



Calorimetric investigation of hydrates of pure isobutane and iso- and normal butane mixtures

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ARTICLE INFO

Article history:

Received 24 September 2017

Received in revised form

15 December 2017

Accepted 13 January 2018

Keywords:

Adiabatic calorimetry

Isobutane

Normal butane

Gas hydrate

Quartz powder

Phase transition

Quadruple and quintuple points

ABSTRACT

This paper shows the accurate calorimetric measurements of the phase equilibrium of pure isobutane, normal butane and their mixture in water-saturated quartz powder and in bulk. The heat capacity, temperature derivative of pressure at constant volume, enthalpy and pressure, as a function of temperature, for binary and ternary systems (water-isobutane, water-normal butane, water-isobutane-normal butane) have been measured in the hydrate's forming range (the temperature range of 234–280 K and pressure up to 10 MPa). Based on experimental data of heat capacity and temperature derivative of pressure at constant volume, the phase diagrams for hydrates of isobutane and mixture of isobutane and normal butane have been constructed. The isobutane-normal butane ratio of gaseous phase has been defined. The lower and upper quadruple points of isobutane hydrate and the quintuple point of isobutane hydrate formed by mixture of butanes have been detected. Isobutane is a hydrate former. Normal butane has an effect on the phase equilibrium of hydrates. An upper quadruple point of the pure isobutane hydrate is transformed into a line of upper quadruple points of the isobutane hydrate, which is in equilibrium with the binary mixture isobutane - normal butane. A line of upper quadruple points starts at the upper quadruple point of pure isobutane hydrate and stretches up to the quintuple point of hydrate formed by the mixture of butanes. The content of normal butane at the quintuple point is $29.9 \pm 0.5\%$ mol and does not depend on its concentration in the original mixture (before hydrate formation). The stability of isobutane and normal butane concentration in mixture is provided due to partial dissociation or formation of hydrate. A three-component system (water - normal butane - isobutane) of five phases (water - ice-hydrate - liquid butanes - gaseous butanes) has zero degree of freedom at the quintuple point. There is only one value of pressure, temperature and content of butanes in which five phases can exist together in equilibrium.

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1. Introduction

Natural gas hydrates are the most important source of hydrocarbon resources as vast reserves of the natural gas which exist in the form of hydrate. Natural gas hydrates are usually formed by mixtures of hydrocarbons such as methane, ethane, propane, isobutane, etc. and associated gases such as carbon dioxide and hydrogen sulfide. Large reserves of natural gases in the hydrate state are concentrated in the hydrate formation zone of the sea-floor and of the permafrost of the earth's crust [1,2]. The hydrate formation zone is a zone of sedimentary rock saturated with water

and gas, in which the thermodynamic conditions are suitable for hydrate formation. An outline of the hydrate formation zone is determined by pressure, temperature, mineralization of reservoir water, and based on the hydrate's phase diagram. Diagrams for detection of hydrate formation zones are widely used by specialists to predict depths of hydrate-bearing intervals in bottom sediments. The development of such diagrams is possible only through experimental hydrate data of multicomponent mixtures [3]. Hydrates are not just a significant source of natural gas, but a source of problems that must be overcome at the production, processing and transport level, as with most hydrocarbons. A crucial step to overcome these problems is construction of phase diagram of hydrates formed by hydrocarbon mixtures.

The content of each component in natural gas hydrates is different and predetermined by the conditions of hydrate

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formation. If the concentration of some component varies the hydrating pressure for mixture is changed as well. For example, in the presence of methane, a nonhydrate former will increase the hydrating pressure for pure methane (a structure-I hydrate former) at any given temperature and a structure-II hydrate former will lower the hydrating pressure somewhat below that for pure methane at the same temperature [4,5].

Research of gas hydrates formed by pure hydrocarbons is very important for a deeper understanding of the fundamental properties of clathrate hydrates. Thermodynamic properties and phase behavior of hydrates formed by pure methane, ethane and propane were thoroughly studied by various researchers [6–22] including our investigations using an adiabatic calorimetry [23–26]. At the same time, the thermodynamics of hydrate formed by pure isobutane has not been well studied, and hydrate from normal butane hasn't been produced. It is unknown, if the pure normal butane forms hydrates [27]. However, there is an opinion that normal butane does enter into the hydrate's lattice when hydrate is formed in the presence of a hydrate former component, for instance in the presence of methane [4,5,28]. Thus, a research on the normal butane and isobutane contribution to the hydrate formation of hydrocarbon mixtures and the analysis of the possibility of hydrate formation by pure normal butane at low temperature is required.

