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Effect of a dispersive surfactant additive on wetting and crystallisation in a system: water–oil–metal substrate. Application to gas hydrates

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Abstract

To control the plugging of oil pipe-lines by the gas hydrate crystals, the dispersive surfactant additives can be injected into oil. We have studied the influence of such an additive (IPE 201 surfactant) on wetting and crystallisation in a simple model system, water–dodecane–steel substrate, having in mind applications to real hydrate crystals. It has been shown that this surfactant changes the wetting properties in the studied system: water wets a steel substrate less than dodecane, containing IPE 201. The morphology of the obtained ice crystals also changes in the presence of this surfactant: the crystal forms become more complex and fractal. As a consequence, the stability of the ice crystals with respect to the mechanical deformations is lowered. The obtained results will allow to understand the effect of the IPE 201 surfactant on the control of the real hydrate crystals formation. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dispersive surfactant additive; Gas hydrate crystals; Wetting; Crystallisation

1. Introduction

Gas hydrates are crystalline compounds that occur when water forms a cage-like structure around smaller guest molecules of natural gases (see Refs. [1,2]). The hydrate crystals may be formed in oil pipelines at high pressures (of the order of several MPa) and low positive temperatures (of the order of several °C). This phenomenon often takes place, for instance, in submarine pipe-lines. The hydrate-crystal formation generally starts at the metal pipe walls, e.g., at the surface, since there are a great number of crystallisation sites. Growing hydrate crystal aggregates may block the oil circulation and even cause serious damages to pipe-lines. That is why the control of the hydrate crystallisation is of key importance for the oil industry.

The usual practice for avoiding the plugging of the oil production facilities by hydrates is the addition of thermodynamic inhibitors such as methanol or glycol [2]. One of the new options under development is the injection of low-dosage additives, such as the 'hydrate dispersants' which prevent the agglomeration of hydrate particles by the formation of the hydrate-in-oil dispersion and allow them to be transported within the flow [3–5].

For the hydrate dispersants, one usually uses the tensioactive (or surfactant) substances—the so-called dispersive surfactants. These surfactants should, in principle, modify the wetting properties of a system, gas–water–oil–steel pipe walls, and diminish the attraction either between gas hydrate crystals and pipe walls or between separate hydrate crystals themselves. Thus, the forming hydrate plugs could be easily destroyed by the oil flow.

We have tried to study the effect of a dispersive surfactant on wetting and crystallisation in a relatively simple model system: water–oil (with a dispersive surfactant)–steel substrate, having in mind the application of the obtained results to real gas hydrate-forming compounds.

The unusual surface properties of water and ice attracted the considerable attention of scientists (see Refs. [6–8] and the literature cited therein). There exists also a number of publications concerning some aspects of the role of a surface in the gas hydrate crystallisation, namely: (i) the formation of hydrate crystals in the presence of the so-called 'third surfaces'—solid substances added into oil for the water absorption [9–11]; and (ii) the influence of the gas–water and gas–solid wall interfacial areas on the crystallisation of hydrates [12–14].

The effect of dispersive surfactants on the hydrate-crystal formation at the pipe walls, however, has not yet been studied in detail under laboratory conditions.

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2. Experimental procedure

2.1. Materials

For our experiments, we used ultra pure (Millipore system) water with a resistance $R = 18.2$ MΩ.

For oil, we used purified dodecane (Merck) with the addition of a 50% solution of the dispersive nonionic polymeric surfactant IPE 201 (product of IFP) in the hydrocarbon solvent Shell Sol. Furthermore, we will call this mixture 'the surfactant-containing oil', and c the concentration of the pure IPE 201 surfactant in it.

For metal substrates, we utilised the plane-parallel rectangular-form optically-polished inox steel plates. These substrates were carefully washed in pure acetone and ethyl alcohol and then dried in the laboratory oven for 1 h at $T = 100°C$, before each experimental test.

Note that we have even tried to study a real hydrate-forming system: water containing tetrahydrofuran (THF)–surfactant-containing oil—inox steel. THF allows the formation of the hydrate crystals at an atmospheric pressure and relatively high temperatures (about +4°C). However, the very high volatility of THF has not permitted us to carry out these experiments.

