Study of oil sludge, waste oil and other auxiliary substances influence on the methane hydrate dissociation

A S Stoporev [1,2,3], A P Semenov [1], A Y Manakov [2,3] and V A Vinokurov [1]

[1] Gubkin University, Department of Physical and Colloid Chemistry, Leninsky prosp. 65, Building 1, Moscow, 119991, Russian Federation

[2] Nikolaev Institute of Inorganic Chemistry SB RAS, Ac. Lavrentiev ave. 3, Novosibirsk, 630090, Russian Federation

[3] Novosibirsk State University, Pirogova Str. 2, Novosibirsk, 630090, Russian Federation

E-mail: stopor89@bk.ru

Abstract. In this paper, classes of oil medium that ensure the methane hydrate self-preservation were identified. The following compounds and substances were studied: asphaltenes, resins, asphaltene-resin-paraffin deposits (ARPD), multiwall carbon nanotubes, meloxicam ($C_{14}H_{13}N_3O_4S_2$), kinetic hydrate inhibitors (KHI) Luvicap 55W (copolymer of N-vinylcaprolactam and N-vinylpyrrolidone) and Luvicap EG (poly(N-vinylcaprolactam)), refined petroleum products (initial and waste) and 2,6-Di-*tert*-butyl-4-methylphenol (antioxidant fuel additive AO-29). Isolated oil components had practically no effect on the decomposition process of methane hydrate. It was observed, that the presence of surface-active additives in refined petroleum products leads to suppression of the investigated effect (self-preservation). It seems to be that in the case of used engine oils, the degree of manifestation of methane hydrate self-preservation effect depends on the duration of its operation (mileage). The obtained results can be the basis of recycling of ARPD and hazardous waste petroleum products in technologies for storage/transportation of natural gas.

1. Introduction

Gas hydrates are inclusion compounds in which the host framework is formed by water molecules bound to each other with hydrogen bonds, while the guest components fill the cavities in this framework [1]. When it comes to the storage and transportation of gas in hydrate form, it may be based on the self-preservation effect [2]. This phenomenon consists in a sharp decrease in the hydrate decomposition rate at temperature below 0 °C [3]. The following models are currently being considered. (1) Hydrate powder-in-liquid hydrocarbon suspensions transported through pipelines at the temperature and pressure within hydrate stability zone. (e.g., [4,5]), and (2) gas hydrate-ice pellets with size range from a few millimeters to several centimeters transported in metastable state at atmospheric pressure and temperature below 0 °C. (e.g., [6,7]). The pellets application for gas storage and transportation by the use of self-preservation effect was patented (see [8], for example). A hydrate granular form creates favorable conditions for its long-term existence outside thermodynamic stability zone in comparison with a hydrate powder. The overland transportation of natural gas hydrate to small consumers located within several hundred kilometers from the gas terminal was approved in the demo project launched by Mitsui Engineering & Shipbuilding CO [9]. The gas hydrates were transported in

the form of pellets sized from 0.50 mm to 30 mm. Their storage at -20 °C led to hydrate preservation for two weeks.

Study of gas hydrates in an oil at temperature below 0°C showed that the self-preservation effect manifestation occurs due to some oil components forming "reinforced shell" on hydrate particles (see [10], for example). A variation in the oil composition allows the hydrate formation and decomposition processes to be controlled [10]. Thus, the hydrates can exist in some oil content systems for a long time in the *p-T* region, where they are thermodynamically unstable. It is known that some oil components can form adsorption layers ("reinforced shell") on the surface of water droplets dispersed in the oil [11]. The layers play an important role in the colloidal chemistry and rheology of oils (in particular they determine stability of oil emulsions). An influence of the adsorption layers on hydrate-in-oil suspensions behavior has almost not been investigated to date. At the same time, temperature interval (below 0 °C) favor the manifestation of self-preservation effect, which is important from both practical and theoretical point of view. This allows one to say that the study performed in this work are of a fundamental nature and offers the challenge to manage the effect of self-preservation in applications to technological processes with the use of waste oils and deposits formed on the oil pipelines walls.

2. Experimental section

TO, EO1, EO2, SOF and T_ARPD (Table 1) were selected as objects of study. TO is a high-quality product that is produced from a mineral base oil with the use of hydrocatalytic processes and contains an antioxidant additive (AO-29); engine oils have high antioxidant and dispersant properties (prevents formation of high- and low-temperature deposits on engine parts). Thus, the oils used contain various additives (antioxidant and dispersant). TO, EO1, EO2, SOF and T_ARPD were taken in pure form, while asphaltenes and resins isolated from the oil of the South-Philippine deposit, multiwall carbon nanotubes, meloxicam (4-hydroxy-2-methyl-N-(5-methyl-2-thiazolyl)-2H-1,2-benzothiazine-3-carboxamide-1,1-dioxide), Luvicap 55W (dry polymer), Luvicap EG (dry polymer) and antioxidant fuel additive AO-29 (2,6-di-*tert*-butyl-4-methylphenol) were dissolved in toluene. Content of KHI Luvicap 55W and Luvicap EG in the solutions obtained was 0.5 mass % (standard concentration of KHI in aqueous phase for hydrate inhibition); content of other auxiliary substances was 1 mass %.

