Formation of Gas Hydrate − Oil Associates in the Aqueous Phase during Hydrate Crystal Growth in Water − Oil − Methane Systems

T. P. ADAMOVA[1], A. YU. MANAKOV[1,2], A. A. SIZIKOV[1], L. K. ALTUNINA[3]

[1]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

E-mail: tata_12345@mail.ru

[2]*Novosibirsk State University, Novosibirsk, Russia*

[3]*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia*

Abstract

Video recording of methane hydrate growth in three-phase water − oil − methane systems was carried out for three crude oils. It was found that the formation of unconventional gas hydrate − oil associates germinating into the aqueous phase volume was likely for two of these oils in the late steps of growth. The paper discusses probable formation mechanisms for these associates.

INTRODUCTION

Gas hydrates are crystalline compounds of gas and water. One hydrate volume may contain as high as 170 volumes of water. Relatively high pressure of a hydrate-forming gas and reduced temperature are required for the existence of the majority of gas hydrates [1]. Natural gas hydrates are currently regarded as a promising source of hydrocarbons with resources not less than 10^{14} m^3 [2]. Industrial technologies of natural gas production from gas hydrate accumulations have been developed in the USA and Japan [3]. The most important technical issue in oil and gas industries related to gas hydrates is the formation of gas hydrate plugs during production and infield transportation of oil and natural gas [4−6]. Preventing the formation of gas hydrates in Russia is an urgent problem, as the main oil and gas production is carried out in cold climate areas. The development of hydrate prevention during oil production and ways to eliminate them require intensive fundamental research of formation and decomposition processes of hydrates in oil media, which causes the interest of a number of large research teams towards this issue (see the review in [4−8]).

During production and infield transportation, gas hydrates are formed in the course of cooling multiphase flows containing oil, associated gas, and water (brine). Currently, the most common model of hydrate formation in systems of this kind assumes that water emulsification in the oil takes place in the first step of the process. Further, the surface of water droplets is covered with a hydrate film; there are its grows up to the complete transformation of water into hydrate and, finally, the adhesion of the generated hydrate particles to form a gas hydrate plug [5−8].

To avoid hydrate formation, so-called thermodynamic inhibitors (methanol, glycols, *etc.*) displacing the thermodynamic conditions of hydrate formation to the range of lower temperatures and high pressures are used [4−6]. In recent decades, "low-dose inhibitors" that slow down the formation of hydrates (kinetic inhibitors) or prevent the adhesion of hydrate particles between themselves (antiaglomerants) have been increasingly used [9, 10]. In some cases, crude oil already contains components that can prevent both the formation and agglomeration of hydrate particles [11−13].

In heterogeneous systems, gas hydrates formation occurs at the phase boundary [14−17]. Visual observing and recording of hydrate nucleation and growth in such systems are powerful research method that allows determining the main regularities and peculiarities of hydrate formation in such systems. It was found that the film growing at the gas-water phase boundary was completely localized in the aqueous phase [18]. As demonstrated in [16, 17, 19−22], the crystallite size of the hydrate film and its thickness are reduced with increasing of the process moving force (overcooling), while the growth rate is increased. Depending on the level of overcooling and growth time, the thickness of the hydrated film ranges from several μm to 100 μm [23, 24]. Herewith, the variation in the overcooling value results in a change in the morphology of the generated crystals [25]. The step of hydrate film growth on the water surface is followed by the stage of sprouting of needle-like crystals in the volume of the aqueous phase [25−30]. It was demonstrated that under the influence of surfactants dissolved in the aqueous phase and kinetic inhibitors of hydrate formation, the morphology of growing hydrate crystals might change [14, 31−33]. In particular, the presence of surfactants leads to the disappearance of a thick film on the water surface and the growth of needle/whisker crystals, both in the volume of water and gas/organic phases. The growth of hydrate crystals at the boundary of water and organic liquid saturated with hydrate-former is similar to their growing at the water-gas contact surface [34−36].

Our research team carries out systematic research on gas hydrates formation in hydrate-former − oil − water systems. During experiments on visual observations of methane hydrate growth in the oil-water surface, a phenomenon related to the formation of hydrate-oil associates in the water volume was recorded. This research paper describes observations made during these experiments.

