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Natural Gas Hydrate Decomposition in the Presence of Methanol

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Abstract

Novel experimental data concerning the reactions kinetics for the formation and decomposition of hydrates synthesized from natural gas of the Irelyakh gas and oil field (Yakutia) are obtained. It is established that the duration of induction period of natural gas hydrate formation depends on the thermobaric conditions of its synthesis. Kinetic data characterizing the effect of methanol on the rate of natural gas hydrate decomposition at atmospheric pressure are obtained. It is established that the effect of methanol on the rate of hydrate decomposition is determined by changing the dissociation mechanism.

Key words: natural gas hydrate, equilibrium condition, kinetics, methanol

INTRODUCTION

The studies on gas hydrates represent a promising technological direction in the development of the gas industry which promotes scaling gas technologies to a significantly new qualitative level. The development of efficient technologies for gas transportation and storage in gas hydrate state requires, first of all, for the creation of scientific foundations in order to control the processes of gas hydrate formation and decomposition [1]. At the same time, the processes of formation and decomposition of gas hydrates are insufficiently studied until now. Therefore, for today only the process of methane hydrate decomposition is most completely investigated, whose temperature range of manifesting a self-conservation effect at atmospheric pressure (242–271 K) is determined [1].

The purpose of the present work consisted in the investigations concerning the reaction kinetics of formation and decomposition for hydrates synthesized from natural gas, as well as their decomposition in the presence of methanol.

EXPERIMENTAL

As a subject of inquiry we have chosen the hydrate synthesized from distilled water and natural gas from the Irelyakh gas and oil field (GOF) (Yakutia) under static conditions under preset pressure and temperature.

The obtaining of gas hydrates requires for data concerning the pressure and temperature of hydrate formation, those are determined by the component composition of hydrates [2, 3]. The individual component composition of the natural gas of the Irelyakh GOF was investigated using the method of gas adsorption chromatography by means of Crystal 2000M chromatographic analytical software complex, according to the State Standard GOST 2378–87, in accordance with the GOST R ISO MEK 17025–2006 at the accredited laboratory of the Institute of Petroleum and Gas Problems, SB RAS (the accreditation certificate No. ROSS RU. 0001.516690). It was established that the natural gas under investigation has the following composition, vol. %: CH₄ 88.86, C₂H₆ 2.25, C₃H₈

TABLE 1

Equilibrium conditions for hydrate formation from the natural gas of the Irelyakh GOF

T, K	273	274	275	276	277	278	279	280	281	282	283	284	285	286
P, atm	10.49	11.98	13.67	15.60	17.78	20.26	23.08	26.28	29.92	34.05	38.75	44.10	45.83	52.10

0.97, *i*-C₄H₁₀ 0.12, *n*-C₄H₁₀ 0.22, C₅₊ 0.04, CO₂ 0.04, N₂ 7.14, He 0.36, M_{aver} 17.55.

Basing on the data obtained using the technique presented in [4, 5], thermobaric conditions were calculated for hydrate formation (Table 1). In order to determine the gas compressibility factor we used an empirical Berthelot equation, which provided a sufficient accuracy for the pressure lower than 100 atm corresponding to hydrate synthesis is used.

Further, the following conditions for the synthesis of hydrates were chosen from calculated values: the temperature of synthesis <278 K at the pressure of 20 atm and <286 K at the pressure of 50 atm. At the pressure amounting to 20 atm, the processing chamber represented a thick-walled cylinder made of plexiglass, whereas at higher temperatures the chamber represented a steel cylinder (Fig. 1).

The successful synthesis of hydrates including natural gas is determined also the

value of a ratio between the amount of water and the amount of hydrate forming gas. For the most complete transforming the system water–natural gas into the hydrate form it is necessary to calculate the ratio required at preset temperature and pressure values. Earlier [6] it was demonstrated, that in 1 L of hydrate can contain up to 200 L of natural gas. Taking into account this ratio, we determined from the ideal gas state equation a necessary amount of water which would completely bind the gas into hydrate under the conditions of synthesizing we chose (Table 2).

In order to immediately obtain natural gas hydrates, to a high pressure chamber was poured a calculated amount of distilled water (see Fig. 1, Table 2), then the chamber was evacuated and filled with natural gas. The pressure in the chamber was created in excess to provide the transition of the water–gas system into the hydrate state with no additional gas supply. The chamber filled thus with water and gas was placed into a cooling chamber with the established equilibrium temperature of the hydrate formation. For increasing the conversion level of the water–gas system into hydrate the temperature was repeatedly raised/lowered within the range of values from 286 to 266 K.