Here, it is necessary to note the peculiarities of hydrate formation, which have been recently revealed and which really have an affect on hydrate formation. Not long ago we had studied phenomena concerning to the state of metastability of water – hydrocarbon system in the hydrate's forming range [24,25,34]. The state of double metastability is the precursor of hydrate formation or ice crystallization. We observed that thermal history of water has an effect on the direction of phase transition of the water - hydrocarbon system if this one is at the state of double metastability.

What is the state of "double metastability"? Water is considered to be supercooled when it exists as a liquid at lower temperatures than melting point. Once the equilibrium curve water – hydrate – hydrocarbon is crossed through cooling and the system temperature become below zero, but solid phases did not occur, this system is at the state of "double metastability".

The hydrate structures are composed of five polyhedra formed by hydrogen-bonded water molecules and the most common solid form of water is known as hexagonal ice [31]. As followed from calculation by comparing the heat of sublimation of ice with the heat of fusion of ice, only 15% of hydrogen bonds break when ice melts [31]. Thus, if the water - hydrocarbon system is at the state of double metastability and the water is obtained by melting ice, the ice crystallization takes place. If the water is obtained by melting hydrate, the hydrate formation takes place. Besides, our experiment shows, that hydrates of hydrocarbon mixtures consist of two coexisting hydrate structures and the ratio of these hydrate structures greatly depends on condition of water preparation (whether the water is obtained by melting hydrate or ice) [26,35].

Another phenomenon is capillary effects on phase behavior of liquid and gaseous hydrocarbons and dynamics of hydrate formation and dissociation in the porous media [23]. Experiment shows that phase behavior of liquid and gaseous hydrocarbons is drastically transformed by the effects of porous media. Due to effects of drying or wetting, a considerable increase or decrease of pressure takes place. Transformation of phase behavior of hydrocarbon in the water saturated porous medium causes the transformation of its hydrate's phase diagram.

The set forth above phenomena have usually a strong effect on the process of hydrate formation and it is necessary to keep in mind these effects during the course of the research on hydrate formation.

In this paper, we discuss the data of our recent experimental

research of the phase equilibrium of hydrates formed by pure isobutane and isobutane and normal butane mixture in water-saturated quartz powder and in bulk, which revealed the contribution of each component to the process of hydrate formation and dissociation by mixture of hydrocarbons.

2. Experimental apparatus and procedures

2.1. Experimental setup

We have performed accurate measurements of the phase equilibrium of pure isobutane, normal butane and their mixture in water-saturated quartz powder and in bulk in the hydrate's forming range. A method of precision adiabatic calorimetry was used. This method was applied for adiabatic calorimeter setup. The experimental setup consists of two adiabatic calorimeters. The first calorimeter is used for measurements of hydrocarbon fluids phase equilibrium in bulk and the second one for measurements in porous media. Measurements of heat capacity, temperature derivative of pressure at constant volume, enthalpy and pressure, as a function of temperature, are performed either independently using each calorimeter or simultaneously using them both. With the simultaneous operation of both calorimeters the same fluid is placed into calorimeter's cell of the first calorimeter (bulk) as well as into calorimeter's cell of the second one (porous media). Comparison of the measured parameters allows us to detect the porous medium effect. Experimental details of the setup are given elsewhere [23].

An advanced adiabatic calorimetry provides the precision data of heat capacity, temperature derivative of pressure at constant volume and equilibrium curves of coexisting phases formed by the pure components and their mixture. A method of precision adiabatic calorimetry allows us to define the type of phase transition (first or second order) and the characteristic properties of coexisting phases. Using the procedure described in Ref. [23] the heat capacity and temperature derivative of pressure at constant volume have been measured and the equilibrium curves of water-hydrate-butananes and ice-hydrate-butananes have been constructed at a temperature ranging from 234 to 280 K and pressure up to 10 MPa.

2.2. Sample preparation and description of measurements

The research on hydrate formation and dissociation is complicated, on one side, due to the slow mass transfer caused by the diffusion of hydrate former gas through water or ice and, on the other side, due to the long-term hydrate nucleation (induction time). Research on hydrates of pure isobutane and iso- and normal butane mixture in bulk is especially complicated due to the slow mass transfer. To overcome this complication a composite porous medium, described in Ref. [23], was used. A composite porous medium is formed from quartz powder grains covered by a water film. In fact, the water film is a mechanical continuation of the quartz powder grains. The composite porous medium, having an increased water - gas interface, overcomes the slow gas diffusion through water or ice and allows us to study the intrinsic peculiarities of hydrates. However, capillary effects on hydrate phase behavior, which are necessary to keep in mind, take place in the composite porous medium. Due to capillary effects, the phase behavior of hydrate former gas and hydrocarbon hydrate is transformed.

The calorimetric research of hydrates of pure isobutane and iso- and normal butane mixture was performed both in porous medium and bulk. The main data were measured in the porous medium, but the long-term bulk research was performed to reveal the capillary effects on the dynamics of hydrate formation and dissociation in

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