



Condensed Matter and Interphases (Kondensirovannye sredy i mezhfaznye granitsy)

Original articles

DOI: <https://doi.org/10.17308/kcmf.2020.22/2963>

Received 21 May 2020

Accepted 15 July 2020

Published online 30 September 2020

ISSN 1606-867X

eISSN 2687-0711

Usage of the Kolmogorov–Johnson–Mehl–Avrami Model for the Study of the Kinetics of the Formation of Natural Gas Hydrate in Inverse Oil Emulsions.

© 2020 V. V. Koryakina[✉], E. Yu. Shitz

Federal Research Centre “The Yakut Scientific Centre”,
Institute of Oil and Gas Problems of the Siberian Branch of the RAS
20, Avtodorozhnaya ul., Yakutsk 677007, Russian Federation

Abstract

The article presents the results of a study of the hydration of the aqueous phase in inverse oil emulsions with natural gas rich in methane (more than 90 vol.%). The aim of the work was to study the kinetics of the crystallisation of oil emulsions during the formation of natural gas hydrates in them using the method of differential scanning calorimetry (DSC).

The objects of the study were inverse oil emulsions containing 20, 40, 60, and 80 wt% of water. DSC is used under quasi-equilibrium experiment conditions to study the kinetics of hydration of oil emulsions with gas.

The study showed the applicability of the Kolmogorov–Johnson–Mehl–Avrami model (KJMA) in order to describe the crystallisation process of inverse oil emulsions in a quasi-equilibrium DSC experiment. The kinetic parameters of the KJMA model in emulsions were determined for the processes of water drops conversion into ice, as well as their hydration with natural gas. It was shown that within the system “natural gas-oil-water” the process of ice formation is characterised by high values of the Avrami exponent ($n > 3$) and the degree of freedom ($\lambda = 3$), and the process of natural gas hydrate formation is characterised by low values of the Avrami exponent ($n < 3$) and medium degree of freedom ($\lambda = 1-3$). It was shown that in a continuous aqueous phase, natural gas hydrates are formed by instantaneous nucleation in the form of separate one-dimensional crystals; while in oil, hydrates are nucleated at a constant rate and, depending on the water content, grow in the form of disparate crystallites, shell, or spherulites. The obtained research results make it possible to deepen our knowledge of the kinetics and hydration mechanisms in oil emulsions, they can be used to complement the scientific basis for creating new technologies for the joint transportation of oil and hydrated natural gas in it.

Keywords: crystallisation, kinetics, Kolmogorov–Johnson–Mehl–Avrami model, differential scanning calorimetry, oil emulsion, natural gas hydrate, hydrate formation.

Funding: The study was supported by state-funded research, development, and engineering project No. AAAA-A17-117040710035-7.

For citation: Koryakina V. V., Shitz E. Yu. Usage of the Kolmogorov–Johnson–Mehl–Avrami model for the study of the kinetics of the formation of natural gas hydrate in inverse oil emulsions. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2020;22(3): 327–335. DOI: <https://doi.org/10.17308/kcmf.2020.22/2963>

✉ Vladilina K. Koryakina, e-mail: koryakinavv@ipng.ysn.ru



The content is available under Creative Commons Attribution 4.0 License.

1. Introduction

Gas hydrates are non-stoichiometric clathrate compounds of water and non-polar gases that are formed at low temperatures and high gas pressure by introducing “guest” molecules of the hydrate-forming gas (G) into the water cavities of the “host” lattice according to the scheme [1]:



At the same time, water hydration, its binding by hydrate-forming gas molecules, occurs without violating the integrity of the clathrate frame consisting of water molecules linked together by hydrogen bonds [2].

In addition to bulk aqueous solutions, water-in-oil emulsions are one of the media for the potential formation of gas hydrates. The practical application of this phenomenon in inverse oil emulsions can be demonstrated using the currently known technologies of joint multi-phase transportation of oil and gas, whose core principle is hydration of the aqueous component of the emulsion with associated gas, turning the emulsion into a suspension of hydrated particles in oil [3].

Almost all kinetic models for the process of hydrate formation in continuous aqueous solutions are improved types of the Englezos-Bishnoi model [4, 5], which is based on the crystallisation theory and two-film interphase mass transfer. In this model, the diffusion factor can be omitted by the forced mixing of the “hydrate-forming gas – continuous liquid” system, and the reaction rate (1) between the process participants is considered proportional to the specific area of the interphase boundary.

The kinetic and thermodynamic parameters of nucleation, growth, and dissociation of gas hydrate particles in the emulsion media have their own differences and peculiarities because of the presence of an oil matrix. Moreover, the mechanisms and kinetics of the formation of gas hydrates are fundamentally different in different types of emulsions. For example, in direct emulsions, hydrate formation usually occurs directly at the “gas-liquid (aqueous phase)” interphase boundary at a higher rate than in inverse emulsions, where hydrate formation occurs at the “liquid (oil)-liquid (water)” interphase, with the necessary stage of diffusion of the hydrate-forming gas to the hydrate growth sites on the surface of the droplets

of the aqueous phase of the emulsion [6, 7].

