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Time-dependent nucleation of methane hydrate in a water-in-oil emulsion: effect of water redistribution

Andrey S. Stoporev*[a,b,c] **and Andrey Yu. Manakov**[b,c]

[a] *Kazan Federal University, 420008 Kazan, Russian Federation. E-mail: andrey.stoporev@kpfu.ru*

[b] *A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation*

[c] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*

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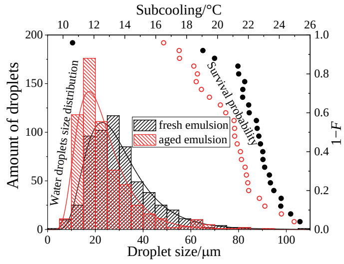
Nucleation is a key step in preventing gas hydrate formation during oil and gas production. Oil can sharply affect the hydrate nucleation with changing the activity of nucleation centers (mainly at the water–oil interface) over time. The spontaneous emulsification of water-in-oil emulsions in the course of aging can lead to a decrease in the size of water drops and, consequently, facilitate the hydrate nucleation and alter hydrate mitigation during the shut-in period.



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The interaction of water with such gases as methane, carbon dioxide, and some Freons under specific thermobaric conditions results in the formation of water frameworks with cavities stabilized by the gases.[1] Note that the polyhedral structure of these compounds, gas hydrates, allows them to contain a large amount of gas [for example, up to 170 volumes (STP) of methane per hydrate]. Thus, these compounds are promising carriers for gas storage and transportation.[2] On the other hand, their formation in water–oil–gas flows often harms the production and transportation of oil and gas.[3] There are several strategies for preventing hydrate complications,[2–4] and some of them seem to be opposite. However, all strategies suppose managing the hydrate formation process. Indeed, one way assumes to avoid the formation of hydrates completely (thermodynamic hydrate inhibition), while others do not exclude the formation of hydrates with controlling their growth (using hydrate growth inhibitors and anti-agglomerants to convert a gas into a hydrate directly in the flow and transfer the hydrate-in-oil suspension). In the latter case, the hydrate phase nucleation is often a critical stage.[5–7] The influence of many factors on the nucleation process has been shown.[8,9] Nucleation at the water–solid substrate interface (without direct contact with the hydrate former) is extremely rare.[10] In general, the nucleation of hydrates can be affected by additives that either form a boundary simultaneously with water and the phase saturated with a hydrate former or modify this interface. Crude oils contain such substances, namely, asphaltenes, resins, waxes, and polar compounds (naphthenic acids).[11–15] The mechanism of hydrate nucleation in oil suspensions is complicated by the alteration in the activity of nucleation centers with time under static conditions (shut-in period).[16] In this work, we determined the contribution of a size redistribution of water droplets during emulsion aging to the nucleation of methane hydrate in a water-in-oil emulsion under static conditions in Teflon (polytetrafluoroethylene) vials.

We used crude oil from the Mamontovskoe oil field (MF oil).[†] The size of water droplets in the emulsion was measured with an optical microscope. In the first type of experiments, two freshly prepared emulsion samples were used. In these experiments, the duration of emulsion saturation with gas was 1.5 or 12 h. In the second type of experiments, the emulsion aged for 10 days was used. Before each experiment, the size of the water droplets in the emulsion was also