One of the main methods for monitoring the kinetics of hydrate formation consists in the measuring the amount of gas transformed into hydrate. For this purpose, volumetric absorption of natural gas was registered each 24 h basing changing the pressure in the chamber. According as the gas hydrate formed, the pressure in the system started to slowly decrease

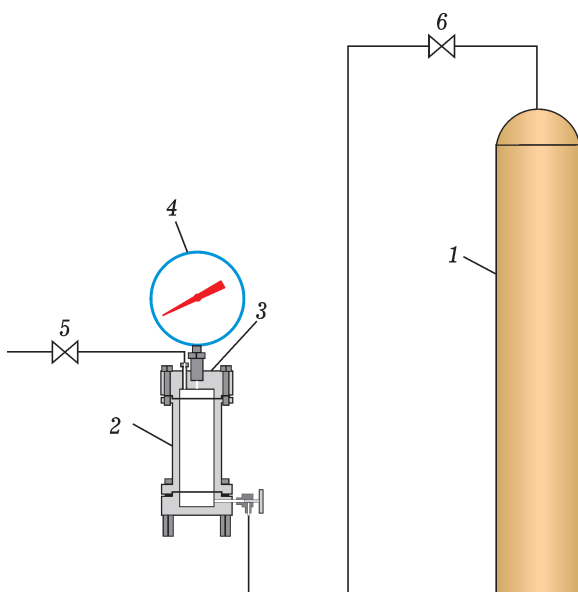


Fig. 1. Scheme of experimental setup for obtaining natural gas hydrates: 1 – cylinder with natural gas; 2 – high pressure chamber; 3 – flange lid; 4 – standard manometer; 5, 6 – intake and escape-cock.

TABLE 2

Calculated ratio values for water and gas amount

Chamber capacity, mL	Volume, mL	
	Water	Gas
213.74	19.50	>3900
521.64	116.00	>23 200

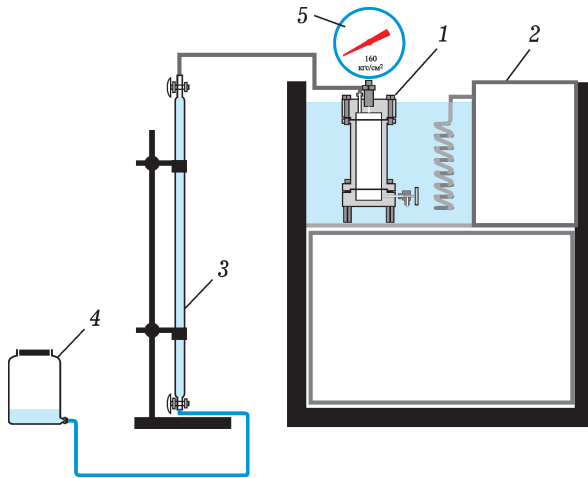


Fig. 2. Experimental setup for the investigation of hydrate decomposition process: 1 - high pressure chamber; 2 - thermostat; 3 - gas burette; 4 - superseding vessel, 5 - exemplary manometer.

up to establishing any constant value, which indicated completing the process of water-gas system conversion into hydrate. Thus, the duration of the process for obtaining synthetic natural gas hydrate depends on the pressure

in the chambers amounting to 20 days at the pressure of 50 atm and 25 days at 20 atm.

The kinetics of natural gas hydrate dissociation was studied using an original experimental setup (Fig. 2). So, for the decomposition of hydrates, the pressure in the chamber was sharply lowered down to an atmospheric value with the help of an escape cock, and then the chamber was evacuated and immersed into a thermostat with the temperature of 298 K.

For the decomposition of hydrates in the presence of methanol, the pressure in the chamber was also lowered down to an atmospheric value to added methanol through the escape cock, at a ratio methanol: hydrate, equal to 0 : 1, 1 : 5, 1 : 1. Further, the chamber was immersed into a thermostat at the temperature of 298 K. Volume of the gas evolved due to the decomposition of the hydrate was measured *via* the method of displacement with the help of a burette.