2.2. Equipment

The following experimental equipment were utilised in our work.

(1) The Wilhelmy balance—for the contact-angle and for the surface-tension measurements.

(2) The optical microscope–goniometer (Krüss), supplied with a video camera, for the contact-angle measurements.

(3) The experimental assembly (Fig. 1), consisting of the Linkam THMS 600 thermostatic cell, the Olympus BH2-UMA optical microscope, the Lauda RC6 thermostat, the video-recording system (the Sony CCD-IRIS video camera, the JVC BR-6400TR video tape recorder (VTR), the Sony Trinitron TV display) and the Macintosh IIx computer, was used for the microscopic observations in the reflected white light at low temperatures and for the stockade and treatment of the obtained video images.

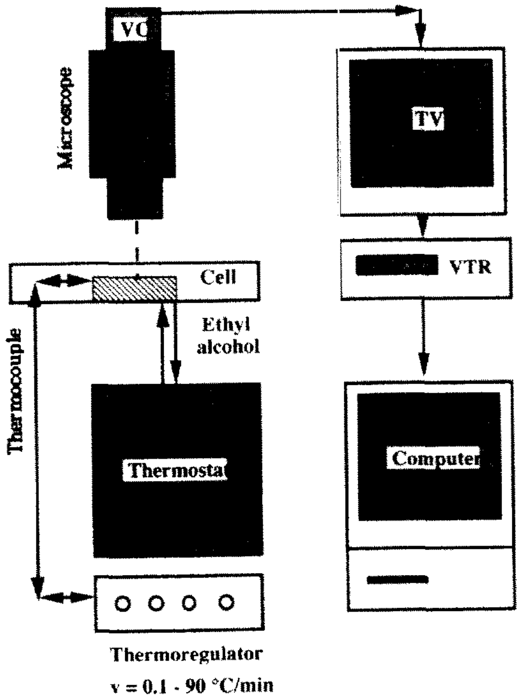

Fig. 1. Schematic representation of the experimental setup for the low-temperature microscopic observations.

Our thermostatic cell allowed us to heat or to cool a sample with rates lying in the limits 0.1–90°C/min. The temperature was measured with a thermocouple with an accuracy of 0.1°C. Heating was done by passing an electric current through the cell wire helix, cooling by circulating cold denatured ethyl alcohol between the thermostat and the cell. The minimal achieved temperature of a sample was about −30°C. The most often used rate of heating–cooling was 5°C/min.

3. Experimental results and discussion

3.1. Wetting

The critical micellar concentration (CMC) of the IPE 201 surfactant solution in oil was evaluated from the measurements of the surface tension γ_{ow} between the surfactant-containing oil and water for different c (Fig. 2). The CMC corresponded to the limit $\gamma_{ow}(c) \rightarrow$ constant at the $\gamma_{ow}(c)$ curve, and was found to be approximately equal to 0.006 mass%.

The wettability was studied by measuring the contact angles α in two different experimental situations:

1. For water drops placed at the inox steel plates in the surfactant-containing oil with different c,
2. For water drops placed at the inox steel plates in the air, with the surfactant-containing oil of different c poured further on.

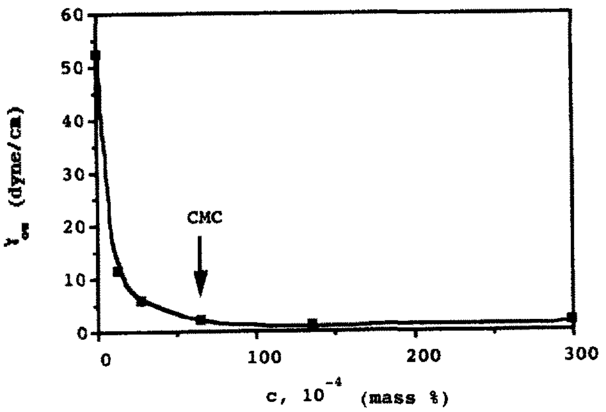

Fig. 2. The dependence of γ_{ow} upon c for the system: pure water–surfactant-containing oil (see the text). The CMC ≈ 0.006 mass%.