When describing the process for the formation of gas hydrates in the aqueous medium of inverse emulsion systems, gas diffusion cannot always be omitted, even with forced mixing of the reacting phases. Therefore, the most famous kinetic model describing hydrate formation in inverse emulsions is the Talatori formal model [8], based on the Kolmogorov–Johnson–Mehl–Avrami equation (KJMA) and originally used for topochemical reactions [9]:

$$\alpha(t) = 1 - \exp[-(kt)^n], \quad (2)$$

where $\alpha(t)$ is the conversion degree, t is time, k is the rate constant, n is the Avrami kinetic exponent, containing information regarding the geometry of the growing formations and the degree of freedom of the crystallisation process.

In modern studies, the KJMA equation is widely used to describe the crystallisation and decomposition of solid substances, including the kinetics of hydrate formation under pressure in various water-containing systems [8, 10–12]. In a study [10], it was shown that the KJMA model satisfactorily describes the initial stage of crystallisation of gas hydrates until the degree of conversion of water to hydrate is no more than 40–50 %. In [8], it was found that in an oil emulsion with 80 % water content, the formation of methane hydrates has two stages. The first is characterised by a slow crystallisation rate $K_c = (2-5) \cdot 10^{-4} \text{ s}^{-1}$, and Avrami exponent $n_1 = 0.9-1.0$. The second stage, compared to the first, is relatively fast, $K_c = (3.5-11) \cdot 10^{-4} \text{ s}^{-1}$ at $n_2 = 1.6-2.9$. It was shown in [11, 12] that the Avrami exponent of the process of methane hydrate formation in distilled water is $n = 0.5-2.5$, depending on the presence of surfactants in the system and forced mixing.

It is known that the KJMA equation is successfully used to describe phase conversions and reactions in various substances, particularly in polymer composites and metal alloys, studied using the method of differential scanning calorimetry (DSC) [13, 14]. The method makes it possible to obtain statistically average values of kinetic parameters of the processes without a range of experiments, including those in emulsions [15–18].

Purpose: To determine the kinetic parameters of the Kolmogorov–Johnson–Mehl–Avrami model during the crystallisation of the aqueous phase of

oil emulsions during the formation of natural gas hydrates in their medium using the DSC method.

2. Experimental

The object of research was water-in-oil emulsions with the oil (o) and water (w) mass ratio of 20o : 80w, 40o : 60w, 60o : 40w, and 80o : 20w, obtained by mechanical mixing of distilled water and oil from the Irelyakh GOF (Yakutia, Russia), with a density of 0.869 g/cm³, containing 1.47 wt% paraffin hydrocarbons, 0.3 wt% asphaltenes, and 10.4 wt% resins. More details about obtaining oil emulsions can be found in [19].

As an atmosphere for the DSC experiment, a naturally-occurring gas was used, with the following composition, vol.%: CH₄ – 92.87, C₂H₆ – 5.25, C₃H₈ – 1.21, *i*-C₄H₁₀ – 0.12, *n*-C₄H₁₀ – 0.12, N₂ – 0.38, CO₂ – 0.05 (Sredneviluyskoe gas-condensate field (Yakutia, Russia)).

The kinetic parameters of the crystallisation processes of water-in-oil systems with the formation of natural gas hydrates in their medium

were determined using a high-pressure differential scanning calorimeter DSC 204 HP Phoenix by Netzsch (Germany). The DSC thermograms showed successive cooling and heating segments, which were obtained in the temperature range from +25 to –10 °C, with a cooling rate of 0.1 °/min and a heating rate of 0.2 °/min. The temperature measurement accuracy was ± 0.1 °C, the gas pressure throughout the experiment was 5.0 MPa, and the sample weight was ~30 mg. The relative enthalpy measurement error was ± 3 %.

The DSC thermograms of water-in-oil systems in the presence of natural gas were obtained (Fig. 1).

It can be seen that in the cooling segment of the emulsion there is one crystallisation peak in the temperature range of –8 ÷ –12 °C, which breaks up into peaks of melting ice and natural gas hydrate in the heating segment at temperature values of –1.2° and +11.3° C, respectively. Thus, it was found that when the emulsion is cooled in the presence of natural gas, water droplets, when frozen, partially hydrate.