The hydrate decomposition level was determined according to the formula

$$\alpha = V_t/V_\infty \tag{1}$$

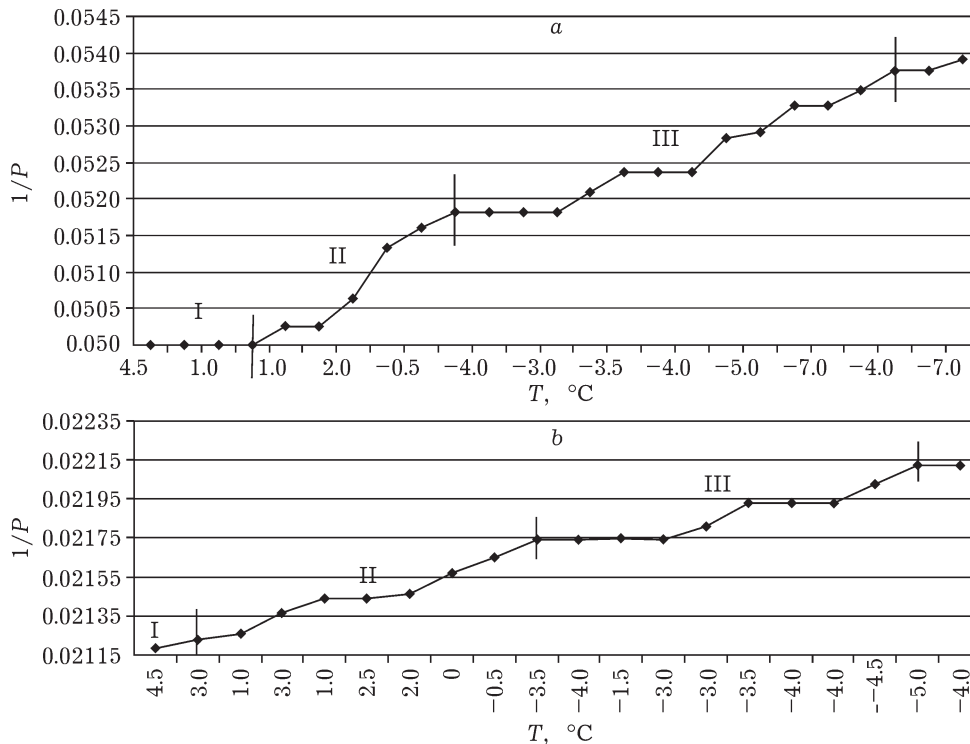


Fig. 3. Formation kinetics for natural gas hydrates at 20 (a) and 50 atm (b). Points were registered each 24 h; I - the induction period, II - surface film growth of hydrates, III - volume diffusion growth.

Here V_t is the volume of gas evolved by the moment of time (t); V_∞ is the volume of gas evolved after complete hydrate decomposition [3].

RESULTS AND DISCUSSION

Formation of natural gas hydrates

In order to determine the influence of synthesis conditions upon the kinetics of natural gas hydrate formation we conducted experiments at various pressure values. Figure 3 demonstrates the results of varying the gas volume depending on temperature at the pressure values amounting to 20 and 50 atm. One can see that the process of hydrate formation is preceded by a time interval corresponding to the water–gas system staying in a metastable state, which time interval is referred to as the induction period. It is established, that the duration of this period grows with decreasing the pressure of hydrate synthesis. Further, resulting from surface hydrate film formation, an abrupt increase in gas absorption is observed. Then transition is observed to the volume diffusion mechanism of hydrate growth that is characterized by a lower rate as compared to surface film formation mechanism since the diffusion of the hydrate-forming agent to the site of crystal growth could be realized already through the bulk of the hydrate film formed. With increasing the thickness of the hydrate film at the interface, the rate of hydrate volume-diffusion growth

decelerates, decreasing exponentially down to zero value. It is established, that at a more high pressure the rate of the hydrate volume-diffusion growth is comparable to the rate of surface hydrate film formation.

Thus, the rate of natural gas hydrate formation depends to a considerable extent on the synthesis pressure being determined by the rate of volume diffusion process.

Decomposition of natural gas hydrates

In order to determine the rate and features of the mechanism of natural gas hydrate decomposition we investigated the kinetics of their dissociation at atmospheric pressure. It is established, that the decomposition of natural gas hydrate under these conditions (Fig. 4, curve 1) occurs in a similar manner as the two-stage process of propane hydrate dissociation described by A. N. Nesterov [3]. So, at the first stage the natural gas hydrate decomposes to yield the gas and metastable water phase. The caloric effect of the reaction ΔH_1 exhibits a positive value, since this reaction is endothermic [3]. The second stage is presented by metastable water phase transition into a thermodynamically stable phase of ice. A stepwise increase in the hydrate decomposition level observed on the kinetic curve could be explained by a rise in the temperature of the system due to the exothermic reaction ($\Delta H_2 < 0$) of water metastable phase transformation into ice. Thus, the reaction scheme for the decomposition of nat-