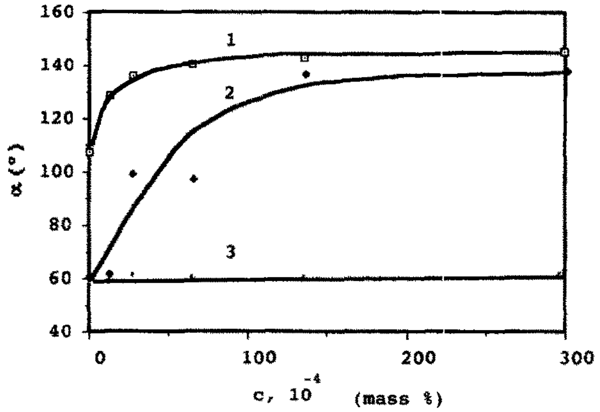

Fig. 3. The dependencies of the contact angle α of the water drops at steel substrate upon c: (1) drops placed into the surfactant-containing oil; (2) drops in the surfactant-containing oil, poured after the drop deposition; (3) drops in the air. All measurements are made after 1 h from the water drops' deposition.

The surfactant concentration dependencies of α exhibit different behaviour in both just-mentioned cases (Fig. 3), i.e., the contact-angle hysteresis (e.g., Ref. [15]). The first situation corresponds to the contact angle of the advancing drop (Fig. 3, curve 1), while the second one, to the contact angle of the retrieving drop (Fig. 3, curve 2).

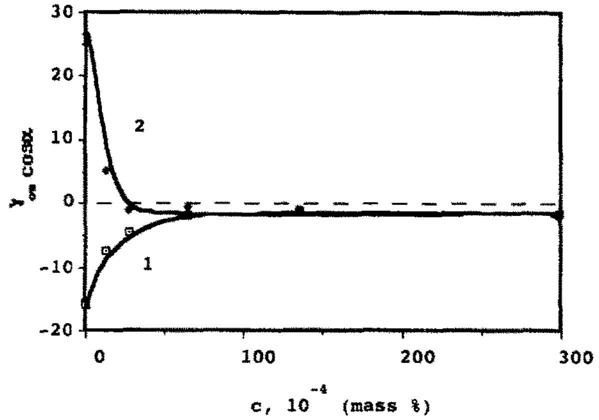

Fig. 4. The dependencies of the value $\gamma_{ow}\cos\alpha$ upon c, plotted from the data of Fig. 3. Curves 1 and 2 correspond to curves 1 and 2 of Fig. 3.

In Fig. 4, we have plotted the c-dependence of the multiplication of two experimentally measured values, γ_{ow} and cos α, which, according to the Young formula, is the difference between the oil–solid (γ_{os}) and water–solid (γ_{ws}) surface tensions:

