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Ostwald ripening in macro- and nanoemulsions

Marina Yu. Koroleva,* Evgeny V. Yurtov

Mendeleev University of Chemical Technology,
Miusskaya pl. 9, 125047 Moscow, Russian Federation

Characteristic features of the Ostwald ripening in oil-in-water and water-in-oil macro- and nanoemulsions are analyzed. Methods for reducing the ripening rate are considered. It is shown that Ostwald ripening is especially relevant for nanoemulsions, and this is often the main process leading to degradation of nanoemulsions, thus limiting their practical applications. Considerable attention is paid to the debatable issue of the role of surfactants in the mass transfer between the droplets of the dispersed phase. Analysis of published sources shows that if the solubility of the dispersed phase substance in the dispersion medium is not extremely low, then the major contribution to Ostwald ripening is made by molecular diffusion. If the solubility of the dispersed phase substance is very low, then micelles and nanodroplets are the most likely carriers of the substances through the dispersion medium. Nanodroplets and slightly larger droplets are formed on the surface of droplets of the starting emulsion because of the interfacial instability (Marangoni effect).
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1. Introduction

Emulsions are formed when two liquids immiscible with each other are dispersed together. Depending on the phase polarity, emulsions are classified into oil-in-water (O/W) emulsions, in which the organic phase is dispersed in water, and water-in-oil (W/O) ones, in which the aqueous phase is dispersed in an organic phase. There are also emulsions consisting of two organic phases sparingly soluble in each other.[1] The main distinction of nanoemulsions from traditional macroemulsions is the size of the dispersed phase droplets. In nanoemulsions, the maximum droplet size does not exceed 100 nm.[2]

Emulsions are widely used in the medical, pharmaceutical and food industry, for the production of latexes by emulsion polymerization and for separation and analysis processes. In all cases, it is required that these colloid systems be highly stable and exist without degradation for

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a required period of time. However, all emulsions are thermodynamically unstable systems. As time goes on, processes decreasing the interfacial area take place in them. Emulsion breakdown is a result of the following processes:

— flocculation — sticking together of droplets of the dispersed phase; and coalescence — droplet fusion;

— sedimentation (creaming) — directed motion of particles (downwards or upwards);

— Ostwald ripening (OR) or isothermal distillation — the transfer of matter from smaller to larger droplets driven by the difference between the curvature radii of drops.

The droplet flocculation, resulting in the formation of flocs, and sedimentation can be efficiently retarded by increasing the viscosity and by structuring the dispersion medium of emulsions. The coalescence rate can be substantially reduced by using appropriate surfactants.

Ostwald ripening is much more difficult to control. Ostwald ripening can be markedly retarded or almost stopped upon the addition of electrolytes to the dispersed aqueous phase in W/O emulsions.[3–5] In oil-in-water emulsions, the OR rate can be considerably decreased, but cannot be prevented, especially in nanoemulsions. Ostwald ripening is often among the key processes leading to degradation of nanoemulsions,[6–9] which restricts their practical applications. Ostwald ripening leads not only to enlargement of droplets in nanoemulsions, but also to changes in their optical properties, which affects the quality of final products used in various branches of industry.[10]

A number of reviews are devoted to the theoretical consideration of OR and its specific features in liquid colloid systems. The most complete and comprehensive review of Taylor[11] focuses on the characteristic features of OR in emulsions and on the applicability of the Lifshitz–Slezov–Wagner (LSW) theory to the description of these systems.

The mechanism of OR in emulsions is still debated. In the 1990s, a vigorous discussion took place in the literature on how the mass transfer between the dispersed phase droplets takes place and whether this can be facilitated by micelles formed by surfactant molecules.[11–16] However, despite the large body of experimental data on the OR in macro- and nanoemulsions accumulated and published to date, this is still an open question.

2. Kinetics and quasi-equilibrium of Ostwald ripening in emulsions. Limitations of the Lifshitz – Slyozov – Wagner theory

The OR process is driven by the difference between chemical potentials of substance within the droplets of different size. As a result, smaller droplets diminish, while larger droplets grow. The chemical potential of the substance in the dispersed phase is described by the equation[17,18]

$$\mu_d = \mu_b + \frac{2\gamma V_m}{r} \quad (1)$$

where μ_d and μ_b are the chemical potentials of the dispersed phase substance in the dispersed state and in the bulk, respectively; γ is the interfacial tension between the aqueous and organic phases in the emulsion; V_m is the molar volume the dispersed phase substance; r is the droplet radius.

The dependences of $\Delta\mu_d = \mu_d - \mu_b$ on the diameter of decane droplets in O/W emulsion and water droplets in W/O emulsion calculated by the authors using Eqn (1) are shown in Fig. 1. In the case of nanoemulsions, the difference between the chemical potentials substantially increases with decreasing droplet diameter. An especially sharp increase in $\Delta\mu$ is typical of O/W nanoemulsions; therefore, these colloid systems are often unstable to OR.

If the dispersed phase of the emulsions does not consist of a single component, but is a solution, the difference between the chemical potentials of the major component of the dispersed phase is decreased by the osmotic component[17]

$$\mu_d = \frac{2\gamma V_m}{r} + RT\ln(1-x) \approx \frac{2\gamma V_m}{r} - RTx \quad (2)$$

where R is the universal gas constant, T is the temperature, x is the mole fraction of the substance in the dispersed phase.

The first term in Eqn (2) reflects the effect of the Laplace pressure, while the second one corresponds to the osmotic pressure. If the osmotic pressure in the dispersed phase droplets is greater than or equal to the Laplace pressure, the emulsions occur in the quasi-equilibrium state and there is no OR.[18] For O/W emulsions, relatively high concentrations of the second component are required to stop the OR; this is especially true for nanoemulsions (Fig. 2). When the mole fraction of the second oil-soluble component is 0.01, the chemical potential difference for the major component is below zero if the droplet diameter exceeds 100 nm; when $x = 0.05$, droplets with a diameter >20 nm are stable to OR; when $x = 0.10$, all nanoemulsions become stable to OR.

Stabilization of W/O emulsions against the OR requires much lower concentrations of the second water-soluble component. Most often, electrolytes are used as the second components. When the mole fraction of the second component is 0.001, the chemical potential difference for the major substance is below zero if the droplet diameter exceeds

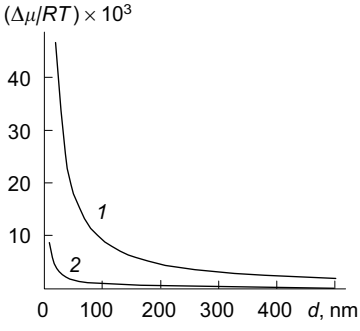


Figure 1. Chemical potential difference *vs* diameter of droplets of decane (*1*) and water (*2*) in O/W and W/O emulsions, respectively. The interfacial tension is 3 mN m^{-1}.

M.Yu.Koroleva. Doctor of Chemical Sciences, Professor at the Department of Nanomaterials and Nanotechnology, MUCT.
E-mail: m.yu.kor@gmail.com
Current research interests: nanoemulsions, emulsions, liquid nanostructured systems.
E.V.Yurtov. Corresponding Member of the RAS, Doctor of Chemical Sciences, Head of the same Department.
E-mail: nanomaterial@mail.ru
Current research interests: nanomaterials and nanostructures, nanoemulsions and emulsions, liquid extraction.

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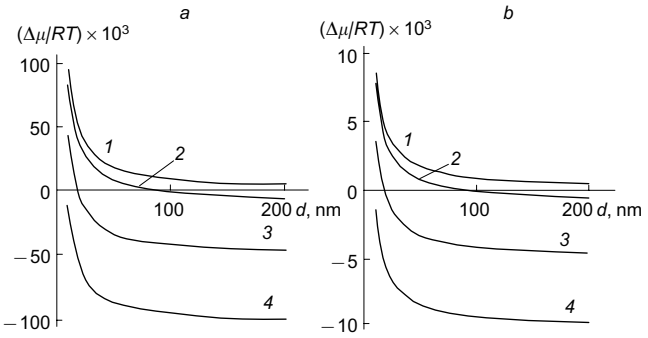


Figure 2. Difference between the chemical potentials of the major component *vs* droplet diameter.
(*a*) Droplets consisting of decane and a second oil-soluble component with a mole fraction: 0 (*1*), 0.01 (*2*), 0.05 (*3*) and 0.10 (*4*);
(*b*) droplets consisting of water and a second water-soluble component with a mole fraction: 0 (*1*), 0.001 (*2*), 0.005 (*3*) and 0.010 (*4*). The interfacial tension is 3 mN m^{-1}.

100 nm; when x is higher, W/O nanoemulsions are stable to OR.

It is noteworthy that droplets always differ in size in real emulsions and nanoemulsions. Correspondingly, smaller droplets would be less stable to the OR at the same initial concentration of the second component in the dispersed phase of the emulsion.

Despite the fact that emulsions are formed from immiscible liquids, the solubility of one phase in the other phase differs from zero. Therefore, some of the dispersed phase substance is dissolved in the dispersion medium (in the same way, the dispersed phase contains dissolved molecules of the dispersion medium). Provided that an ideal solution is formed, the chemical potential of the dispersed phase substance dissolved in the dispersion medium is given by

$$\mu_C = \mu_{C_0} + RT\ln C \tag{3}$$

where μ_{C_0} and C are the standard chemical potential and the concentration of the dispersed phase substance, respectively.

For a single-component dispersed phase at equilibrium, at $\mu_C = \mu_d$, the concentration of the dispersed phase substance in the dispersion medium can be found from the relation [18]

$$RT\ln C(r) = \frac{2\gamma V_m}{r} + \mu_b - \mu_{C_0} \tag{4}$$

Above a flat surface at $r = \infty$

$$\mu_b - \mu_{C_0} = RT\ln C_b^\infty$$

where C_b^∞ is the concentration of the saturated solution of the dispersed phase substance in the bulk dispersion medium, *i.e.*, in a non-emulsion system. Therefore, the concentration of the substance in the dispersion medium directly above the droplet surface can be expressed as [19, 20]

$$C(r) = C_b^\infty \exp\frac{2\gamma V_m}{r\,RT} \tag{5}$$

As the droplet radius decreases, the solubility increases. This results in mass transfer from smaller droplets to larger ones. The kinetics of this process in emulsions and nanoemulsions is usually described in terms of the LSW theory, which has been developed to describe the substance transport in supersaturated solid solutions.[19–21] The equations of the LSW theory were derived with the following assumptions. It was assumed that particles consist of only one substance, the transfer of which in a continuous medium occurs *via* molecular diffusion. Also, no kinetic restrictions to mass transfer across the interface exist. This model is applicable to dilute emulsions stabilized by low-molecular-mass surfactants. In the colloid systems stabilized by bulky polymer films at the interface, substsnce diffusion across the interface can be markedly retarded.[22–25]

The LSW theory was developed to describe spherical particles of the dispersed phase with the assumption that they do not move (no Brownian motion occurs in the system) and do not interact with one another. This is true only for dilute colloid systems, in which the dispersed phase particles are located at distances much greater than their sizes.