Table 1. Characteristics of the initial liquids.

Property	Sample				
	TO[a]	EO1[a]	EO2[a]	SOF[a]	T_ARPD[a]
Content of asphaltenes (mass %)	< 0.1	–	–	1.5	1.8
Content of resins (mass %)	0.69	–	–	10.7	5.5
Pour point (°C)	–	-36	-39	–	–
Density at 20°C (kg/m^3)	837	878	856	865	859
Viscosity at 20°C (mPa·s)	4.9	127.5	90.9	17.3	–

[a] TO, EO1, EO2, SOF, T_ARPD – are acronyms of transformer oil (LUKOIL VG), engine oil 1 (LUKOIL SUPER 10W-40, semi-synthetic), engine oil 2 (IDEMITSU 5W-40, fully-synthetic), petroleum from Sovetskoe oil field, asphaltene-resin-paraffin deposits from Irelyakhskoe oil field diluted with toluene respectively.

The approach to control the hydrate decomposition process proposed in this work was not previously used in practice. The pure methane hydrate with stoichiometry of $CH_4 \cdot 6.1H_2O$ synthesized from distilled water and methane (Moscow Gas Refinery Plant, >99.99 % pure) was mixed with additives either at 1 °C under methane pressure (10 MPa) or at liquid nitrogen temperature (atmospheric pressure). The mixing process under methane pressure was described in [10]. As for mixing at the boiling point of liquid nitrogen, the procedure was performed by careful grinding of

hydrate and a frozen organic liquid. The obtained mixture was put into an autoclave and heated to 10 °C at 10 MPa. The samples were held at these *p-T* conditions for day to provide redistribution of components in the system. Then the obtained sample of methane hydrate-in-organic liquid suspension was pulled out at liquid nitrogen temperature. The synthesized samples were carefully powdered (the particle size was less than 250 μm [10]) and studied by thermovolumetry at atmospheric pressure and temperature below 0 °C [10] (two measurements were carried out for each sample). The average hydrate content was 40.1 ± 0.1 %. The procedure of pure methane hydrate synthesis was described in [10].

3. Results and discussion

Comparison of the curves of gas evolution from the samples obtained by mixing pure methane hydrate and organic liquid under different conditions (at 1 °C under methane pressure (10 MPa) or at liquid nitrogen temperature, followed by heating the sample) showed that the decomposition of these samples proceeds in the same way (Figure 1). The part of hydrate self-preserved in T_ARPD was 21.0 ± 1.0 and 19.0 ± 2.8%, for different preparation modes respectively. However, the preparation of a hydrate suspension by grinding pure hydrate with an organic liquid at nitrogen boiling point can significantly expand the range of test substances as mixing liquids under pressure is limited to the ones with low viscosities.
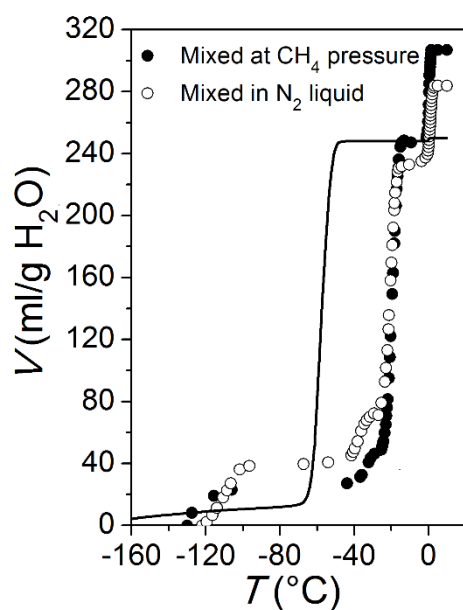

