

Selection of Surfactants for Stable Paraffin-in-Water Dispersions, undergoing Solid–Liquid Transition of the Dispersed Particles

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A new experimental procedure is proposed for express evaluation of the coalescence stability of dispersions, in which the dispersed particles undergo solid–liquid phase transition. The procedure includes centrifugation of the dispersion concurrently with the phase transition of the particles and allows precise quantification of dispersion stability in terms of a critical pressure, at which the coalescence between the dispersed particles/drops takes place. The method is applied for studying the effects of surfactant type and concentration on the stability of paraffin-in-water dispersions, which have potential application in energy storage and transportation systems. Several types of water-soluble surfactants (anionic, nonionic, and polymeric) are compared, whereas hexadecane or tetradecane is used as a dispersed phase. Most of the studied individual surfactants are found to be inefficient stabilizers (except for the nonionic Tween 40 and Tween 60). However, the dispersion stability increases significantly after the addition of appropriate cosurfactants, such as hexadecanol, Brij 52, or cocoamidopropyl betaine. Surfactants and cosurfactants with longer hydrophobic tails are better stabilizers than those with shorter tails. The obtained results are discussed from the viewpoint of the mechanisms of particle/drop coalescence during the solid–liquid-phase transition. The consistency and the undercooling temperatures of the studied dispersions are also discussed, because these properties are important for their practical applications. The proposed procedure for evaluation of dispersion stability and some of the conclusions could be relevant to food emulsions, in which dispersed fat particles undergo solid–liquid-phase transition of similar type.

1. Introduction

Phase change materials (PCMs) are used in energy storage and transportation systems, because of their high “latent” heat, which can be released/absorbed during the phase transition of the material.^{1–7} While undergoing the phase transition, PCMs maintain the temperature of the system within a relatively narrow range, thus acting as a thermostating material. The most common PCMs are the ice slurries. Other examples are some gas clathrates, salt hydrates (CaCl₂·6H₂O; Na₂SO₄·10H₂O), poly(ethylene glycol), and paraffins (*n*-alkanes). PCMs find application in heat or cool storage devices, air-conditioning systems, and for cooling of electronic systems.

The paraffins have several advantages, which make them preferred PCMs in various applications: they have relatively large latent heat, low degree of undercooling,^{1,3,7–10} and low

vapor pressure; they are chemically inert, and they are stable. A serious problem for the application of bulk paraffins as PCMs is their low thermal conductivity, which hampers the heat exchange and, thus, makes the bulk paraffins applicable only in static energy storage and thermal insulation systems.

The paraffin dispersions in aqueous medium are more suitable for many applications, because the paraffin particles dispersed in a carrier fluid can be used for heat transport and for dynamic cooling/heating. As the surface-to-volume ratio is larger for the dispersed paraffins, the heat-exchange is greatly accelerated, which is a serious advantage in the applications. Three main methods have been proposed to stabilize paraffin-in-water dispersions of this type: micro-encapsulation, shape stabilization, and stabilization with surfactants.

In the case of microencapsulation, the paraffin is enclosed in a polymeric capsule.^{4–7,11} This method suffers from the disadvantage that the capsule walls can be mechanically damaged, as the paraffin expands and shrinks during phase transition and/or when the dispersion passes through pumps and other mechanical devices. To avoid this problem, the capsule walls must be relatively thick, which, however, leads to significant thermal resistance and a reduced heat exchange rate.¹¹

In the shape-stabilization method, the paraffin is impregnated in a supporting porous material.^{2,12} The shape-stabilized paraffins are appropriate bulk material for static energy storage and thermal insulation. Shape-stabilized paraffins can be used also for dynamic

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(1) Kurklu, A. Energy storage applications in greenhouses by means of phase change materials (PCMs): A review. *Renewable Energy* **1998**, *13*, 89.

(2) Xiao, M.; Feng, B.; Gong, K. Preparation and performance of shape stabilized phase change thermal storage materials with high thermal conductivity. *Energy Convers. Manage.* **2002**, *43*, 103.

(3) Choi, M.; Cho, K. Liquid cooling for a multichip module using Fluorinert liquid and paraffin slurry. *Int. J. Heat Mass Transfer* **2000**, *43*, 209.

(4) Maguire, M. T. Microwavable gel containing microencapsulated phase change material. U.S. Patent WO0122779, 2001.

(5) Akamatsu, Y.; Yoshikawa, M.; Chikazawa, A.; Ishiguro, M.; Kishimoto, A.; Maeda, S.; Nakahira, T.; Nakanishi, Y.; Setoguchi, T. Heat-accumulating microcapsule dispersion. U.S. Patent 5,916,478, 1999.

(6) Sengupta, S. Microencapsulated phase change material slurry heat sinks. U.S. Patent 5,007,478, 1991.

(7) Cho, K.; Choi, S. H. Thermal characteristics of paraffin in a spherical capsule during freezing and melting processes. *Int. J. Heat Mass Transfer* **2000**, *43*, 3183.

(8) Kraack, H.; Sirota, E. B.; Deuthsch, M. Measurement of homogeneous nucleation in normal-alkanes. *J. Chem. Phys.* **2000**, *112*, 6873.

(9) Uhlmann, D. R.; Kritchevsky, G.; Straff, R.; Scherer, G. Crystal nucleation in normal alkane liquids. *J. Chem. Phys.* **1975**, *62*, 4896.

(10) Turnbull, D.; Cormia, R. L. Kinetics of crystal nucleation in some normal alkane liquids. *J. Chem. Phys.* **1961**, *34*, 820.

(11) Brown, R. C.; Rasberry, J. D.; Overmann, S. P. Microencapsulated phase-change materials as heat transfer media in gas-fluidized beds. *Powder Technol.* **1998**, *98*, 217.

(12) Hong, Y.; Xin-shi, G. Preparation of polyethylene-paraffin compound as a form-stable solid-liquid phase change material. *Solar Energy Mater. Solar Cells* **2000**, *64*, 37.

thermal regulation in the form of dispersions containing relatively large particles ($> 100 \mu\text{m}$).

Alternatively, paraffin dispersions in aqueous medium can be stabilized by surfactants, which adsorb on the oil–water interface and, if appropriately chosen, prevent the particle coalescence. Surfactant-stabilized paraffin dispersions (SSPDs) have several advantages as compared to the microencapsulated and shape-stabilized paraffins. Micrometer-sized droplets/particles can be easily obtained by using standard and relatively cheap emulsification procedures. Such small particles exhibit efficient heat-exchange (due to the high surface-to-volume ratio) and do not cream rapidly. If significant coalescence between the dispersed particles occurs after a certain period of application, the initial drop-size distribution can be restored for minimal costs, by passing the used dispersion through a standard homogenizer. Another advantage of the surfactant stabilized PCM dispersions is the negligible thermal resistance of the protective surfactant layer. Last but not least, the surfactants prevent the deposition of the paraffin particles on the walls of the cooling/heating system and thus reduce the probability for obstruction of the equipment channels and pipes.

One of the most significant difficulties in the formulation of paraffin-in-water emulsions for thermal applications is the choice of appropriate surfactants, which should be able to stabilize the dispersed drops/particles in the moment of the phase transition. Another problem for the application of SSPDs, is the possible undercooling of the micrometer-sized paraffin droplets (decrease of the freezing temperature below that of the respective bulk paraffin). It was experimentally found that, although the undercooling of bulk paraffins is usually negligible, the dispersed paraffin drops could crystallize at temperatures well below the freezing temperature of the bulk paraffin.^{13–16} The degree of undercooling depends not only on drop size but also on the used surfactant.^{17–19} For these reasons, the appropriate choice of surfactants for stabilizing paraffin dispersions is of crucial importance for the practical application of these systems.

The standard procedure for testing the stability of paraffin dispersions is to subject them to multiple freeze–thaw cycles of the dispersed phase, possibly while circulating the dispersion through a model heat-exchange system.¹⁹ If the dispersion is unstable, the aqueous and paraffin phases separate partially after a given number of cycles; this number is used as a measure of dispersion stability. The circulation method requires special equipment, it is time-consuming (especially for the more stable systems), and no precise quantification of dispersion stability is possible. Furthermore, in the actual technological devices (air-conditioners, heat transportation systems), the dispersion is typically subject to strong local mechanical stresses, which may lead to drop–drop coalescence in emulsions that are otherwise

stable under static conditions or under pressure variations of lower magnitude.