EXPERIMENTAL

Visual observations of hydrate nucleation and growth were carried out in a high-pressure apparatus with a cylindrical operating chamber of 32 mm diameter and 45 mm height (NIIC SB RAS design and manufacture, Fig. 1). From butt ends, the device is closed by leikosapphire windows that allow observing processes taking place inside. The video camera coupled with the cathetometer optical system recorded all events occurring in the cell (Fig. 1). Continuous video recording and photographing were carried out in the transmitting geometry. The apparatus is equipped with a gas inlet/outlet system and a thermocouple that allows monitoring the temperature inside the cell with an accuracy of ±0.2 °C. The instrument pressure was measured by a Bourdon pressure gauge with an accuracy of ±0.1 MPa. Samples were placed in an open glass cuvette with parallel walls. The internal cuvette size is 3 mm thickness × 18 mm width.

Water was poured into the cuvette, after which oil was layered on the top. Next, the cuvette was placed in the high-pressure apparatus, cell volume was purged with methane, and the operating pressure of CH_4 was set. The sample was kept for 6−12 h to saturate oil and water with methane, after which a predetermined temperature was set. Experiments were carried out at 12.5−13.5 MPa and −5 °C, overcooling, in this case, was 19.8−20.4 °C. Methane with a purity of 99.98 %, distilled water, Span 80 surfactant (Sigma-Aldrich), and three types of crude oils hereinafter referred to as KA, CK and CH were used (Table 1).

RESULTS AND DISCUSSION

Hydrates in water − oil systems (CH, CK, and KA) were produced during the long-term isothermal ageing of samples at −5 °C and methane pressure of 12.5−13.3 MPa. Hereafter, a stepwise increase in temperature up to the complete dissociation of the generated hydrate was carried out. In all cases, the formation of hydrate began after the induction period (from a few hours to a day or more).

The initial hydrate formation and growth were carried out in a similar fashion (Fig. 1). Hydrate nucleation began near the water-oil contact surface. It was impossible to observe the film itself using the available optical devices due to oil non-transparency and a small thickness of the hydrate film. Therefore the hydrate formation and growth was recorded by the appearance and
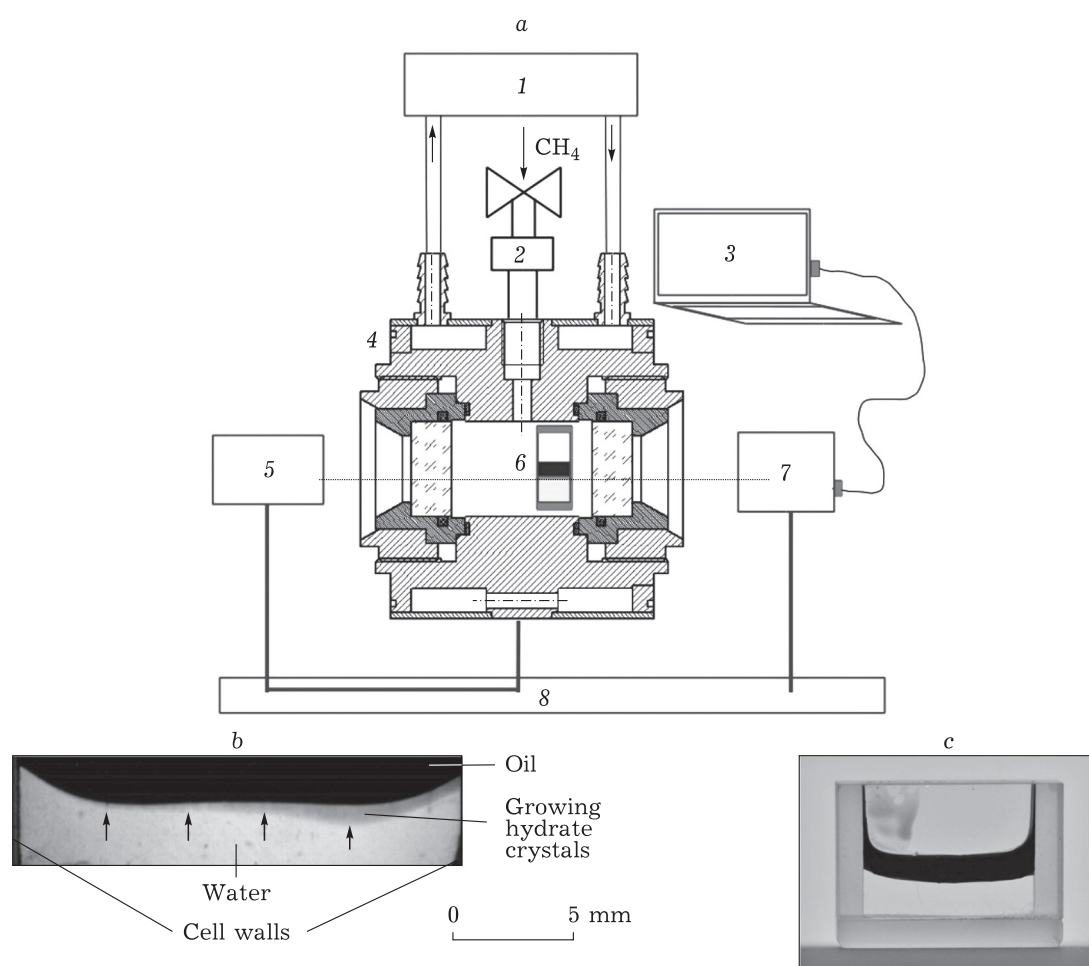
Fig.1. *a* − Schematic representation of the experimental setup (*1* − thermostat, *2* − pressure and temperature sensors, *3* − computer, *4* − high pressure cell, *5* − illuminator, *6* − cell with oil and water, *7* − cathetometer with video camera, *8* − optical bench); *b* − typical frame showing the interface between oil and water during the hydrate formation process (arrows show the boundary of spreading massive of whisker crystals); *c* − cell with oil and water.