$$\gamma_{ow}\cos\alpha=\gamma_{os}-\gamma_{ws}. \qquad (1)$$

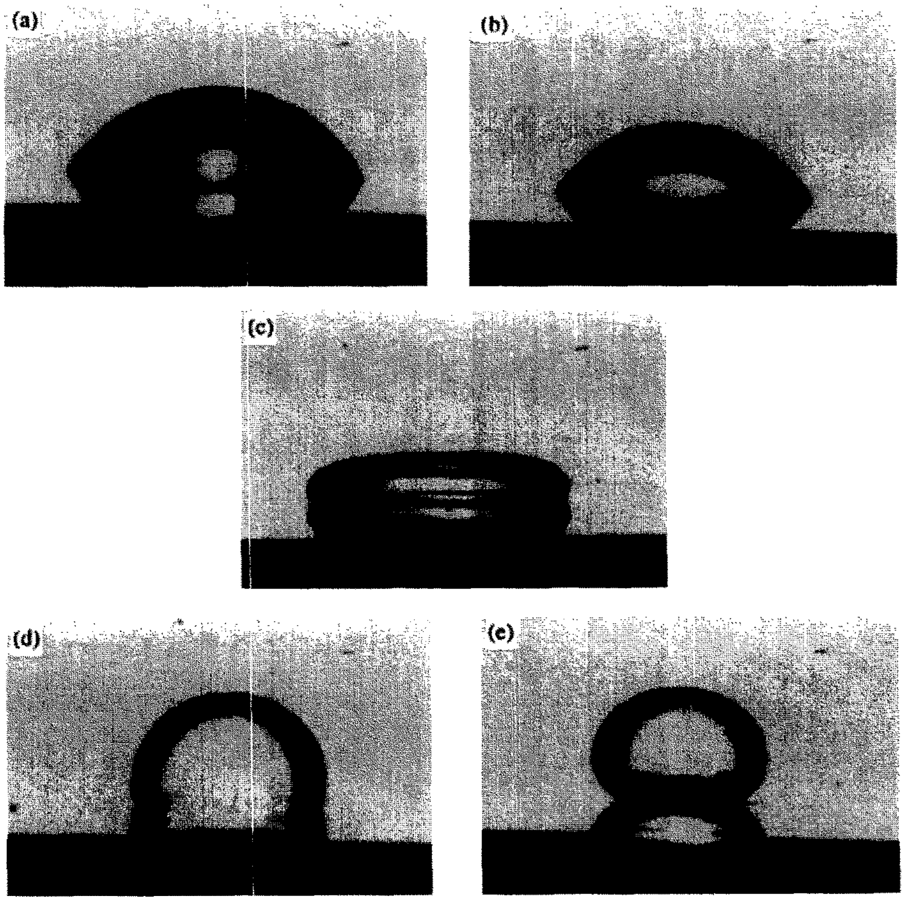

Fig. 5. Photographs of water drops placed on the inox steel plates: (a) a drop in the air; (b) the same drop in the poured pure dodecane; (c) a drop into the poured surfactant-containing oil ($c=0.03$ mass%); (d) a drop placed into the pure dodecane; (e) a drop placed into the surfactant-containing oil ($c=0.03$ mass%). All photographs are taken after 1 h from the water drops' deposition.

It is evident from Fig. 4 and Eq. (1), that for $c < \mathrm{CMC}$, the value $\gamma_{os} - \gamma_{ws}$ grows or diminishes with increasing c. Contrarily, for $c > \mathrm{CMC}$ $\gamma_{os} - \gamma_{ws} = \text{constant} < 0$. It means that at $c \approx \mathrm{CMC}$, the wettability in the studied system is changed considerably: for $c < \mathrm{CMC}$, water partially wets a steel surface and oil does not wet it, while for $c > \mathrm{CMC}$, water does not wet a steel surface, and oil partially wets it. The water drop photographs represented in Fig. 5 illustrate the just described wetting behaviour.

Thus, one should expect that the presence of the IPE 201 surfactant will influence the morphology of ice crystals in the studied system.

3.2. The water-in-oil emulsion formation

The water-in-oil emulsion was obtained as follows. An oil (the pure dodecane or the surfactant-containing oil) massive drop (about 1 mm in diameter) was placed at the inox steel substrate. Temperature was lowered gradually. As soon as small water droplets started to condensate from the atmosphere at the steel substrate, the initially flat front of the oil drop was deformed, and oil rapidly started to expand in the direction of the condensed water droplets, i.e., the water-in-oil emulsion forming wetting transition took place. Thus, the following condition was fulfilled:

