Phase behavior of hydrocarbon systems in water-saturated sand reservoir at hydrate formation conditions

In connection with forthcoming development of Chayandinskoye oil/gas condensate field (OGCF) with low reservoir temperatures of production level it is necessary to estimate the risks of hydrating in bottom-hole zone of formation. With this objective, using the method of adiabatic calorimetry, thermodynamics and kinetics of alkanol-type hydrates of individual hydrocarbons formation and disintegration processes have been investigated, as well as those of six-component gas mixture, modeling composition of formation gas at Botuobinskaya deposit of Chayandinskoye oil/gas/condensate field.

Testing rig, research method

The experimental complex of adiabatic calorimeters allows carrying out measurements of thermodynamic parameters (temperature, pressure, enthalpy) for hydrocarbon systems in the temperature range of 110–420 K at pressures up to 60 MPa. Measurements have been carried out using the method of the State Standard Reference Data Service registered in the Russian Scientific /Technical Information Center for Standardization, Metrology, and Estimation of Conformity described in detail in [1, 2]. There, one can also find description of methods for sample preparation, and filling of calorimetric cell with water and gas, as well as research procedures. Porous medium has been modeled by granulated quartz sand, grain size 25–38 microns (average grain size – 31,5 microns). As gas hydrating agents both pure components (methane, ethane and propane) and a model six-component mix have been used.

Thermal background of ‘water / gas / hydrating agent’ system and specifics of kinetics in hydrating and ice formation processes

On regard of analysis of calorimetric studies, several kinds or conditions of water have been specified: ‘fresh water’, ‘melt water’, and ‘water after decomposition (dissolution) of hydrate’. Such division is based on experimental data for induction periods of phase transitions in the metastable system ‘water / gas’ into hydrate or ice, depending upon its thermal background.

Fresh water is the water for the first time introduced into porous medium, or the water obtained by heating water-saturated porous medium above ice-melting temperature of 20 °C or higher. Hydrating and ice formation processes for such water are characterized by the greatest induction periods, as compared with other kinds of water.

Melt water is the water after ice melting. At that, heating of the system above ice melting temperature should not exceed 0,2–0,5 °C. In this case, the beginning of hydrate formation process is characterized by rather long induction period (24 hours or more). At the same time, ice crystallization process is characterized by shortest, as compared with other kinds of water, induction period.

Water after hydrate decomposition (dissolution) is the water obtained as a result of gas hydrate decomposition at temperature increase in the cell or at gas extraction from the cell. In our experiments, heating was done above the temperature of hydrate decomposition which is 0,5–2,0 °C. For such water, the repeated ice crystallization process is characterized by shortest, as compared with other kinds of water, induction period. Moreover, for water obtained as a result of hydrate decomposition in the course of gas extraction (pressure decrease in the cell at fixed temperature), induction period in the beginning of repeated hydrates formation is practically absent.

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ice.
Thermal background effects of considered systems on kinetics of hydrating and/or ice formation processes, as indicated by experimental data below, provide rather accurate test-to-test reproducibility. One of potential reasons for such behavior of ‘water / light hydrocarbons’ systems is connected with saturation and over-saturation of water with dissolved gases at hydrate dissolving, or with under-saturation water with dissolved gases at ice dissolving. It means that over-saturated gas condition in water can promote hydrates homogeneous nucleation at repeated hydrating process. It should be pointed out that not all experimental data obtained by the authors match water over-saturation / under-saturation with gas concept, so the discussed question needs further investigation. Heterogeneous nucleation processes can be affected by local concentrations of micro-impurities at ice or hydrate formation, and also – porous medium. In literature, similar thermal effects affecting the induction period have been observed during crystallization of water droplets in ice at atmospheric pressure [3]. ‘Simplified’ effect of secondary hydrates formation was also pointed out in literature with interpretation as ‘hydrate water memory’ (e.g., [4], p. 115–116). Nevertheless, before [4] there have been no systematic calorimetric studies of thermal background of system in regard of induction periods and crystallization processes (in ice or hydrate).