The current paper describes an alternative procedure, which includes thawing of the dispersed particles while the dispersion is subject to centrifugation. The centrifugal field compresses the particles in the dispersion with controlled force (defined by the applied centrifugal acceleration), which can be precisely evaluated. In our procedure, the dispersion stability is quantified by the critical pressure, at which a continuous oil layer is released on top of the emulsion cream after melting of the dispersed paraffin particles. This pressure can be easily and accurately calculated from the experimental data, as explained in section 2.4. Important advantages of the current method are the use of a standard centrifuge and a relatively simple procedure, the precise quantification of the dispersion stability for wide range of systems (from very unstable to very stable), the possibility to compare the stability of 4–6 systems within 1–2 days. All of these advantages suggest that the method can be used as a standard procedure for comparing the stability of SSPDs, while varying the surfactant composition, drop size, oil phase, etc. In our previous studies, we successfully applied a similar procedure (without the thawing cycles) to study the effect of various factors on the coalescence stability of protein-stabilized emulsions, related to food systems.^{20–24}

To illustrate the applicability of the suggested procedure to SSPDs, in the current study, we compare the efficiency of various surfactants as dispersion stabilizers of hexadecane-in-water and tetradecane-in-water dispersions. The effects of the surfactant type, concentration, and chain-length were studied. Various surfactant mixtures were also studied and shown to be superior to the individual surfactants, if appropriate blends are formulated.

Beside the coalescence stability, the fluidity of the PCM dispersion is also important for many applications to ensure the dispersion circulation through the heat-exchange apparatus. The temperature range, in which the particles undergo the phase change, is another important property of these dispersions: the paraffin droplets should crystallize in a relatively narrow temperature range to maintain the temperature of the system within given limits. For these reasons, the crystallization temperature and the consistency of the paraffin dispersions are also studied.

2. Materials and Methods

2.1. Materials. Hexadecane or tetradecane (products of Merck) were used as oil phase in the studied PCM dispersions. The melting temperatures and the enthalpies of melting/freezing of these bulk paraffins are: $T_M = 5.8 \text{ }^\circ\text{C}$ and $\Delta H = 45.1 \text{ kJ/mol}$ for tetradecane and $T_M = 18.3 \text{ }^\circ\text{C}$ and $\Delta H = 53.4 \text{ kJ/mol}$ for hexadecane.²⁵

Two series of nonionic surfactants with the commercial names Brij (products of Aldrich) and Tween (products of ICI) were used as dispersion stabilizers. The Brij surfactants are polyoxyethylene

(13) Montenegro, R.; Antonietti, M.; Mastai, Y.; Landfester, K. Crystallization in miniemulsion droplets. *J. Phys. Chem. B* **2003**, *107*, 5088.

(14) Dickinson, E.; McClements D. J.; Povey, M. J. W. Ultrasonic investigation of particle size dependence of crystallization in *n*-hexadecane-in-water emulsions. *J. Colloid Interface Sci.* **1991**, *142*, 103.

(15) Phipps, L. W. Heterogeneous and homogeneous nucleation in supercooled triglycerides and *n*-paraffins. *Trans. Faraday Soc.* **1964**, *60*, 343.

(16) McClements, D. J.; Dungan, S. R.; German, J. B.; Simoneau, C.; Kinsella, J. E. Droplet size and emulsifier type affect crystallization and melting of hydrocarbon-in-water emulsions. *J. Food Sci.* **1993**, *58*, 1148.

(17) Awad, T.; Hamada, Y.; Sato, K. Effects of addition of diacylglycerols on fatty crystallization in oil-in-water emulsions. *Eur. J. Lipid Sci. Technol.* **2001**, *103*, 735.

(18) Katsuragi, T.; Kaneko, N.; Sato, K. Effects of addition of hydrophobic sucrose fatty acid oligoesters on crystallization rates of *n*-hexadecane in oil-in-water emulsions. *Colloids Surf. B* **2001**, *20*, 229.

(19) Coupland, J. N. Crystallization in emulsions. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 445. Vanapalli, S. A.; Palanuwech, J.; Coupland, J. N. Stability of emulsions to dispersed phase crystallization: effect of oil type, dispersed phase volume fraction, and cooling rate. *Colloids Surf. A* **2002**, *204*, 227.

(20) Tcholakova, S.; Denkov, N.; Ivanov, I. B.; Campbell, B. Coalescence in β -lactoglobulin stabilized emulsions: effects of protein adsorption and drop size. *Langmuir* **2002**, *18*, 8960.

(21) Tcholakova, S.; Marinov, R.; Denkov, N. D.; Ivanov, I. B. Evaluation of short-term and long-term stability of emulsions by centrifugation and NMR. *Bulg. J. Phys.* **2004**, *31*, 96.

(22) Tcholakova, S.; Denkov, N. D.; Sidzhakova, D.; Ivanov, I. B.; Campbell, B. Effects of electrolyte concentration and pH on the coalescence stability of β -lactoglobulin emulsions: Experiment and interpretation. *Langmuir* **2005**, *21*, 4842.

(23) Tcholakova, S.; Denkov, N. D.; Ivanov, I. B.; Campbell, B. Coalescence in protein stabilized emulsions. In *Proc. Third World Congress on Emulsions* Lyon, 2002; Paper No. 200.

(24) Denkov, N. D.; Tcholakova, S.; Ivanov, I. B.; Campbell, B. Methods for evaluation of emulsion stability at a single drop level. In *Proc. Third World Congress on Emulsions*, Lyon, 2002; Paper No. 198.

(25) Domalski, E. S.; Hearing, E. D. Heat capacity and entropies of organic compounds in the condensed phase. *J. Phys. Chem. Ref. Data* **1996**, *3*, 1.

alkyl ethers, which differ in the number of oxyethylene groups and the length of the alkyl chain. The following Brij surfactants were used: Brij 30 (polyoxyethylene-4 dodecyl ether), Brij 35 (polyoxyethylene-23 dodecyl ether), Brij 52 (polyoxyethylene-2 hexadecyl ether), and Brij 58 (polyoxyethylene-20 hexadecyl ether). Two mixtures of Brij surfactants were also tested: Brij 52/Brij 58 (45:55 wt %, both surfactants have hexadecyl chains with 16 C-atoms) and Brij 30/Brij 35 (80:20 wt %, both surfactants have dodecyl chains with 12 C-atoms). Each of these mixtures contains one water-soluble and one oil-soluble surfactant, and the weight ratios are chosen to ensure hydrophile-lipophile balance of the mixture $HLB \approx 11$. The latter value is recommended in the literature for stabilization of paraffin emulsions containing liquid droplets (see, e.g., ref 26).

Tween surfactants are polyoxyethylene-sorbitan alkylates, which have a sorbitan ring bound to hydrophilic chains of 20 oxyethylene groups and a hydrocarbon tail. The surfactants in this group differ in the length of the alkyl chain only. The series studied includes: Tween 20 (polyoxyethylene-20 sorbitan-monododecanoate with 12 C-atoms in the alkyl chain), Tween 40 (polyoxyethylene-20 sorbitan-monopalmitate with 16 C-atoms in the alkyl chain), Tween 60 (polyoxyethylene-20 sorbitan-monostearate with 18 C-atoms in the alkyl chain), and Tween 80 (polyoxyethylene-20 sorbitan-monooleate with 18 C-atoms and one double bond in the alkyl chain). As oil-soluble nonionic cosurfactant, we used hexadecanol (Chameleon).

The ionic surfactants were α -olefin sulfonate (α OS, product of Teocomb Bulgaria), sodium dodecyl trioxyethylene sulfate (SDP3S, product of KAO), sodium dodecyl sulfate (SDS, product of Acros), hexadecyltrimethylammonium bromide, and dodecyltrimethylammonium bromide (HTAB and DTAB, both products of Aldrich). As amphoteric water-soluble cosurfactant we used cocoamidopropyl betaine (Betaine, product of Goldschmidt Chemical Co.).

As polymer emulsifier, we tested poly(vinyl alcohol) (PVA, with $M_n \approx 12\,600$, $M_w \approx 63\,000$, degree of hydrolysis $\approx 88\%$, product of Rhodia).