[†] The MF oil contained 0.5 wt% asphaltenes and 4.0 wt% resins; its density and viscosity were 0.841 g cm^{-3} and 18.8 mPa s, respectively. Water-in-MF oil emulsions were prepared at room temperature with a magnetic stirrer at 800 rpm for 20 min without surfactant additives. The water to oil weight ratio was 1 : 1. When stored in sealed vessels (to avoid evaporation), these emulsions did not coalesce under room conditions. The study was carried out using an autoclave into which four K-type thermocouples (accuracy, ± 0.2 °C) were introduced. The pressure in the autoclave was measured using an electronic pressure sensor (accuracy, ± 0.25%). An aluminum block inside the autoclave contained four Teflon vials (internal diameter, 10 mm; height, 35 mm). Emulsion samples of 0.902 ± 0.002 g were loaded into each of the Teflon vials. The thermocouple junctions were placed at the geometric centers of the emulsion samples. In the typical experiments, the aluminum block with the vials filled with the emulsion samples was placed in the autoclave. The autoclave volume was rinsed with methane; a required pressure was set, and the samples were saturated with gas for 1.5 or 12 h at 20 °C. Next, the autoclave was immersed in a thermostat; the temperature was varied with a rate of 0.136 K min^{-1} according to the program + 20 °C → – 15 °C → + 20 °C (ramp experiment). The moment of methane hydrate nucleation in the samples was determined by an exothermic effect detected with the thermocouples. The pressure in the system was within a range of 11.8–12.8 MPa. The subcooling value (ΔT) was calculated for each nucleation event based on the temperature and pressure in the cell and the known equilibrium conditions of methane hydrate formation.[17] The measurement technique was described elsewhere.[18,19] Experiments with 24 emulsion samples were performed for each system. Micrographs with clearly visible spherical droplets were taken to determine the size of the droplets, and these data were used to plot the droplet size distribution diagrams.

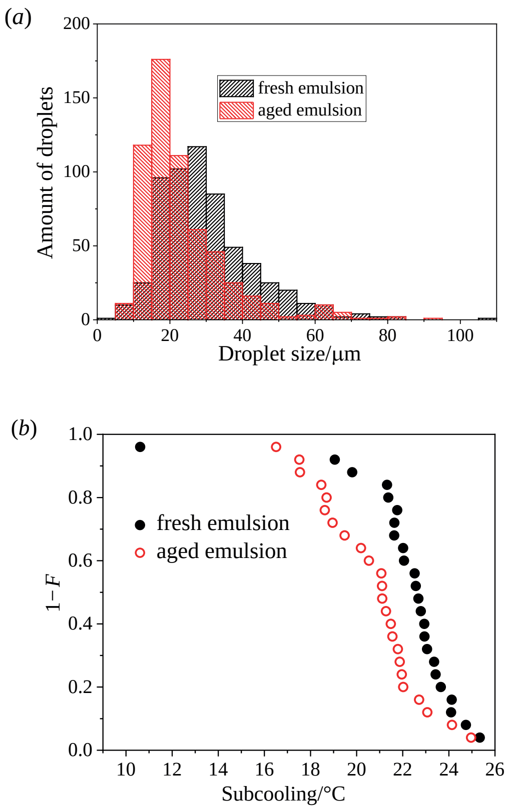

Figure 1 (*a*) Water droplet size distribution in the fresh and aged emulsions. (*b*) Survival probability of hydrate nucleation in the samples *vs.* the subcooling value.

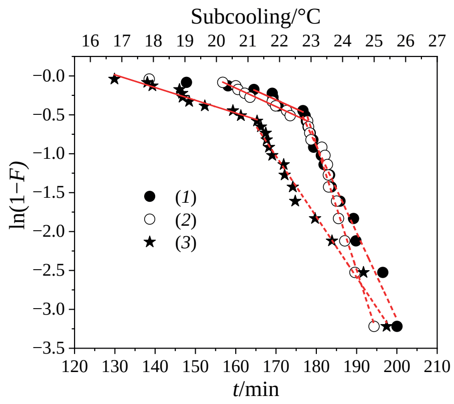

Figure 2 Linearization of survival curves obtained in constant cooling ramp experiments with (*1*) a fresh emulsion saturated for 1.5 h, (*2*) a fresh emulsion saturated for 12 h, and (*3*) an emulsion aged for 10 days and saturated for 12 h; time is counted from crossing the metastability boundary and linked with the subcooling axis.

determined. In this case, saturation of the emulsion with the gas was carried out in 12 h. The aim of this study was to determine the effect of emulsion aging on methane hydrate nucleation.