growth of a colony of whisker crystals spreading along the water-oil interface and growing towards cuvette bottom. Hydrate growth continued for 2−3 minutes. Note that the observed crystals were hydrate, not ice, as they did not disappear at temperatures above 0 °C (the temperature of hydrate decomposition under these conditions is not less than 14.8 °C). There was water freezing only in one experiment, herewith, the sample lost transparency. A more detailed description of hydrate growth processes is beyond the scope of this work.

Further changes in the appearance of the samples under investigation were much slower. There was a change in the appearance of the colony of whisker crystals within a few hours in all cases. This was related to their overgrowing and enlargement. After hydrate formation in the sample, its temperature rose stepwise, as a rule, to 5 and

11 °C. Sample ageing duration at each of these temperatures ranged from 12 h to several days. Herewith, there were no significant changes in

TABLE 1

Composition and properties of oils used in the study

Parameter	Sample number		
	1	2	3
Asphaltene, mass %	3.46	0.22	0.67
Paraffins, mass %	4.84	5.83	4.39
Resins, mass %	10.23	4.36	5.07
Oils + aromatics, mass %	86.31	95.42	94.26
Temperature of the fluidity loss, °C	−7.6	−11.0	−10.4
Density, kg/m^3	0.845	0.841	0.835
Viscosity, mPa · s (20 °C)	5.95	1.85	7.29
Acidity, mg KOH/g	0.21	abs.	abs.

Note. abs. − absent.

sample appearance. Experiments with CH and CK oils at this stage demonstrated an intense growth of hydrate layers on the inner surfaces of the cuvette lying above the oil layer. Furthermore, there was the formation of unconventional oil associates in the aqueous phase. This is the formation that is the subject of the present report.

The considered associates were oil drops gradually germinating into the aqueous phase (Fig. 2). These drops appeared only several hrs after hy-