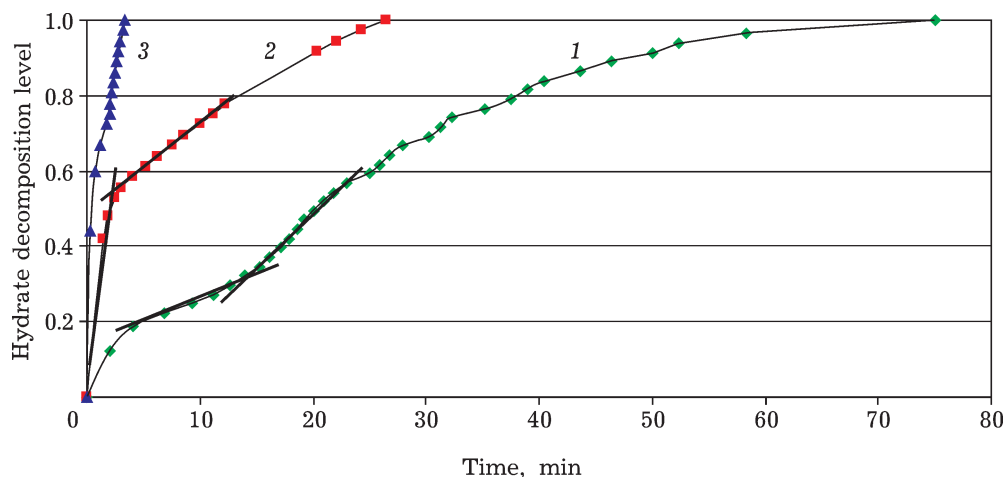
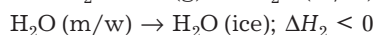
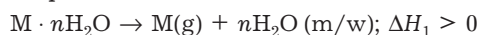


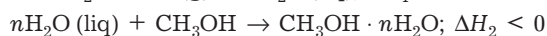
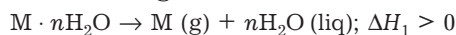
Fig. 4. Kinetics of natural gas hydrate decomposition for the gas from the Irelyakh GOF ($P = 1$ atm, $T = 298$ K). Methanol : hydrate ratio: 0 : 1 (1), 1 : 5 (2), 1 : 1 (3).

ural gas hydrate at atmospheric pressure could be presented as



Here $H_2O(m/w)$ is metastable water.

In order to determine the role and to estimate the accelerating action of the hydrate formation inhibitor on the process of hydrate dissociation we investigated the dissociation process in the presence of methanol. The results of natural gas hydrate decomposition at atmospheric pressure and constant temperature equal to 298 K in the presence of methanol are presented in Fig. 4 (curves 2, 3). It is established, that the average rate of hydrate decomposition at a ratio methanol : hydrate, equal to 1 : 5, triply increases, whereas at the ratio of 1 : 1 a 15-fold increase is observed, as compared to the rate of hydrate decomposition without no methanol added. This fact might be connected with the hydration of alcohol molecules by the molecules of water formed due to the decomposition of the hydrate, which could results in the redistribution of hydrogen bonds between the molecules of water. An increase of methanol concentration in the solution results in an increase in the number of hydrogen bonds between water and alcohol molecules and thus in forming proper alcohol supramolecular structural entities with water. So, methanol quickly destroys the clatrate lattice of the hydrate. Thus, the reaction mechanism for the dissociation of natural gas hydrates under the influence of methanol could be formulated in the following manner:



where $H_2O(liq)$ is liquid water.

Thus, it is first demonstrated that the decomposition of natural gas hydrate at atmospheric pressure occurs involving two stages with the intermediate formation of metastable water and ice. It is established, that the mecha-

nism of decomposition changes in the presence methanol, since the process of dissociation is characterized by the absence of this intermediate stage as well as by a higher rate. The accelerating action of the inhibitor could be caused by the formation of alcohol-water supramolecular structural entities, whereby that equilibrium in the reaction is shifted towards an active liberation of the hydrate-forming agent.

CONCLUSION

Resulting from the studies carried out, the duration of natural gas hydrate synthesis depending on pressure has been obtained. It has been established that there is no stage of metastable water and ice formation under gas hydrate decomposition accelerated by an inhibitor. The data obtained should be taken into account in considering problematic questions concerning man-caused hydrate formation under the conditions of gas extraction, preparation, transportation and innovation technologies connected with the necessity for transforming the natural gas into the clatrate form, as well new methods for the development of gas hydrate fields.

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