As it was indicated in sources [5, 6], information about thermal background of the system in calorimetric cell with porous medium, in principle, makes it possible to predict kinetic specifics of subsequent formation of hydrate / ice solid phases. Obtained experimental data concerning the influence of thermal prehistory of ‘water / six-component gas mix’ system on hydration and/or ice formation processes in comparison with ‘water / light hydrocarbon’ systems are analyzed below. Model mix was prepared in special sampling apparatus using chemically pure components of alkane hydrocarbons, nitrogen and carbon dioxide. Averaged composition of initial (real) formation mix of Botuobinsky field (see row 1), and also composition of simulating it six-component mix (see row 2) are given in the table.

Preliminary thermodynamic modeling was carried out using calculation method [7, 8], which showed that these two gas mixes have very close both compressibility factors and hydrating curves (lines of three-phase ‘gas / water / hydrate’ balance). At experimental studies of six-component mix, main attention was paid at metastability and kinetics of hydrate formation with fresh water and dissolved hydrate water. Influence of the system thermal background manifests itself:

a) in potential formation of different hydrate structures;

b) different duration of induction periods and metastable evolution conditions of ‘water / gas mix’ system with phase transition into hydrate or ice.

Influence of system thermal background on hydrate structures formation

The induction period before the beginning of hydrate formation in the fresh water system was significantly longer than the induction period at beginning of hydrate formation in the dissolved hydrate system. At calorimetric studies of hydrate formation processes in the cooling mode, it is manifested in different immersion depths of metastable zone (at similar cooling speed). Typical examples of hydrates formation and decomposition processes in fresh water, dissolved hydrate water, and also in ‘intermediate state’ water systems thermograms for gas mix density of 74,336 kg/m³ are given on fig. 1 and 2. System with fresh water has the greatest induction period in the beginning of hydrates formation process, and at cooling it most strongly ‘interferes’ into metastability zone (see point B on fig. 1). However, the depth of immersion into metastability zone (see point B₁ on fig. 1) for ‘water with dissolved hydrate’ system is the smallest (the induction period is short). While for water in ‘intermediate state’, the depth of immersion into metastability zone has ‘intermediate value’ (see point B₂ on fig. 1).

Hydrates formation begins in points B, B₁ and B₂, and passes away with heat release. Theoretically, we can assume that in zones BC, B₁C₁, and B₂C₂...
hydrate of cubic II structure (here and hereinafter designated as sII) is formed, and in zones CD, C1D1 and C2D2 hydrate of I structure (sI) is formed. The share of sI hydrate (CD) obtained from fresh water is significantly less than shares of hydrate of the same structure obtained from dissolved hydrate water (C1D1). Quantitatively, these shares have been calculated by measured thermal effects (enthalpy curves). Hydrates dissolution has been investigated in the heating mode as it is shown on fig. 1, curves C′A, D1C′1 and D2C′2. Dissolution (decomposition) of sI hydrate occurred in zones DC′, D1C′1 and D2C′2, and sII hydrate was melting in zones C′A, C′1A and C′2A.

On fig. 2, \( \left( \frac{\partial P}{\partial T} \right)_{V} \) derivative relationships between ‘water / six-component gas mix’ system and gas hydrate dissolving temperature are represented. At dissolving of gas hydrate formed in fresh water, two extrema of the \( \left( \frac{\partial P}{\partial T} \right)_{V} \) derivative vs temperature (E1 and E2) are observed. The first of these (E1) corresponds to dissolution of sI hydrate, the second (E2) – to sII hydrate dissolution. In case of hydrate obtained from dissolved hydrate water, the situation proves to be more complicated. Here, three extrema at thermodynamic \( \left( \frac{\partial P}{\partial T} \right)_{V} \) derivative dependence from temperature (F1, and also F′2 and F″2) are already observed. The first of these (F1) corresponds to dissolution of sI hydrate, the second and third, as it seems, – to dissolution of the metastable structures ‘close’ to sII.