drate formation in the system and, as a rule, at temperatures above 0 °C. In two cases, it was possible to observe the formation of oil "snakes" of sufficiently complex shape in the aqueous phase (Fig. 3, 4). As demonstrated by analysis of video records, there was the quickest growth of oil drops at the start (up to 1.5 mm/min); further growth slowed down to a complete halt. The rate at the intermediate steps of the process was several hundredths of mm/min. The growth rate of
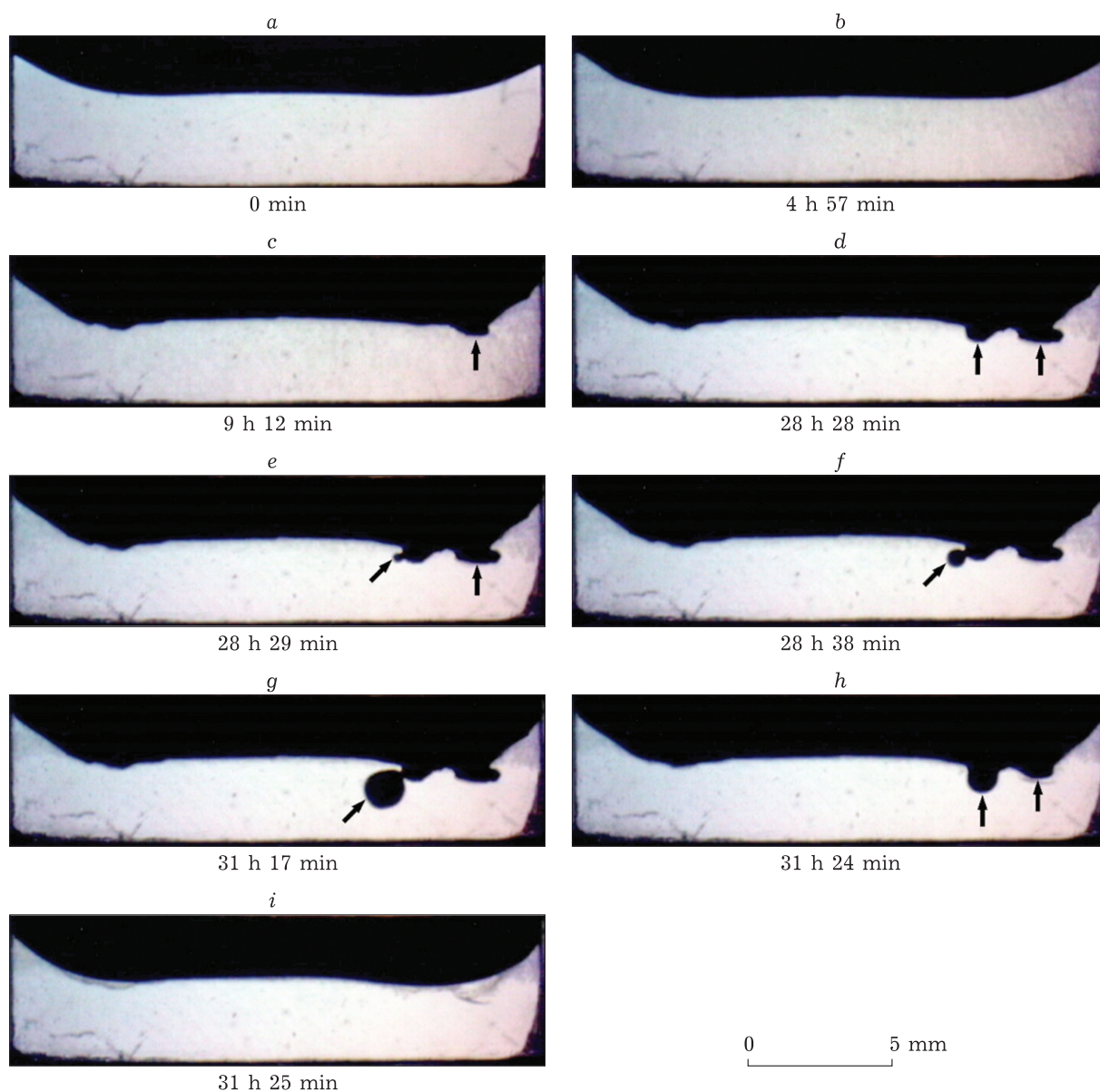

Fig. 2. Formation of oil inclusions ("snakes") into aqueous phase in the experiment with the oil sample No. 3 (time passed since the beginning of the experiment is shown): *a* − cell appearance at the experiment beginning, *b* − cell appearance with the formed hydrate (it shows itself as light ripple on the cell wall in the region of aqueous phase), *c*−*d* different stages of the "snakes" growth till its complete stop (*d*); *e*−*g* − different stages of the new "snakes" growth; *h* − oil snakes during the hydrate decomposition; *i* − cell appearance after the hydrate decomposition. Arrows show on oil inclusions into the aqueous phase. Methane pressure, MPa: 13.3 (*a*, *b*), 14.2 (*c*−*i*). The hydrate was formed at ca. −5 °C (*a*, *b*), the inclusions growth took place at −5 °C (*c*−*i*).

oil "snakes" at the beginning of the increase was 0.02−0.05 mm/min; the growth stopped in 3−5 h. After the temperature increase, the oil drops either merged with oil volume (Fig. 2) or turn into petroleum balls stuck to cuvette bottom or walls.