To prevent the formation of ice crystals during the experiments, the aqueous phase contained 30 wt % of ethylene glycol as an antifreeze agent (product of Teokom). Thus, the freezing temperature of the aqueous phase was reduced down to $-14\text{ }^\circ\text{C}$. Sodium azide (0.1 g/L NaN_3 , product of Riedel-de Haën) was added to some of the surfactant solutions to prevent possible bacteria growth.

2.2. Dispersion Preparation. Paraffin-in-water emulsions were prepared by intensive stirring of 35 mL surfactant solution and 15 mL liquid oil (30 vol. % oil) with a rotor-stator homogenizer Ultra Turrax (Janke & Kunkel GmbH & Co, IKA-Labortechnik), operating at 13 500 rpm. The duration of stirring was fixed at 5 min, and the temperature was $25\text{ }^\circ\text{C}$, so that the paraffins were in a liquid state during this emulsification procedure.

2.3. Determination of Drop Size Distribution in the Emulsions. The drop size distribution was determined by optical microscopy.^{27,28} Specimens from the studied emulsions were taken immediately after emulsion preparation and were inserted in capillaries of rectangular cross-section, specially designed for microscope observations. The oil drops were observed in transmitted light with microscope Axioplan (Zeiss, Germany), equipped with objective Epiplan, $\times 50$, and connected to a CCD camera (Sony) and video-recorder (Samsung SV-4000). The diameters of the recorded oil drops were afterward measured (one by one), by using custom-made image analysis software, operating with Targa+ graphic board (Truevision, USA). The diameters of 1000 droplets of each sample were measured. The mean volume-surface diameter (called also "Sauter diameter"),

d_{32} , was calculated from the measured drop diameters by using the relation

$$d_{32} = \frac{\sum_i N_i d_i^3}{\sum_i N_i d_i^2} \quad (1)$$

where N_i is the number of drops with diameter d_i .

2.4. Evaluation of Dispersion Stability by Centrifugation. Since the procedure for evaluating the coalescence stability of the paraffin dispersions is essential for the current study and contains some original elements, it is described in more detail.

The following protocol for the centrifugation experiments was used. First, the studied dispersions were stored at $T = -10\text{ }^\circ\text{C}$ for 1 h 30 min to solidify the dispersed hexadecane or tetradecane drops (the aqueous medium remained in a liquid state). These pre-cooled dispersions were afterward centrifuged at a given acceleration, g_k , at $0\text{ }^\circ\text{C}$ for 1 h. Note that this temperature is lower than the melting point of the studied paraffins. Therefore, during this first period of centrifugation, the cream of particles compacted in the upper zone of the test tube, without particle melting. Afterward, the temperature in the centrifuge was gradually raised to $25\text{ }^\circ\text{C}$ (for about ≈ 30 min) without stopping the centrifuge, and the samples were centrifuged for additional 1 h. After stopping the centrifuge rotor, the temperature in the studied dispersions was measured to be always $> 22\text{ }^\circ\text{C}$, which is above the melting point of the studied oils. Therefore, the dispersed particles certainly melted during the second period of centrifugation, while being compressed under the action of a known centrifugal acceleration, g_k . The centrifuged samples were visually inspected for the presence of a continuous layer of oil, which could be released on top of the emulsion cream during centrifugation, as a result of drop coalescence. If no oil was seen on the surface of the dispersion, a new sample of the same composition was prepared and the experiment was repeated at higher centrifugal acceleration. Once the minimal acceleration was established, at which a continuous oil layer was released on top of the cream, the experiment was repeated to check the reproducibility of the result.

A standard 3K15 centrifuge (Sigma Laborzentrifugen, Germany) was used, and following our previous studies, we characterized the dispersion stability by the critical osmotic pressure, $P_{\text{OSM}}^{\text{CR}}$, at which a continuous oil layer was observed after finishing the centrifugation.²⁰ $P_{\text{OSM}}^{\text{CR}}$ was calculated from the experimental data, by using the equation²⁰

$$P_{\text{OSM}}^{\text{CR}} = \Delta\rho g_k (V_{\text{OIL}} - V_{\text{REL}})/A \quad (2)$$

where $\Delta\rho$ is the difference between the mass densities of the aqueous phase and the paraffin; g_k is the centrifugal acceleration; V_{OIL} is the total volume of oil used for preparation of the emulsion; V_{REL} is the volume of released oil at the end of centrifugation; and A is the cross-sectional area of the centrifuge test tube. The higher $P_{\text{OSM}}^{\text{CR}}$, the more stable is the dispersion. The typical reproducibility of $P_{\text{OSM}}^{\text{CR}}$, determined as described above, was $\pm 10\%$.

The method allows a rapid (~ 2.5 h) comparative test of 4–6 samples with relatively small volume required (~ 30 mL from each sample). The emulsion stability can be rated qualitatively by comparing the amount of oil released on top of the emulsion cream after centrifugation. The determination of $P_{\text{OSM}}^{\text{CR}}$ requires one to find the centrifugal acceleration leading to a release of a thin (1–2 mm) continuous oil layer on top of the cream, which demands typically 2–4 measurements with a given sample. More explanations about the principle of the method, along with various tests for its accuracy and many results obtained with protein-stabilized emulsions relevant to food systems can be found in refs 20–24.

2.5. Observation of Paraffin Particles in Polarized Light. Microscope observations of hexadecane-in-water dispersions were performed to assess the effect of surfactants on the freezing temperature of the hexadecane drops. A specimen of the studied

(26) Tsujii, K. *Surface activity*; Academic Press: San Diego, CA, 1998.

(27) Denkova, P. S.; Tcholakova, S.; Denkov, N. D.; Danov, K. D.; Campbell, B.; Shawl, C.; Kim, D. Evaluation of the precision of drop-size determination in oil/water emulsions by low resolution NMR spectroscopy. *Langmuir* **2004**, *20*, 11402.

(28) Sather, O. Video-enhanced microscopy investigation of emulsion droplets and size distributions. In *Encyclopedic Handbook of Emulsion Technology*; Sj blom, J., Ed.; Marcel Dekker: New York, 2001; Chapter 15, p 349.

Table 1. Critical Osmotic Pressure for Coalescence, P_{OSM}^{CR} , for Hexadecane Dispersions Stabilized by Individual Surfactants or Surfactant Mixtures^a

main surfactant	N_C	P_{OSM}^{CR} , kPa				
		without cosurfactant	cosurfactants with $N_C = 12$		cosurfactants with $N_C = 16$	
			Betaine	Brij 30	hexadecanol	Brij 52
SDP3S	12	≈ 0	≈ 0	≈ 0	> 120	not measured
DTAB	12	≈ 0	not measured	≈ 0	not measured	> 120
Brij 35	12	≈ 0	41 ± 5	35 ± 5	104 ± 5	> 120
HTAB	16	≈ 0	> 120	95 ± 5	> 120	> 120
α OS	16	≈ 0	120 ± 5	≈ 0	> 120	> 120
Tween 60	18	18 ± 2	102 ± 5	110 ± 5	100 ± 5	110 ± 5

^a The concentration of the main surfactant is 1 wt %, the cosurfactant is 0.5 wt %. N_C is the number of C atoms in the hydrophobic surfactant tail.

Table 2. Critical Osmotic Pressure, P_{OSM}^{CR} , for Tetradecane and Hexadecane Dispersions Stabilized by Mixtures of Brij Surfactants^a

surfactant mixture		N_C	dispersed phase	P_{OSM}^{CR} , kPa
surfactants	wt:wt ratio			
Brij 52/Brij 58	45:55	16/16	hexadecane tetradecane	> 120 > 120
Brij 30/Brij 35	80:20	12/12	hexadecane tetradecane	0 110 ± 5

^a The total surfactant concentration is 1 wt %. N_C is the number of carbon atoms in the hydrophobic surfactant tail.