The thickness of the diffusion layer around a particle should be equal to or greater than the particle diameter. In this case, the diffusion rate of the dissolved substance of the dispersed phase does not depend on the presence of other particles, which is also possible only for dilute emulsions. The concentration of the dispersed phase substance in the dispersion medium is the same at any distance from the particle (except from near-interface layers), *i.e.*, diffusion of the dispersed phase substance from smaller to larger droplets does not give rise to a gradient of the concentration in the dispersion medium.

The LSW theory implies that a quasi-steady state is established with time in a colloid system. In this case, at any given time, there exist droplets with the critical radius r_{cr}, the size of which does not change, since the concentration of the dispersed phase substance in the dispersion medium is equal to its solubility [see Eqn (5)]. The droplets smaller than those with the critical radius diminish, while larger droplets grow.

As time goes on, the r_{cr} value increases. The rate of increase in the cube of the critical radius is equal to the OR rate (ω) and, according to the LSW theory, it obeys the equation

$$\omega = \frac{dr_{cr}^3}{dt} = \frac{8\,D\,C_b^\infty\,\gamma M}{9\,\rho^2\,RT} \tag{6}$$

where D is the diffusion coefficient of the dispersed phase substance in the dispersion medium, M and ρ are the molecular mass and the density of the dispersed phase substance, respectively, and t is time.

The size distribution of droplets in the quasi-steady state is described by equations

$$f(u) = \frac{81\,e\,u^2 \exp\left(2u/3 - 1\right)^{-1}}{32^{1/3}(u+3)^{7/3}(1.5-u)^{11/3}} \text{ for } u < 1.5 \tag{7}$$

$$f(u) = 0 \text{ for } u \geqslant 1.5 \tag{7a}$$

where u is the normalized radius r/r_{cr}, e is the base of the natural logarithm (Euler number).

The LSW distribution is shown in Fig. 3. This size distribution is time invariant. For comparison, the same Figure shows other types of size distribution of droplets that are used in calculations described in Section 6.

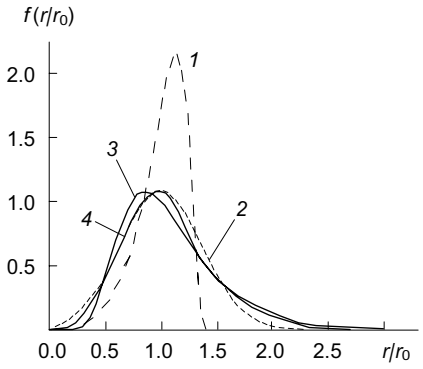


Figure 3. Steady state LSW distribution (*1*), normal (*2*) and log-normal distributions (*3*) and normalized experimental droplet size distribution in the emulsion with an initial average droplet size r_0 = 160 nm (*4*).

Before the quasi-steady state is attained, the OR rate depends, in most cases, on the polydispersity of particles; wider particle size distribution leads to a higher rate of OR.[11]

Since in real colloid systems, the concentration of the dispersed phase is not equal to zero, the diffusion layers overlap and the OR rate increases. Some authors made attempts to take account of the cooperative effect of droplets on the OR rate. Enomoto *et al.*[26] proposed a multiplication factor $k(\varphi)$ such that the OR rate at a given fraction of the dispersed phase (φ) is expressed as

$$\omega(\varphi) = k(\varphi)\omega \quad (8)$$

where ω is the OR rate calculated by Eqn (6).

Other studies demonstrated that the OR rate in emulsions depends on the fraction of the dispersed phase at $\varphi > 0.05$, while at $\varphi < 0.05$, the OR rate can be considered to be constant.[11] It was shown experimentally[16] that in the 0.01 – 0.30 range of the dispersed phase fractions, the OR rate is almost invariable.

Mathematical modelling of OR in O/W emulsions showed that if the mass transfer across the interfacial layer on the droplet surface is the rate-limiting step, the OR rate depends, first of all, on the solubility and, to a much lesser extent, on the fraction of the dispersed phase.[27]

3. Ostwald ripening rates in oil-in-water emulsions calculated by the Lifshitz – Slyozov – Wagner equation and determined experimentally

Many authors studied the OR kinetics in O/W emulsions and compared the experimental OR rates with the rates calculated using the LSW theory. The effect of the solubility of the dispersed phase substance on the OR rate was studied[28 – 33] using homologous series, most often, n-alkanes.†

The OR rates determined for emulsions with alkanes and stabilized by various surfactants are summarized in Table 1. The theoretical OR rates differ because authors used different values for the solubility of alkanes in water, for interfacial tension and for diffusion coefficients. Therefore, the theoretical values from several publications are given.[28, 29, 33] It is noteworthy that in all cases, except for the study of Kabalnov and Makarov,[28] the emulsions were stabilized by surfactants taken in amounts exceeding the critical micelle concentration (CMC) in the dispersion medium.

Despite the differences between the data reported by different authors, it can be seen that the OR rate decreases with increasing length of the hydrocarbon chain. This is due to decreasing solubility of alkanes in the aqueous phase. Almost in all cases, the experimentally determined OR rates were greater than the values calculated using the LSW equation.

Sodium dodecyl sulfate (SDS)-stabilized alkane-in-water emulsions were diluted with water until the fraction of the dispersed phase was 3.3×10^{-5} and the surfactant concentration was 3.3×10^{-5} mol L^{-1} (Ref. 28). As the hydrocarbon chain length increased, the solubility of alkanes in the aqueous phase decreased and, hence, the OR rate decreased. However, it is noteworthy that the experimental OR rates were several time higher than those calculated by the LSW equation (see Table 1).

The Ostwald ripening rates for nanoemulsions of paraffin oil in water were 1.5×10^{-29} and 1.1×10^{-29} m^3 s^{-1} in the case of stabilization with Brij 30 and a mixture of Tween 80 (polyoxyethylene glycol sorbitan monooleate) and Span 80 (sorbitan monooleate), respectively.[37]

In nanoemulsions of triglycerides in water stabilized by 5.6 mass % SDS and 16.6 mass % PEG ($M \approx 6600$), an increase in the hydrocarbon chain length of triglycerides was accompanied by a decrease in the OR rate.[32] For example, for triglycerides such as tributyrin (TBT), tricaproin (TCP), tricaprylin (TCPr) and trilaurin (TL), the experimental OR rates were as follows:

Compound	TBT	TCP	TCPr	TL
ω_{exp}, m^3 s^{-1}	1.1×10^{-25}	4.2×10^{-27}	3.5×10^{-28}	5.8×10^{-31}

The rate of OR was 4.4×10^{-26} m^3 s^{-1} in the emulsion of *N*,*N*-dimethyldecanamide in water stabilized by polyoxyethylene glycerol fatty acid ester (Glycereth-17 cocoate) (Ref. 38).

In nanoemulsions of isohexadecane in water stabilized by mixtures of nonionic surfactants — polyoxyethylene (4) lauryl ether ($\overline{C}_{12}\overline{E}_4$) and polyoxyethylene (6) lauryl ether ($\overline{C}_{12}\overline{E}_6$), — an increase in the percentage of $\overline{C}_{12}\overline{E}_6$ in the mixture brought about a decrease in the OR rate from $\sim 8 \times 0^{-27}$ m^3 s^{-1} to lower values.[39]

Sodium dodecylbenzenesulfonate-stabilized emulsions of tetradecane in water were studied by cryo-scanning electron microscopy (cryo-SEM). The droplet size distribution in the emulsion was initially close to log-normal (the root-square deviation was $\sigma = 0.5$), and then it was rapidly transformed into a more symmetrical one. However, during 51 days of observation, the distribution did not arrive to the LSW distribution. The experimental OR rates of 0.2×10^{-27} and 0.7×10^{-27} m^3 s^{-1} for surfactant concentrations of 0.05 and 0.15 M, respectively, were approximately equal to the calculated OR rate equal to: 0.2×10^{-27} m^3 s^{-1} (Ref. 40).

In hexadecane nanoemulsions stabilized by a mixture of PEG-60, hydrogenated castor oil and Span 80, the OR rate was 1.4×10^{-29} m^3 s^{-1} (Ref. 41).

Using Tween 80 and Span 80 for stabilization, kerosene-in-water nanoemulsions with a droplet size of

† Hydrocarbons described in the review are mainly normal isomers, for which letter n- before the name is omitted; the full name contains the appropriate prefix for other isomers.

Table 1. Theoretical and experimental Ostwald ripening rates in emulsions of hydrocarbons in water.

ω, $m^3 s^{-1}$		Surfactant		Fraction of the dispersed phase
calculation	experiment	type	concentration	
		Octane – water emulsion		
6.1×10^{-25} (Ref. 33)	$(1.8 – 3.7) \times 10^{-24}$ (Ref. 33)	Aerosol OT	0.15 mass %	–
	1.9×10^{-21} (Ref. 30)	–	–	0.001 mol L^{-1}
		Nonane – water emulsion		
7.2×10^{-25} (Ref. 28)	2.1×10^{-24} (Ref. 28)	SDS	3.3×10^{-5} mol L^{-1}	3.3×10^{-5}
		Decane – water emulsion		
2.0×10^{-26} (Ref. 29)	5.3×10^{-25} (Ref. 28)	SDS	3.3×10^{-5} mol L^{-1}	3.3×10^{-5}
1.8×10^{-25} (Ref. 28)	6.1×10^{-24} (Ref. 29)	SDS	20 mmol L^{-1}	5 mass %
	1.2×10^{-24} (Ref. 30)	–	–	0.001 mol L^{-1}
	7.2×10^{-26} (Ref. 34)	Phosphatidylglycerol	0.4 mass %	10 vol.%
	2.1×10^{-25} (Ref. 35)	SDS	30 mmol L^{-1}	5 vol.%
	3.5×10^{-26} (Ref. 36)	SDS + pentanol	10.5 mass % + 15 mass %	15 mass %
		Udecane – water emulsion		
5.0×10^{-26} (Ref. 28)	1.2×10^{-26} (Ref. 36)	SDS + pentanol	10.5 mass % + 15 mass %	15 mass %
	2.4×10^{-25} (Ref. 28)	SDS	3.3×10^{-5} mol L^{-1}	3.3×10^{-5}
		Dodecane – water emulsion		
1.7×10^{-27} (Ref. 29)	1.1×10^{-25} (Ref. 29)	SDS	20 mmol L^{-1}	5 mass %
1.4×10^{-26} (Ref. 28)	4.9×10^{-26} (Ref. 28)	SDS	3.3×10^{-5} mol L^{-1}	3.3×10^{-5}
	2.3×10^{-26} (Ref. 32)	SDS + PEG ($M \approx 6600$)	5.6 mass % + 6.6 mass %	15 mass %
	4.0×10^{-26} (Ref. 30)	–	–	0.001 mol L^{-1}
	3.9×10^{-27} (Ref. 36)	SDS, pentanol	10.5 mass %, 15 mass %	15 mass %
		Tridecane – water emulsion		
3.8×10^{-27} (Ref. 28)	1.2×10^{-27} (Ref. 36)	SDS + pentanol	10.5 mass % + 15 mass %	15 mass %
	1.4×10^{-28} (Ref. 28)	SDS	3.3×10^{-5} mol L^{-1}	3.3×10^{-5}
		Tetradecane – water emulsion		
1.4×10^{-28} (Ref. 29)	1.5×10^{-27} (Ref. 32)	SDS + PEG ($M \approx 6600$)	5.6 mass % + 16.6 mass %	15 mass %
	8.9×10^{-26} (Ref. 29)	SDS	20 mmol L^{-1}	5 mass %
	2.4×10^{-27} (Ref. 32)	–	–	0.001 mol L^{-1}
	5.6×10^{-28} (Ref. 36)	SDS + pentanol	10.5 mass % + 15 mass %	15 mass %
		Hexadecane – water emulsion		
1.1×10^{-29} (Ref. 29)	8.0×10^{-27} (Ref. 29)	SDS	20 mmol L^{-1}	5 mass %
8.0×10^{-29} (Ref. 28)	1.8×10^{-30} (Ref. 28)	SDS	3.3×10^{-5} mol L^{-1}	3.3×10^{-5}
	1.7×10^{-28} (Ref. 32)	SDS + PEG ($M \approx 6600$)	5.6 mass % + 16.6 mass %	15 mass %
	1.2×10^{-27} (Ref. 30)	–	–	0.001 mol L^{-1}
		Octadecane – water emulsion		
8.4×10^{-31} (Ref. 29)	1.8×10^{-29} (Ref. 32)	SDS + PEG ($M \approx 6600$)	5.6 mass % + 16.6 mass %	15 mass %
	9.6×10^{-28} (Ref. 29)	SDS	20 mmol L^{-1}	5 mass %