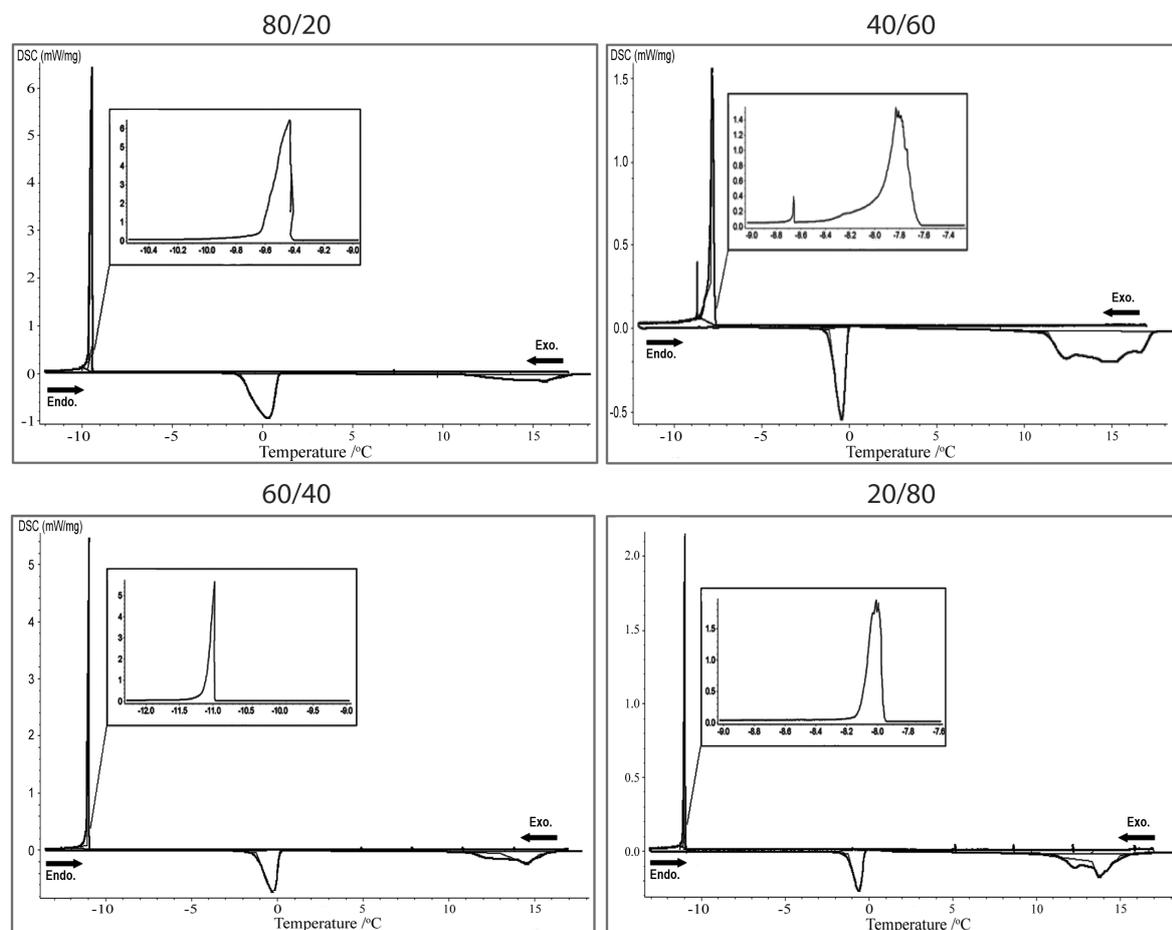


Fig. 1. The DSC thermograms of water-in-oil systems cooling in the presence of natural gas

The curves of the degree of water conversion during crystallisation were obtained according to the ratio:

$$\alpha(t) = \frac{\int_{t_0}^t \left(\frac{dH_c}{dt} \right) dt}{\int_{t_0}^{t_\infty} \left(\frac{dH_c}{dt} \right) dt} = \frac{S_t}{S_\infty}, \quad (3)$$

where α is the degree of conversion of the liquid phase of emulsion to the solid hydrate-containing phase; index 0 is the initial time of crystallisation; ∞ is the total time of crystallisation; H_c is the heat of crystallisation, S is the peak area. On the obtained kinetic curves, we graphically determined the reaction half-life $t_{1/2}$.

The obtained curves of the degree of water conversion to the hydrate-containing phase were analysed according to the KJMA equation (2). The Avrami exponent n was found by double logarithmic transformation of equation (2):

$$\ln[-\ln(1-\alpha)] = n \ln(t) + \ln(k), \quad (4)$$

and construction for the process a kinetic anamorphosis of the second order in the coordinates $\ln[-\ln(1-\alpha)] - \ln(t)$. In this case, the slope angle of the kinetic anamorphosis, which has the form of a straight line, equals to the constant n . The Avrami exponent is $n = \varphi + \lambda$, where φ is the number of stages of a nucleus formation, usually it is 1 or 0 for nucleation at continuous rate or instantaneous nucleation, respectively; and λ is the number of degrees of freedom, or the nuclei effective growth directions, it is 3 when spheres are formed; 2 when two-dimensional surfaces are formed; and 1 for rod-like structures and unidirectional one-dimensional growth processes [20].

By constructing an anamorphosis of the first order in the coordinates $\ln(1-\alpha) - t^n$ we defined the k^n value by the slope angle of the line. The crystallisation rate constants (K_c) were determined using the Sakovich ratio in accordance with [21]:

$$K_c = nk^{1/n}. \quad (5)$$

The water conversion degree of the water-in-oil system to the natural gas hydrate (γ) was calculated using the ratio:

$$\gamma = \frac{\Delta H_m}{500} \times 100\%, \quad (6)$$

where ΔH_m is the heat of fusion of the natural gas hydrate released during the heating segment, 500 kJ/kg is the theoretical amount of heat released during the fusion of the natural gas hydrate at a 100% degree of conversion [22].