Analysis of conditions of formation of the associates under discussion unambiguously points to their close relation with gas hydrates formation in the corresponding systems. Indeed, the spontaneous embedding of oil droplets into the water volume is nonsense. Accordingly, in order to form such formations, the formation of a solid phase, the crystals of which would penetrate into the water and tighten the oil, is required. Fig. 5 gives the schematically assumed formation mechanism of oil host-guests in water.

The sole solid phase that may form in the cuvette under our experimental conditions is methane gas hydrate. An opportunity to form long (whisker) crystals and their bundles is well known for gas hydrates (for example, [37]). It is most likely that there was their formation in our experiments, too. We assume that in order to form hydrate − oil associates in the aqueous phase, a combination of three circumstances is required. First of all, $P−T$ conditions of the experiment and the composition of the oil phase should be in favour to the growth of colonies and/or beams of whisker hydrate crystals growing into the aqueous phase. As far as we know, there are no current satisfactory ways to purposefully produce whisker crystals of gas hydrates; accordingly, the fulfilment of
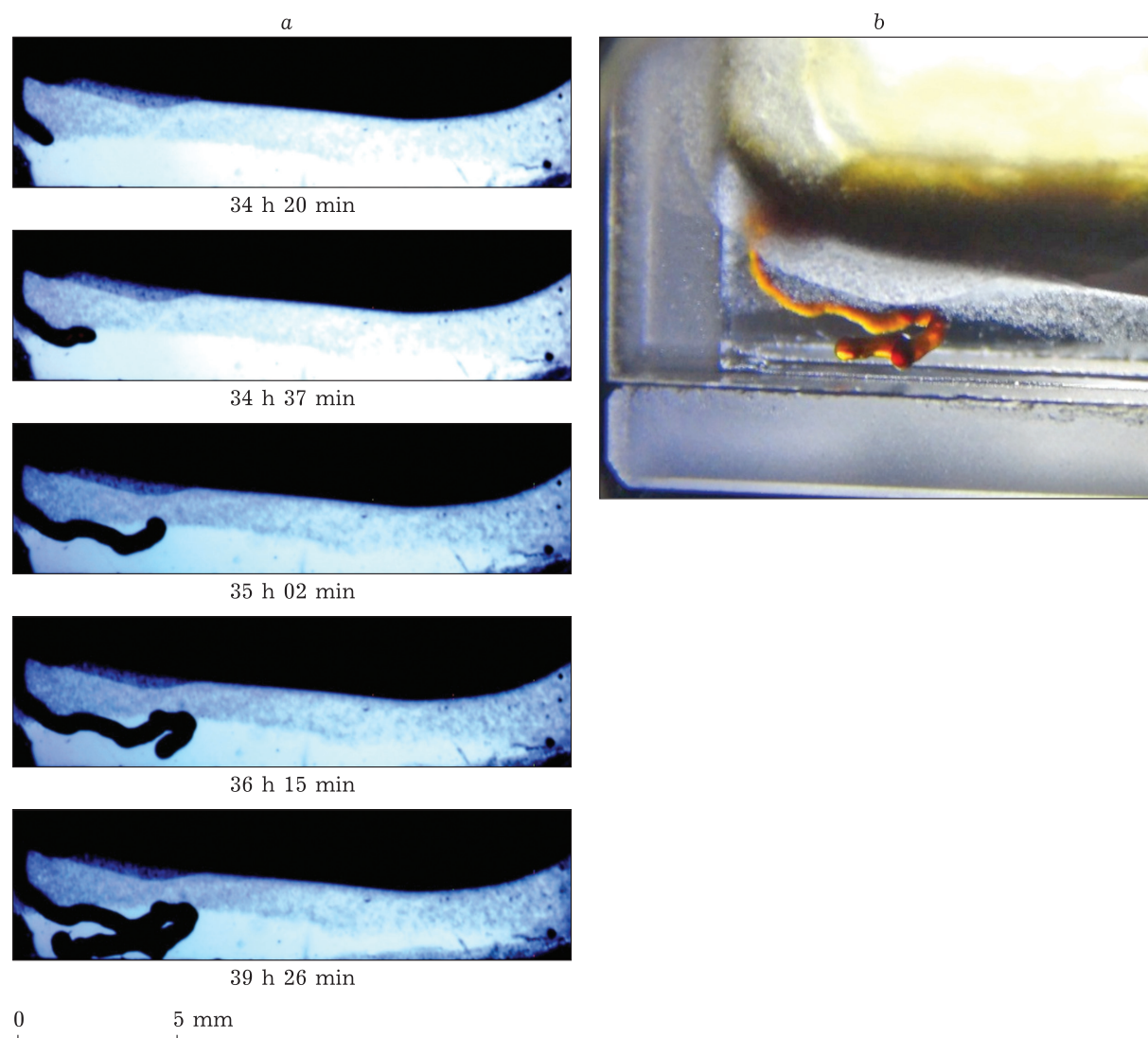

