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Influence of petroleum fractions on the process of methane hydrate self-preservation

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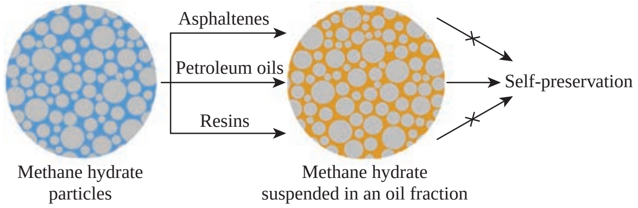
The dissociation of methane hydrate doped with a petroleum fraction (resins, asphaltenes, or oils) by its cryogenic mixing with pure hydrate particles has been studied at temperatures below 0 °C. An oil fraction of petroleum (a mixture of saturated, aromatic and polar compounds) was close to crude oil in terms of efficiency with respect to the self-preservation of methane hydrate. The effect of asphaltenes on hydrate dissociation was negligible, whereas resinous substances occupied an intermediate position between the fractions of oils and asphaltenes in the degree of influence.



The self-preservation effect of gas hydrates is associated with the formation of an ice film on the surface of hydrate particles when they decompose at temperatures below 0 °C. The formation of this film leads to a considerable slowdown of hydrate dissociation up to almost complete stop of the process.[1,2] The phenomenon has been intensively studied since the early publications.[3,4] The temperature boundaries of an anomalous preservation area of methane hydrate were determined.[5] A detailed study of hydrate dissociation showed that hydrate particles decompose to gas and supercooled water above the temperature of hydrate–supercooled water–gas metastable equilibrium curve.[6,7] It was found that the efficiency of self-preservation of gas hydrates depends on their particle size (this effect was observed only for hydrate particles larger than 250 μm),[8,9] the guest molecules,[10] and *p*–*T* conditions under which the ice shell forms.[11,12] The possibility of managing the self-preservation of gas hydrates by selecting an appropriate dispersion medium was demonstrated.[13–15] Fine methane hydrate particles (< 10 μm) placed within hydrophilic beads were preserved up to an ice melting point, while quick decomposition of the same particles within hydrophobic beads occurred above –73 °C.[13] It was shown[14,15] that the suspension of methane hydrate in crude petroleum undergoes effective self-preservation even with a hydrate particle size of several tens of micrometers. In this case, the medium components adsorbed on the hydrate surface exert a predominant influence on the decomposition of the hydrate phase. The effect of petroleum components adsorbed at the solid–liquid interface on the system properties was also indicated.[16] Meantime, data on the effect of auxiliary components on the decomposition of gas hydrates at low temperatures are almost absent from the literature,[15,17,18] although the influence of complex mixture compositions on the stabilization / destabilization of metastable systems is of considerable interest.[19–23] The physicochemical processes of gas hydrate interactions with various substances at the dissociation stage should be known to develop methods for controlling the rate of decomposition of these compounds using auxiliary substances, in particular, oil sludges. Here, we consider for the first time the influence of petroleum fractions surrounding hydrate particles on the process of their decomposition.

The approach implemented in this work is the use of a new method of controlling the self-preservation of gas hydrates, namely, the surface modification of hydrate particles by auxiliary substances. Thus, the decomposition of methane hydrate with surface modified by additional components not participating in hydrate formation (petroleum fractions, Table 1) was studied.[†]

In the cases of the initial petroleum and the oil fractions, three stages of gas evolution from the sample were observed. It was

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[†] Separation of crude petroleum into oils (O), resins (R) and asphaltenes (A) was carried out in accordance with GOST (Russian State Standard) 189995.1-73 (similar to NIGOGA – The Norwegian Industry Guide to Organic Geochemical Analyses).[24] The additives were introduced by their deposition on the surface of gas hydrate particles with the stoichiometry $CH_4{\cdot}6H_2O$. The mixture was prepared by thoroughly blending the hydrate samples and a petroleum fraction, which were previously ground to powder. All mixing stages were carried out at the liquid nitrogen temperature. The initial petroleum and O were taken in pure forms, while R and A were dissolved in a hexane–toluene mixture (7 : 3, by volume); the concentrations of R and A in the solutions were the same as in the original petroleum. The resulting mixture (hydrate : petroleum fraction = = 1 : 1.3 by weight) was loaded in an autoclave and heated to +10 °C for 24 h under methane pressure to ensure the stability of the hydrate. Then, the high-pressure cell was cooled with liquid nitrogen, the residual pressure was dropped, and the sample of a methane hydrate suspension in the petroleum fraction was taken. The synthesized samples were thoroughly ground (to particle sizes of < 250 μm) and studied by the thermovolumetry at atmospheric pressure and low temperatures.[25]

Table 1 Concentrations of the petroleum fractions and data obtained by the thermovolumetry of frozen suspensions of methane hydrate-in-petroleum fraction.

Fraction	Verkhnechonskoe oil field (VchOF)					Mayskoe oil field (MaOF)				
	Fraction content (wt%)	V_1/ml per gramm H_2O^a	T_1/°C^b	V_2/ml per gramm H_2O^a	T_2/°C^b	Fraction content (wt%)	V_1/ml per gramm H_2O^a	T_1/°C^b	V_2/ml per gramm H_2O^a	T_2/°C^b
Petroleum	100	29.3	–40.7 to –17.2	193.6	–12.7 to 3.9	100	23.5	–37.3 to –4.6	199.0	–4.6 to 3.4
Asphaltenes	2.13	222.5	–60.0 to –28.1	–	–	0.22	222.8	–65.6 to –25.1	–	–
Resins	7.79	76.2	–51.7 to –28.3	146.8	–28.3 to 0.2	2.73	172.1	–47.5 to –17.3	50.5	–11.6 to 2.8
Oils	90.08	130.1	–67.0 to –52.5	92.5	–11.0 to 0.7	97.05	37.5	–23.8 to –16.3	185.5	–3.2 to 4.1

[a] Volume of methane released in different temperature ranges and normalized to 1 g of water. [b] The temperature range of gas emission peak at the corresponding stages.

previously shown that gas evolution in a temperature range from –130 to –100 °C corresponded to the decomposition of a supersaturated gas solution in oil (Figure 1, curves *1* and *2*).[15] The subsequent stages (see Table 1) relate to hydrate decomposition at different temperatures.

