

Effects on phase behavior of Multi-phase flows 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.

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 theoretical and experimental data concerning adsorption effect, which can be

use in oil and gas practice [1]. Our previous experimental research [2] ; [3] is one of the steps in this direction.

It should be pointed that there are many important papers (see for review[4-11]) concerning the influence of pore water on three phase equilibrium line (equilibrium liquid pore water - gaseous phase - hydrate phase) primary for methane and carbon dioxide gases. In these papers pore water inside porous media are significantly differ from bulk water (at low pore water saturation). The pore water chemical potential depends on water content in porous media and at high saturation it becomes equal to bulk water potential. The shift of hydrate equilibrium line depending on water saturation is take place (due to the chemical potential of pore water is not equal to the chemical potential of bulk water). At this paper we discuss another type effect - propane phase capillary effect which was detected by calorimetric experiments.

2. EXPERIMENTAL

A method of precision adiabatic calorimetry was applied for investigation of phase behavior of liquid and gaseous propane with water in bulk and in porous media. Principal scheme of this complex is depicted in Fig. 1. An experimental complex consists of two adiabatic calorimeters [2]. The first calorimeter (I) is used for investigation of phase behavior of hydrocarbon fluids in bulk and the second one (II) in porous media. Measurements of the thermodynamic parameters are performed either independently on each calorimeter or simultaneously on both calorimeters.

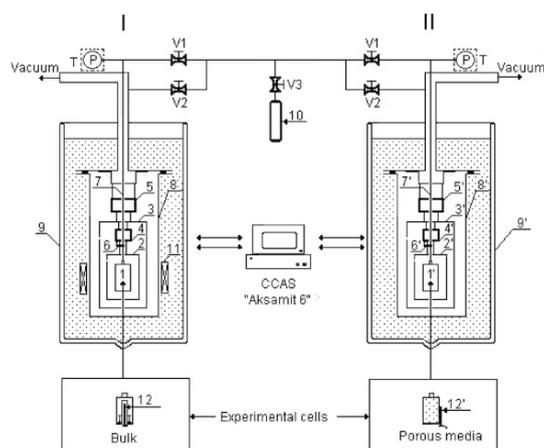


Fig. 1 Principal scheme of experimental adiabatic complex. Prime corresponds to the porous media (PM) investigations.

The calorimeter cell for measurements in bulk (1) contains the magnetic mixer, which is set in action by solenoid (11) with the period of 10 s. Platinum thermometer (12) is placed into the copper cylindrical case inside this cell. The calorimeter cell for measurements in porous media (1') is collapsible. Thermometer is placed on its side (12').

3. RESULTS AND DISCUSSION

Phenomenon of capillary condensation of propane we have experimentally observed in dry (waterless) quartz powder. If the density of propane is less than the critical density ($\rho_c = 221.56 \text{ kg/m}^3$), this phenomenon takes place. Measurements were performed for isochoric processes in the density range of propane from 3 to 200 kg/m^3 . As example, transformation of the liquid - vapour equilibrium line of propane as a part of propane isochore of density $\rho = 91.34 \text{ kg/m}^3$ is depicted in Fig. 2. Red line in Fig. 2 (A'B'C') corresponds to the pressure-temperature dependency of propane in quartz powder. Blue line (ABC) corresponds to the pressure-temperature dependency of propane in bulk. AB corresponds to the liquid - vapour equilibrium state of propane in bulk and BC corresponds to the vapour phase of propane in bulk. A'B'C' corresponds to the liquid - vapour equilibrium of propane in quartz powder.

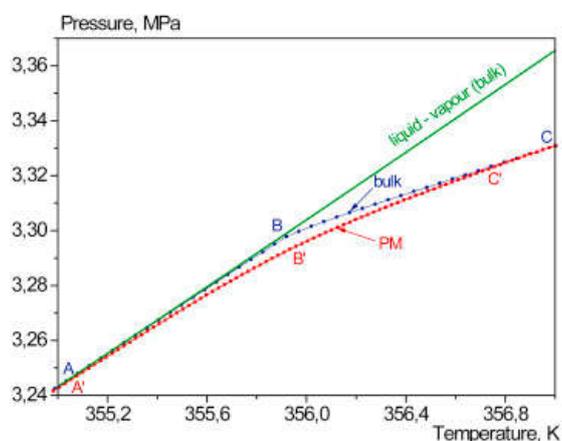


Fig. 2 A downward shift of the liquid – vapour equilibrium line of propane (A'B'C') as a result of capillary condensation in dry quartz powder compared to the liquid – vapour equilibrium line of propane in bulk (AB).