a − Stages of the growth of oil inclusions

34 h 20 min

34 h 37 min

35 h 02 min

36 h 15 min

39 h 26 min

0   5 mm

Fig. 3. *a* − Stages of the growth of oil inclusions (snakes) into the aqueous phase in the experiment with the oil sample No. 2 (time passed since the beginning of the experiment is shown); *b* − appearance of the inclusion at a late stage of the growth (the snake growth occurs in the volume of the aqueous phase). The growth took place at 4.9 °C and 13.0 MPa.
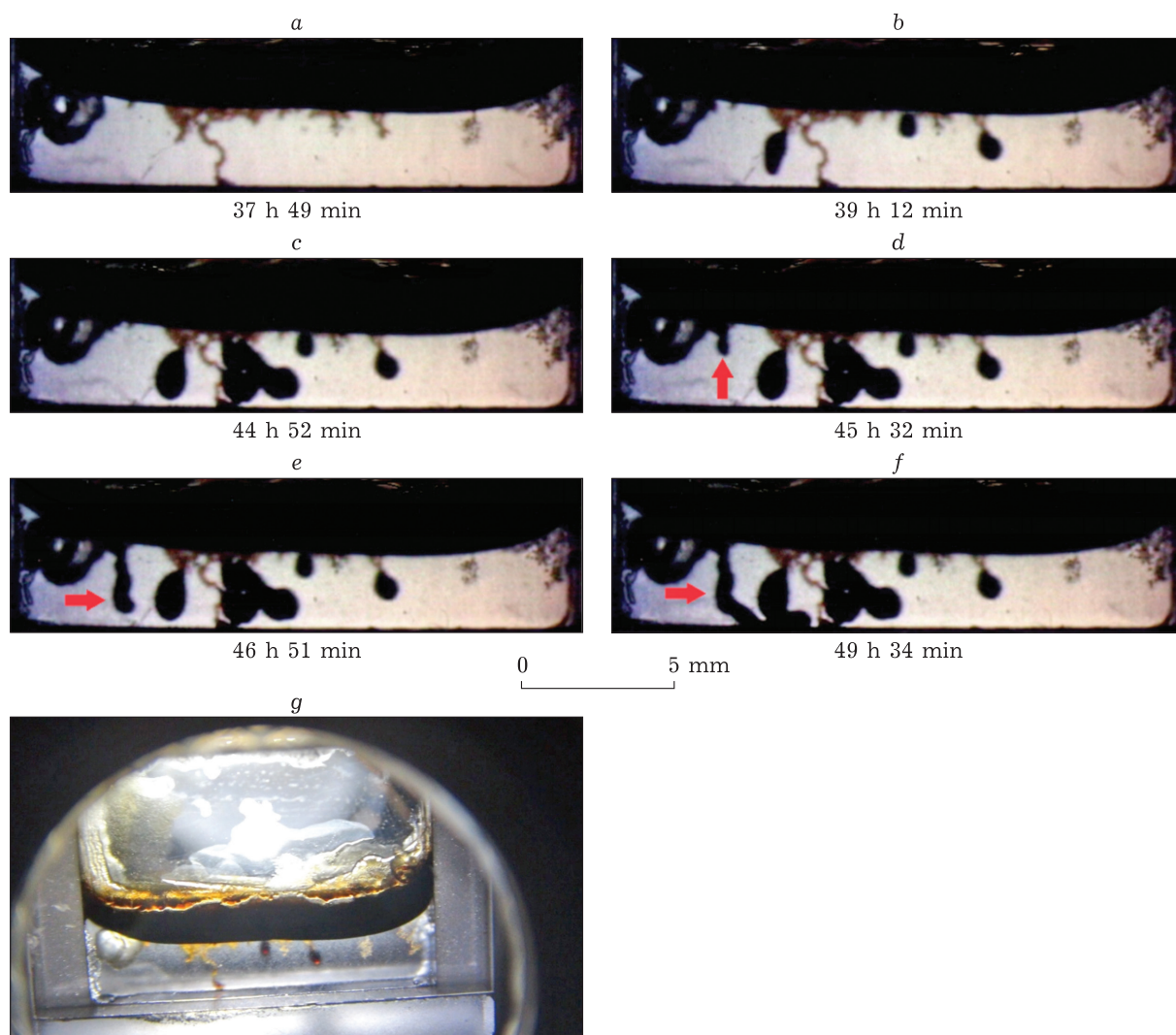
Fig. 4. Formation of oil inclusions ("snakes") into aqueous phase in the experiment with the oil sample No. 3 (with ice freezing, time passed since the beginning of the experiment is shown): *a* − cell appearance immediately after ice melting; *b−c* − different stages of the inclusions growth; *d−g* − different stages of the growth of oil snakes (shown by red arrows); *h* − cell appearance at the stage of the growth of the oil inclusions. The growth took place at 5.5 °C and 13.4 MPa.