Note. The dash means the absence of surfactant, PEG ($M \approx 6600$) is polyethylene glycol with molecular mass of 6600.

20 – 45 nm were obtained. The rate of OR in these nanoemulsions varied in the range of $(0.6 – 2.2) \times 10^{-29}$ m^3 s^{-1} (Ref. 42).

The OR rate in limonene-in-water emulsions stabilized by Span 85 (sorbitan trioleate) and Brij O20 [polyoxyethylene (20) oleyl ether] was 0.39×10^{-29} m^3 s^{-1} (Ref. 43).

In many cases, experimentally determined OR rates were equal to or higher than the calculated values. A possible reason is that, the particles are assumed to be immobile in the LSW theory, while in real emulsions, droplets of the dispersed phase are involved in the Brownian motion. Nevertheless, despite the difference between the theoretical assumptions made to derive LSW equations and experimental conditions used to study OR in emulsions, many publications reveal that LSW equation is applicable for descrip-

tion of the OR rates in O/W emulsions, since the cube of the average radius obeys a linear dependence on time.

4. Stability conditions for two-component emulsions. Ostwald ripening in oil-in-water macro- and nanoemulsions upon the addition of a second poorly soluble component

4.1. Theoretical consideration of the stability of two-component emulsions

It was shown in Section 2 that, in the presence of a second component dissolved in the dispersed phase, there appears an osmotic pressure, which decreases the chemical potential of the major component of the dispersed phase in the dispersed state compared to the bulk state. The idea of stabilizing mist droplets by adding a non-volatile compound was stated for the first time by Köhler,[44] and the thermodynamic description of this phenomenon was given by LaMer and Gruen.[45]

The use of this approach to slow down OR in emulsions was first demonstrated by Higuchi and Misra.[46] The authors showed that the OR rate in O/W emulsions sharply decreases when a second component, much less soluble in the dispersion medium than the first component, is added to the dispersed phase. The more soluble component moves more rapidly from smaller droplets to larger ones. This changes the composition of droplets: the concentration of the low-soluble component increases in smaller droplets and decreases in larger ones.

A theoretical consideration of the effect of solubility of the second component of the dispersed phase on the OR in emulsions was reported by Kabalnov *et al.*[17] The authors considered the case when the second component was almost insoluble in the dispersion medium, which is typical of W/O emulsions containing electrolytes in the dispersed phase. Another case they considered was inclusion into the dispersed phase of a second component low-soluble in the dispersion medium. This condition can occur both in O/W and in W/O emulsions.

4.1.1. The second component is poorly soluble in the dispersion medium

If the dispersion medium solubility of the second component of the dispersed phase was extremely low, the diffusion of the major component from smaller droplets to larger ones led to a state in which the chemical potentials of substances within the droplets differing in size were nearly equal. The capillary effects were counterbalanced by concentration effects, and the mass transfer ceased, since all droplets were in equilibrium with one another.

In the equilibrium state

$$x_1^* - x_2^* = \frac{2\gamma V_{m1}}{RT}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) = \text{const} \tag{9}$$

where x_1^* and x_2^* are the mole fractions of the poorly soluble component in two equilibrium droplets with the radii r_1 and r_2, respectively, and V_{m1} is the molar volume of the major component.

The equilibrium state is attained if [17]

$$x_1^* > \frac{2\gamma V_{m1}}{RT r_{cr}} \tag{10}$$

If the initial concentration of the second component of the dispersed phase is high ($x^* \gg \gamma V_{m1}/r_i RT$), the size distribution of droplets is changed little upon reaching the equilibrium state (Fig. 4 *a*). Furthermore, according to authors' calculations, the maximum of the normal distribution shifted towards greater size.

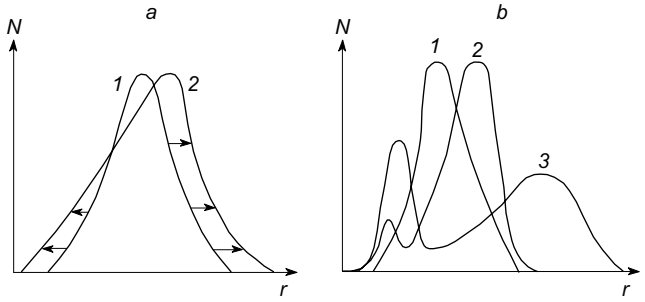


Figure 4. Transformation of the initial droplet size distribution (*1*) to equilibrium one (*2*) at $x^* \gg \gamma V_{m1}/r_i RT$ (*a*) and transient size distributions (*2* and *3*) at $x^* \ll \gamma V_{m1}/r_i RT$ (*b*).[17] *N* is the fraction of droplets.

The authors assumed that under the condition that $x^* \ll \gamma V_{m1}/r_i RT$, smaller droplets did not disappear during the OR, but only diminished down to a certain volume. For this case, a bimodal size distribution of the droplets was obtained (Fig. 4 *b*). This assumption is not always valid for emulsions stabilized by surfactants. When the droplet size decreases down to the size of micelles, the droplets cease to exist.

The change of the shape and position of the maximum corresponding to larger droplets (see Fig. 4 *b*) was described by the LSW equation. The height of the peak corresponding to smaller droplets increased as OR proceeded.[17] If this approach is applied to the case of infinitely low concentration of the second component, the height of the peak for smaller droplets should infinitely increase, which is unlikely for real colloid systems.

4.1.2. The second component is low-soluble in the dispersion medium

If the solubility of the second component in the dispersion medium is low, the OR rate depends on the solubility. Here diffusion of the less soluble substance is the rate-limiting stage. In this case, the time dependence of the cube of the average droplet radius is also linear, and the process rate is determined by the following expressions [47]

$$\omega = \frac{\mathrm{d}r_{cr}^3}{\mathrm{d}t} = \frac{\gamma M}{\rho RT}\left(\frac{f_1}{C_{b_1}^{\infty} D_1} + \frac{f_2}{C_{b_2}^{\infty} D_2}\right)^{-1} \tag{11}$$

$$V_m = f_1 V_{m_1} + f_2 V_{m_2} \tag{11a}$$

$$f_1 + f_2 = 1 \tag{11b}$$

where f_1 and f_2 are the volume fractions of components in the dispersed phase, $C_{b_1}^{\infty}$ and $C_{b_2}^{\infty}$ are the concentrations of saturated solutions, D_1 and D_2 are the diffusion coefficients of the components in the dispersion medium.

If the molar volumes of the single components and the interfacial tension between these components and the dispersion medium differ insignificantly, then

$$\omega = \left(\frac{f_1}{\omega_1} + \frac{f_2}{\omega_2}\right)^{-1} \tag{12}$$

where ω_1 and ω_2 are the rates of OR of single components.

If $C_{b_2}^{\infty}/C_{b_1}^{\infty} \ll 1$, then under the conditions that

$$f_2 \gg \frac{\omega_2}{\omega_1} \approx \frac{C_{b_2}^{\infty}}{C_{b_1}^{\infty}} \quad (12a)$$

the OR rate depends on the rate of diffusion of the second component. The process rate is described by the relation

$$\omega = \frac{\omega_2}{f_2} \quad (12b)$$

The lower the solubility of the second component in the dispersion medium and the higher the concentration of this component in the dispersed phase, the lower the OR rate.[47]

Thus, if even a very small amount of a substance with extremely low solubility in the dispersion medium is incorporated into the dispersed phase, the emulsion is kinetically stabilized to OR.

4.2. Experimental study of the Ostwald ripening in oil-in-water macro- and nanoemulsions upon addition of a second low-soluble component to the dispersed phase

Experimental studies showed a decrease in the OR rate in O/W emulsions upon the addition of a second component, poorly soluble in the dispersion medium, to the dispersed phase. Taylor and Ottewill[36,48] investigated the effect of added tetra-, hexa- or octadecane on the OR rates in octadecane-in-water emulsions stabilized by SDS and pentanol. Upon the elongation of the hydrocarbon chain of the added component, its solubility in the aqueous dispersion medium decreased and, hence, the OR rate in the emulsions decreased.

If the addition of the second component is accompanied by a decrease in the interfacial tension, this gives rise to an additional stabilization of the emulsion to OR. During OR, the size of droplets, in which the second component is concentrated, decreases. The amount of the surfactant on the droplet surface increases, and this results in decreasing interfacial tension. The droplets to which the more soluble component migrates are enlarged and, as long as the surfactant adsorption is not finished, the interfacial tension increases. This further reduces the rate of transport of the major component and, hence, retards the growth of the dispersed phase droplets in the emulsions.[17,49]

The emulsions with tetradecane as the dispersed phase became more unstable to OR when ethanol was added to the dispersion medium, due to higher solubility of tetradecane in the water – ethanol mixture. The addition of octadecane as the second low soluble component to the dispersed phase resulted in a considerable decrease in the OR rate, including the case with ethanol in the dispersion medium.[50]

Davis *et al.*[49] studied the effect of addition of perfluorinated oils on the stability of hexane-in-water emulsions stabilized by a 5×10^{-2} M solution of SDS. It was shown that in the presence of perfluorotributylamine, perfluorodecalin or perfluoromethylcyclohexane, the emulsions were stable to OR.