The mean sizes of water droplets in the fresh and aged water-in-oil emulsions were 30 and 23 μm, respectively [see Figure 1(*a*)]. The areas of water–oil interfaces were 0.063 and 0.069 m^2 per sample in fresh and aged emulsions, respectively. Hydrate formation was detected by an exothermal effect in the cooling curve. Ice crystallization also occurred because the system was in a metastable state with respect to both methane hydrate and ice at a temperature below –0.8 °C. Based on previous data, the formation of hydrate was unambiguously distinguished from ice crystallization by the values of thermal effects.[18,19] In this work, we omitted ice crystallization and considered only hydrate nucleation. This stochastic process was described by the following distribution function (survival function):[20,21]

$$1 - F = 1 - \frac{N}{N_0 + 1}, \quad (1)$$

where F is a probability function, N_0 is the total number of samples, and N is the number of hydrate nucleation events that occurred up to a certain temperature (subcooling). The resulting survival functions are shown in Figure 1(*b*). The nucleation rate J can be calculated as the time t derivative of the survival function

$$J = -\frac{d[\ln(1 - F)]}{dt}. \quad (2)$$

We can reliably distinguish two regions in each nucleation curve in semilogarithmic coordinates. Each part is approximated by a straight line, the slope of which gives the nucleation rate (Figure 2, Table 1). Note that the survival curve for the aged emulsion is significantly shifted to the region of lower subcooling [on average by 1.5–2 °C, see Figure 1(*b*)]. Previously, the influence of emulsion aging on gas hydrate nucleation was not reported.

The most likely reason for this effect can be a redistribution of water between drops. Usually, the Ostwald ripening leads to the rise of droplet size in the dispersed phase of emulsions.[22] In our case, a decrease in the size of water droplets was observed. Evaporation can be excluded because the emulsion was aged in tightly closed vials and condensation on the walls did not occur. It is likely that spontaneous emulsification was the main reason for water redistribution. Indeed, micellar solutions of surfactants are widely used to stabilize water-in-oil microemulsions and obtain various nanoparticles.[23–26] Asphaltenes can also participate in self-emulsifying process.[27,28] The adsorption of asphaltenes and/or other oil components can change interfacial tension at the oil–water interface. This can facilitate the formation of nanodroplets near this interface. The ripening of droplets leads to the formation of an emulsion with a new size distribution. Comparison of the methane hydrate nucleation rates in fresh and aged emulsions at close supercooling showed an increase in their difference when the rates were normalized to the water–oil surface areas. Thus, the formation of a sorption layer (emulsion aging) of oil components on the water–oil surface somewhat slows down the hydrate nucleation. Note that the time of emulsion saturation with methane had almost no effect on the rate of hydrate nucleation (compare the survival curves in Figure 2 and the nucleation rates in Table 1). Earlier, we found that the undersaturation of another water-in-oil emulsion (with

Table 1 Nucleation rates of methane hydrate in 50 wt% water-in-MF oil emulsions at different subcooling (see Figure 2); standard deviations are given in parentheses.

Temperature/°C	Pressure/MPa	Δ*T*/°C	Nucleation rate	
			min^{-1}	$min^{-1}\,m^{-2}$ [a]
Fresh emulsion (1.5 h saturation)				
–9.1	12.8	24.1	0.112(3)	1.78
–6.8	12.1	21.4	0.023(6)	0.36
Fresh emulsion (12 h saturation)				
–9.2	12.2	23.8	0.161(7)	2.56
–6.4	11.8	20.8	0.024(1)	0.38
Aged emulsion (10 days exposure under ambient conditions; 12 h saturation)				
–8.5	12.4	23.3	0.078(3)	1.13
–4.0	12.0	18.5	0.016(1)	0.23

[a] Nucleation rates are normalized per water–oil surface area.

similar viscosity and density) led to a noticeable shift of the hydrate nucleation to lower temperatures under identical experimental conditions.[29] Nevertheless, 4 h was not sufficient for saturation in that case, while 1.5 h was sufficient in this work. Unfortunately, the diffusion coefficients of methane in these oils are unknown, but we can assume that the formation/activation of nucleation centers is here a rate-limiting stage.

Thus, we found the effect of water-in-oil emulsion aging on methane hydrate nucleation. The aging resulted in water droplet size redistribution, while hydrate nucleation turned to a lower subcooling region. The time of emulsion saturation had no influence on the nucleation process compared to a previous study of a similar system. Spontaneous emulsification with the subsequent ripening can be responsible for water redistribution. It can be expected that the development of kinetic hydrate inhibitor formulations with surface active substances[30,31] can enhance the water redistribution due to the solubilization of micelles. This effect can have a significant impact on hydrate mitigation under static conditions (shut-in period).

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