

HYDRATE FORMATION IN THE SYSTEM "PARAFFIN DEPOSIT + WATER"

Ivanova I. K.¹, Semenov M. E.², Koryakina V. V.²

¹ Ammosov North-Eastern Federal University

² Institute of Oil and Gas Problems, Siberian Branch of Russian Academy of Sciences,
iva-izabella@yandex.ru

With the development of oil industry in the territories of the Far North, West and East Siberia they met the processes, significantly complicating the work of the exploration and production wells. These processes include asphaltene-resin-paraffin depositions (ARPD), hydrate formation and formation of complex composite depositions. One should emphasize that these oil fields are located in the zone of low temperatures and are characterized by specific thermobaric conditions of occurrence, caused by the influence of a thick layer of permafrost. This is a cause of high-molecular compounds deposition on the surface of the oil-producing equipment, up to the formation of paraffin plugs in an oil producing wellbore. In its turn, the paraffin deposits on the walls of the tubing create a local constriction, which leads to an increased pressure drop and temperature reduction, so the process of the hydrate formation is intensified. Consequently, the hydrate formation is a final stage of forming complex plugs, the main cause of which is the deposition of paraffin on the walls of the pipes. The formation of gas hydrates complicates the oil production technology, its transport, storage and processing. For the development of technological and technical solutions aimed at the fighting with complex plugs a fundamental research in the field of phase transitions and growth kinetics of hydrates in a "paraffin deposits + water" systems is needed.

Thus, the purpose of the work - the definition of temperature and pressure conditions of formation and decomposition (melting) of natural gas hydrate (NGH) in the systems, consisting of commercial ARPD and water in various ratios. The results of this research were first published in [1].

As a model of the hydrate forming oil-associated gas we took the natural gas (NG) from Srednevilyuiskoe gas condensate field (GCF) with high content of methane (92.9 vol. %). The objects of the study were the hydrates of this natural gas, synthesized in the systems formed with various mass proportions by ARPDs of paraffinic type and distilled water: sample # 1, ARPD/H₂O = 80/20; # 2, ARPD/H₂O = 60/40; # 3, ARPD/H₂O = 40/60; and # 4, ARPD/H₂O = 20/80. The ARPD samples were taken from the surface of the lifting pipes (LPs) at the Irelyakhskoe gas-and-oil field (GOF). The samples were prepared at room temperature using a household electric mixer (blade rotation speed 11 000 rpm) during 30 min without addition of synthetic surfactants. Weighed portions of ARPDs were prepared on a technical balance at an accuracy of 0.001 g and agitated in a mixer pot. The resulting samples were kept for two days in a separating funnel; the samples remained stable. When APRDs

and water were mixed at the 20/80 component ratio, a limiting saturation of ARPDs with water was observed, the actual component ratio in this sample being 40/60. Therefore, the sample # 4 was excluded from the objects of study. Thus, natural gas hydrates (NGHs) were synthesized in the samples # 1–3.

The thermodynamic characteristics of phase transitions in the hydrates were determined with a Netzsch DSC 204 HP Phoenix high-pressure differential scanning calorimeter (Germany). The relative error of enthalpy measurements was $\pm 3\%$, and the error of temperature measurements, $\pm 1^\circ\text{C}$. The experiments were performed in steel vessels closed with perforated aluminum caps. The thermograms were recorded in the mode described in [2]. Each sample was measured not less than two times. The NGH growth kinetics in ARPD/ H_2O systems was studied in the installation schematically shown in Fig. 1a.

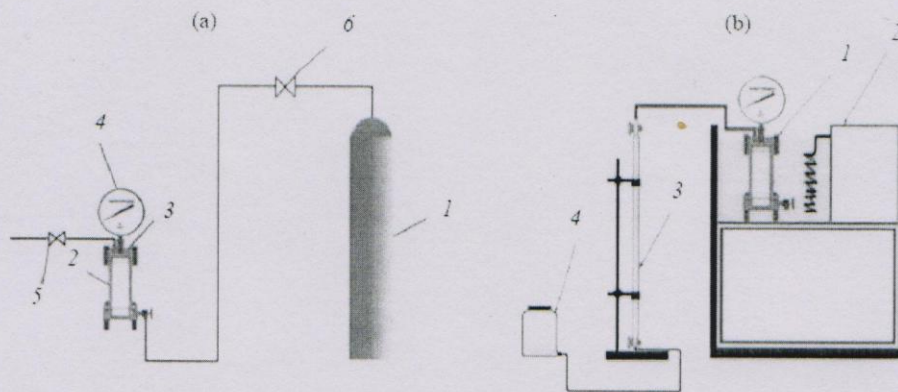


Fig. 1. The experimental installations for (a) synthesis and (b) decomposition of hydrates. (a) (1) Cylinder with gas, (2) high-pressure chamber; (3) cover-flange, (4) pressure gage, and (5, 6) valves. (b) (1) High-pressure chamber, (2) thermostat, (3) burette, and (4) displacement vessel