Thus, we found that the individual petroleum fractions R and A had almost no effect on the self-preservation of methane hydrate. Hydrate samples with the addition of fraction A decompose with a certain shift with respect to the equilibrium dissociation temperature (–80 °C) without a self-preservation effect (see Figure 1, for fractions A, isolated from VchOF and MaOF petroleum, respectively). At the same time, a significant part of the hydrate modified with the oil fraction O separated from the petroleum decomposes only at 0 °C (41.6% in the case of VchOF and 83.2% in the case of MaOF, see Table 1, Figure 1). Similar behavior was observed in the case of initial petroleum.[14,15] The effect is more pronounced in the presence of petroleum compared to an individual oil fraction (86.8% for VchOF and 89.4% for MaOF, see Table 1, Figure 1). Resins occupy an intermediate position between the fractions of oils and asphaltenes in the degree of influence. This indicates that compounds ensuring the effective self-preservation of gas hydrates are predominantly in the oil fraction. We assume that the subsequent separation of oil fractions will allow us to reveal the mechanism of this process. Two effects of the dispersion medium are possible here: (i) the adsorption of various compounds/functional groups at the surface of hydrate particles and (ii) the formation of a specific hydrophobic-hydrophilic environment around the particle that contributes to the creation of a protective ice coating on the surface of hydrate particles/suspension. Resin, asphaltene or oil fractions seem to be likely to influence the morphology of the protective ice film. As water does not wet oil, it is most likely that, in the presence of oil, the supercooled water formed during hydrate dissociation spreads over the entire surface of hydrate particles leading to the formation of a dense ice layer around them. However, the medium composition affects this process since self-preservation was not observed in the cases of *n*-decane, toluene[15] and diesel oil.[17]

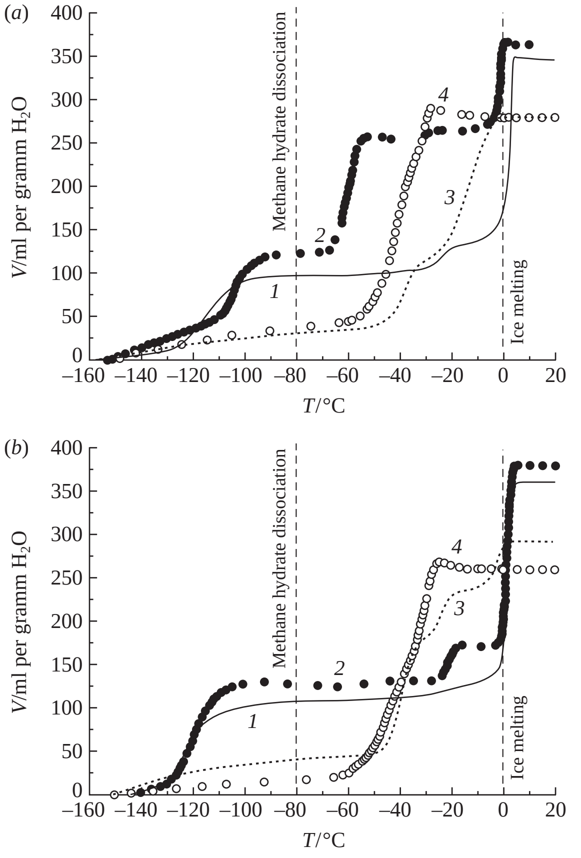

Figure 1 Hydrate dissociation in the fractions of (*a*) VchOF and (*b*) MaOF petroleum: (*1*) crude petroleum, (*2*) oils (O; saturated, aromatic and polar compounds), (*3*) resins (R), and (*4*) asphaltenes (A).

The versatility of the method used in this work for the preparation of methane hydrate suspensions in petroleum fractions should be noted. As indicated above, the mixing of hydrate with petroleum/petroleum fractions was carried out at the liquid nitrogen temperature. Previously, similar suspensions were prepared either by the direct synthesis of gas hydrate from water-in-petroleum emulsion[14,17] or by blending the hydrate and the petroleum under the pressure of hydrate-forming gas.[15] These techniques have a number of limitations and drawbacks, such as the requirement of water emulsification in a dispersion medium and the complexity of equipment. The method proposed facilitates the preparation of gas hydrate suspensions and makes it possible to use any liquid as a dispersion medium, which greatly extends the choice of the objects for study.

Thus, a new method for obtaining gas hydrate suspensions in liquids from frozen constituent parts has been proposed, which makes it possible to prepare finely dispersed hydrate suspensions without auxiliary components (surfactants). Various petroleum fractions have different effects on the decomposition of gas hydrates. The process under the experimental conditions is retarded in the case of methane hydrate placed in a solution of asphaltenes or resins. Hydrate begins to dissociate at a temperature above –80 °C, but self-preservation is not observed, whereas the fraction of oils isolated from the petroleum contributes to the manifestation of this effect. The obtained data can be used for the development of hydrate storage / transportation technologies of hydrate-forming agents by reducing gas losses when hydrate particles are placed in a dispersion medium that inhibits their decomposition. The further isolation of components/subfractions from the oil fractions, which cause self-preservation of methane hydrate, will contribute to a deeper understanding of the mechanism of this process.

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