Table 3. Undercooling Temperature, ΔT [°C] $\approx 18 - T_{FD}$, for Hexadecane Drops, Stabilized by Different Surfactants^a

surfactant	cosurfactant	N_C	ΔT , °C	consistency	P_{OSM}^{CR} , kPa
SDS	no	12	14	gellike	≈ 0
α OS	no	16	12	gellike	≈ 0
	Brij 52	16/16	12	fluid	> 120
	hexadecanol	16/16	10	fluid	> 120
Brij 35	no	12	15	fluid	≈ 0
Brij 58	no	16	7	gellike	≈ 0
	Brij 52	16/16	4	gellike	> 120
Tween 60	no	18	8	fluid	18 ± 2
	Brij 52	18/16	5	fluid	110 ± 5
	hexadecanol	18/16	5	fluid	100 ± 5

^a T_{FD} is the freezing temperature of the dispersed drops. The consistency and the critical osmotic pressure, P_{OSM}^{CR} , for hexadecane-in-water dispersions pre-cooled at $T_0 = -10$ °C are also presented. The total surfactant concentration is 1.0 wt % for the individual surfactants and for the Brij52/58 mixture. In the other mixtures, the concentrations are 1 wt % for the main surfactant and 0.5 wt % for the cosurfactant.

emulsion was introduced into a capillary with a rectangular cross-section ($50 \times 2 \times 0.1$ mm³), which was afterward placed in a metal cell with optical windows, connected to a thermostat (Digital One, Thermo Neslab). The sample was cooled with a cooling rate of ≈ 0.3 °C/min. The particles were observed in transmitted polarized light with the video-enhanced microscope system described in section 2.3. The crystallization was detected by the onset of optical birefringence of the paraffin particles.^{9,15} The temperature at which about 50% of the dispersed particles crystallized is quoted in Table 3 as the crystallization temperature of the respective sample.

2.6. Measurements of the Hexadecane/Surfactant Solution Interfacial Tension. The interfacial tension, σ , at the hexadecane/surfactant solution interface, was measured by drop shape analysis on DSA10 instrument (Kruss GmbH, Germany).

3. Results and Discussion

3.1. Effects of Paraffin Freeze–Thaw Cycle and of Surfactant Type on Dispersion Stability. To demonstrate the

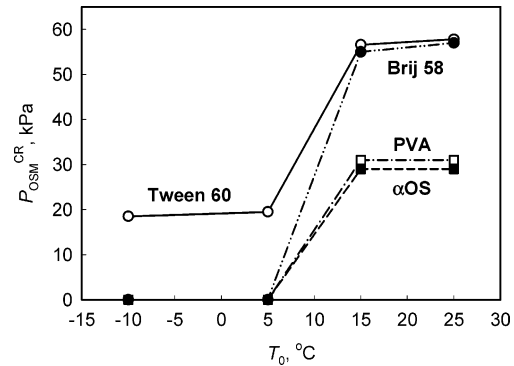


Figure 1. Critical osmotic pressure, P_{OSM}^{CR} , as a function of the pre-cooling temperature, T_0 for hexadecane-in-water dispersions stabilized by 1 wt % of Tween 60 (empty circles), Brij 58 (filled circles), PVA (empty squares), and α OS (filled squares). The mean volume-surface diameters, d_{32} , for these dispersions are 8 (Tween 60 and Brij 58), 12 (α OS), and 16 μ m (PVA).

effect of a paraffin freeze–thaw cycle on dispersion stability, we measured the critical pressure, P_{OSM}^{CR} , as a function of the temperature, T_0 , at which the dispersion was initially pre-cooled. Hexadecane-in-water emulsions, stabilized by 1 wt % of surfactant (Tween 60, Brij 58, α OS, or PVA), were pre-cooled for 1 h 30 min at three different temperatures, $T_0 = -10, 5,$ and 15 °C. In the meantime, reference samples of the same emulsions were shelf-stored at 25 °C. The dispersion pre-cooled at -10 °C was centrifuged for 1 h at 0 °C, as described in section 2.4, whereas the emulsions pre-cooled at 5 and 15 °C were centrifuged for 1 h at 5 and 15 °C, respectively. Then the temperature in the centrifuge was increased up to 25 °C and all dispersions were centrifuged for another 1 h. The reference emulsions were centrifuged for 3 h at 25 °C.

The obtained results for the dependence of P_{OSM}^{CR} on T_0 are presented in Figure 1. One sees that the stability of the dispersions stored at room temperature was similar to that of the emulsions pre-cooled at 15 °C (e.g., $P_{OSM}^{CR} \approx 58$ kPa for Tween 60 and Brij 58 stabilized samples), which was due to the fact that this pre-cooling temperature was not sufficiently low to induce freezing of the hexadecane drops (see Table 3). Therefore, the particles did not pass through a freeze–thaw cycle when the pre-cooling was performed at $T_0 = 15$ °C. In contrast, the stability of the dispersions pre-cooled at $T_0 = +5$ and -10 °C was significantly lower ($P_{OSM}^{CR} \approx 18$ kPa for Tween 60 and virtually zero for all other surfactants).

It is evident from Figure 1 that, for all surfactants, the emulsion stability decreased in a stepwise manner, when the pre-cooling temperature was changed from 15 to 5 °C. This was a clear indication that the phase transition of the hexadecane drops

(occurring within this temperature interval) destabilized these dispersions significantly. The respective mechanisms of dispersion destabilization are discussed in section 3.5.

Let us compare now the efficiency of the individual surfactants in stabilizing the hexadecane-in-water dispersions. Three different types of surfactant are compared in Figure 1: nonionic Brij 58 and Tween 60, anionic α OS, and polymeric PVA. The comparison shows that the noncooled emulsions containing nonionic surfactants have about two times higher stability, as compared to that of emulsions stabilized by PVA and α OS ($P_{\text{OSM}}^{\text{CR}} \approx 58$ kPa vs 30 kPa). This difference is at least partially due to the smaller mean drop diameter, d_{32} , in the emulsions stabilized by nonionic surfactants ($\approx 8 \mu\text{m}$ vs 12 and $16 \mu\text{m}$ for the other emulsifiers). Indeed, in our previous study, we showed that the critical osmotic pressure leading to drop-drop coalescence is approximately proportional to the inverse mean drop diameter, $P_{\text{OSM}}^{\text{CR}} \propto 1/d_{32}$.²⁰

For all of the individual emulsifiers studied, except Tween 60, almost all of the emulsified oil separated as a bulk oil phase after a single freeze-thaw cycle even without centrifugation; see Figure 1 and the results for the individual surfactants in Table 1. This means that the freezing/melting cycle of the dispersed paraffin particles led to a complete destabilization of most of the dispersions studied, which were stabilized by individual surfactants. Only Tween 60 was able to stabilize the dispersion to a certain extent after a freeze-thaw cycle, though the dispersion stability decreased about 3 times when passing through the phase transition of the particles ($P_{\text{OSM}}^{\text{CR}} \approx 18$ kPa vs ≈ 55 kPa).

The noticeable difference in the stability of pre-cooled dispersions containing Brij 58 and Tween 60 (0.5 vs 18 kPa), which had similar mean drop size, could be partially due to the different shape of the paraffin crystals formed upon freezing of the drops in these systems. Microscope observations showed that the paraffin crystals formed in the presence of Tween 60 were more compact and regular in shape, whereas many crystallites with needlelike and irregular shapes were formed in the dispersions stabilized by Brij 58. As discussed in section 3.5 below, needlelike and irregularly shaped crystals could destabilize significantly the system during the freezing-thaw cycles, due to the "pin effect" of the sharp particle edges.

3.2. Effect of Surfactant Chain-Length on Dispersion Stability. One series of experiments was aimed at evaluating the effect of the hydrocarbon chain length of the surfactant molecules on dispersion stability. For this purpose, we measured the critical osmotic pressure for hexadecane-in-water dispersions, pre-cooled at $T_0 = -10$ °C, which were stabilized by a series of surfactants from the Tween group, which had the same headgroup and different hydrocarbon tails. Thus, we compared Tween 20 (with 12 C atoms in the alkyl chain, including the carbon atom in the carboxyl group), Tween 40 (with 16 C atoms), Tween 60 (with 18 C atoms), and Tween 80 (again with 18 C atoms, but the alkyl chain contains a double bond).

The dependence of $P_{\text{OSM}}^{\text{CR}}$ on the length of the hydrocarbon chain is presented in Figure 2 and shows that Tween 40 and Tween 60 (with 16 and 18 C atoms, respectively) are much more efficient stabilizers in comparison with Tween 20 and Tween 80. In fact, the dispersion stabilized by Tween 20 was destroyed after the freeze-thaw cycle even without centrifugation.