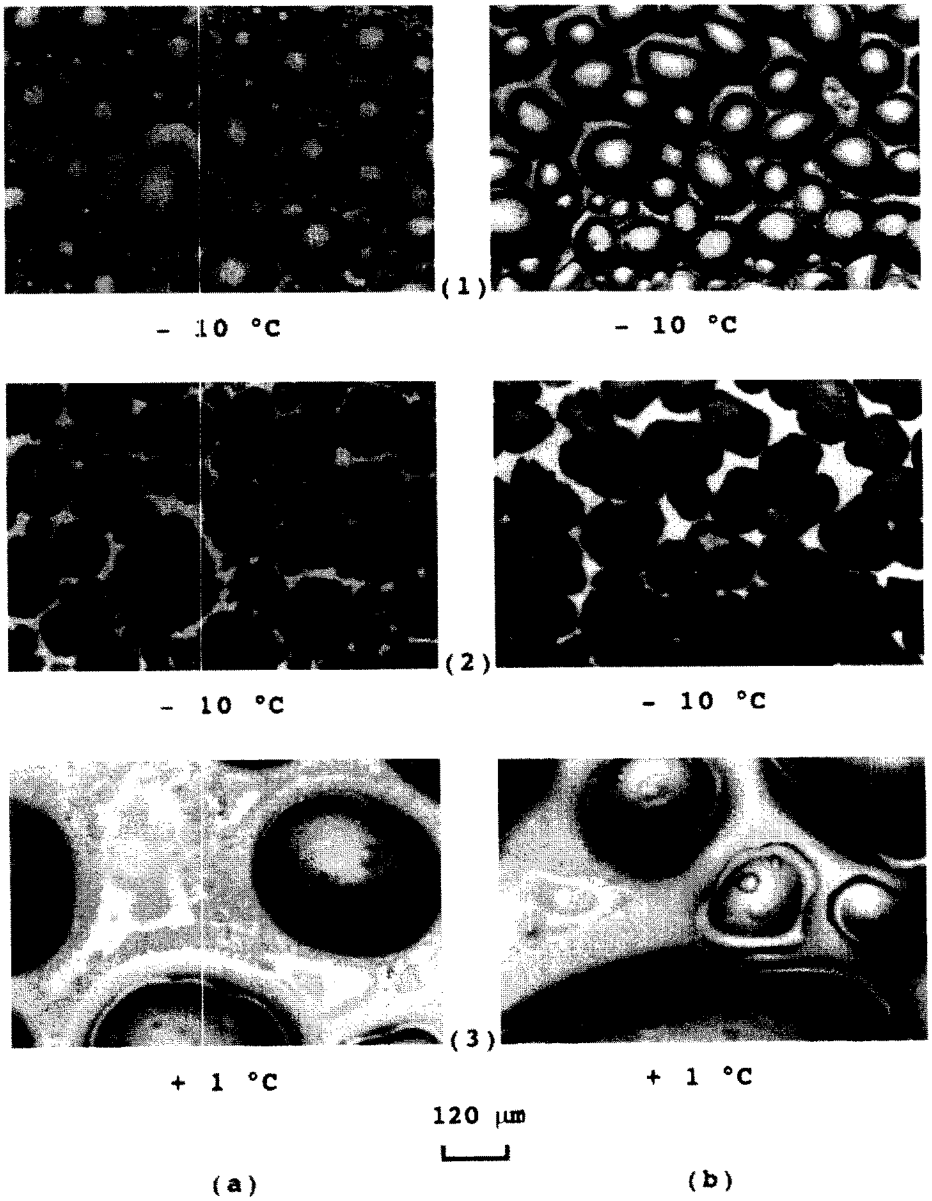

Fig. 6. Cooled (1), frozen (2) and melted (3) water-in-oil emulsions at the inox steel substrates for the following compositions of the emulsion oil part: (a) the pure dodecane; (b) the surfactant-containing oil ($c = 0.03$ mass%). Correspondent temperatures are shown below the photographs.

$$\gamma_{ow} < \gamma_{os}. \tag{2}$$

Here, γ_{ow} and γ_{os}, the surface tensions between oil and water and between oil and solid respectively, are fulfilled (for more details, see Ref. [16]).

As a result, all the substrate was covered with oil, and the water-in-oil emulsion was obtained.

No distinguished differences in the dynamics of the just-described wetting transition for drops of the pure dodecane and of the surfactant-containing oil have been observed, since the addition of the surfactant diminishes both γ_{ow} and γ_{os} (see Eq. (2)) [16].