Delmas *et al.*[8] investigated O/W nanoemulsions with a mixture of soybean oil and wax dispersed in an aqueous solution of electrolytes. The nanoemulsions were stabilized with PEG stearates — Myrj s40, Myrj s50 and Myrj s100 (PEG 40, 50 and 100 stearates, respectively) and lecithin. If $\geqslant 10$ mass % wax was added to the dispersed phase, OR was almost prevented in the emulsions.

In the lecithin-stabilized nanoemulsions with a mixture of Mirenat-TT (commercial product containing $\sim 15\%$ lauryl alginate, propylene glycol and polysorbate) and eugenol or thymol as the dispersed phase, the average droplet diameter was 90 and 100 nm, respectively. Since the dispersed phase was a mixture of components with different solubility in the aqueous phase, the nanoemulsions were stable to OR.[51]

Sodium dodecyl sulfate-stabilized emulsions with dispersed phase containing tetradecan-1-ol and menthol in 1 : 2 molar ratio (in the eutectic ratio) were investigated. The OR rate in these emulsions was equal to $(1.3-2.3) \times 10^{-27}$ m^3 s^{-1}, and this value was lower than the RO rate in similar emulsions of decane in water — $(2.7-2.9) \times 10^{-27}$ m^3 s^{-1}. The solubility of tetradecan-1-ol is more than three orders of magnitude lower than the solubility of menthol; therefore, the former acted as the second component retarding OR.[52]

In Tween 80-stabilized emulsions of heptane in water, the rate of OR was 4.2×10^{-24} m^3 s^{-1}. Similar emulsions stabilized by hydroxypropyl cellulose were characterized by a lower OR rate — 1.9×10^{-24} m^3 s^{-1}. The inclusion of felodipine as a second component into the dispersed phase induced a more sharp decrease in the OR rate than the addition of amlodipine.[53]

The incorporation of a second component retarding the OR into droplets of the dispersed phase is important for emulsion polymerization.[54] Most often, hexadecane or cetyl alcohol is added to the monomer in order to inhibit OR.[55] It was shown[56] that the size of styrene droplets (150 and 80 nm, respectively) almost did not change during 3 – 4 h after the emulsion preparation if the concentrations of hexadecane were equal to 3.6 mass % and 10.0 mass %.

Tauer[57] investigated the effect of a second low-soluble component on the stability of O/W emulsions formulated with such monomers as methyl methacrylate, butyl acrylate, styrene, 4-*tert*-butylstyrene or lauryl methacrylate that are most commonly used for emulsion polymerization. It was shown that the addition of a polymer chemically similar to the monomer and almost insoluble in the aqueous phase made it possible to reduce the OR rate with no changes being introduced into the composition of the produced latex.

Analogous results were reported by Kamogawa *et al.*[58] Emulsions containing benzene and polystyrene with a molecular mass of 450 000 in 9 : 1 mass ratio as the dispersed phase were stable for more than a year.

Fryd and Mason[59] used mixtures of two polydimethylsiloxanes with molecular masses of 160 and 6000 in various ratios as the dispersed phases. Emulsions were stabilized by SDS. They were resistant to OR if the dispersed phase consisted only of macromolecular dimethylsiloxane. If the concentration of macromolecular siloxane was low and the concentration of low-molecular-mass siloxane was high, OR proceeded at a high rate. Upon evaporation of the low-molecular-mass siloxane, the size of droplets decreased, and the emulsions were stabilized to OR. This method can be used not only to stabilize emulsions, but also to obtain ethylcellulose and polylactide particles,[60] polylactide with carotene particles[61] and microspheres with medical drugs.[62]

Studies of emulsions of food orange oil in water stabilized by modified starch demonstrated that ester gum in a concentration of >9 mass % (Ref. 63) or corn oil in a concentration of >10 mass % (Ref. 64) added to the dispersed phase decreased the OR rate due to lower solubility of these compounds in the aqueous phase of these emulsions compared with orange oil.

Table 2. Effect of eugenol concentration (C_{eu}) in the oil phase on the experimental rate of OR in emulsions stabilized by Tween 20 (polyoxyethylene glycol sorbitan monolaurate).[66]

C_{eu} (%)	ω, $m^3 s^{-1}$				
	decane	dodec-1-ene	dodecane	tetradec-1-ene	tetradecane
0	$4.6 \pm 0.9 \times 10^{-25}$	$1.4 \pm 0.3 \times 10^{-25}$	$3.8 \pm 1.5 \times 10^{-26}$	$7.4 \pm 0.1 \times 10^{-27}$	$3.2 \pm 1.2 \times 10^{-27}$
1	$2.7 \pm 1.5 \times 10^{-25}$	$9.0 \pm 0.1 \times 10^{-26}$	$2.1 \pm 0.2 \times 10^{-26}$	$4.5 \pm 1.9 \times 10^{-27}$	$2.2 \pm 0.3 \times 10^{-27}$
10	$2.4 \pm 0.3 \times 10^{-26}$	–	–	–	$2.3 \pm 0.2 \times 10^{-28}$
20	$5.4 \pm 2.8 \times 10^{-27}$	$7.0 \pm 2.0 \times 10^{-28}$	$2.0 \pm 0.8 \times 10^{-27}$	$1.1 \pm 0.5 \times 10^{-28}$	$8.7 \pm 1.1 \times 10^{-29}$

The results reported by Li *et al.*[65] indicate that emulsions with tributyrin as the dispersed phase have very low stability to OR due to the rather high solubility of tributyrin in the aqueous dispersion medium. The addition of >15 mass % – 25 mass % corn oil to the dispersed phase resulted in a considerable decrease in the OR rate because of low solubility of corn oil in the aqueous phase.

The addition of 1 mass % to 20 mass % eugenol to the dispersed phase of O/W emulsions with decane, dodec-1-ene, dodecane, tetradec-1-ene and tetradecane resulted in a decrease in the rate of OR (Table 2).[66] In the authors' opinion, coalescence is the predominting mechanism at higher concentrations of eugenol.

The additions of rosin gum,[67–70] medium-chain triglycerides[71–73] and various oils such as silicone,[67] corn,[64, 71, 73–79] olive,[80] sunflower,[81–83] soybean,[84] sesame seed[85] and rapeseed[86] oils were used to retard OR in O/W emulsions and nanoemulsions with the dispersed phase composed of essential oils with a relatively high solubility in the dispersion medium.

Natural oils consisting of substance mixtures are often used in food emulsions as dispersed phases. For example, the OR rate was very low in Tween 80-stabilized emulsions of lemon essential oil[87] and soy polysaccharide-stabilized emulsions of thyme oil.[88] Meanwhile, Tween 80-stabilized nanoemulsions of thyme oil and oregano oil were unstable to OR, while in nanoemulsion of lemongrass oil or mandarin oil, the average droplet size barely changed over a period of 56 days.[89] The emulsions of lemongrass oil or clover oil, also stabilized by Tween 80, were stable for more than 6 months.[90]

Emulsions that contained diacylglycerol oil and steroid glycosides in 4 : 1 mass ratio as the dispersed phase and stabilized by Tween 80 (0.1 mass %) were stable, in particular, to OR. The size distribution of droplets in these emulsions remained almost unchanged during a year.[91] However, in this case, steroid glycosides acted not only as the second component reducing the OR rate, but also as an additional stabilizer because of its amphiphilic properties.

The second component added to the dispersed phase of nanoemulsion can act as an agent retarding OR and can also increase antibacterial activity of nanoemulsions.[92]

Linear time dependences of the cube of the droplet radius were observed in a nanoemulsion of a mixture of biodiesel and bifenthrin in water stabilized by a mixture of nonionic [polyoxyethylated nonylphenol (NP-6)] and anionic [calcium dodecylbenzenesulfonate (ABSCa)] surfactants. The OR rate decreased with increasing mass ratio between the organic phase and the surfactant mixture from 1.2 to 1.8.[93]

When a preliminarily produced nanoemulsion of corn oil and lemon essential oil was mixed with a macroemulsion of corn oil, it was impossible to determine the OR rate. The rapid droplet flocculation and creaming took place in the mixture of macro- and nanoemulsions, and the OR was not the predominant process in the mechanism of phase separation.[94]

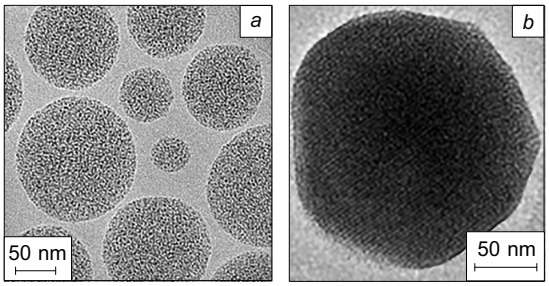


Figure 5. Cryo-SEM images of a dodecane-in-water emulsion (*a*) and an assembly of gold nanoparticles after diffusion of dodecane from a small droplet (*b*).[95]

The incorporation of hydrophobized nanoparticles into the dispersed phase of O/W emulsions apparently does not influence the intensity and the rate of OR. However, the decrease in the size of small droplets due to OR can be used to fabricate functional nanostructures. When the droplet size decreases, the concentration of nanoparticles in the droplets increases, and nanoparticle assemblies with an ordered structure are formed. The cryo-SEM images of assemblies of 2-nm gold nanoparticles in various hydrocarbons — toluene, cyclohexane, dodecane and hexadecane — were obtained (Fig. 5).[95]

5. Compositional ripening as a way to stabilize macro- and nanoemulsions

The kinetic stabilization of emulsions can also occur during their compositional ripening. This process takes place on mixing of two emulsions with dispersed phases differing both in the composition and in the size of droplets. The substance redistribution and mixing results in increasing entropy. If the substance in larger droplets is better soluble in the dispersion medium than the substance in smaller droplets, the diffusion from larger to smaller droplets occurs at a higher rate than diffusion in the opposite direction. As a result, the size of large droplets decreases, while the size of small droplets increases until the chemical potentials of substances within the droplets become equal.[96–98]

If the substance of the dispersed phase of one emulsion has a finite solubility in the dispersion medium, while that of the other emulsion is almost insoluble, the mass transfer takes place until the droplets of the first emulsion completely disappear. The substance from these droplets would