PM is the liquid – vapour equilibrium line of propane in porous medium.

Phenomena of capillary condensation and evaporation of propane we have experimentally observed in water saturated quartz powder. Shifts of the liquid - vapour equilibrium line of propane are depicted in Fig. 3. The upward (CB) or downward (C''B'') shifts of the liquid – vapour equilibrium line of propane in the porous medium, compared to the bulk equilibrium, were observed.

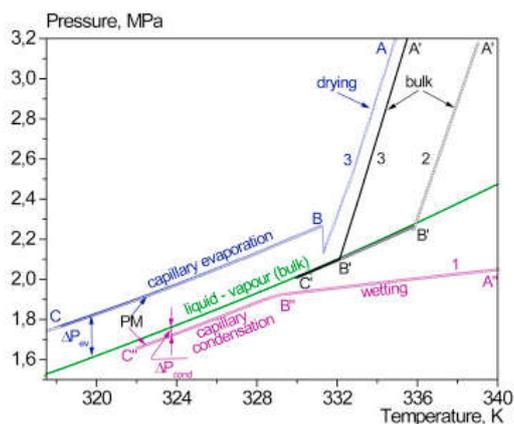


Fig. 3 Shifts of the liquid – vapour equilibrium line of propane as a result of capillary evaporation

(CB) and capillary condensation (C''B'') in quartz powder grains covered by water film compared to the liquid – vapour equilibrium line of propane in bulk (C'B'). AB, A'B' is liquid propane, A''B'' is gaseous propane. PM is the liquid – vapour equilibrium line of propane in porous medium. Numbers are density of propane isochores: 1 - $\rho = 41,90 \text{ kg/m}^3$, 2 - $\rho = 420,48 \text{ kg/m}^3$, 3 - $\rho = 430,46 \text{ kg/m}^3$.

Pressure as a function of temperature at the isochoric dissociation of propane hydrate is depicted in Fig.4. Density of propane for isochors 1, 2, 3, 5 is less than the critical density. To demonstrate a phenomenon of the partial wetting of hydrate surface by propane at high density ($\rho > \rho_c$), the isochore 4 of density $\rho = 458,135 \text{ kg/m}^3$ is depicted.

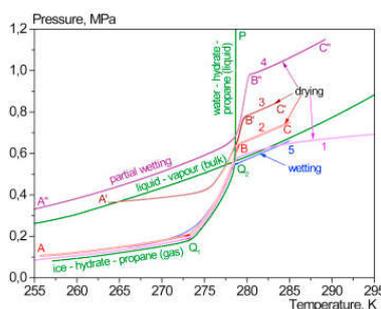


Fig. 4 Pressure as a function of temperature at isochoric dissociation of propane hydrate. Numbers are density of propane isochores: 1 - $\rho = 12,57 \text{ kg/m}^3$, 2 - $\rho = 24,23 \text{ kg/m}^3$, 3 - $\rho = 49,28 \text{ kg/m}^3$, 4 - $\rho = 458,14 \text{ kg/m}^3$, 5 - $\rho = 44,74 \text{ kg/m}^3$. Q₂B, Q₂B', Q₂B'' are superheated hydrate. AQ₁Q₂P is phase diagram for pure propane hydrate.

Fig. 4 shows that each isochore consists of three sections. AQ₁ corresponds to the hydrate – ice – gaseous propane equilibrium. Q₁Q₂B corresponds to the hydrate – water – gaseous propane equilibrium.

Based on the data of specific heat (extrema of the specific heat), phase transitions were localized, and phase diagrams have been constructed. Heat capacity, as a function of temperature at the isochoric dissociation of propane hydrate, is depicted in Fig. 5. Extrema of the specific heat near the lower quadruple point are concerned to the ice melting and extrema of

the specific heat near the upper quadruple point are concerned to the propane hydrate dissociation.