The higher stability of emulsions containing Tween 40 and Tween 60 in comparison with that of Tween 20 and Tween 80 could not be explained by different drop sizes in these emulsions, because the mean drop diameter was almost the same for all Tween surfactants studied, $d_{32} \approx 7 \mu\text{m}$. Since the headgroup of these surfactants is also the same, the different emulsion stability

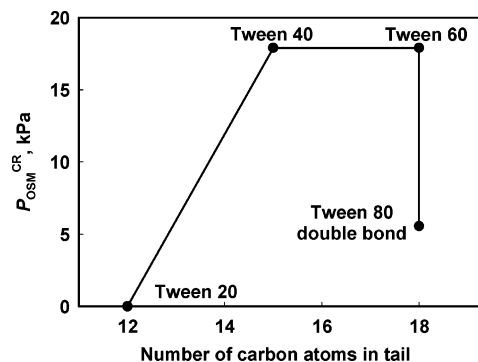


Figure 2. Critical osmotic pressure, $P_{\text{OSM}}^{\text{CR}}$, for hexadecane-in-water dispersions stabilized by 1 wt % Tween surfactants having different number of carbon atoms in the hydrophobic tail. The dispersions are initially pre-cooled at -10 °C for 1 h 30 min. The mean volume-surface diameters of the drops in these dispersions are very similar, $7.5 \pm 0.5 \mu\text{m}$.

could be related to variations in the length and structure of the hydrocarbon tails only.

The observed differences in the stability of these dispersions are probably due to different packing of the molecules in the adsorption layer. First, due to the longer chain lengths of Tween 40 and Tween 60 molecules, their adsorption free energy is higher than the respective energy of Tween 20 molecules. Presumably, the stronger adsorption energy leads to denser adsorption monolayer on the oil/water interface, which ensures higher dispersion stability. On the other hand, the presence of a double bond in the tail of Tween 80 molecules probably results in looser adsorption layers (despite the long chain-length), due to geometrical constraints, which preclude the formation of compact adsorption monolayers.

3.3. Effect of Cosurfactants on Dispersion Stability. The addition of appropriate cosurfactants is known to significantly improve foam and emulsion stability.^{26,29–35} For example, Betaine and other amphoteric cosurfactants are widely used to improve foam stability, when ionic surfactants such as SDS and SDP3S are used as main stabilizers.^{29–35} This effect is explained by the formation of denser adsorption layers, which stabilize more efficiently the emulsion and foam films against rupture.

For this reason, we studied the effect of Betaine as a water-soluble cosurfactant, on the stability of hexadecane dispersions pre-cooled at $T_0 = -10$ °C, see Table 1. As explained in section 3.1, for all individual surfactants (except Tween 60), separation of bulk oil was observed after 1 freeze-thaw cycle even without centrifugation, see Table 1. Similar results were obtained with the mixtures SDP3S + Betaine, evidencing that Betaine was an inefficient cosurfactant for the systems, in which the main surfactant contained 12 C atoms in the hydrophobic tail.

(29) Rosen, M. J. *Surfactants and interfacial phenomena*; Wiley-Interscience Publication: New York, 1989; Chapter 11.

(30) Lomax, E. G., Ed.; *Amphoteric surfactants*; Surfactant Science Series, Vol. 59; Marcel Dekker: New York, 1996.

(31) Patist, A.; Axelberd, T.; Shah, D. O. Effect of long chain alcohols on micellar relaxation time and foaming properties of sodium dodecyl sulfate solutions. *J. Colloid Interface Sci.* **1998**, *208*, 259.

(32) Domingo, X. Betaines. In *Amphoteric Surfactants*; Lomax, E., Ed.; Marcel Dekker: New York, 1996; Vol. 59, Chapter 3.

(33) Basheva, E.; Ganchev, D.; Denkov, N. D.; Kasuga, K.; Satoh, N.; Tsujii, K. Role of betaine as foam booster in the presence of silicone oil drops. *Langmuir* **2000**, *16*, 1000.

(34) Basheva, E.; Stoyanov, S.; Denkov, N. D.; Kasuga, K.; Satoh, N.; Tsujii, K. Foam boosting by amphiphilic molecules in the presence of silicone oil. *Langmuir* **2000**, *17*, 969.

(35) Danov, K. D.; Kralchevska, S. D.; Kralchevsky, P. A.; Ananthapadmanabhan, K. P.; Lips, A. Mixed solutions of anionic and zwitterionic surfactant (Betaine): Surface-tension isotherms, adsorption, and relaxation kinetics. *Langmuir* **2004**, *20*, 5445.

On the other hand, the dispersion stability was significantly enhanced when mixtures of Betaine and HTAB, α OS, or Tween 60 (surfactants with 16 or 18 C atoms) were used, see Table 1; the critical pressure was above 100 kPa in all these systems. This result could not be explained with the reduced drop size only (about twice smaller in the surfactant mixtures) and indicated that efficient protective layers of adsorbed surfactants were formed in these systems.

In another series of experiments, hexadecanol, Brij 52, and Brij 30 were evaluated as oil-soluble cosurfactants for dispersions stabilized by SDP3S, DTAB, Brij 35, HTAB, α OS, or Tween 60 as main water-soluble surfactant, see Table 1. As expected, the addition of oil-soluble cosurfactants led to significant improvement of dispersion stability. The addition of Brij 52 and hexadecanol (both with 16 C atoms in the chain) led to very high critical pressures, $P_{OSM}^{CR} > 100$ kPa, in all systems studied. On the other hand, the addition of Brij 30 (with 12 C-atoms) gave no or moderate improvement of emulsion stability for SDP3S, DTAB and Brij 35 (also with 12 C atoms) and significantly improved the stability of emulsions containing HTAB and Tween 60 containing 16 or 18 C atoms.

Summarizing, the data in Table 1 demonstrate a clear correlation between dispersion stability and the chain length of the surfactants. The surfactant mixtures containing only components with short tails (12 C atoms) are the poorest stabilizers, see the results for the systems SDP3S + Brij 30 or Betaine; DTAB + Brij 30; and Brij 35 + Brij 30 or Betaine. Most efficient are the mixtures containing oil-soluble and water-soluble components with 16 C atoms: e.g., α OS + hexadecanol or Brij 52 and HTAB + hexadecanol or Brij 52. Dispersions stabilized by a mixture of surfactants with tails of different lengths (16 and 12 C atoms) in most cases exhibited relatively high stability: SDP3S + hexadecanol; DTAB or Brij 35 + Brij 52; HTAB or α OS + Betaine. The only significant exception from these trends was the mixture of α OS and Brij 30, which showed rather low stability.

To check whether only the chain-length of the surfactants is important, or it is also the matching of the surfactant tails with the oil molecules, we compared the critical osmotic pressures for tetradecane and hexadecane emulsions, stabilized with two mixtures of Brij surfactants, see Table 2. Each mixture contained one water-soluble and one oil-soluble surfactant with equal alkyl chain-lengths: the surfactants in the Brij 30/35 mixture had 12 C atoms, whereas the surfactants in the Brij 52/58 mixture had 16 C atoms. Both mixtures had the same HLB ≈ 11 , which is considered to be appropriate for stabilizing alkane-in-water emulsions without phase transition of the dispersed drops.³⁶

As seen from Table 2, the mixture Brij 52/58 (16 C-atoms) is very efficient for stabilization of both the tetradecane and hexadecane emulsions. On the other hand, the Brij 30/35 mixture (12 C atoms) stabilizes relatively well only the tetradecane emulsion. These experiments show that only surfactants with sufficiently long hydrophobic tails are efficient in stabilizing the hexadecane dispersions undergoing phase transition. For tetradecane dispersions, one can use surfactants with somewhat shorter tails (12 C atoms). These results indicate also that the HLB number, used to choose surfactants for conventional emulsions,³⁶ cannot be employed directly for dispersions, in which the particles undergo freeze–thaw cycles; the chainlength of the surfactants is also very important in the latter systems.

3.4. Effect of Surfactant Concentration on Dispersion Stability. The effect of total surfactant concentration on the

stability of hexadecane dispersions was studied with the mixture Brij 52/58. The critical pressure, P_{OSM}^{CR} , increased from ≈ 0 to 76 kPa when the total surfactant concentration was increased from 0.1 up to 0.3 wt %. At even higher concentration, $C_{TOT} = 1$ wt %, P_{OSM}^{CR} was higher than 120 kPa, which was the upper limit of the critical pressures that could be measured in our equipment.