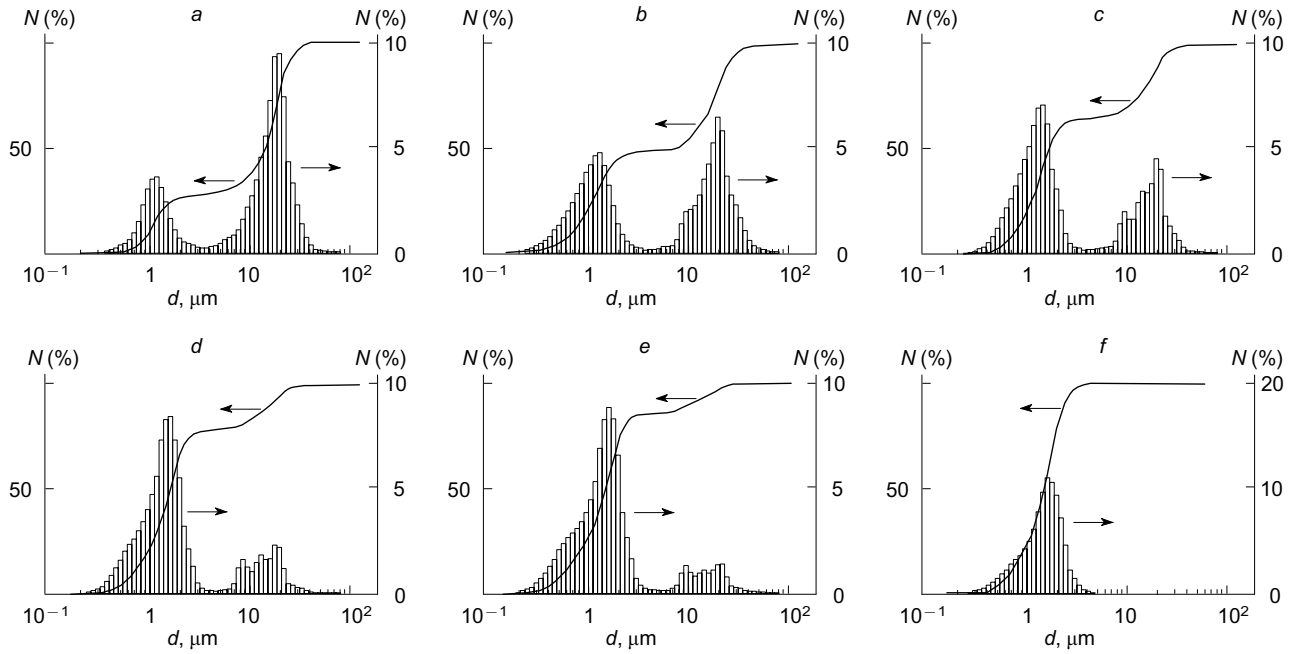


Figure 6. Differential and integral (continuous lines) droplet size distributions 60 (*a*), 1200 (*b*), 2640 (*c*), 5880 (*d*), 8460 (*e*) and 86 400 s (*f*) after mixing of squalane and decane emulsions stabilized by $\overline{C}_{12}\overline{E}_8$.[100]

migrate into the second emulsion droplets, which would proportionally increase in size $[(\varphi_1 + \varphi_2)/\varphi_2]^{1/3}$, where φ_1 and φ_2 are the initial fractions of the dispersed phase in the first emulsion (with the soluble component) and in the second emulsion, respectively.[99]

Binks *et al.*[100] investigated swelling of squalane droplets in water upon the addition of an emulsion containing decane droplets. Both emulsions were stabilized by an nonionic surfactant, octaethylene glycol dodecyl ether $\overline{C}_{12}\overline{E}_8$. The size distributions of droplets for various times after mixing are shown in Fig. 6. The initial radius of squalane droplets was 0.39 μm and the size of decane droplets was 8.6 μm. As time went on, the height of the second peak decreased due to the diffusion of decane to the squalane droplets. The height of the first peak increased and the peak position shifted towards greater sizes. The mass transfer rate increased with increasing surfactant concentration.

In most studies related to the OR, size variation of the dispersed phase droplets over time was monitored by optical and electron microscopy methods and by dynamic light scattering. McClements and Dungan[101] studied the OR process by monitoring the melting point variations of droplets, which was manifested as shifts of peaks in the differential scanning calorimetry (DSC) curves. The compositional ripening in a 1 : 1 mixture of Tween 20 stabilized emulsions with hexa- and octadecane resulted in averaging of the droplet composition. The DSC curves first exhibited two minima, which corresponded to hexa- and octadecane droplets mixed in 1 : 1 ratio (Fig. 7 *a*). These minima shifted with time. When an additional amount of Tween 20 was added to the dispersion medium of ready emulsions, the rate of OR increased (Fig. 7 *b* – *d*). During the experimental time, the minima merged into a single one corresponding to droplets of the averaged composition.

Analogous dependences were obtained for a mixture of emulsions stabilized by Tween 80. The highest OR rate was observed on mixing of emulsions of hexa- and octadecane in 3 : 1 mass ratio.[102]

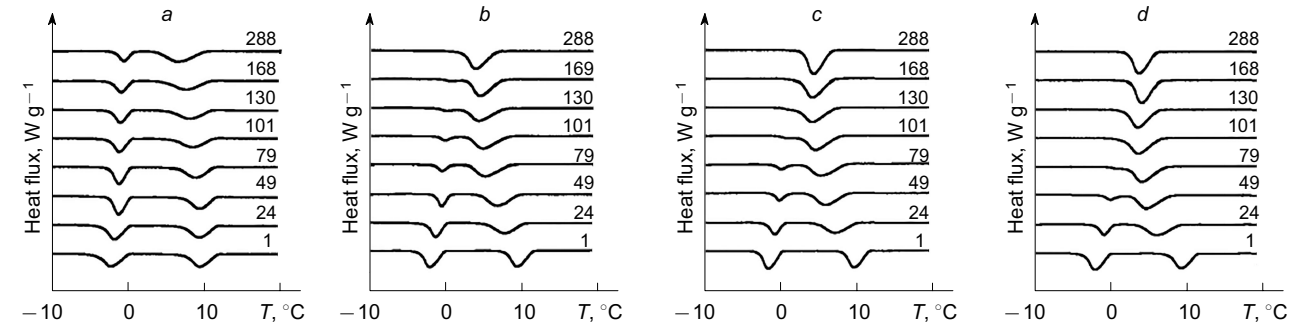


Figure 7. DSC thermograms of a mixture of hexa- and octadecane emulsions in 1 : 1 ratio. Concentration of Tween 20 added to the emulsion after producing (mass %): (*a*) 0, (*b*) 1, (*c*) 2, (*d*) 4; the time of emulsion storage in hours is indicated in the plots.[101]

Peña and Miller[103] investigated the rate of dissolution of decane and squalane droplets and their mixtures in an aqueous solution of $\overline{C}_{12}\overline{E}_8$ (2.5 mass %) with eiher empty micelles or micelles partly solubilized with decane. Considering their experimental data and modelling results, the authors concluded that in emulsions studied by Binks *et al.*,[100] the OR rate was determined by mass transfer across the interface and, perhaps, by adsorption and desorption of micelles at the droplet surface, but not by the diffusion of micelles.

Taisne *et al.*[104] observed the mass transfer between tetradecane and 1-bromotetradecane droplets stabilized by SDS. The water solubility of hexa- and tetradecane was 1.4×10^{-10} and 2.3×10^{-10} m^3 m^{-3}, respectively. These values were used for estimation of 1-bromotetradecane solubility. No mass transfer was detected between the hexadecane and 1-bromohexadecane droplets.

When O/W emulsions of hexadecane and octadecane stabilized by Tween 20 or sodium caseinate were mixed, compositional ripening did not take place either.[105]

Drelich *et al.*[106] studied O/W emulsions of hexadecane and tetradecane stabilized by silica nanoparticles in the presence of several surfactants such as Tween 20, SDS and Synperonic F127 (oxyethylated polymeric surfactant). Tetradecane migrated to the hexadecane droplets only in the presence of low-molecular-mass surfactants — Tween 20 and SDS.

Thus, on mixing of emulsions with different dispersed phases stabilized by low-molecular-mass surfactants, compositional ripening took place.

6. Ostwald ripening in water-in-oil macro- and nanoemulsions. Electrolytes as insoluble components

The OR process in W/O emulsions is studied much less extensively than that in O/W emulsions. Only few publications report data on the OR rates in W/O emulsions.[107 – 112] The addition of electrolytes into the dispersed aqueous phase resulted in decreasing droplet growth and coalescence rates.[113] In the dispersed phase of W/O emulsions containing a solution of high ionic strength, OR did not take place.[3] However, W/O emulsions containing a solution with a low electrolyte concentration and especially distilled water in the dispersed phase were unstable to OR.

6.1. Experimental study of the Ostwald ripening rate in water-in-oil macro- and nanoemulsions

The number of publications dealing with the OR kinetics in W/O emulsions is not high. Jiao and Burgess[107] described the results of studying OR in W/O emulsions with heptane, decane, dodecane, tetradecane or hydrocarbon oil as the dispersion medium. The volume fraction of distilled water as the dispersed phase was 0.005. The emulsions were stabilized by Span 83 (sorbitan sesquioleate) with concentrations from 1.8×10^{-4} to 1.8×10^{-2} mol L^{-1}. The average diameter of the dispersed phase droplets was $\sim$300 nm.

The linear time dependences of the cube of the normalized average droplet radius in these W/O emulsions at 25 °C are shown in Fig. 8. The OR rate increased with decreasing length of the hydrocarbon chain and, correspondingly, decreasing viscosity of the dispersion medium in the W/O emulsions.[107]

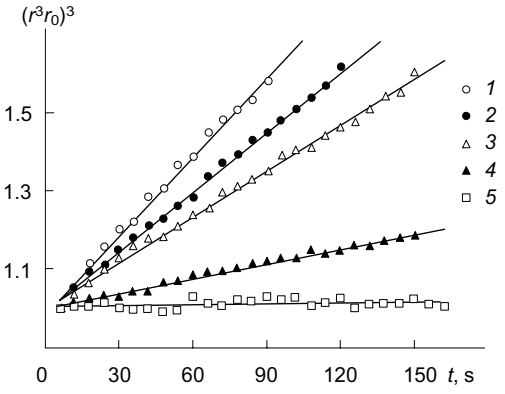


Figure 8. Time dependence of the cube of the normalized average droplet radius of the dispersed phase in W/O emulsions stabilized by Span 83 at 25 °C.[107]
Emulsions: (*1*) water in heptane, (*2*) water in decane, (*3*) water in dodecane, (*4*) water in tetradecane, (*5*) water in paraffin oil.

Table 3. Ostwald ripening rates in W/O emulsions with different dispersion media.[107]

Dispersion medium	ω_{exp}, m^3 s^{-1}	ω_{theor}, m^3 s^{-1}	$\omega_{exp}/\omega_{theor}$
Heptane	3.0×10^{-24}	2.6×10^{-24}	1.15
Decane	2.3×10^{-24}	1.7×10^{-24}	1.35
Dodecane	1.8×10^{-24}	9.9×10^{-25}	1.82
Tetradecane	5.8×10^{-25}	6.1×10^{-25}	0.95

Comparison of the OR rates (Table 3) demonstrated that the experimental ω values exceeded the theoretical ones, except those for emulsions with tetradecane.