Figure 1. Dissociation of methane hydrate in T_ARPD; method of suspension preparation is indicated on the graph; the black line corresponds to the pure hydrate dissociation.
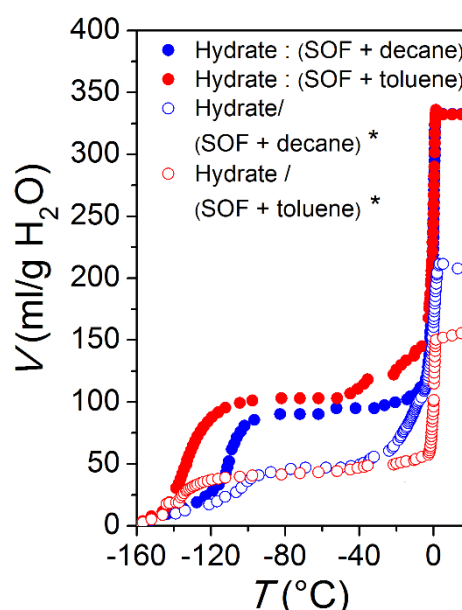
Figure 2. Dissociation of methane hydrate in SOF oil diluted with decane or toluene (1:1 by weight); filled circles indicate suspension prepared by mixing at liquid nitrogen temperature; open circles * correspond to data of [10] on dissociation of hydrate formed directly from water emulsified in the oil.

At the same time, Figure 2 clearly shows that the decomposition of methane hydrate in suspensions obtained by either mixing at liquid nitrogen temperature with subsequent heating or direct synthesis from the emulsion had some differences. This can be explained by the different morphology of hydrate particles. It was shown that the morphology of hydrate growing at a water–organic interface was varied considerably depending on the composition of organic phase [12]. Thus, the method chosen for

preparing of hydrate suspensions allowed one to study the effect of an organic liquid composition on the hydrate dissociation at a constant composition, size, and morphology of hydrate particles. The first experiments showed that TO promoted the effective self-preservation of methane hydrate (96.3 ± 1.9%), whereas EO had no effect and the decomposition began at the equilibrium temperature (-80°C) as well as in the case of pure methane hydrate (Figure 3; the dissociation of the hydrate in EO1 and EO2 proceeded in the same way). It is known that various types of oils are prepared from the base oil by the addition of different additives. There is a wide range of additives in engine oils (anticorrosion, antioxidant, antifriction, detergent and dispersant, etc.), whereas in the transformer oil only an antioxidant additive is present. Thereby, there are types of additives capable of suppressing the self-preservation effect (most likely, surfactants providing a detergent and dispersant effect).
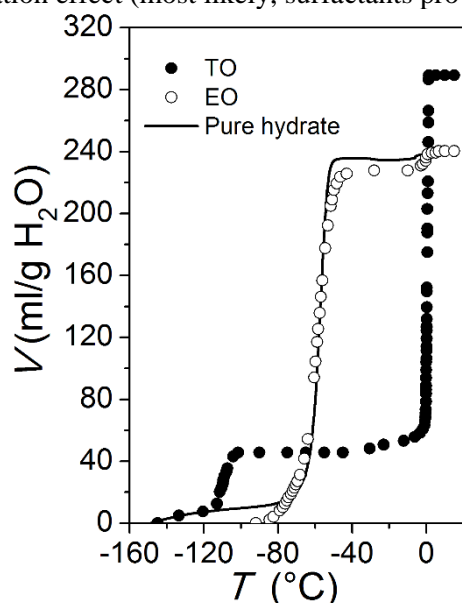

Figure 3. Dissociation of hydrate in the initial oils; dispersion media are indicated on the graph.
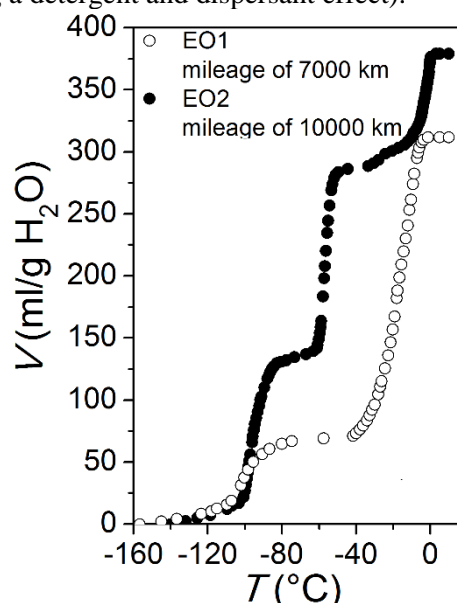
Figure 4. Dissociation of hydrate in the used oils; dispersion media are indicated on the graph.

Similar experiments with these engine oils differed in mileage (7000 and 10000 km in the case of EO1 and EO2, respectively) showed that the oils modified in this way had some influence on the process of hydrate decomposition (Figure 4). It seems to be that the part of methane hydrate, which decomposes in used engine oils at a temperature close to 0°C, depends on the duration of its operation (mileage). Dispersant additives are most likely destroyed or bound with solid deposits formed during cocking. These observations can contribute to the development of a new trend in the use of waste oils to stabilize the hydrate phase for storage and transportation of gas in hydrate form. Discussion of this possibility requires to provide additional experiments and goes beyond the scope of this paper.