3. Results and discussion

During the initial stage of using the Kolmogorov–Johnson–Mehl–Avrami model to analyse the crystallisation process of any system, it is necessary to verify its applicability under the specific conditions of the experiment.

3.1 Applicability of the KJMA model for the interpretation of the DSC data from the process of crystallisation of water-in-oil emulsions in the presence of natural gas

It is known that the shape of the DSC signal is significantly affected by the cooling rate of the system and its effect becomes noticeable in the experiments involving high cooling rates $\beta > 1-5$ °/min [23]. It is difficult to apply the KJMA equation in such cases, since processing the conversion curves leads to significant deviations and errors. Therefore, with high cooling rates ($\beta > 1$) of the experiment, the non-isothermal model of KJMA is used to process the DSC signal [24].

With lower cooling rates $\beta \ll 1$ °/min, quasi-isothermal crystallisation conditions are implemented. Under them the application of the isothermal KJMA equation provides satisfactory results, and the applicability of the KJMA model for interpreting the kinetics of the process is estimated by the form of anamorphosis curves. Such an approximation is known as a quasi-isothermal condition for the realisation of a DSC experiment [23]. The curves of the degree of conversion of water to the hydrate-containing phase obtained under such conditions are provided in Fig. 2.

It can be seen (Fig. 2) that all curves of the degree of conversion of water to the crystalline phase are S-shaped.

It was found that, at $\alpha < 0.05$ (or 5%), the crystallisation curves of the water phase in water-in-oil systems have a small acceleration period. It is an induction period, which, as can be seen from Fig. 2, is absent on the crystallisation curve of distilled water. It is apparently due to the instantaneous nucleation of many crystallisation centres ($\varphi = 0$), while the presence of an induction period in emulsions can be associated with the fact that only part of the hydrate nuclei survive

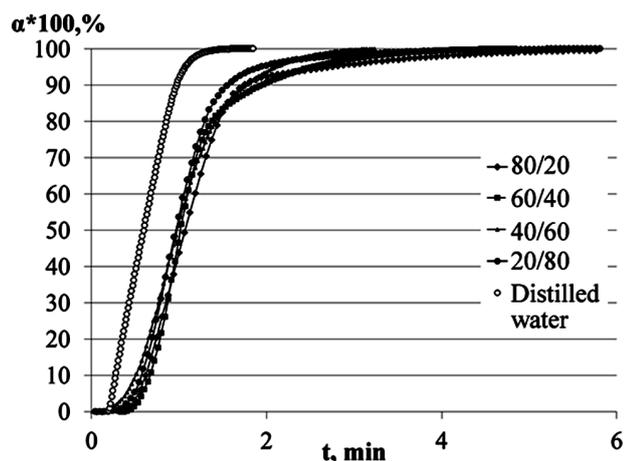


Fig. 2. The curves of the degrees of conversion α to the hydrate-containing phase, when cooling distilled water and water-in-oil emulsions in the presence of natural gas

and keep growing [25], that is nucleation at a constant rate ($\varphi = 1$). Thus, it was shown that the mechanisms of hydrated nucleation in the continuous water phase and in the dispersed water-in-oil medium are different.

With $\alpha > 0.80$ (or 80 %), the crystallisation process in water-in-oil systems slows down and is associated with a change in the crystallisation mode from kinetic to diffusion-controlled. The duration of this period is more than half of the total crystallisation time of the system. The formation of natural gas hydrate in this section of the crystallisation curve is explained by the slow advance of the hydrate formation front deeper into the reaction zone (water droplets). It can be described by the model that is described in detail in [26].

Thus, in the range of degrees of conversion of water into a hydrate-containing phase $0.05 < \alpha < 0.80$, there is a zone of active nucleation and crystal growth, whose formation can be described without taking into account the diffusion of natural gas across the water-oil boundary.

Secondary anamorphoses of the curves of the degrees of conversion of water from water-in-oil systems into a hydrate-containing phase are shown in Fig. 3. It was determined that all obtained secondary anamorphoses are straight-lined ($R^2 > 0.98$) in the range of the function $f = \ln[-\ln(1 - \alpha)] \in [-0.09; -2.97]$, which corresponds with the range of conversion degrees $\alpha \in [0.05; 0.60]$.

Therefore, in the range of conversion degrees α from 0.05 to 0.60, the kinetic DSC curves of the process of quasi-isothermal crystallisation in water-in-oil systems with the formation of natural gas hydrate can be analysed using the KJMA equation.

3.2. Kinetic parameters of crystallisation of the water phase of water-in-oil systems during the formation of natural gas hydrates in them

The kinetics of hydrate formation in oil emulsions, as a crystallisation process, can be characterised by the Avrami exponent, the number of nucleation stages, the degree of freedom, and the direction of the process of crystallisation of water droplets.