The increased dispersion stability with C_{TOT} is related to two effects: (1) The mean drop size of the dispersions, d_{32} , decreased from ≈ 15 to 5 μm with the increase of C_{TOT} from 0.1 to 1 wt %, and (2) the higher surfactant concentration, C_{TOT} , probably led to the formation of a denser adsorption layer on the drop surface. It is difficult to make analysis of the second effect without a large set of additional experiments, because the surfactants in the used mixture can redistribute between the oil and water phases, and their partitioning coefficient could depend on temperature, surfactant concentration, and other factors.

Following the approach from ref 37, one could estimate approximately the minimal surfactant concentration needed to ensure stable dispersion with a given mean drop diameter. By making a mass balance of the surfactant initially dissolved in the aqueous phase and the adsorbed surfactant after the dispersion formation, one obtains the following expression, which relates the surfactant adsorption, Γ , with the change in the surfactant concentration as a result of adsorption:

$$\Gamma = \frac{d_{32}(C^{INI} - C^{END})(1 - \Phi)}{6\Phi} \quad (3)$$

Here C^{INI} is the initial surfactant concentration before emulsification, C^{END} is the final surfactant concentration in the aqueous phase after emulsification, d_{32} is the mean surface–volume drop diameter, and Φ is the oil volume fraction in the emulsion. Assuming that almost all of the dissolved surfactant is adsorbed on the drop surface, $C^{INI} \gg C^{END}$, and taking typical values for the adsorption, $\Gamma \approx 2$ mg/m², one derives that the minimal surfactant concentration needed to obtain a dispersion with given d_{32} is

$$C_{MIN}^{INI} \approx \frac{1.2\Phi}{d_{32}(1 - \Phi)} \quad (4)$$

where d_{32} is expressed in micrometers, C is expressed in wt %, and the oil volume fraction Φ is dimensionless. The comparison of eq 4 with the experimental data showed a reasonable agreement; we needed about 0.05 wt % of water-soluble surfactant (0.1 wt % in total) to obtain stable dispersion with $d_{32} \approx 15$ μm and $\Phi = 0.3$, against 0.034 wt % predicted by eq 4. For further discussion of the effect of emulsifier concentration and adsorption on the coalescence stability of emulsions, see refs 37–39.

3.5. Mechanisms of Emulsion Destabilization during Solid–Liquid-Phase Transition of the Dispersed Particles. Two possible scenarios of emulsion destabilization due to solid–liquid phase transition of the particles have been discussed in the literature and are briefly reproduced here in view of our experimental results.^{40–45}

(37) Tcholakova, S.; Denkov, N. D.; Sidzhakova, D.; Ivanov, I. B.; Campbell, B. Interrelation between drop size and protein adsorption at various emulsification conditions. *Langmuir* **2003**, *19*, 5640.

(38) Tcholakova, S.; Denkov, N. D.; Danner, T. Role of surfactant type and concentration for the mean drop size during emulsification in turbulent flow. *Langmuir* **2004**, *20*, 7444.

(39) Tcholakova, S.; Denkov, N. D.; Ivanov, I. B.; Campbell, B. Coalescence stability of emulsions containing globular milk proteins. *Adv. Colloid Interface Sci.* **2006**, in press.

(40) Garrett, P. R. The mode of action of antifoams. In *Defoaming: Theory and Industrial Applications*; Garrett, P. R., Ed.; Marcel Dekker: New York, 1993.

(36) *The HLB System*; Guide from ICI Surfactants; ICI Surfactants: Wilmington, DE, 1992.

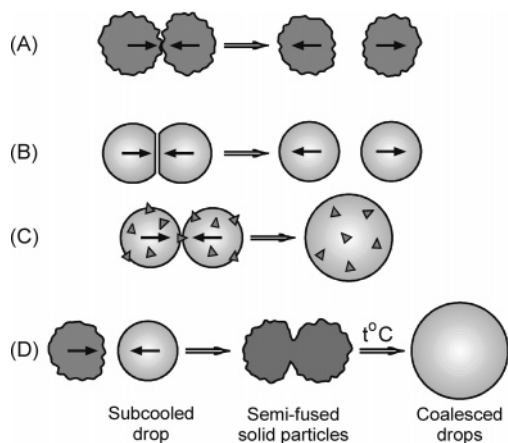


Figure 3. Possible scenarios for destabilization of dispersions due to solid–liquid-phase transitions: (A) two solid particles collide and rebound; (B) stable emulsion film is formed between two colliding drops; no particle/drop fusion is expected in A and B; (C) particles undergoing phase transition: the solid crystals are able to break the films between the droplets and the drops can coalesce; (D) crystallization induced by contact between solid particle and undercooled drop.

The first mechanism involves coalescence, which occurs when two semi-liquid droplets collide with each other, whereas the collision between the liquid drops or two solid particles of the same composition might not lead to coalescence. By way of illustration, in Figure 3A, we show schematically two solid paraffin particles which collide and rebound, because the point contacts between them do not lead to sufficiently strong adhesion force (the contact area is too small) so that the particles can be easily separated after contact. On the other hand, when two liquid drops collide with each other, a plane-parallel film is formed between them, see Figure 3B. If appropriate surfactants are used, the emulsion film that intervenes between the colliding drops is stabilized by steric or electrostatic repulsive forces and the drop–drop coalescence is again difficult (no direct contact between the drop surfaces is realized). However, if semisolid droplets collide, the paraffin crystals protruding from the drop surface into the aqueous phase can tear the film between the drops, see Figure 3C. This “pin” effect of the solid particles, which could facilitate the coalescence of liquid drops, is well documented in the studies on the antifoam effect of oil–solid compounds used to destroy undesirable foam (see, e.g., refs 40–42). A similar pin effect of the fat crystals is known from the studies of food emulsions.^{43,44}

We were able to observe microscopically the pin effect of the crystals in semisolid hexadecane particles, formed during the solid–liquid-phase transition. Figure 4 shows photos obtained by optical microscopy of pre-cooled hexadecane particles, dispersed in 2 wt % SDS solutions. The studied dispersion was contained in a thermostated capillary with rectangular cross-section, as described in section 2.3. In Figure 4A, the temperature was maintained below 18 °C, which is the melting temperature of hexadecane – the particles behaved as distinct entities and could be easily separated from each other upon stirring of the

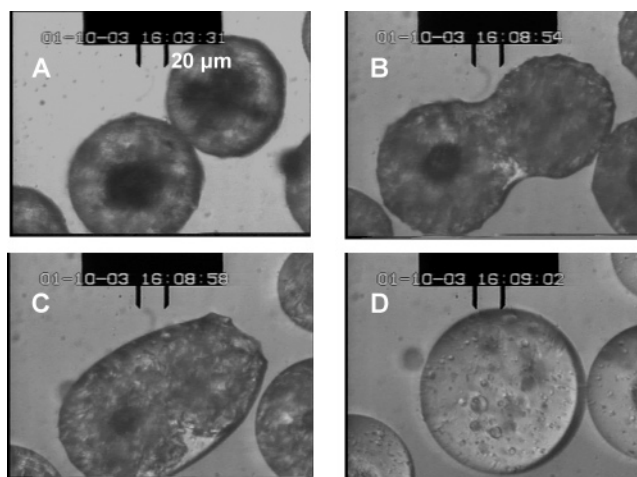


Figure 4. Fusion of hexadecane particles, assisted by the solid–liquid-phase transition, as observed by optical microscopy: (A) $T < 18$ °C, (B) $T \approx 18$ °C, (C and D) $T > 18$ °C. The hexadecane melts at $T = 18$ °C. The particles are stabilized by 2 wt % SDS (the distance between the dark vertical bars is 20 μm).

dispersion. In Figure 4B, the temperature of the sample had been raised to 18 °C. There was a partial fusion of the semisolid particles formed at the hexadecane melting temperature. The further increase of temperature led to a complete fusion of the two contacting hexadecane particles, Figure 4C. Once liquid drops were formed at higher temperature, they did not coalesce upon contact, see Figure 4D.