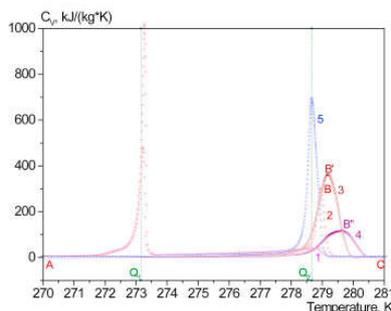


Fig. 5 Heat capacity as a function of temperature at isochoric dissociation of propane hydrate.

Notations are the same as in Fig. 4

Due to a shift of the liquid - vapour equilibrium line of propane (CD is moved to C'D'), a section of the hydrate – water – gaseous propane equilibrium line (Q₁Q₂) is extended to the region of higher pressure and temperature (section Q₂Q'₂) as depicted in Fig. 6 As a result, an upper hydrate quadruple point Q₂ is moved to the point Q'₂. If the capillary phenomena do not effect, the upper quadruple point is not shifted into the region of the higher temperature.

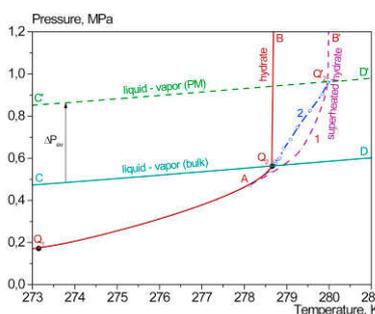


Fig. 6 Phase diagrams for water – propane system.

The maximal effects of capillary phenomena are displayed in the range of high densities of liquid propane (see curve 4 in Fig. 4 and curves 1, 2, 3 in Fig. 7). Pressure as a function of temperature at the isochoric formation and dissociation of liquid propane hydrate for various wetting properties of propane on water: wettability, partial wettability and non-wettability (drying) is depicted in Fig. 7 The heating and cooling regimes of measurements were used. ABC corresponds to the heating regime of measurements and CB'A corresponds to the cooling regime of measurements.

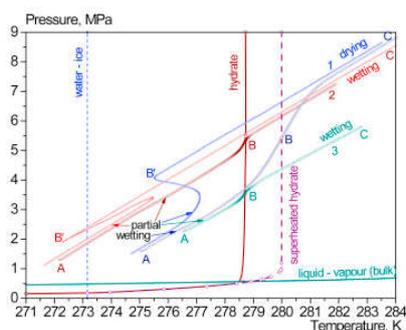


Fig. 7 Pressure as a function of temperature at isochoric formation and dissociation of liquid propane hydrate.

Numbers are density of propane isochores: 1 - $\rho=527,802\text{kg/m}^3$, 2 - $\rho=530,082\text{kg/m}^3$, 3 - $\rho=523,946\text{kg/m}^3$.

Processes of formation and dissociation of superheated hydrate, predetermined by capillary effects, are differed from the processes of hydrate formation and dissociation without capillary effects. This fact is followed from comparison of the data of heat capacity measurements. The results of comparison of heat capacity measurements are depicted in Fig. 8a and b. These figures show that character of heat capacity at the superheated hydrate dissociation (Fig. 8b) is drastically differed from character of heat capacity at the hydrate dissociation without capillary effect (Fig. 8a).

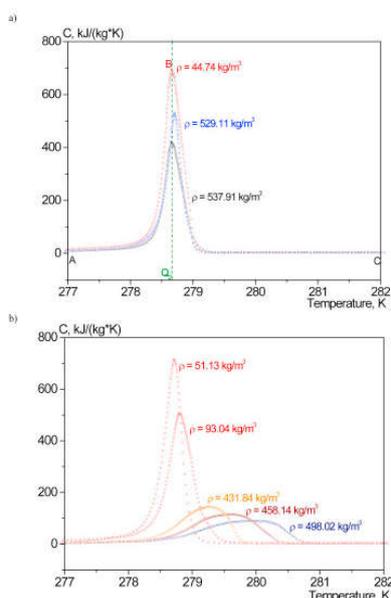


Fig. 8 Heat capacity as a function of temperature at isochoric dissociation of propane hydrate. Numbers are density of propane at isochores.