Courrier *et al.*[114] studied emulsions of water in perfluorooctyl bromide stabilized by 11-(perfluorooctyl)undecyldimorpholinophosphinate. The rate of OR was almost invariable — $(1.1-1.4)\times10^{-31}$ m^3 s^{-1} — in the surfactant concentration range from 1.5 mass % to 4.0 mass %, which is $\sim$1000 times lower than the theoretical value.

Koroleva and Yurtov[108, 109] studied OR in concentrated W/O emulsions with a dispersed phase fraction of 0.65. The emulsions were stabilized by Span 80, and the dispersion medium consisted of hydrocarbon oil. The experimental rate of OR was determined from the linear region of the time dependence of r^3 in the range from 0 to $\sim$40 days (Fig. 9) to be 2.1×10^{-26} m^3 s^{-1}.

Porras *et al.*[110] investigated the droplet growth in W/O nanoemulsions stabilized by mixtures of Tween 80, Span 20 (sorbitan monolaurate) and Span 80 in various combinations. The dispersed phase consisted of distilled water and

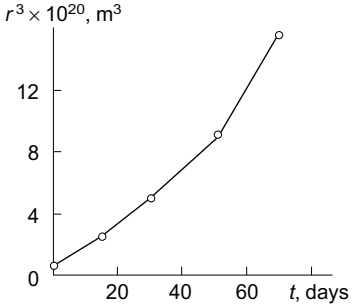


Figure 9. Time dependence of the cube of the average droplet radius in W/O emulsion stabilized by Span 80.[108]

Table 4. Experimental OR rates in water-in-decane nanoemulsions with different fractions of the dispersed phase (φ) and mass ratios of surfactants.[110]

Span 80 : Tween 80	φ (mass %)	$\omega \times 10^{28}$, $m^3 s^{-1}$
51 : 49	11.4	8.0
51 : 49	14.0	3.2
51 : 49	16.6	0.7
51 : 49	3.9	1.0
51 : 49	5.4	0.3
62 : 38 [a]	19.0	21.3
62 : 38 [a]	20.0	10.3

[a] Span 20 : Tween 80 ratio is given.

the dispersion medium was decane. The OR rates in these emulsions are summarized in Table 4.

El-Din *et al.*[111] reported data on the OR rates in nanoemulsions of distilled water in diesel fuel stabilized by a mixture of Tween 20 and Span 80. As the concentration of the dispersed phase was increased from 5 vol.% to 9 vol.%, the radius of water droplets in the nanoemulsions increased from 50 to 104 nm. The OR rate also increased from 2×10^{-22} to 10×10^{-22} $m^3 s^{-1}$, respectively.

El-Din *et al.*[111, 115, 116] prepared W/O nanoemulsions in diesel fuel stabilized by a mixture of Tween 85 (polyoxyethylene sorbitan trioleate) and Span 80. The initial average droplet diameter varied from 26 to 78 nm. When the fraction of the dispersed phase increased from 5 mass % to 7 mass %, the OR rate decreased from 9.0×10^{-23} to 0.8×10^{-23} m^3 s^{-1}. An increase in the surfactant concentration resulted in increasing OR rate in all studied nanoemulsions with any fraction of the dispersed phase. For example, when the dispersed phase fraction was 7 mass %, the ω value increased from 8×10^{-26} to 7×10^{-24} $m^3 s^{-1}$ as the surfactant concentration increased from 4 mass % to 10 mass %.

The rate of OR was 2.27×10^{-29} m^3 s^{-1} in emulsions of water in diesel fuel stabilized by Triton X-100 (polyethylene glycol tert-octylphenyl ether) and Span 80 with a droplet diameter of 25 nm (Ref. 117). In Span 80-stabilized water-in-oil emulsions with chitosan in the dispersed aqueous phase, the rate of OR was 3.58×10^{-24} m^3 s^{-1} (Ref. 118). However, the authors emphasized that droplet coalescence took place in the emulsions, in addition to OR.

When W/O nanoemulsions with isohexadecane as the dispersion medium were stabilized by mixtures of $\overline{C}_{12}\overline{E}_2$ [polyoxyethylene (2) lauryl ether] and $\overline{C}_{12}\overline{E}_4$, the OR rate depended on the surfactant ratio (Table 5).[112] The minimum OR rates were detected in W/O nanoemulsions with the $\overline{C}_{12}\overline{E}_2$ and $\overline{C}_{12}\overline{E}_4$ molar ratio ~ 2. The water droplet size in these nanoemulsions almost did not change for 200 days; the authors attributed this to the formation of a tougher and stronger film on the surface of droplet that prevented Ostwald ripening.

The OR rates reported by various researchers for W/O emulsions vary over a very broad range, from 10^{-22} to 10^{-31} m^3 s^{-1}. The high values of ω found by El-Din *et al.*[111] can be explained by higher polarity of diesel fuel compared with saturated hydrocarbons and, hence, higher solubility of water in the fuel. The OR rate in nanoemulsions stabilized by mixtures of Span 80 and Tween 80 [110] was two orders of magnitude lower than that in Span 80-stabilized emulsions [108, 109] and 3 – 4 orders of magnitude lower than that in Span 83-stabilized emulsions.[107] When

Table 5. Experimental OR rates in water-in-isohexadecane nanoemulsions at different surfactant ratios.[112]

$\overline{C}_{12}\overline{E}_2 : \overline{C}_{12}\overline{E}_4$ ratio		$\omega \times 10^{27}$, $m^3 s^{-1}$
mass	molar	
0 : 10	0	3.1
1 : 9	0.15	7.1
2 : 8	0.33	16.0
3 : 7	0.57	21.2
4 : 6	0.88	9.3
5 : 5	1.32	1.3
6 : 4	1.98	5×10^{-6}
7 : 3	3.08	24.5
8 : 2	5.28	39.0
9 : 1	11.89	61.0
10 : 0	∞	98.4

the emulsions were stabilized by $\overline{C}_{12}\overline{E}_2 : \overline{C}_{12}\overline{E}_4$ mixtures, ω values ranged from nearly zero to 10^{-25} m^3 s^{-1}.

The macro- and nanoemulsions considered above were stabilized by various surfactants and the dispersion medium consisted of various hydrocarbons; therefore, it is difficult to compare data and draw unambiguous conclusions. The only fact confirmed experimentally is that the W/O emulsions and nanoemulsions without electrolytes in the dispersed phase are unstable to OR.

For increasing the stability to OR, electrolytes are usually added into the dispersed phase of W/O emulsions, and the OR intensity can be controlled by varying the electrolyte concentrations. For example, in the fabrication of highly porous polymers by polymerization of the dispersion medium in the highly concentrated W/O emulsions, electrolytes were added to the dispersed phase in order to control the droplet size in the starting emulsion and, hence, the pore size in the resulting highly porous polymer.[119, 120]

Water-in-oil emulsions were studied as reservouirs for the storage of *Lagenidium giganteum* and *Chlorella vulgaris* bacteria. Most likely, the vital activity of microorganisms in the dispersed phase resulted in the release of compounds that were dissolved in the aqueous phase and retarded the OR. The average droplet size increased only from 5.4 to 7.1 μm over a period of 150 days. In the authors' opinion, the increase in the droplet size was correlated with cell death.[121]

6.2. Effect of electrolyte concentration on the Ostwald ripening in water-in-oil emulsions

For O/W emulsions, it was shown that the addition, to the dispersed phase of a second component, the solubility of which in the dispersion medium is much lower than the solubility of the major component, is the most efficient method for lowering the OR rate.[17, 46, 48] In the case of W/O macro- and nanoemulsions, electrolytes soluble in the dispersed phase are used most often as the second components.

Koroleva and Yurtov[4] calculated the concentration ranges of electrolytes in the dispersed phase of W/O emulsions in which OR takes place. For determining the total pressure acting on the surface of water droplets, the following components were taken into account:

— the pressure increase in the emulsion droplets caused by the curvature of the droplet surface was calculated using the Laplace equation

$$\Delta P_{\mathrm{Lp}} = \frac{2\gamma}{r} \tag{13}$$

where ΔP_{Lp} is the Laplace pressure;

— osmotic pressure generated in the presence of electrolytes in the water droplets

$$P_{\mathrm{os}} = \phi CRT \tag{14}$$

where ϕ is the osmotic coefficient, C is the electrolyte concentration in the droplets. The considered W/O emulsions had a dispersed phase fraction of $< 74\%$; therefore, the osmotic pressure arising in the emulsions upon the droplet deformation [122] was neglected.

In the modelling of OR in W/O emulsions, polydisperse systems were investigated. In the calculations, the transfer of water from smaller droplets to larger ones took place until excess pressures in all droplets of the W/O emulsion became constant and equal to the equilibrium pressure (P^{∞})

$$P^{\infty} = \frac{\sum_i (P_{\mathrm{os}} - \Delta P_{rmLp})}{N} \tag{15}$$

The dependence of the difference between the osmotic pressure and the Laplace pressure in W/O emulsions with NaCl aqueous solutions of various concentrations in the droplets is shown in Fig. 10.[4] It can be seen that in nanoemulsions especially with droplets < 25 nm, the osmotic pressure is higher than the Laplace pressure only at high concentrations of the electrolyte.

The effect of NaCl concentration on OR in W/O emulsions was calculated using the size distributions of dispersed phase droplets shown in Fig. 3. The experimental droplet size distribution corresponded to the size distribution in a Span 80-stabilized W/O emulsion with a dispersed phase fraction of 0.65. The experimental histogram was approximated by a normal (root-mean-square deviation $\sigma = 0.37$), log-normal ($\sigma = 0.4$) and steady-state LSW distributions.

The existence of three ranges of electrolyte concentrations was assumed. The first range is $C^0 < C_1$. When the electrolyte concentration in the dispersed phase is low, smaller droplets decrease in size, as a result of OR, down to the size of micelles and, after that, they cease to exist. In course of time, the total number of dispersed phase droplets in such emulsions decreases. The C_1 value is the critical concentration for OR: below this value, the number of droplets in the emulsion decreases due to OR, while above this concentration the droplet number remains invariable.

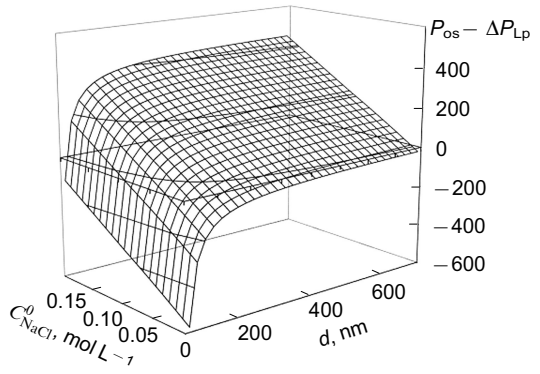


Figure 10. Difference between the osmotic pressure and Laplace pressure *vs.* diameter of water droplets and the initial concentration of NaCl in the droplets.[4]

The second range is $C_1 \leqslant C^0 < C_2$. At a higher concentration of the electrolyte, the size of smaller droplets decreases, while the size of larger droplets increases. The process goes on until the excess pressure in all droplets in the emulsion becomes equal. In this case, the number of droplets in the system does not decrease.