It was determined (Table 1) that during the crystallisation of the continuous phase of distilled water, only a small part of it (not more than 5%)

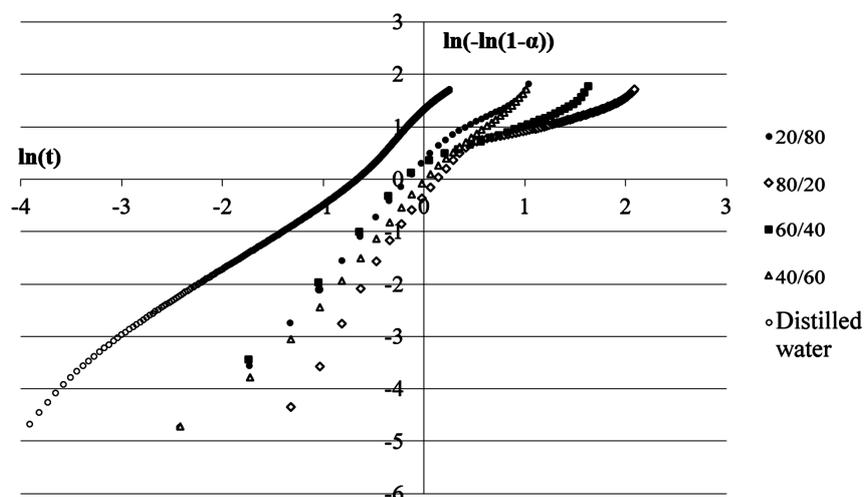


Fig. 3. The second-order anamorphoses of the curves of the degrees of conversion to the crystal phase, when cooling distilled water and water phase within water-in-oil emulsions

Table 1. The values of the fraction of hydrated water (γ), the Avrami parameter (n), the degree of freedom (λ), the number of nucleation stages (φ), and the crystal geometry upon crystallisation of water-in-oil emulsions and continuous water phase in the presence of natural gas and in its absence (*) (R^2 is the regression coefficient)

Object, %	γ , %	n	φ	λ	Object, %	R^2
Distilled water	5	1.5	0	1	Filaments, single crystallites	0.991
80o:20w	60	2.5	1	1	Single crystallites	0.998
60o:40w	60	2.5	1	1	Single crystallites	0.999
40o:60w	44	2.7	1	2	Shell	0.997
20o:80w	26	3.9	1	3	Spherulite	0.984
80o:20w*	0	4.2	1	3	Spherulite	0.999

undergoes hydration, while the crystals of natural gas hydrate are formed by instant nucleation of the nuclei ($\varphi = 0$) with subsequent unidirectional growth ($\lambda = 1$) in the form of filaments or separate formations (Fig. 4, I). It is consistent with the morphology of natural gas hydrates growing from the surface of distilled water deep into the continuous phase in the form of single crystallites and dendritic formations [27].

In water-in-oil systems, an increase in the Avrami exponent of the crystallisation process is observed, both due to the number of stages of the nucleation process φ , and due to the degree of freedom λ , which determines the shape of the growing crystals of natural gas hydrate (Table 1).

It was determined that in water-in-oil systems, the hydration crystals nucleate continuously, with their subsequent growth throughout the entire crystallisation process ($\varphi = 1$). In this case, the remaining part of the water phase, which are drops, turns into ice.

It was found that the crystallisation degree of freedom increases with the increase in water content in a water-in-oil system, which entails

changes in the geometry of growing crystals. So, with a water content of up to 40 wt%, single hydrate crystallites are formed in oil (Fig. 4, II). In these emulsions with a low water content, the formation of “serpentine” hydrates can probably occur that are growing from the surface of a water droplet [28] up to the formation of “wool balls”. It can be explained by the presence of a high surfactant content in oil: both synthetic and natural. [29]. It is possible that oil surfactants concentrated on the surface of water droplets interfere with the free growth of hydrate crystals, forcing it to “cling” between the surfactant macromolecules.

When the water content in the emulsion is 60 wt%, the hydrate is formed in the form of a shell on the droplet surface (Fig. 4, III), and at 80 wt% of water in the oil, spherulitic formations grow (Fig. 4, IV), which is confirmed by generally accepted models of hydrate formation in emulsions on the surface of water droplets [30]. It was found that the formation of the ice phase in the water-in-oil system (80o:20w*) is characterised by a high degree of freedom ($\lambda = 3$),

