



# Pressure dependence of gas hydrate formation in triple systems water – 2-Propanol–methane and water – 2-Propanol–hydrogen



Artem A. Sizikov<sup>a</sup>, Andrey Yu. Manakov<sup>a, b, \*</sup>, Eugeny Ya. Aladko<sup>a</sup>

<sup>a</sup> Nikolaev Institute of Inorganic Chemistry SB RAS, Ac. Lavrentiev ave. 3, Novosibirsk, 630090, Russian Federation

<sup>b</sup> Novosibirsk State University, Pirogova Str. 2, Novosibirsk, 630090, Russian Federation

## ARTICLE INFO

### Article history:

Received 23 March 2016

Received in revised form

13 June 2016

Accepted 15 June 2016

Available online 16 June 2016

### Keywords:

Gas hydrate

2-Propanol

Methane

Double hydrate

Composition

## ABSTRACT

The compositions of the cubic structure II double hydrates of 2-propanol and methane have been determined. The hydrates have been prepared at 274.2 K, under methane pressure of  $10.0 \pm 0.3$  MPa from solutions with 2-propanol content varying from 4.2 to 18.1 wt%. The combination of thermovolumetric measurements, powder X-ray diffraction and Raman spectroscopy has given evidence that the double hydrate formed is a substitutional solid solution in the whole range of studied 2-propanol concentrations in the starting aqueous solutions. It has been shown that the maximal extent of substitution of 2-propanol by methane grows with the increasing pressure of the synthesis. The composition of the double hydrate with the largest gas content prepared under methane pressure of  $10.0 \pm 0.3$  MPa corresponds to  $(3.0\text{PA} + 5.0\text{CH}_4)_\text{H} \cdot (12.6\text{CH}_4)_\text{D} \cdot 136\text{H}_2\text{O}$  (PA – 2-propanol, indexes H and D denote molecules situated in H and D cavities, respectively). When the synthesis is carried out at methane pressure of 5.2 MPa, the composition of the double hydrate with the largest gas content is  $(4.3\text{PA} + 3.7\text{CH}_4)_\text{H} \cdot (13.3\text{CH}_4)_\text{D} \cdot 136\text{H}_2\text{O}$ . In addition, high-pressure DTA has been employed to demonstrate that the double hydrate of 2-propanol and water is formed only at hydrogen pressure exceeding 50 MPa.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Gas hydrates form one of the classes of inclusion compounds in which the molecules of a gas, readily volatile liquid, or (in some cases) solid substance are located in the cavities of a polyhedral framework composed of water molecules. The most common structural types of gas hydrates are cubic structure I (sI), cubic structure II (sII), and structure H (sH) [1]. Unit cell of a sI hydrate framework consists of six large T-cavities ( $5^{12}6^2$ ; the cavity has 12 pentagonal faces and 2 hexagonal faces) and two small D-cavities ( $5^{12}$ ). The formula of the unit cell is  $6\text{T} \cdot 2\text{D} \cdot 46\text{H}_2\text{O}$ . Typical guest molecules which form sI hydrates are methane, carbon dioxide and hydrogen sulfide. The unit cell of a sII hydrate framework consists of eight large H-cavities ( $5^{12}6^4$ ) and sixteen small D-cavities ( $5^{12}$ ), unit cell formula is  $8\text{H} \cdot 16\text{D} \cdot 136\text{H}_2\text{O}$ . Gas hydrates of this structural type are formed by  $\text{N}_2$ ,  $\text{O}_2$  and larger guest components like propane, tetrahydrofuran or mixtures of guests. sH hydrate discovered

by Ripmeester et al. [2] are double hydrates requires the largest guest such as isoamyl alcohol along with a smaller guest like methane [3]. The unit cell of a sH framework consists of three types of cavities: one large E ( $5^{12}6^8$ ), two medium D' ( $4^35^66^3$ ), and three small D ( $5^{12}$ ).