**Effect of the system thermal background on direction of solid phase process formation (evolution into hydrate or ice)**

As it has been already noted, at temperature over 0 °C and pressure exceeding the one on the line of three-phase ‘gas / water / hydrate’ balance, duration of metastable state of ‘water / gas mix’ system existence depends on the background of the system. For water after hydrate decomposition (dissolution), the induction period is small, and that for fresh or melt water is significantly longer. At temperatures less than 0 °C and pressure in the system exceeding that on the three-phase ‘gas / water / hydrate’ balance line, metastable ‘water / gas mix’ system can evolve with formation of ice or hydrate. Such state can be called ‘double metastability’: the system is metastable both in relation of ice formation and in relation of hydrate formation. For fresh and melt water, evolution of this system primarily in ice formation, and for
dissolved hydrate water – in hydrate formation is typical. The authors connect this significant difference in the induction periods with different content of dissolved gas in water (up to possible over-saturation of water with gas after hydrate decomposition).

On fig. 3, phase diagrams obtained by the authors in calorimetric test (three-phase balance lines: ‘gas / water / hydrate’ and ‘gas / ice / hydrate’) for ‘water – light hydrocarbon’ and ‘water / six-component gas mix’ systems.

On fig. 4, experimental data concerning the influence of thermal background on direction and nature of phase transition into solid stable phase (hydrate, ice) of ‘water / propane’ system is reflected. For this system, the influence of thermal background is most obvious. At positive Celsius temperature for ‘water / propane’ system, the temperature range of potential metastability is minimal in comparison with other considered systems. This range for ‘fresh (or melted) water / propane’ system is limited, on the one hand, by overcooled water crystallization temperature, and, on the other hand, – by hydrate decomposition temperature, and does not exceed 5–6 °C. In thermobaric area above the top quadrupole point \( Q_2 \), hydrate decomposition curve is practically vertical.

Three cases with different thermal background of this system with fresh water, melt water and dissolved hydrate water have been investigated. In zones \((AB, A'B', A''B'')\) isochoric cooling for these three cases is shown (see fig. 4). Zones of isochoric coolings in all cases coincide in both water and propane equal contents. In the course of cooling (after crossing of three-phase balance of ‘water / hydrate / propane’ phases \((Q_1N)\) and those of ‘ice / water / propane’), systems prove to be in the ‘double metastability’ state. At the further cooling, the nature of behavior depends upon thermal background.

For cases with fresh or melt water, the prevailing tendency of the system evolution is appearance of ice with preservation of the system metastability in relation to hydrates formation. On fig. 4, processes of fresh \((BC)\) and melt \((B'C')\) water crystallization are shown. Temperature in the beginning of melt water crystallization (point \( B' \)) exceeds the crystallization temperature of water (point \( B \)). Further, because of emitted heat at crystallization, ‘ice / water’ systems \((CC_1, C'C_1)\) heat up and reach phase balance condition. At that, metastability of the ‘water (ice) / propane’ system in relation to hydrate formation is preserved. Further cooling was carried out along isochore curves. At deepening into metastable zone \((C, D \text{ and } C'D')\) hydrates formation from ice and propane hydrate begins in points \( D \) and \( D' \). Finally, the systems come to the ‘ice / hydrate / propane’ phase balance condition.

However, if the system contains water after hydrate decomposition, at its isochoric cooling
Fig. 3. Experimental phase diagrams for ‘water / methane’, ‘water / ethane’, ‘water / propane’ (black lines) and ‘water / six-component gas mix’ systems (red line)