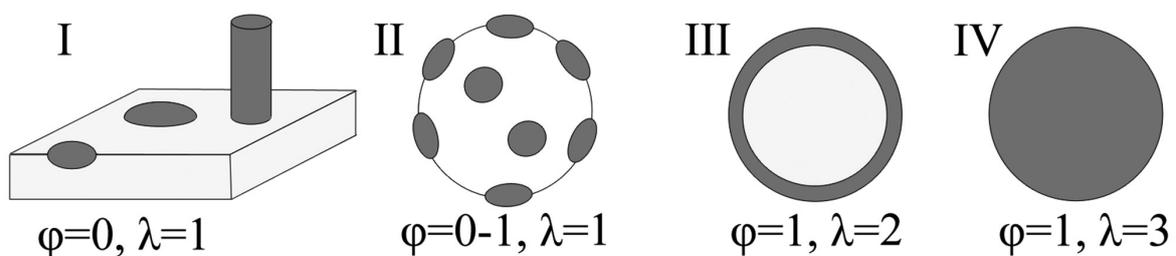


Fig. 4. Crystal growth patterns of natural gas hydrate on: I) the surface of distilled water; and on the drops of water-in-oil emulsion with a water content of: II) no more than 40 wt%; III) 60 wt% (sectional view); IV) 80 wt% (sectional view). The hydrate phase is marked in grey, and the ice phase is white

it goes in all directions and leads to the formation of a spherulite.

It should be noted that the growth patterns of natural gas hydrate crystals shown in Fig. 4, are theoretically-calculated, model schemes that need further confirmation and more detailed study using direct methods of studying the supramolecular structure (TEM, AFM, etc.).

It was determined that with an increase in the water content in oil, the fraction of hydrated water (γ) decreases and, consequently, the proportion of ice in the system increases, which leads to an increase in the Avrami exponent and the degree of freedom of crystallisation. When the Avrami exponent $n < 3$, water in the emulsion predominantly crystallises into natural gas hydrate, and when $n \geq 3$ the formation of ice prevails in the system. Thus, it is shown that the Avrami exponent is inversely related to the amount of natural gas hydrate formed in the water-in-oil system.

Differences in the nature of the processes of natural gas hydrate and ice formation in oil emulsions also affect their kinetic characteristics (Table 2).

It was found that the crystallisation rate constants of oil emulsions of all compositions in the presence of natural gas are 38.3–56.7 s⁻¹, which is 13–20 times higher than that for an 80o:20w* emulsion containing no natural gas (Table 2) and 7–11 times higher than the rate of emulsion hydration with methane [8].

Thus, the formation of natural gas hydrate in the water-in-oil system occurs faster than ice formation.

It was found that the reaction half-life of the aqueous phase conversion into a crystalline hydrate-containing phase is almost the same for all compositions of water-in-oil emulsions and is ~60 s, which is 3 times less than the ice formation process (Table 2).

The process of ice formation in the absence of natural gas in water-in-oil systems proceeds at a lower speed at a temperature of 255 K, that is, under conditions of deeper supercooling of the system, and it is longer than hydrate formation, which is characteristic of the process of homogeneous crystallisation.

Moreover, it was found that a decrease in the temperature of the water-in-oil system

Table 2. The values of kinetic exponents and temperature of the process of crystallisation of water in water-in-oil systems in the presence/absence (*) of natural gas in the system

Object	T_c, K	$K_c, 10^{-3} s^{-1}$	$t_{1/2}, s$
80o:20w	265	48.3	58
60o:40w	266	38.3	59
40o:60w	262	56.7	61
20o:80w	264	53.3	64
80o:20w*	255	2.8	181

from 266 to 262 K results in an increase in the crystallisation rate constant of the aqueous phase by 1.5 times. Thus, the overcooling of the system is the driving force of the crystallisation of water-in-oil emulsions, leading to the formation of natural gas hydrate in them.

4. Conclusions

Therefore, it was shown that the Kolmogorov-Johnson-Mehl-Avrami model is suitable for describing the experimental data of the DS calorimetry of the process of nucleation of natural gas hydrate in water-in-oil systems. The use of the KJMA model in studying the crystallisation of the aqueous phase of oil emulsions in the presence of natural gas allowed us to draw the following main conclusions:

1. The growth of hydrate crystals on the surface of water droplets in oil depends on the water content in the oil and proceeds in the form of a rod-like unidirectional growth: in oil with low water content (< 40 wt%), or completely taking the surface of a water droplet (> 60 wt%);

2. The Avrami exponent indirectly characterises the prevailing process during crystallisation of the “water-oil-natural gas” system: when $n < 3$, natural gas hydrate predominantly forms in the emulsion, and when $n \geq 3$ the formation of ice prevails in the system;

3. The crystallisation rate of oil emulsions with the formation of natural gas hydrate is 13–20 times higher than the rate of ice formation in the emulsion.

The obtained experimental data allow us to deepen our knowledge of the kinetics and mechanisms of nucleation of natural gas hydrates in water-in-oil systems, and can be used to model the process of hydrate formation in a water-oil emulsion medium.

Knowledge of the fundamental physical and chemical parameters of the process of formation of natural gas hydrates in inverse oil emulsions is one of the key factors for the successful and effective development of oil and gas fields with high water content that are located in the regions of the Far North, Eastern Siberia, and the Arctic.

In practical terms, the results of the study of the features and differences of the formation of natural gas hydrates in oil emulsions can be helpful in creating the scientific foundations of new technologies for the joint transportation of oil and hydrated natural gas in it.