The second scenario of dispersion destabilization involves collision between a solid particle and an undercooled droplet, see Figure 3D.⁴⁵ This scenario is possible when the emulsion droplets crystallize primarily via homogeneous nucleation.^{8,9,14} Since the nucleation is a stochastic process, it probability rapidly decreases with the decrease of drop size, i.e., statistically averaged the bigger droplets crystallize at higher temperatures. The inherent polydispersity of the emulsions leads to existence of a certain temperature range (which could be as large as 10–15 °C), in which the dispersed drops crystallize. In this interval, the probability for collision of solid particles and undercooled liquid drops is rather high. Upon such a collision, the solid particle can initiate crystallization in the liquid droplet, accompanied with partial fusion between them. After subsequent heating and melting of the frozen hexadecane particles, such partially fused particles coalesce and form bigger drops. Therefore, subsequent freeze/thaw cycles would lead to an increase of the mean drop size and to eventual release of bulk oil on the emulsion surface. This mechanism was also observed in some of the systems studied, as explained in the following section 3.6.

3.6. Fluidity of the Paraffin Dispersions. For many applications, the PCM dispersions should be fluid in order to circulate through a heat-exchange system. All emulsions in the current study were fluid when the dispersed paraffin was in a liquid state, which is due to the moderate volume fraction of the dispersed drops, $\Phi = 30\%$ (the yield stress of emulsions usually appears when Φ is above the close-packing concentration of spherical drops, $\Phi > 74\%$). On the other hand, many of the studied dispersions acquired significant yield stress and appeared gellike after the temperature was reduced down to -10 °C and the dispersed particles solidified, see Table 3. Note that the aqueous phase remained liquid at -10 °C, due to the added antifreeze (30 wt % ethylene glycol), so that the observed gelling of these dispersions could be due only to strong interaction between the solidified particles.

(41) Hadjiiski, A.; Tcholakova, S.; Ivanov, I. B.; Gurkov, T. D.; Leonard, E. F. Gentle film trapping technique with application to drop entry measurements. *Langmuir* **2002**, *18*, 127.

(42) Denkov, N. D. Oil based antifoams. *Langmuir* **2004**, *20*, 9463.

(43) Rousseau, D. Fat crystals and emulsion stability – A review. *Food Res. Int.* **2000**, *33*, 3.

(44) Boode, K.; Walstra, P. Partial coalescence of oil-in-water emulsions. I. Nature of the aggregation. *Colloids Surf. A* **1993**, *81*, 139.

(45) Hindle, S.; Povey, M. J. W.; Smith, K. Kinetics of crystallization in n-hexadecane and cocoa butter oil-in-water emulsions accounting for droplet collision-mediated nucleation. *J. Colloid Interface Sci.* **2000**, *232*, 370.

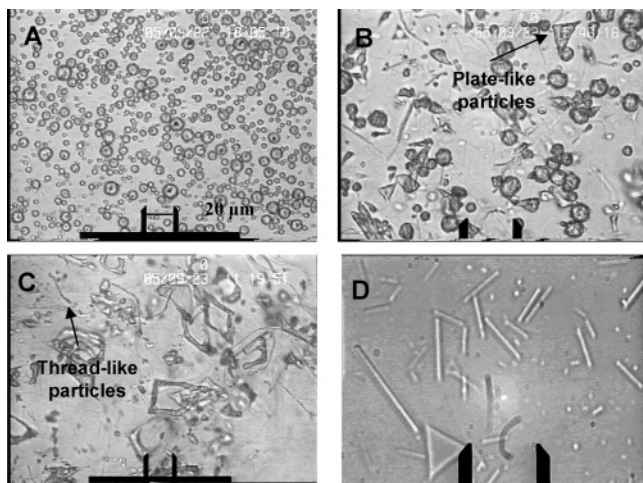


Figure 5. Hexadecane particles frozen in different surfactant solutions: (A) 1 wt % SDS; (B) 1 wt % α OS + 0.5 wt % hexadecanol; (C) 1 wt % Brij 58/Brij 52; (D) intermediate phases observed during the freezing process of the drops in Brij 58/Brij 52 solution. The distance between the vertical dark bars is 20 μ m

The observations of the gellike dispersions revealed that they could be classified into two distinct groups:

(a) Unstable after a freeze–thaw cycle. The aqueous and the paraffin phases completely separated after 1 freeze–thaw cycle, even without centrifugation. All hexadecane emulsions stabilized with individual ionic surfactants were of this type.

(b) Stable after freeze–thaw cycles. For example, the hexadecane and tetradecane dispersions stabilized by Brij 58/52 mixture proved to be very stable with respect to drop-drop coalescence after many freeze–thaw cycles, despite the emulsion gelling at low temperatures (see Table 3).

The origins of the yield stress of these two types of dispersions are rather different:

The low stability and the significant yield stress of the unstable dispersions were interrelated, because the microscope observations showed that their gelling structure consisted of a network of partially fused particles. The formation of this network can be easily explained by considering the second mechanism of dispersion destabilization described in section 3.5. When an undercooled drop collides with a solid particle, they can partially fuse in the process of drop freezing (see Figure 3D). As a result, aggregates of partially fused particles form, which arrange at a certain stage into a three-dimensional paraffin network, impregnated by the aqueous phase. Thus, a bicontinuous paraffin/water structure is formed which prevents the free flow of the system. The subsequent increase of temperature melts the paraffin and the particles coalesce, forming larger drops as depicted in Figure 3D and, eventually, a separate bulk oil phase.

The dispersions in the second group were very stable despite their significant yield stress below the freezing temperature of the drops. The hindered flow in these dispersions is attributed to the highly elongated shape of the frozen particles (see Figure 5 for photos showing particles of different shapes in the systems studied). Indeed, microscopic observations showed that the crystallization of hexadecane and tetradecane droplets, stabilized with the Brij 58/52 mixture, resulted in the formation of particles with highly elongated shapes, see Figure 5C,D. These elongated particles could form a three-dimensional (3D) structure even without direct contacts between the particle surfaces. In these systems, short-ranged electrostatic or steric repulsion between the particles prevents their fusion, but the geometrical constraints, imposed by the particle shape, hinder the free flow of the

suspension. The particle melting in such dispersions leads to restoration of the spherical drop shape without drop–drop coalescence, so that the original free-flowing emulsion is restored after a freeze/thaw cycle. Such gelling dispersions could be used for static energy storage devices but are inappropriate for dynamic heat exchangers.

The observations showed that, as a general trend, the droplets stabilized with long-chained nonionic surfactants (Tween 40, Tween 60, and Brij 58) solidified in platelike and threadlike shapes, whereas the particles were spherical in solutions of the anionic surfactants α OS, SDS, and SDP₃S. Some cosurfactants were found to affect the shape of the frozen particles. For example, the frozen hexadecane particles stabilized with α OS were spherical, whereas the addition of hexadecanol as an oil-soluble cosurfactant led to the formation of some fraction of platelike particles, see Figure 5B.

3.7. Effect of Surfactants on Temperature of Particle Freezing. The practical application of PCM dispersions is often related to a requirement for maintaining a narrow temperature range of the dispersion, while it circulates through the heat-exchange system. This temperature range is determined to a large extent by the temperature interval, in which the dispersed particles freeze and thaw. The thawing of the particles occurs at temperatures close to the melting point of the bulk material. However, the freezing of the dispersed drops could be strongly hampered by the low probability for formation of solid nuclei in the small volume of micrometer-sized drops.^{13–19} This undercooling effect could be very significant for paraffin-in-water dispersions, despite the fact that the bulk paraffins exhibit a very low degree of undercooling in comparison with many other organic liquids.^{8–10}

The reason for the more pronounced paraffin undercooling in emulsions could be explained by comparing the nucleation mechanisms in bulk materials and emulsions.^{8–19} The nucleation in bulk phases is known to be predominantly heterogeneous, which implies that the solid nuclei are first formed on the solid walls of the container and on the surface of solid particles, which are always present as contaminations. Thus, one solid particle could induce the nucleation and subsequent freezing of the entire bulk material. When the paraffin is dispersed into small drops, the contact of the paraffin with solid walls is eliminated and the contaminating solid particles are distributed among the drops. In typical emulsions, the probability to find a solid particle in a droplet is relatively low, and therefore, the freezing of dispersed drops in emulsions occurs predominantly through a homogeneous nucleation. The smaller the droplets, the lower the probability for formation of homogeneous or heterogeneous nucleus, which results in a higher degree of undercooling.