Fig. 4. Influence of water thermal background on evolution of ‘water / propane’ system double metastability state: $MQ_1$ – ‘ice / propane hydrate’ balance; $OQ_1$ – ‘water (overcooled) / propane hydrate’ balance; $Q_1$ – bottom quadrupole point; $FW$, $IW$ – crystallization of fresh and melt water in accordance with subsequent hydrate formation; $HW$ – hydrate formation from dissolved hydrate water with the subsequent crystallization, which has not passed into overcooled water hydration phase
below 273.15 K no ice crystallization is still observed, and at temperature ~270 K (point B’’), formation of hydrate from the overcooled water and propane begins. In the course of hydrate crystallization, no ice is formed yet. And only after approaching to the ‘metastable (overcooled) water/hydrate/propane’ (OQ1) phase balance curve, but without crossing it, ice crystallization begins. Due to heat emitted at ice crystallization the system is heating up, thus resulting in a partial decomposition of previously formed propane hydrate. Hydrate, because of its heating, passes to metastable condition (D’D’’). In course of further isochoric cooling (D’’E’’) the system reaches the ‘ice/hydrate/propane’ (MQ1) phase balance curve.

Thus, the ‘water/propane’ system visually indicates that its evolution at isochoric cooling is clearly defined by thermal background.

Phase balance curves of ‘water (ice)/hydrate – hydrocarbons of other hydrate-forming components system and of their mixes’ (including investigated by authors six-component gas mix) cover a more extensive metastable area. For these systems, kinetic specifics of solid phase formation process is also predetermined by thermal background, but only at low pressures (for methane – below 4 MPa, for ethane – below 0.7 MPa, for six-component gas mix – below 1.2 MPa). At higher pressures, phase balance curves of ‘water (ice)/hydrate/hydrocarbons’ system will stay away from ice dissolution curve by 20 K and more, and therefore observable thermal background effects begin to manifest themselves less clearly.

On fig. 5 and 6, results of calorimetric studies of thermal background effects produced by ‘water/six-component mix’ system on direction and nature of transition into solid phase (hydrate, ice) or metastable phase are represented. For comparison, data for ‘water/propane’ system are also given.

Fig. 5 reflects that the behavior of ‘fresh water/six-component mix’ system in the course of ice crystallization and subsequent hydrate formation is similar to behavior of ‘fresh water/
propane’ system. In both cases, at isochoric cooling (curves $AB$ and $A'B'$) in the area of negative Celsius temperatures, ice crystallization occurs with emission of heat (curves $BC$ and $B'C'$). And at further cooling of the system, after the induction period ($CD$ and $C'D'$), ice transition into hydrate phase occurs ($DE$ and $D'E'$).

Behavior of ‘dissolved hydrate water / six-component mix’ system in the course of hydrate formation and subsequent ice crystallization (see fig. 6) is similar to behavior of ‘dissolved hydrate water / propane’ system. In both cases of isochoric cooling ($AB$ and $A'B'$), in the area of negative Celsius temperatures, at first hydrate formation is going on ($BC$ and $B'C'$), while ice is not formed. In a course hydrate formation, pressure decrease is observed. After curve has achieved the ‘metastable overcooled water / hydrate / propane’ phase balance ($C$), water crystallization of with ice formation begins. Process in the ‘metastable overcooled water / hydrate / gas mix’ system ($C'$) is of a similar nature.

Due to heat emitted at crystallization, systems are heating (at that, there occurs a partial decomposition of propane hydrate or gas mix hydrate, curves $CC_1$ and $C'C_1$, change more sharply than relevant isochores) and reach ‘ice / water’ equilibrium phase conditions bordering with the metastable phase of propane hydrate ($C_1$) or gas mix hydrate ($C_1'$). In the course of further isochoric cooling ($C,D$ and $C',D'$), systems reach relevant ‘ice / hydrate / propane’ or ‘ice / hydrate / gas mix’ phase balance curves.

Thus, the adiabatic calorimetry method has been used to investigate phase behavior of ‘water / six-component mix’ system at thermobaric conditions for potential hydrate formation of rather complicated nature. New aspects of metastability occurrence in hydrocarbon systems with hydrates formation have been found. Influence of thermal background on the nature of the system and sequence of phase transitions of hydrates into ice has been revealed. Behavior of ‘water / light hydrocarbons’ in similar experiments has been compared. A hypothesis in relation to physical reasons of thermal background impact effects in systems under consideration has been suggested.

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**References**

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