4. CONCLUSION

An original experimental method with two adiabatic calorimeters was applied for investigation of capillary effects on phase behavior of liquid and gaseous propane and dynamics of hydrate

formation and dissociation in composite porous media (lyophilic quartz particles covered by water film). Based on the experimental data of specific heat and of temperature derivative of pressure at constant volume, the phase diagrams for propane in bulk and in water saturated and dry quartz powder have been constructed (including the gas hydrate field of phase diagram). The results of experiments showed that phase behavior of liquid and gaseous propane is drastically transformed by the porous media effects. Due to effects of drying or wetting, the considerable growth or lowering of pressure takes place. Transformation of phase behavior of propane occurs in water saturated as well as in dry porous media. Transformation of propane phase behavior in the water saturated porous media leads to alteration of propane hydrate's phase diagram. A shift of the upper quadruple point of propane hydrate into the region of the higher temperature and pressure takes place. Domain of the propane hydrate thermodynamic stability is enlarged and the state of superheated hydrate is developed.

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REFERENCES

- [1] Y. C. Yortsos, A.K. Stubos Phase change in porous media *Curr. Opin. Colloid & Interface Sci.*, 6 (2001), pp. 208–216.
- [2] V. M. Buleiko, B.A. Grigoriev, V.A. Istomin Experimental Investigation of the Quartz Powder Specific Surface Effect on Phase Behavior of Ternary Mixtures of Hydrocarbons vol. 17, *Vestnik of the Kazan Technological University* (2014), pp. 101–107 No 23, (in Russian).
- [3] V. M. Buleiko, V.P. Voronov, S.N. Zakirov, E.S. Zakirov, I.M. Indrupskii Regularities in the behavior of hydrocarbon systems of oil and gas pools *Dokl. Earth Sci.*, 1028-334X, 415 (No 5) (2007), pp. 686–689.
- [4] D. H. Smith, K. Seshadri, J.W. Wilder Thermodynamics of methane, propane, and carbon dioxide hydrates in porous glass *AIChE J.*, 50 (No. 7) (2004), pp. 1589–1598.
- [5] M. Zarifi, J. Javanmardi, H. Hashemi, A. Eslamimanesh, A.H. Mohammadi Experimental study and thermodynamic modelling of methane and mixed C1, C2, C3 clathrate hydrates in the presence of mesoporous silica gel *Fluid Phase Equilibria*, 423 (2016), pp. 17–24.
- [6] Seo Yongwon, S. Lee, I. Cha, J.D. Lee, S.-P. Kang Phase equilibria of ethane and propane hydrates in porous silica gels *J. Phys. Chem. B*, 113 (16) (2009), pp. 5487–5492.
- [7] Seo Yongwon, S. Lee, I. Cha, J.D. Lee, S.-P. Kang Phase equilibria of ethane and propane hydrates in porous silica gels *J. Phys. Chem. B*, 113 (16) (2009), pp. 5487–5492.
- [8] T. Uchida, T. Ebinuma, S. Takeya, J. Nagao, H. Narita Effects of pore sizes on dissociation temperatures and pressures of methane, carbon dioxide, and propane hydrates in porous

- media *J. Phys. Chem. B*, 106 (4) (2002), pp. 820–826.
- [9] A.H. Mohammadi, A. Eslamimanesh, D. Richon, F. Gharagheizi, M. Yazdizadeh, J. Javanmardi, H. Hashemi, M. Zarifi, S. Babaee Gas hydrate phase equilibrium in porous media: mathematical modeling and correlation *Ind. Eng. Chem. Res.*, 51 (2012), pp. 1062–1072.
- [10] V.K. Saw, G. Udayabhanu, A. Mandal, S. Laik Methane hydrate formation and dissociation in the presence of silica sand and bentonite clay *Oil Gas Sci. Technol. – Rev. IFP Energies nouvelles*, 70 (No. 6) (2015), pp. 1087–1099.
- [11] Q. Wu, B. Pang, B. Zhang, T. Xu Progress in the Research on Phase Equilibrium of Gas Hydrates in Porous Medium, the Second China Energy Scientist Forum (2010), pp. 141–145.