The above consideration suggests two possible ways for suppressing the undercooling phenomenon in the studied emulsions:

(1) Addition of solid particles. One can introduce solid particles in the paraffin phase to act as nucleation sites in each droplet. The particles should be of nanometer size (preferably with diameter below 10–20 nm) for two reasons: First, to avoid the possible “pin” effect of these particles, which could deteriorate emulsion stability. Second, because a low weight concentration of such small particles would be sufficient to ensure at least one or several particles in each drop. This approach would require a very good chemical compatibility of the particles with the paraffin phase, to avoid the possible ejection of the particles from the paraffin drops after several freeze–thaw cycles. Thus, appropriate surface treatment of the particles might be needed.⁴⁶ We have not tested this approach to reduce the undercooling

phenomenon (it goes beyond the scope of our study), although it presents a distinct interest from scientific and application viewpoints.

(2) Choice of appropriate surfactants. There is extensive evidence that surfactant adsorption layers could trigger nucleation and growth of the solid phase in some systems.^{16–18,47–49} Although the exact mechanism is still a matter of discussion,^{16–19,47} several studies showed that surfactants with longer tails (e.g., with 16 C atoms) are more efficient in suppressing the undercooling phenomenon. For example, a Langmuir monolayer of long-chain aliphatic alcohols was shown to induce freezing of undercooled water droplets.⁴⁹ In another study, it was shown⁵⁰ that mixed surfactant monolayers at the air/water interface “melt” at higher temperatures for surfactants with longer tails. These results indicate that dense adsorption layers of long-chain surfactant molecules could act as templates for oil crystallization; that is, a heterogeneous nucleation could be realized in the paraffin emulsions, with the nucleation site being the drop surface.

To check whether the surfactants affected the undercooling phenomenon in our systems, we measured the drop freezing temperature in dispersions stabilized by several surfactant systems. Table 3 presents results for the undercooling temperature, $\Delta T = T_B - T_{FD}$, where $T_B \approx 18^\circ\text{C}$ is the melting/freezing temperature of bulk hexadecane and T_{FD} is the freezing temperature of the dispersed drops, which was determined by microscope observations. As expected, the drops in all emulsions crystallized at temperatures lower than the phase-transition temperature of bulk hexadecane. In addition, a correlation between the type of used surfactant and the degree of undercooling was noticed. The droplets stabilized with short-chain surfactants (SDS and Brij 35) exhibited the highest degree of undercooling, $\Delta T \approx 14^\circ\text{C}$. The droplets stabilized with long-chain individual surfactants (Tween 60 and Brij 58) had a lower degree of undercooling ($\Delta T < 10^\circ\text{C}$), and the addition of oil-soluble cosurfactants (hexadecanol and Brij 52) suppressed the emulsion undercooling even more (ΔT between 4 and 5°C). We did not find a clear correlation between the interfacial tensions with the degree of undercooling in the systems studied. The only clear trend we could notice is that the undercooling was less pronounced (small ΔT) in the presence of long-chained surfactants (C16 and C18). The only long-chain surfactant, which was inefficient as a nucleating agent, was αOS . This could be due to the presence of a double bond in the αOS chain, which could prevent the efficient packing of the surfactant molecules in the adsorption layer (similarly to the explanation for the low dispersion stability in the systems stabilized by Tween 80, Figure 2).

It is worthwhile noting that the paraffin drops in the systems with low degree of undercooling ($\Delta T < 10^\circ\text{C}$, see Table 3) exhibited rather complex drop-shape transformations during freezing. The drops were observed to change first their shape from spherical to rod- or platelike, Figure 5D, without showing optical birefringence upon observation in polarized light (a similar

phenomenon was reported by Phipps¹⁵). After several subsequent shape transformations, the particles finally crystallized into true crystals exhibiting birefringence. In contrast, the paraffin droplets in the systems with high degree of undercooling ($\Delta T > 10^\circ\text{C}$) crystallized directly into true crystals, without passing through intermediate phases. It is known from the literature that n -paraffins could undergo first a phase transition into the so-called “rotator phases”,^{8,51,52} These are intermediate, metastable phases without a long-range order in the rotational degree of freedom of the molecules around their long axis. These phases have no complete crystal order, and as a result, they do not exhibit optical birefringence. Thus, we suppose that the complex shape transformations observed in some of the dispersions during drop freezing were due to formation of intermediate rotator phases.

It is rather possible that the observed rotator phases were directly related to the lower degree of undercooling of the respective systems. It is known from the literature that the pure bulk n -even alkanes have high degree of undercooling and do not pass through rotator phases.⁵³ In contrast, the pure bulk n -odd alkenes have a much lower degree of undercooling and pass through rotator phases before crystallization. Thus, one can assume that the transient rotator phases induce nucleation and subsequent crystallization of the paraffins at higher temperature.⁵³ Transferring this assumption to our systems, we could speculate that the surfactants triggering a liquid-to-rotator phase transition facilitate the solid paraffin nucleation, thus reducing the degree of undercooling.

Concluding, surfactants with straight long tails (16 or 18 C atoms) lead to more stable emulsions and to a lower degree of undercooling, most probably due to the formation of more compact and ordered adsorption layers.

4. Summary and Conclusions

New rapid procedure for testing emulsion stability to freeze–thaw cycles of the dispersed particles is proposed. The dispersion stability is quantified by the critical pressure leading to formation of continuous oil layer on the surface of a centrifuged dispersion, in which the particles undergo solid-to-liquid transition. The application of this procedure to a series of selected surfactants and surfactant mixtures allowed us to quantify the following effects:

- As expected, the solid–liquid phase transition of the dispersed paraffin particles lowers significantly the dispersion stability, which is due to the piercing of the emulsion films by the paraffin crystals with subsequent fusion of the liquid contents of the particles.
- The surfactant mixtures comprising hydrophilic and hydrophobic components were found to be very efficient in stabilizing the dispersions, which can be attributed to the formation of denser adsorption layers in the mixed systems.
- The length of the hydrocarbon tails of the used surfactants is very important; at least one of the surfactants in these mixtures should have a long hydrocarbon tail (16 or 18 C atoms) for efficient dispersion stabilization. This experimental fact is explained by the formation of more compact and probably ordered adsorption layers by the surfactant molecules with longer tails. This assumption is indirectly supported by the fact that the surfactants with longer tails suppress significantly the undercooling phenomenon, which could be also explained by the

(46) Marinova, K. G.; Christova, D.; Tcholakova, S.; Eftremov, E.; Denkov, N. D. Hydrophobization of glass surface by adsorption of poly(dimethylsiloxane). *Langmuir* **2005**, *21*, 11729.

(47) Grange, G.; Levis, A.; Mutafchiev, B. Solidification of stearic acid–water and laurone–water emulsions: Role of the droplet–medium interface on nucleation kinetics. *J. Colloid Interface Sci.* **1986**, *109*, 542.

(48) Davey, R. J.; Hilton, A. M.; Garside, J.; Fuente, M.; Edmondson, M.; Rainsford, P. Crystallization of oil-in-water emulsions: Amphiphile directed nucleation in aqueous emulsions of m -chloronitrobenzene. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 1927.

(49) Gavish, M.; Popovitz-Biro, R.; Lahav, M.; Leiserowitz, L. Ice nucleation by alcohols arranged in monolayers at the surface of water drops. *Science* **1990**, *250*, 973.

(50) Casson, B. D.; Bain, C. D. Phase transitions in mixed monolayers of cationic surfactants and dodecanol at the air/water interface. *J. Phys. Chem. B* **1999**, *103*, 4678.

(51) Sirota, E. B.; King, H. E.; Singer, D. M.; Shao, H. H. Rotator phases of the normal alkanes: an X-ray scattering study. *J. Chem. Phys.* **1993**, *98*, 5809.

(52) Sirota, E. B.; Singer, D. M. Phase transitions among the rotator phases of the normal alkanes. *J. Chem. Phys.* **1994**, *101*, 10873.

(53) Sirota, E. B.; Herold, A. B. Transient-phase induced nucleation. *Science* **1999**, *5401*, 529.

formation of compact adsorption layers acting as nucleation substrates for paraffin crystallization in the drops.

- Some of the dispersions exhibit a significant yield stress after freezing of the dispersed particles, which might be a problem in their application as phase-change material (note that the dispersion gelling could be a benefit in some food applications). For the stable dispersions, the observed yield stress is explained by the strongly elongated shape of the solid paraffin particles. In these systems, a 3D-network of interacting but distinct particles is formed, which hampers the suspension flow. In contrast, the

yield stress of the unstable dispersions is due to formation of a 3D-network of partially fused particles, which coalesce upon melting of the paraffin phase.

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