The third range is $C^0 \geqslant C_2$. At even higher electrolyte concentrations in the dispersed phase, the OR process is virtually absent. The C_2 value was conventionally chosen in such a way that the change in the average droplet radius was $< 1\%$ as the quasi-equilibrium is established in the system.

We calculated and plotted the equilibrium droplet size distributions in systems with experimental, normal, log-normal and LSW initial distributions (Fig. 11). Curves *4* for each distribution correspond to the critical concentration C_1. As the NaCl content in the emulsions decreases, the maximum in the curves diminishes and the droplet size distribution is broadened.

The critical concentrations of OR were different depending on the type of distribution and mainly on the distribution skewness. The skewness of the log-normal and experimental distributions was positive, while that for the LSW distribution was negative. In the case of the normal distribution, the skewness was equal to zero.

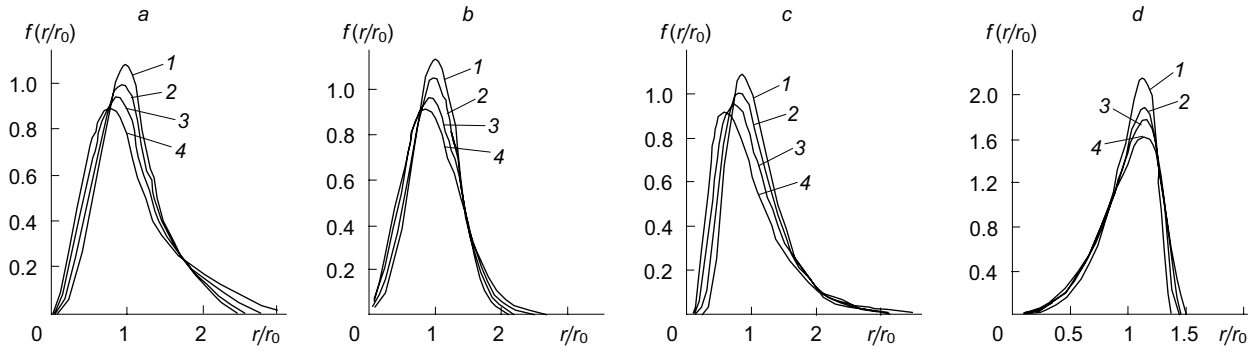


Figure 11. Initial (*1*) and equilibrium (*2*–*4*) droplet size distributions for various initial NaCl concentrations in the aqueous phase of W/O. Distribution: (*a*) experimental, (*b*) normal, (*c*) log-normal, (*d*) LSW. C_{NaCl}, mol L^{-1}: (*2*) 0.05, (*3*) 0.02, (*4*) 0.0118 (*a*), 0.0134 (*b*), 0.0102 (*c*), 0.0163 (*d*).

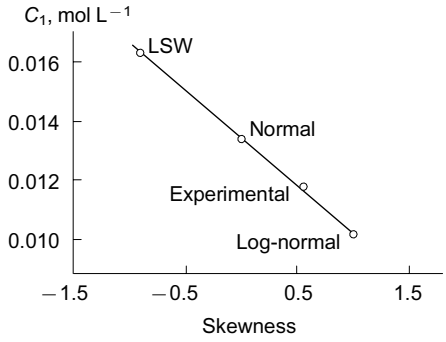


Figure 12. Critical concentration of OR in W/O emulsions *vs.* the skewness of the initial size distribution of dispersed phase droplets.

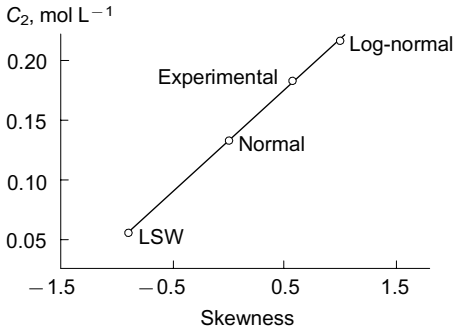


Figure 13. Concentration of NaCl above which OR in W/O emulsions is almost absent *vs.* the skewness of the initial size distribution of dispersed phase droplets.[4]

The dependence of the OR critical concentration for W/O emulsions with different droplet size distributions on the skewness of the initial distribution is shown in Fig. 12. This dependence is linear, and the C_1 value decreases with increasing skewness.

The lowest critical concentration of OR was found for emulsions with the highest skewness, *i.e.*, for the log-normal size distribution of droplets. The C_1 value for the normal distribution with a zero skewness was higher, and this value for the LSW distribution with a negative skewness was even higher. Similar results were obtained for W/O emulsions with aqueous solutions of KCl, $CaCl_2$, Na_2SO_4 or $MgSO_4$ in the dispersed phase.

Thus, the higher the skewness of the initial droplet size distribution, the lower the electrolyte concentration required to stabilize the emulsions. In these W/O emulsions, water partly migrates from smaller droplets to large ones, but the total number of droplets does not decrease.

The obtained results are in line with experimental data. Indeed, a 0.005 M solution of NaCl is required for stabilizing emulsions with a droplet size of $\sim$0.5 μm.[123] Correspondingly, lower NaCl concentrations are needed to substantially retard OR if droplets are larger.

6.3. Calculation of electrolyte concentrations at which Ostwald ripening is prevented in water-in-oil emulsions

Koroleva and Yurtov[4] calculated the NaCl concentration (C_2) at which the average droplet radius in the dispersed phase changed by less than 1% at OR equilibrium, *i.e.*, at the concentration above which the intensity of OR is low and the effect of OR on the W/O emulsion breakdown can be neglected.

The dependence of C_2 on the skewness of the droplet size distribution was linear (Fig. 13). Unlike analogous dependence for C_1 (see Fig. 12), in this case, the skewness had an opposite effect: the lowest C_2 value was observed for the stationary LSW distribution, while the highest C_2 was found for the log-normal distribution.

A comparison of C_1 and C_2 (see Figs 12 and 13) leads to the following conclusions. The dispersed phase of emulsions with a log-normal droplet size distribution and also experimentally prepared emulsions should contain an electrolyte in a lower concentration in order that the total number of droplets is not decreased as a result of OR. However, for almost complete suppression of OR in emulsions with these droplet size distributions, higher electrolyte concentrations are needed than in emulsions with the normal or LSW distribution.

An opposite trend was manifested for emulsions with the steady-state LSW distribution. These emulsions had the lowest stability to OR at low electrolyte concentrations. Meanwhile, the OR process was nearly absent at lower C_2 values.

7. Does the average droplet size increase or decrease with Ostwald ripening?

It is commonly accepted that the average droplet radius can only increase during OR. Certainly, in the steady state of OR, the droplet radius always increases. However, what happens to the average droplet size before the process has reached the steady state and occurs in the transient state?

We performed calculations to determine the variation of the average droplet size in W/O emulsions at a NaCl concentration equal to C_1 for different droplet size distributions. The change in the average radius as a function of skewness of the distribution is depicted in Fig. 14. It can be seen that the average radius increases only for emulsions with the LSW distribution. In emulsions with normal, log-normal and experimental distributions, the average droplet radius decreases and, furthermore, the greater the skewness of the distribution, the greater the decrease in the equilibrium average radius.

It should be emphasized once again that these results refer to emulsions with the electrolyte concentration C_1 in

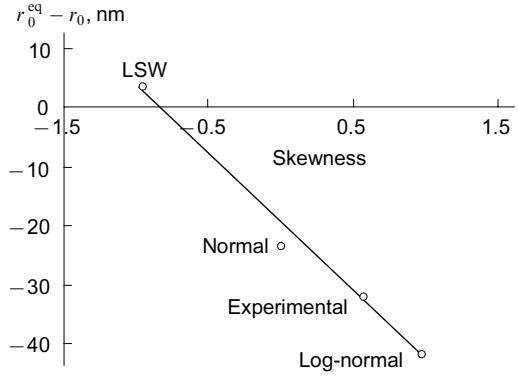


Figure 14. Effect of the type of droplet size distribution on the change in the equilibrium average droplet radius (r_0^{eq}) in W/O emulsions in comparison with the initial average radius (r_0).

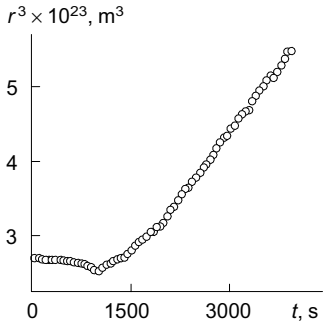


Figure 15. Calculated time dependence of the cube of the average droplet radius in a dodecane-in-water emulsion with a dispersed phase fraction of 2.29×10^{-4}; $\omega = 1.17 \times 10^{-26}$ m^3 s^{-1} (Ref. 124).

the dispersed phase, *i.e.*, to the limiting concentration at which the total number of droplets remains unchanged and OR is ceased as the quasi-equilibrium is reached.

If the electrolyte concentration in the dispersed phase of a W/O emulsion is lower than the critical concentration for OR (provided that the skewness $\geqslant 0$), then the average droplet radius decreases only in the early period. When the steady state is reached and mass-transfer leads to the dissolution of small droplets, the average radius inevitably increases.

Results of the same type were obtained by mathematical modelling of OR in a dodecane-in-water emulsion with the normal initial size distribution of droplets. According to an assumption of the LSW theory that the particles are fixed in space, it was also assumed in the modelling that the dodecane droplets did not undergo the Brownian motion. The results of simulations showed that during the initial transient period of OR, the average droplet radius decreased, passed through a minimum and, as the steady state has been reached, started to increase (Fig. 15).[124]

The simulation results account for the decrease in the size of the dispersed phase droplets observed experimentally by various authors for both O/W and W/O emulsions in the initial periods of OR.[11, 110, 125]

In emulsions containing 20 vol.% dodecane as the dispersed phase stabilized by SDS (1.2 g L^{-1}), the average droplet diameter decreased in the initial period and then increased (Fig. 16).[125]

In nanoemulsions, a decrease in the droplet size was also observed experimentally in the initial period of time. Jiméenez *et al.*[126] investigated nanoemulsions with the dispersed phase of black pepper essential oil, cinnamon oil and their mixtures stabilized by mixtures of Span 20, Tween 80, Tween 40 (polyoxyethylene glycol sorbitan monopalmitate) and Tween 20. The nanoemulsions were prepared by ultrasonic agitation and high-pressure homogenization. The initial droplet diameter was in the range of 32 – 77 nm.