Acknowledgements

The authors are grateful to the staff members of the technogenic gas hydrate laboratory for their assistance in conducting experiments and discussing the results of the study (research fellow M. E. Semenov, leading research fellow I. K. Ivanova).

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Carroll J. *Natural Gas Hydrates: A Guide for Engineers*. Oxford, UK: Gulf Professional Publishing; 2020. 392 p.
2. Maninder K., Zhenyuan Y., Praveen L. A Review of clathrate hydrate nucleation. *Sustainable Chemistry & Engineering*. 2017;5(12): 11176–11203. DOI: <https://doi.org/10.1021/acssuschemeng.7b03238>
3. Straume E. O., Morales R., Sum A. K. Perspectives on gas hydrates cold flow technology. *Energy & Fuels*. 2019;33(1): 1–15. DOI: <https://doi.org/10.1021/acs.energyfuels.8b02816>
4. Ribeiro C. P., Lage P. L. C. Modelling of hydrate formation kinetics: State-of-the-art and future directions. *Chemical Engineering Science*. 2008;63(8): 2007–2034. DOI: <https://doi.org/10.1016/j.ces.2008.01.014>
5. Englezos P., Kalogerakis N. E., Dholabhai P. D., Bishnoi P. R. Kinetics of gas hydrate formation from mixtures of methane and ethane. *Chemical Engineering Science*. 1987;42(11): 2659–2666. DOI: [https://doi.org/10.1016/0009-2509\(87\)87016-1](https://doi.org/10.1016/0009-2509(87)87016-1)
6. Song G., Li Y., Wang W., Zhao P., Jiang K., Ye X. Experimental study of hydrate formation in oil-water systems using a high-pressure visual autoclave. *AIChE Journal*. 2019;65(9): e16667. DOI: <https://doi.org/10.1002/aic.16667>
7. Liu Z., Song Y., Liu W., Lang C., Zhao J., Li Y. Formation of methane hydrate in oil–water emulsion governed by the hydrophilic and hydrophobic properties of non-ionic surfactants. *Energy & Fuels*. 2019;33(6): 5777–5784. DOI: <https://doi.org/10.1021/acs.energyfuels.9b01046>
8. Talatori S., Barth T. Rate of hydrate formation in crude oil/gas/water emulsions with different water cuts. *Journal of Petroleum Science and Engineering*. 2012;80(1): 32–40. DOI: <https://doi.org/10.1016/j.petrol.2011.10.010>
9. Avrami M. Kinetics of phase change. II Transformation-time relations for random distribution of nuclei. *Journal of Chemical Physics*. 1940;8(2): 212–224. DOI: <https://doi.org/10.1063/1.1750631>
10. Palodkar A. V., Mandal S., Jana A. K. Modeling growth kinetics of gas hydrate in porous media: Experimental validation. *Energy & Fuels*. 2016;30(9): 7656–7665. DOI: <https://doi.org/10.1021/acs.energyfuels.6b01397>
11. Susilo R., Ripmeester J. A., Englezos P. Methane conversion rate into structure H hydrate crystals from ice. *AIChE Journal*. 2007;53(9): 2451–2460. DOI: <https://doi.org/10.1002/aic.11268>
12. Naeiji P., Varaminian F. Differential scanning calorimetry measurements and modeling of methane + THF hydrate growth kinetics based on non-equilibrium thermodynamics. *Journal of Molecular Liquids*. 2018; 263: 22–30. DOI: <https://doi.org/10.1016/j.molliq.2018.04.107>
13. Choupin T., Fayolle B., Régnier G., Paris C., Cinquin J., Brule B. A more reliable DSC-based methodology to study crystallization kinetics: Application to poly(ether-ketone-ketone) (PEKK) copolymers. *Polymer*. 2018; 155: 109–115. DOI: <https://doi.org/10.1016/j.polymer.2018.08.060>
14. Tan C., Zhu J., Wang Z., Zhang K., Tian X., Cai W. The crystallization kinetics of Co doping on Ni–Mn–Sn magnetic shape memory alloy thin films. *RSC Advances*. 2018;8(45): 25819–25828. DOI: <https://doi.org/10.1039/c8ra04618b>
15. Derkach S. R., Kolotova D. S., Simonsen G., Simon S. C., Sjöblom J., Andrianov A. V., Malkin A. Y. Kinetics of crystallization of aqueous droplets in water-in-crude oil emulsions at low temperatures. *Energy & Fuels*. 2018;32(2): 2197–2202. DOI: <https://doi.org/10.1021/acs.energyfuels.7b03457>
16. Liu Z., Liu W., Lang C., Li Y., Yang M., Zhao J., Song Y. DSC studies of methane hydrate formation and dissociation in water-in-mineral oil emulsions. In: *Proc. 16th International Heat Transfer Conference (IHTC-16)*. 2018, 10-15 August, Beijing, China: 2018. p. 1607–1613. DOI: <https://doi.org/10.1615/ihtc16.cat.023453>

