  - Curvature Coefficient [K·mk].

 $\sigma_{hw}$  - Surface Tension on the Hydrate – Water Interface  $[J \cdot m^{-2}]$ .

T<sub>m</sub>, T'<sub>m</sub> - Melting Temperatures on the Planar and Curved Surfaces [K].

 $\rho_h$  - Density of Hydrate [kg · m<sup>-3</sup>].

 $q_m$  - Heat of Hydrate Dissociation [J · mol<sup>-1</sup>].

r<sub>1</sub>, r<sub>2</sub> - Principal Radii of Curvature of the Meniscus [mk].

#### **1** Introduction

The phase behavior of fluids in porous media attracts much attention due to transformation of phase diagrams in comparison with bulk phases. Traditionally the confined geometry effects in mesoscale level are described as capillary and/or adsorption phenomena [1].

Effect of adsorption depends on the value of specific surface of interface boundary as well as the physical and chemical properties of surface. The influence of adsorption on phase equilibria in low permeable porous media may be essential at high pressure. Up to now there are no sufficient theo-

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