However, there are some morphological differences between the water-in-oil emulsions, obtained in those two cases. If the emulsion is kept at a low temperature for some time (not sufficient for the ice formation), additional water will condense from the atmosphere, and the already existing water droplets will grow and coalesce with one another. In the case of pure dodecane, the water-in-oil emulsion is not stable: any two approaching water droplets will coalesce immediately. That is why such an emulsion consists of a great number of isolated spherical water droplets submerged in the oil (Fig. 6a,1). For the surfactant-containing oil, the water-in-oil emulsion, contrarily, will be more stable. Each water droplet in such an emulsion is surrounded by a surfactant monolayer, which prevents the immediate coalescence of the approached water droplets (see Ref. [17]). The water-in-oil emulsion in this case consists of a great number of water

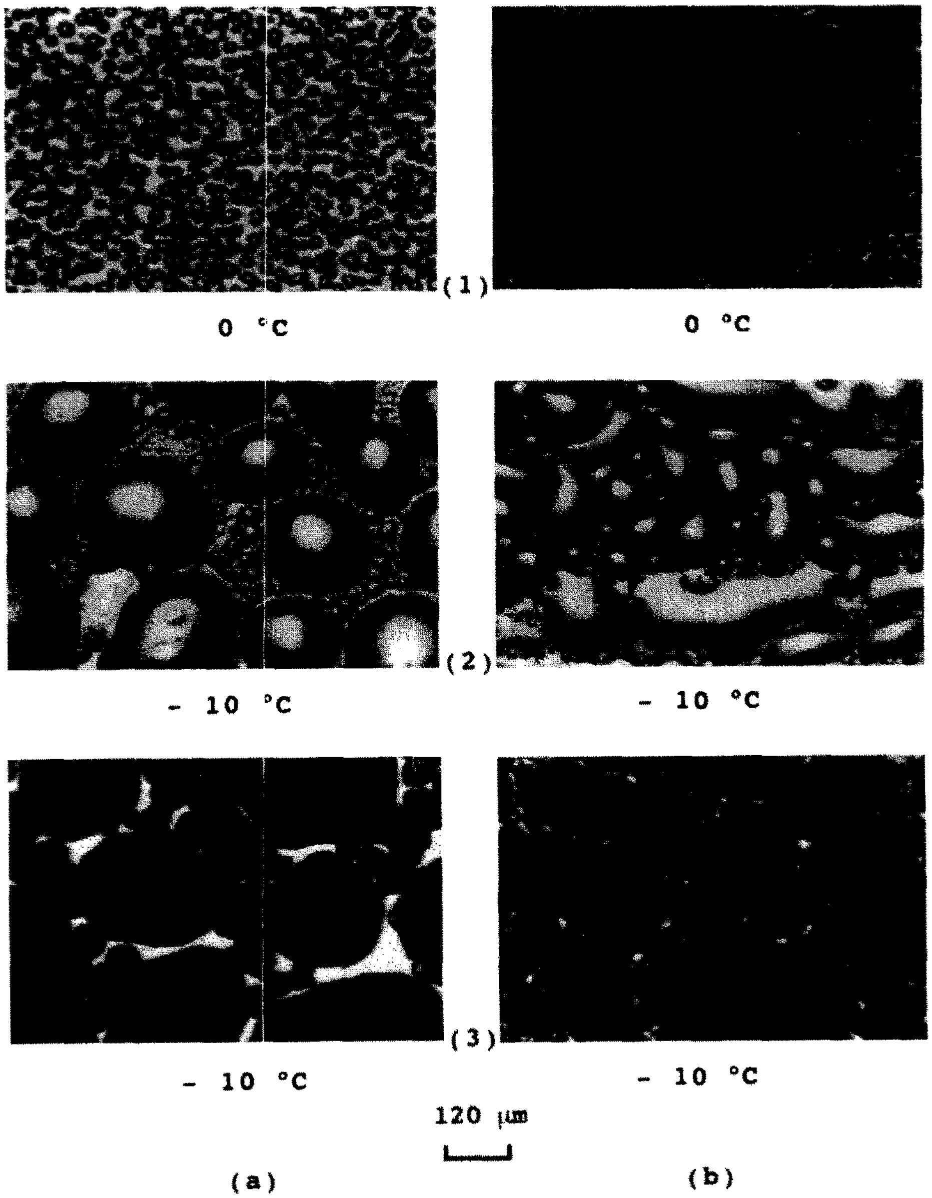

Fig. 7. Condensed (1, 2) and frozen (3) water droplets at the following solid substrates: (a) the pure inox steel; (b) the same steel covered with a dried layer of the surfactant-containing oil ($c = 0.03$ mass%). Correspondent temperatures are shown below the photographs.

aggregates submerged in the oil. Each such aggregate is composed of several mutually approached deformed water droplets in the process of coalescence (Fig. 6b,1).

3.3. *The ice crystallisation*

We kept the obtained water-in-oil emulsions (Fig. 6a,1 and b,1) at $T \approx -10°C$ (just above the crystallisation point of dodecane) for several minutes. As a result, water droplets were transformed into ice crystals, while oil rested in a liquid state (Fig. 6a,2 and b,2). It is clear from these figures that the morphological differences between the ice crystals, formed in the pure dodecane and in the surfactant-containing oil, are similar to those for the emulsions (see Fig. 6a,1 and b,1). Indeed, in the first case, the ice crystals are greater; they have a circular form and are separated form one another. In the second case, they are smaller, have more complicated (fractal) forms and are often associated in clusters.

If, further on, we heat our crystallised system, the ice aggregates melt at $T = 0°C$, and the water-in-oil emulsions with bigger (than the initial ones) water droplets are formed. The morphologies of these emulsions are similar in both just mentioned cases (Fig. 6a,3 and b,3).