17. Drelich A., Dalmazzone C., Pezron I., Liggieri L., Clause D. DSC (Differential Scanning Calorimetry) used to follow the evolution of W/O emulsions versus time on ground and in space in the ISS. *Oil & Gas Sciences and Technology – Revue d'IFP Energies Nouvelles*. 2018;73(16): 1–9. DOI: <https://doi.org/10.2516/ogst/2018003>
18. Leister N., Karbstein H. Evaluating the stability of double emulsions – A review of the measurement techniques for the systematic investigation of instability mechanisms. *Colloids and Interfaces*. 2020;4(8): 1–18. DOI: <https://doi.org/10.3390/colloids4010008>
19. Koryakina V.V., Ivanova I.K., Semenov M.E., Rozhin I.I., Fedorova A.F., Shits E.Y. Specific features of the growth, composition, and content of natural gas hydrates synthesized in inverted oil emulsions. *Russian Journal of Applied Chemistry*. 2017;90(8): 1258–1265. DOI: <https://doi.org/10.1134/s1070427217080110>
20. Dill E. D., Folmer J. C. W., Martin J. D. Crystal growth simulations to establish physically relevant kinetic parameters from the empirical Kolmogorov–Johnson–Mehl–Avrami Model. *Chemistry of Materials*. 2013;25(20): 3941–3951. DOI: <https://doi.org/10.1021/cm402751x>
21. 2. Sakovich G.V. Zamechaniya o nekotorykh uravneniyakh kinetiki reaktsii s uchastiem tverdykh veshchestv, primenyaemykh v nastoyashchee vremya [Remarks on some equations of the kinetics of reactions involving solids currently used]. *Uchenye zapiski Tomskogo universiteta*. 1955; 26: 103–110. (In Russ.)
22. 3. Groysman A. G. *Teplofizicheskie svoystva gazovykh gidratov* [Thermophysical properties of gas hydrates]. Novosibirsk: Nauka Publ.; 1985. 95 p. (In Russ.)
23. 4. *Principles and Applications of Thermal Analysis*. Ed. P. Gabbott. Oxford, UK: Blackwell Publishing Ltd.; 2008. 464 p.
24. Ruitenbergh G., Woldt E., Petford-Long A. K. Comparing the Johnson–Mehl–Avrami–Kolmogorov equations for isothermal and linear heating conditions. *Thermochimica Acta*. 2001;378(1–2): 97–105. DOI: [https://doi.org/10.1016/s0040-6031\(01\)00584-6](https://doi.org/10.1016/s0040-6031(01)00584-6)
25. Stoporev A. S., Manakov A. Yu., Kosyakov V. I., Shestakov V. A., Altunina K. A., Strelets L. A. Nucleation of methane hydrate in water-in-oil emulsions: role of the phase boundary. *Energy & Fuels*. 2016;30(5): 3735–3741. DOI: <https://doi.org/10.1021/acs.energyfuels.5b02279>
26. Kislitsin A. A., Drachuk A. O., Molokitina N. S., Podenko L. S. Diffusion model of methane hydrate formation in “Dry Water”. *Russian Journal of Physical Chemistry A*. 2020;94(2): 405–411. DOI: <https://doi.org/10.1134/s003602442002017x>
27. Kodama T., Ohmura R. Crystal growth of clathrate hydrate in liquid water in contact with methane + ethane + propane gas mixture. *Journal of Chemical Technology & Biotechnology*. 2014; 89(12): 1982–1986. DOI: <https://doi.org/10.1002/jctb.4292>
28. Adamova T. P., Stoporev A. S., Manakov A. Y. Visual studies of methane hydrate formation on the water – oil boundaries. *Crystal Growth & Design*. 2018;18(11): 6713–6722. DOI: <https://doi.org/10.1021/acs.cgd.8b00986>
29. Dong S., Liu C., Han W., Li M., Zhang J., Chen G. The effect of the hydrate antiagglomerant on hydrate crystallization at the oil–water interface. *ACS Omega*. 2020;5(7): 3315–3321. DOI: <https://doi.org/10.1021/acsomega.9b03395>
30. Guo D., Ou W., Ning F., Fang B., Liu Z., Fang X., He Z. The effects of hydrate formation and dissociation on the water–oil interface: Insight into the stability of an emulsion. *Fuel*. 2020; 266: 116980. DOI: <https://doi.org/10.1016/j.fuel.2019.116980>

Information about the authors

Vladilina V. Koryakina, research fellow, Federal Research Centre “The Yakut Scientific Centre of the Siberian Branch of the RAS”, autonomous division of the Institute of Oil and Gas Problems of the Siberian Branch of the RAS, Technogenic Gas Hydrate Laboratory No. 3, Yakutsk, Russian Federation; e-mail: koryakinavv@ipng.ysn.ru. ORCID ID: <https://orcid.org/0000-0002-6650-0038>.

Elena Yu. Shitz, DSc in Engineering, Associate Professor, retired; e-mail: l.u.shitz@mail.ru.

All authors have read and approved the final manuscript.

Translated by Anastasiia Ananeva

Edited and proofread by Simon Cox