the first condition is a matter of chance. Secondly, hydrophobic-hydrophilic components that may be sorbed on the hydrophilic surface of hydrate crystals and make this surface wetted with oil should be a part of the oil. This opportunity has been repeatedly discussed in the literature. It is assumed that the oils showing anti-agglomerating properties do not form hydrate plugs [11−13].

Observations that testify an opportunity to wet out hydrate surfaces with oil are described in the literature. For example, the authors of [14] observed pulling on an oil film on the growing surface of the hydrate. Reference [38] describes oil capture into the inter-crystalline space. At last, the film grown on the oil-water interface should have defects that ensure growth contact of the colony of whisker crystals with bulky oil and tight-

ening this oil into the inter-crystalline space. Note that the mechanical movement of oil occurring herewith may facilitate hydrate crystal growth due to methane-rich oil portions feeding to a growth area. The above discussion gives us the right to refer to the observed objects as gas hydrate-oil associates.

We acquired an interesting opportunity to illustrate a model for generating hydrate-oil associates during one of the experiments with oil CH, whereat aqueous phase freezing occurred (Fig. 4). After ice melting, in the liquid water volume, there were left several dark fibres identified as beams of whisker crystals with a small amount of oil tightened up there between. These beams were able to be formed during water freezing, for instance, due to the presence of the earlier gener-
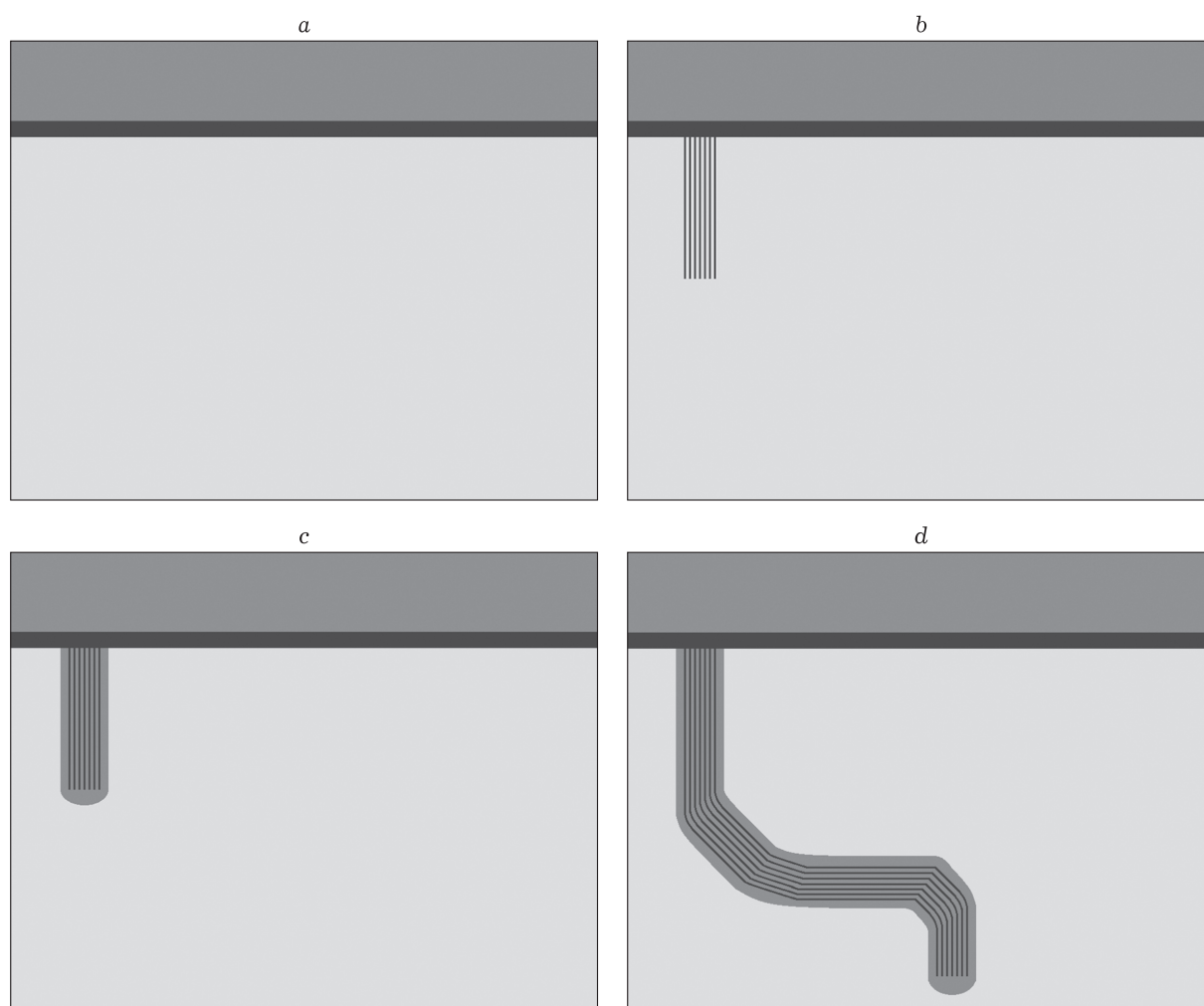
Fig. 5. Schematic representation of the mechanism of the growth of the oil inclusions into the aqueous phase: a − initial state, b − ingrowth of the bunch of needle crystals into the volume of the aqueous phase, c − capillary dragging of oil into the bunch of needle crystals, d − further growth of hydrate-oil associates.

ated whisker crystals of growing frost mass or during ice melting. Figure 4 demonstrates the formation of a large number of hydrate-oil associates in these samples resulting from these crystals outgrowth. Here, we also observed the growth of one of the hydrate "snakes" (Fig. 4, $d-f$). The findings prove the suggested model.