In addition, the effect of the following compounds on the decomposition process of methane hydrate was studied: KHI Luvicap 55W and Luvicap EG, polyfunctional compound meloxicam, AO-29 (antioxidant additive in TO), asphaltenes and resins isolated from the oil of South-Philippine field and multiwall carbon nanotubes (MWCN) (Figure 5, on the examples of asphaltenes, MWCN and Luvicap 55W). The listed compounds had practically no effect on the decomposition process of methane hydrate. Samples with the addition of these compounds behaved themselves in a similar manner and decomposed without self-preservation. Since the substances were dissolved in toluene to mix it with hydrate, the similarity of decomposition curves for methane hydrate dispersed in pure toluene and with the addition of any substances showed that only toluene influenced in these cases (Figure 5).
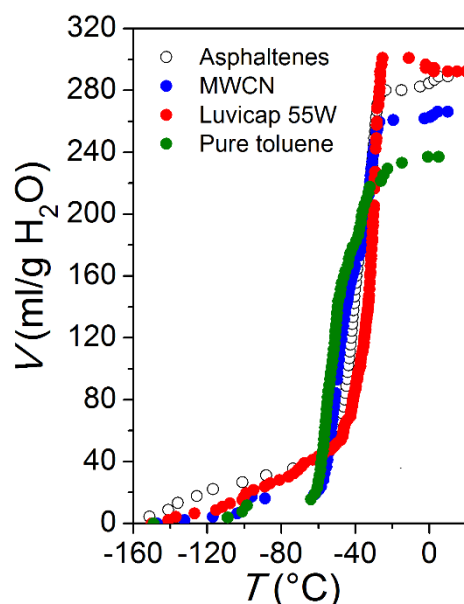
Figure 5. Dissociation of methane hydrate in the presence of different substances indicated on the graph.

Thus, it was demonstrated experimentally that self-preservation effect in TO and ARPD is possible. The increase in the duration of EO operation may also lead to the observation of this effect in the waste oils. The obtained data can be used to develop gas hydrate technologies for storage and transportation of hydrate-forming agents by reducing gas losses when placing hydrates particles in a medium that ensures their slow decomposition. It has been established that artificial additives (kinetic hydrate inhibitors Luvicap 55W and Luvicap EG, polyfunctional compound meloxicam and antioxidant additive) had practically no effect on the kinetic characteristics of gas hydrate decomposition process. The use of ARPD, residual heavy fractions after refining or waste petroleum products for hydrates treatment will not only increase the stability of the hydrate phase during storage, but will also open up a new way to use the listed hazardous wastes accumulated during the oil transportation and refining.

Acknowledgements

References
[1] Sloan E D and Koh C A 2008 *Clathrate Hydrates of Natural Gases* 3rd ed (Boca Raton, London, New-York: CRC Press) p 752
[2] Ershov E D, Lebedenko Y P, Chuvilin E M, Istomin V A and Yakushev V S 1991 *Dokl. Akad. Nauk SSSR* **321** 788–91
[3] Stern L A, Circone S, Kirby S H and Durham W B 2001 *J. Phys. Chem. B* **105** 1756–62
[4] Fitzgerald A and Taylor M 2001 Offshore gas-to-solids technology *Offshore Europe. Soc. Petrol. Eng*. SPE 71805
[5] Lv Y N, Jia M L, Chen J, Sun C Y, Gong J, Chen G J, Liu B, Ren N, Guo S D and Li Q P 2015 *Energy Fuels* **29** 5563–72
[6] Rehder G, Eckl R, Elfgen M, Falenty A, Hamann R, Kähler N, Kuhs W F, Osterkamp H and Windmeier C 2012 *Energies* **5** 2499–523
[7] Mimachi H, Takahashi M, Takeya S, Gotoh Y, Yoneyama A, Hyodo K, Takeda T and Murayama T 2015 *Energy Fuels* **29** 4827–34
[8] Yanagisawa N, Takanashi S, Yamaguchi T and Yamazaki T 2009 *Method of Production, Storage and Transportation for Gas Hydrate* EP2128228 A1 (Mitsui Engineering & Shipbuilding CO., LTD)

[9] Mimachi H, Takeya S, Yoneyama A, Hyodo K, Takeda T, Gotoh Y and Murayama T 2014 *Chem. Eng. Sci.* **118** 208–13

[10] Stoporev A S, Manakov A Yu, Altunina L K and Strelets L A 2016 *Energy Fuels* **30** 9014–21

[11] Mullins O C, Sheu E Y, Hammami A and Marshall A G 2007 *Asphaltenes, Heavy Oils, and Petroleomics* (New York: Springer Science & Business Media) p 669

[12] Stoporev A S, Semenov A P, Medvedev V I, Sizikov A A, Gushchin P A, Vinokurov V A and Manakov A Yu 2018 *J. Cryst. Growth* **485** 54–68