The chamber-reactor is constituted by cylinder 2 into which a sample is charged and cover-flange 3 to which reference pressure gage 4 (accuracy class 0.4) and feeding pipe 5 are attached. An NG was fed via valve 6 into the chamber. The prescribed pressure was 80 bar. The charged chamber placed in the refrigerator was statically kept at a temperature of 20°C for approximately 17 hrs. to saturate the sample with gas. The Sanyo MIR-254 incubator-refrigerator with a programmable temperature control unit (accuracy $\pm 0.3^\circ$) served as refrigerator. After the samples were saturated, hydrates were synthesized in the temperature range $+20 \dots -10^\circ\text{C}$ with a cooling gradient of 0.1 deg min^{-1} . The hydrate formation was monitored by the pressure decrease. The synthesized hydrates were decomposed to determine their specific gas content at $+25^\circ\text{C}$ in the installation shown schematically in Fig. 1b. The chamber 1 was placed in the Huber CC410 thermostat 2 and burette 3 with the displacement vessel 4 connected to the chamber. The released gas was collected in a calibrated burette over a saturated solution of sodium chloride in water. The specific gas content Y of the hydrates was calculated from the ratio between the measured volume of the gas released from a hydrate and the amount of the weighed portion of the hydrate. The decomposition time of each sample was about 1 hr. The synthesis and decomposition of each sample were performed no less than two times.

Table 1 presents the results of the DSC analysis obtained in two experiments on formation and decomposition of NGH in the ARPD/H₂O samples.

Table 1

Thermobaric conditions of phase transformations of NGHs in ARPD/H₂O systems

№	Sample	Crystallization conditions	Melting conditions		α*, %
	Run no.		ice	hydrate	
1	ARPD/H ₂ O=80/20	1st peak: t=-17.60°C; P=41.50 bar; ΔH=2.57 J/g	absent	t=9.11°C; P=37.61 bar; ΔH= - 12.56 J/g	100
	1				
2		1st peak: t=-18.20°C; P=40.60 bar; ΔH=8.13 J/g; 2st peak: t=-21.80°C; P=34.70 bar; ΔH=0.30 J/g	absent	t=7.87°C; P=33.03 bar; ΔH= - 12.38 J/g	100
2	ARPD /H ₂ O=60/40	1st peak: t=-7.64°C; P=48.46 bar; ΔH=20.57 J/g	t=-1.74°C; P=44.35 bar; ΔH= - 8.03 J/g	t=9.98°C; P=43.65 bar; ΔH= -19.76 J/g	71.1
	1				
2		1st peak: t=-7.22°C; P=46.86 bar; ΔH=12.43 J/g; 2st peak: t=-9.49°C; P=45.80 bar; ΔH=3.12 J/g	t=-1.87°C; P=42.88 bar; ΔH= - 2.96 J/g	t=10.40°C; P=42.30 bar; ΔH= -28.40 J/g	90.6
3	ARPD/H ₂ O=40/60	1st peak: t=-1.87°C; P=50.12 bar; ΔH=11.73 J/g	absent	t=10.70°C; P=45.40 bar; ΔH= - 19.96 J/g	100
	1				
3		1st peak: t=-7.54°C; P=43.02 bar; ΔH=13.71 J/g; 2 st peak: t=-9.74°C; P=40.34 bar; ΔH=2.50 J/g	t=-2.06°C; P=39.91 bar; ΔH= - 2.07 J/g	t=9.32°C; P=39.14 bar; ΔH= -25.04 J/g	92.4
4	Distilled water	1st peak: t=-11.40°C P=43.26 бар ΔH=49.82 J/g	t=-1.10°C P=42.06 бар ΔH=-64.38 J/g	t=10.60°C P=41.24 бар ΔH=-1.481 J/g	2.3

* α is the degree of water-to-hydrate conversion.