An opportunity to generate hydrate-oil associates in experiments with CH and CK oils and the lack of these associates in experiments with the KA oil catches the eye. As it can be seen from Table 1, a differential characteristic of KA oil is (1) higher contents of resins and asphaltenes, and also (2) the presence of acid components in oil composition that are naphthenic acids with surfactant properties. In order to discuss the issue regarding the effect of the contents of resins and asphaltenes on generating gas hydrate − oil associates in the aqueous phase, there are not enough

experimental data. In order to elucidate the effect of surfactant additives on crystals growth in water-oil systems, several experiments with CH oil, whereat the addition of 1 mass % of Span 80 surfactant was added to the oil, were performed. As it turned out, hydrate-oil associates were not formed in experiments with Span 80 additives. The resulting outcome points to the significant effect of oil surfactant content level on generating associates of this type. One may assume that surfactant additives (both natural and artificial) result in a changed nature of hydrate crystal growth. This may be related to the competitive nature of sorption on hydrate and cuvette walls surface, on the one hand, and carboxylic acids/Span 80 molecules, on the other one, and changes in the nature of wettability of cuvette walls and hydrate crystals surface with oil and water related thereto. We do not have enough data at the present time to dis-

cuss this issue in detail. Additional research is required for further understanding of this effect.

CONCLUSION

In this manner, an opportunity to generate gas hydrate − oil associates embedded into the aqueous phase was demonstrated in our experimental research. As it turned out, the presence of natural surfactants in oils might change the hydrate particles growth mode. This results in generating such formations in oil disperse systems and has an effect on the dynamics of the corresponding processes.

Acknowledgements

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