The hot spots in technological application of gas hydrates include gas storage and transportation in the hydrate form [4–6], as well as separation of gas mixtures with the use of hydrate formation [7–9]. The reduction of operating costs, as well as simplification and cheapening of the relevant facilities, demands for changing the existence conditions of hydrates to “softer” temperatures and pressures. The only currently known technique of shifting the equilibrium conditions of hydrate formation/decomposition is the employment of double hydrates of the target gas and some secondary component. Partial filling of the hydrate cavities with the molecules of the secondary component diminishes the content of the target gas in the hydrate. Therefore, the search of secondary hydrate-forming components providing fairly large content of the gas in the hydrate and, at the same time, reasonable hydrate decomposition temperature at the operating pressure, is important and topical task. For example, tetrahydrofuran was

\* Corresponding author. Nikolaev Institute of Inorganic Chemistry SB RAS, Ac. Lavrentiev ave. 3, Novosibirsk, 630090, Russian Federation.

E-mail address: [manakov@niic.nsc.ru](mailto:manakov@niic.nsc.ru) (A.Yu. Manakov).

suggested as the secondary component increasing decomposition temperature of hydrogen hydrate [10–12]. Double hydrates H<sub>2</sub>-TBA fluoride [5,13], H<sub>2</sub>-TBA chloride [14] and H<sub>2</sub>-TBA bromide [5,12,15] (TBA – tetrabutylammonium) have been studied for the same purpose. For a given temperature the equilibrium decomposition pressures of such double hydrates are essentially lower than for the hydrate of pure hydrogen [12,16,17].

It is well known that formation of gas hydrates on gas and oil recovery can cause suspension of operation and malfunctions [18,19]. The most common approach to prevention of gas hydrate plugs uses thermodynamic inhibitors of gas hydrate formation, such as various salts, methanol and glycols. The inhibitor molecules decrease the chemical potential of water in the water-alcohol mixture, thus reducing decomposition temperatures of the hydrates formed from this solution [20,21]. For a long time it was generally accepted that lower alcohols are not included in hydrate framework cavities to a noticeable extent [18]. Relatively recently it has been found that methanol molecules can be included in hydrates at limited amount [22], while such alcohols as ethanol [23–29], 1-propanol [27,28,30–33], 2-propanol [27,28,34–36] and tert-butanol [27,37] form sII double hydrates with methane and natural gas. Inclusion of these alcohols in the cavities of the hydrate framework may increase or decrease the stability of the corresponding gas hydrates depending on the gas component [33,36,38]. Large molecular alcohols such as pinacolyl alcohol (3,3-dimethyl-2-butanol) and tert-amyl alcohol (2-methyl-2-butanol) form sH double hydrates with methane [38–40]. Spectroscopic studies have revealed that there is no strong hydrogen-bonding interaction between enclathrated guest and host species for sH hydrates of these compounds [39], as well as for sII hydrate of 1-propanol [41]. The analysis of the available data has shown that below 0°C 2-propanol can be used as the secondary component in gas hydrate technologies [42]. It is cheap, relatively non-toxic, and is produced at industrial scale. At the temperatures below 0°C the equilibrium pressures of the double hydrate of 2-propanol and methane (hence, also of the natural gas) are essentially lower than for pure methane hydrate. These considerations have determined our interest to thorough investigation of the double hydrate of 2-propanol and methane.

The determination of precise gas hydrate composition is a complex experimental task due to difficulties in preparation of an ice-free hydrate sample and the prevention of gas release from the sample. Another problem arises from the nature of these compounds. As a rule, gas hydrates are non-stoichiometric compounds and their composition depends on the conditions of their synthesis and storage [1]. At the same time information concerning composition of gas hydrates is essential for scientific studies and technological applications. In our recent work [42] composition and structure of 2-propanol and methane double hydrate synthesized from 2-propanol solutions with concentrations from 6.2 to 17.9 mass.% were studied by means of thermovolumetric and X-ray powder diffraction methods. All samples of the double hydrates were synthesized at pressure 5.2 MPa and temperature 274.2 K. In this work we present new experimental data on the composition and structure of the samples of 2-propanol + methane double hydrate, which were synthesized from solutions with 2-propanol concentration 4.1–18.0 wt% at the pressure of methane 10.0 MPa and temperature 274.2 K and some reinterpretation of the data presented in the previous work [42].