The DSC study of the processes in which NGHs are formed and decompose in the ARPD/H₂O systems demonstrated that the degree of water-to-hydrate conversion is high (71.1—100%) against 2.3% of hydrate formation in distilled water (Table 1). A possible explanation is that the water is in the dispersed state in the samples under study and, compared with bulk water, has a larger specific surface area, which leads to its intense transition to hydrate. The melting endotherms of all the samples differ only by the presence or absence of the ice melting peak (the melting peaks of the hydrates are present in all the samples under study), whereas the shapes of the signals in the crystallization exotherms of the samples under study reflect the hydrate/ice formation mechanism. Their thermobaric characteristics depend on the component ratio in the ARPD/H₂O systems because the lowest crystallization temperatures were recorded for the samples with the minimum amount of water, the ARPD/H₂O samples with the component ratio 80/20. At the next stage, the formation and decomposition kinetics of NGH in the ARPD/H₂O systems and, for comparison, that in distilled water, were studied in the installations with the basic element being a high-pressure chamber-reactor, are shown schematically in Fig. 1. The obtained data are presented in the Table 2.

Table 2

Gas content of NGHs synthesized in ARPD/H₂O systems and in Distilled water

Sample	ARPD/H ₂ O			Water
Component ratio	80/20	60/40	40/60	-
Volume of released gas, cm ³	1420	1100	1180	850
Specific gas content, cm ³ /g	160	72	56	28.7
Degree of water-to-hydrate conversion, %	97.5	43.8	34.0	17.5

One may see (Table 2) that the highest gas content is observed in the hydrate synthesized in the ARPD/H₂O sample with the component ratio 80/20. In this case, the degree of conversion to hydrate is 97.5% against 17.5% in distilled water. The rest of the samples of water-to-hydrate conversion for the ARPD/H₂O samples with the component ratios of 60/40 and 40/60 had 43.8 and 34.0%, respectively. It should be noted that, despite the nearly identical synthesis conditions, the degree of water-to-hydrate conversion of the samples under study in the DSC calorimetric cell and high-pressure chambers reactors are markedly different and, consequently, the hydrate formation process depends on whether it occurs in a micro- or macro-volume.

The experimental data we have obtained were compared with the equilibrium hydrate-formation conditions calculated by the Sloan procedure [3] for the NG used in the study (Fig. 2). For comparison, the same figure presents the results of a study of the NGH formation in the systems based on distilled water (points 1, 8—10), published in [2].

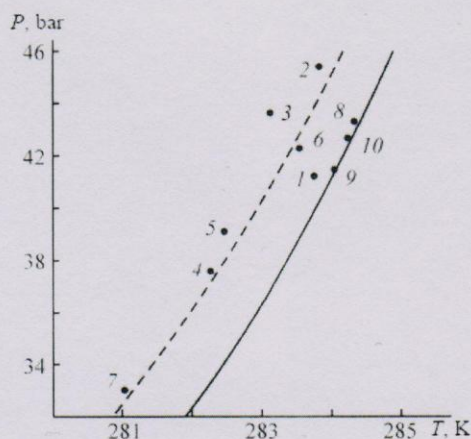


Fig. 2. Comparison of the calculated (curves) and experimental (points) conditions of hydrate formation of natural gas from the Srednevelyuiskoe oil field for various systems. (*P*) Pressure and (*T*) temperature. (1) Distilled water, (2, 5) ARPD/H₂O = 40/60, (3, 6) ARPD/H₂O = 60/40, (4, 7) ARPD/H₂O = 80/20, (8) distilled water + sand, (9) water with thermal history, and (10) water with thermal history + sand. The solid line is the equilibrium curve for natural gas; the dashed line is the approximation of the conditions for ARPD/H₂O systems.

The experimental data (points 2–7) can be certainly used to delineate the thermobaric region of NG hydrate formation in the systems formed by paraffinic ARPDs and H₂O. It can be seen that the hydrate-formation curve is shifted in the systems under study to high pressures. Therefore, no hydrates are expected in the oil extraction systems at the equilibrium parameters lying below this curve.

CONCLUSIONS

A high-pressure DSC method was used to examine phase transitions of natural gas hydrates synthesized in systems constituted by a Asphaltene–Resin–Paraffin Deposits and H₂O. The kinetics of their formation and decomposition was studied in high-pressure chambers reactors. It has been shown that the system constituted by a paraffinic Asphaltene–Resin–Paraffin Deposits and H₂O at the lowest content of water (20 wt %) has the lowest crystallization temperature, large degree of water-to-hydrate conversion, and the highest specific gas content. It was found experimentally that the equilibrium hydrate-formation conditions in the systems constituted by paraffin deposits and water differ from those for bulk water. The experimental data can be used to develop recommendations for precluding the formation of combined obtrusions of hydrates and paraffin, which appear in oil extraction from oil-and-gas fields located in the zone of perennially frozen rocks.

The study was financially supported by the Ministry of Education and Science of the Russian Federation in line with the base part of a State assignment (project no. 1896 “Organization of research activities”).

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