To clarify the role of the surfactant in the ice crystallisation, we also carried out the two following test experiments.

(1) A clean inox steel substrate was gradually cooled. First, a lot of water droplets were condensed at a steel surface from the atmosphere (Fig. 7a,1 and a,2). These droplets were then frozen (Fig. 7a,3). The further heating of the obtained ice aggregates evidently led to their melting and the water droplets' evaporation.

(2) A procedure analogous to (1) was made with the inox steel substrate covered with the IPE 201 surfactant layer.

This layer was obtained as follows: A clean inox steel substrate was totally covered by a massive surfactant-containing drop ($c = 0.03$ mass%). Then, oil was evaporated in the laboratory oven at $T = 100°C$. As a result, only the surfactant IPE 201 macroscopic layer (possibly, containing a small amount of the Shell Sol solvent) rested at the steel surface.

The solid substrate prepared in this manner was gradually cooled. The water droplets condensed on it (Fig. 7b,1 and b,2) were then frozen (Fig. 7b,3). Further heating of the obtained crystalline structure led to melting of the ice aggregates and to the formation of the water-in-oil emulsions, similar to those shown in Fig. 6a,3 and b,3.

The difference between water droplets crystallised at the pure steel and at the steel covered with the IPE 201 surfactant film is clearly visible from Fig. 7a,3 and b,3. It is evident that the obtained crystalline structures are similar to those shown in Fig. 6a,2 and b,2.

Thus, the presence of the IPE 201 surfactant initiates the formation of more complex and, as a consequence, less mechanically stable ice crystals.

4. Conclusion

In conclusion, we have seen that the addition of the dispersive IPE 201 surfactant into the system water–dodecane–inox steel substrate, changes its wetting properties: water wets a steel substrate less than does the surfactant-containing oil. The ice crystals formed in the presence of IPE 201, are assembled in the more complex and, as a consequence, mechanically fragile aggregates, than those obtained without the surfactant. Further studies of the anchoring between ice crystals themselves and between glass crystals and a steel wall made, for instance, by the shear flow of an oil or by the mechanical vibration of a solid substrate are, however, needed.

The obtained experimental results will allow to understand the effect of the IPE 201 surfactant on the control of the real hydrate-crystal formation.

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