## 2. Materials and methods

The synthesis of the double hydrate samples was performed in an autoclave (200 ml in volume), equipped with a manometer and a shutoff valve. The data concerning the reactants used are presented

in Table 1. The aqueous solutions of 2-propanol were prepared by weighing the components. The following experimental procedure was used. The autoclave was cooled to the temperature of liquid nitrogen (77 K) and then the powder of frozen 2-propanol solution (particle diameter < 0.1 mm) was loaded into the autoclave. The autoclave was closed and purged with methane three times to remove any residual air. After that, we set the working pressure of methane at  $10.0 \pm 0.3$  MPa. Then the autoclave was heated to 274.2 K, and the pressure in it was kept constant by release of excessive gas. The sample was kept for two or three days at a temperature of 274.2 K, then the autoclave was frozen to liquid nitrogen temperature, the quenched sample was taken out, ground thoroughly and again loaded into the autoclave using the same procedure as above. To achieve the equilibrium state, this operation was made 4–5 times for each sample. The formation of the hydrate manifested itself as a drop in pressure in the autoclave. During the last cycles of hydrate formation pressure in the autoclave changed only due to temperature change.

Thermovolumetric measurements are described elsewhere [43]. The hydrate sample (0.3–0.5 g) at liquid nitrogen temperature was placed into a cell, which was then heated at a rate of 1–2 K/min. Cell temperature was measured with a chromel-alumel thermocouple (type K). The evolved gas was collected in a burette above the saturated NaCl solution. Temperature dependence of the volume of gas evolved from the hydrate was recorded. The measured gas volume was reduced to the normal conditions; corrections for atmospheric pressure and water vapour pressure were made. The random error of the method is 1.5%.

X-ray powder diffraction studies were performed on a BrukerD8 Advance diffractometer (CuK<sub>α</sub> radiation,  $\lambda = 1.5418$  Å) equipped with Anton Paar refrigerating and heating device. Samples for powder diffractometry were finely ground in a mortar at liquid nitrogen temperature and placed into a sample holder that had been pre-cooled. The data were treated with the help of FIT2D [44] and XLAT [45] programs. Raman spectra were recorded in back-scattering geometry with use of Triplemate SPEX spectrometer equipped with multichannel detector LN-1340PB and home-made refrigerating device. The 514.5 nm line of an argon ion laser was used for excitation.

Hydrate decomposition temperatures in the system 2-propanol – water – hydrogen were measured by means of differential thermal analysis (DTA) in a cell specially developed for the studies of hydrate formation in the presence of a gaseous guest at high hydrostatic pressure [46]. A gas was taken in excess with respect to the expected hydrate composition. Hydrate decomposition temperatures were measured with a chromel-alumel thermocouple (type K) calibrated over standard compounds; the error of temperature measurement was  $\pm 0.3$  K. Scale reading of a thermocouple of this type is almost independent of pressure. Pressure was measured with a manganine manometer calibrated at high pressures with respect to mercury melting. Error of pressure measurements was not more than 1%. The experimental procedure was described in detail in Refs. [46,47].

## 3. Results and discussion

Typical experimental volume-temperature dependences are illustrated in Fig. 1. The results of methane content determination in the samples of the double hydrate of 2-propanol and methane prepared from aqueous solutions with varying fraction of 2-propanol under pressure  $10.0 \pm 0.3$  MPa and the temperature of 274.2 K are shown in Fig. 2. For comparison, the same Figure presents the data for the samples of the double hydrate of 2-propanol and methane prepared at  $5.2 \pm 0.3$  MPa and 274.2 K [42]. Hereafter, for convenience, we use sample notation PmHn, where

Download English Version:

<https://daneshyari.com/en/article/201120>

Download Persian Version:

<https://daneshyari.com/article/201120>

[Daneshyari.com](https://daneshyari.com)