The authors subdivided the change in the droplet diameter into two stages. The diameter decreased during the first

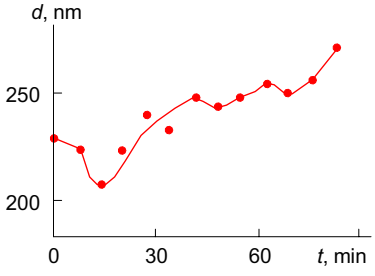


Figure 16. Initial part of the time variation of the droplet diameter in an SDS-stabilized dodecane-in-water emulsion.[125]

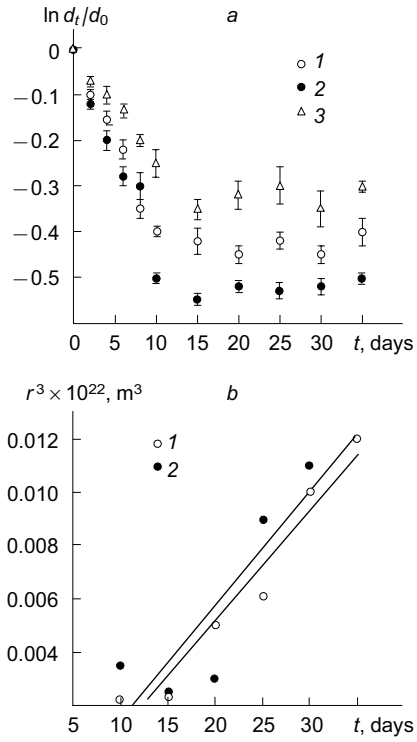


Figure 17. Time dependence of normalized diameter (*a*) and cube of the droplet radius (*b*) in O/W nanoemulsions at 4 °C.[126] (*a*) First stage of breakdown: cinnamon (*1*), black pepper (*2*), cinnamon and black pepper (*3*) essential oils; (*b*) second stage of breakdown; method of the nanoemulsion preparation: ultrasonic agitation (*1*), high-pressure homogenization (*2*); straight lines are linear dependences approximating the experimental data.

10 days (Fig. 17 *a*). This decrease was attributed to the dynamic equilibrium between micelles and the continuous phase, with the micelles being continuously disintegrated and reformed. In the second, steady-state period of OR, the size of droplets increased and the cube of the average droplet radius was linearly correlated with time (Fig. 17 *b*).

In O/W nanoemulsions with dodecane and octadecane in the dispersed phase, the average droplet radius of the dispersed phase decreased (Fig. 18).[11] This was attributed to the fact that in the initial period of OR, dodecane diffused from small droplets and it crystallized as the mole

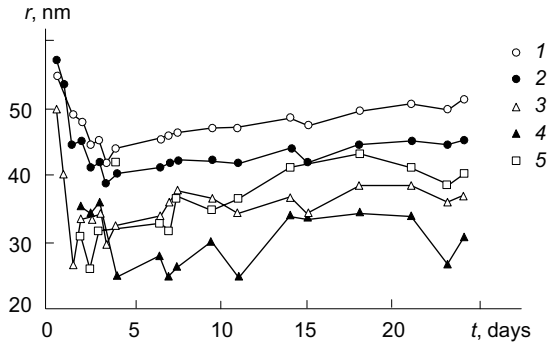


Figure 18. Time dependences of the dodecane droplet radius in an O/W nanoemulsion at different mole fractions of octadecane (the second poorly soluble component): 0.05 (*1*), 0.075 (*2*), 0.1 (*3*), 0.2 (*4*), 0.3 (*5*).[11]

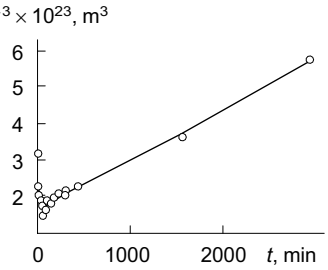


Figure 19. Time dependence of the cube of the average droplet radius in an SDS- and hexanol-stabilized nanoemulsion of decane and hexadecane dispersed in the aqueous phase.[127]

fraction of octadecane became ~0.7 (at 25 °C). In the droplets of the dispersed phase, the concentration of octadecane in dodecane sharply decreased, which weakened the action of octadecane as the second component retarding OR. However, as indicated by Taylor,[11] the mechanism of this phenomenon has not been sufficiently studied.

A study of nanoemulsions with the dispersed phase of decane and hexadecane demonstrated that the average radius also decreased in the initial period of time and then increased (Fig. 19). Similar dependences were obtained for emulsions with decane and squalane or octane and tetradecane as the dispersed phases. During the first 30 min, the size of droplets decreased from 70 to 50 nm and then increased.[127]

It is quite possible that the initial droplet size distribution in the studied emulsions was close to log-normal, which is typical of experimentally prepared emulsions. Therefore, the OR process had not yet reached the steady state in an early period, and the radius decreased. Over time the process reached the steady state and the average radius increased.

Obviously, the decrease in the droplet size observed by various authors in the early period is related to mass transfer from smaller droplets to larger ones, while the total number of droplets in emulsion remains constant. When smaller droplets have completely dissolved, that is, the numerical concentration of droplets in the emulsion decreased, the average droplet size starts to increase. This phenomenon is observed in both macro- and nanoemulsions.

8. Effect of the rheological properties of the interfacial layer on the droplet surface in emulsions on the Ostwald ripening rate

The equation for the OR rate in the LSW theory was derived with the assumption that there are no kinetic restrictions to mass transfer across the interface. In real emulsions, packed adsorption layers and films can exist at the interface and can affect the OR rate. One of the ways to decrease the OR intensity is to increase the Gibbs elasticity of the adsorption films (ε)[22, 25]

$$\varepsilon = \frac{\mathrm{d}\gamma}{\mathrm{d}\ln A} \tag{16}$$

where A is the surface area of the droplet.

The Gibbs elasticity of interfacial films can be increased *via* adsorption of polymeric surfactants that are poorly soluble in the dispersion medium and are, therefore, strongly adsorbed on the droplet surface.

Experimental attempts to produce emulsions stabilized to OR using interfacial films have been undertaken by various researchers.

8.1. Polymer films at the interface

The effect of the elastic modulus of the interfacial layer on the OR rate was studied[128, 129] by numerical methods

$$\omega = \frac{\mathrm{d}r_{\mathrm{cr}}^3}{\mathrm{d}t} = \frac{8\,DC_{\mathrm{b}}^{\infty}\,M\left[\gamma_0 + 2\,E\ln(r_t/r_0)\right]}{9\rho^2\,RT} \tag{17}$$

where γ_0 is the interfacial tension at the initial time, E is the elastic modulus of the interfacial layer, r_0 is the initial droplet radius, r_t is the droplet radius at time t.

It was assumed that a decrease in the droplet size during OR would be accompanied by decreasing interfacial tension, whereas an increase in the droplet size would lead to increasing interfacial tension. This approach is valid for proteins and other high-molecular-mass compounds because their adsorption rate is relatively low. In emulsions stabilized by low-molecular-mass surfactants, the rate of adsorption is higher than the rate of OR; therefore, in the course of OR, surfactant molecules are desorbed from smaller droplets and are adsorbed on larger ones. The interfacial tension of small and large droplets remains almost equal (if the dependence of the interfacial tension on the curvature radius of the droplet is neglected) and decreases only upon the decrease in the total interfacial surface area in the emulsion caused by complete dissolution of small droplets.

Meinters *et al.*[128, 129] modelled OR in emulsions with a zero elastic modulus of the interfacial layer taking into account the decrease in the number of droplets with time. Their simulation results coincided with the LSW theory. In the calculations with a nonzero elastic modulus of the interfacial layer, the number of droplets in the system was assumed to be invariable, *i.e.*, smaller droplets reached a minimum size, but did not disappear. The initial LSW distribution transformed with time into a bimodal distribution if elastic modulus of the interfacial layer was low (Fig. 20).

The position of the first peak, which corresponded to smaller droplets, shifted depending on the $E:\gamma_0$ ratio. As this ratio changed from 0.25 to 0.50, the first maximum shifted towards a greater size of smaller droplets. At great $E:\gamma_0$ ratios, the droplet size almost did not change with time. For droplets to be stable to OR, the following inequality should hold:[24, 128]

$$h > 1.5\,r\frac{\gamma_0}{E} \tag{18}$$

where h is the minimum film thickness.

The simulations showed that the OR rate considerably decreased only when the interfacial film thickness increased to values comparable with the droplet radius. For example, for interfacial films formed by proteins, $E:\gamma_0 \approx 3$; that is, the thickness of such film should exceed half the radius of a droplet in order to prevent OR.[24, 128]

With this approach, it turns out that with increasing droplet size, the thickness of the interfacial film on the droplet surface should increase to stabilize the emulsion to OR. This is at variance with many experimental results. In addition, as the droplets in the emulsions grow, the Laplace pressure decreases and, hence, OR is slowed down.

Experimental studies of the effect of different polymer films on the emulsion stability were reported by various authors. Mun and McClements[24] showed that SDS- and chitosan-stabilized emulsions of tetradecane in water are stable to OR. In these emulsions, the average droplet radius

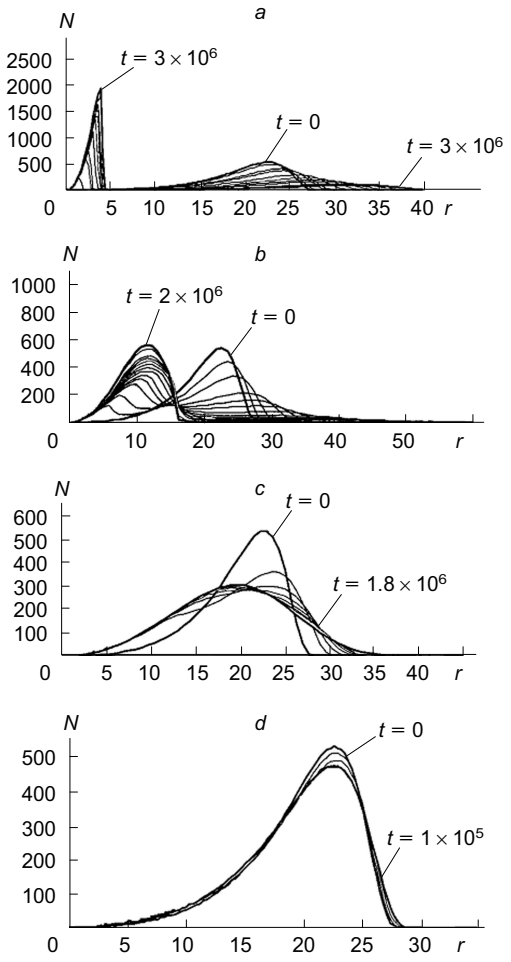


Figure 20. Transformation of the droplet size distribution during OR in emulsions with different interfacial layer elasticity.[129] E/γ_0 = 0.25 (*a*), 0.50 (*b*), 1.00 (*c*), 5.00 (*d*); the *N*, *r* and *t* in the calculations are expressed in relative units.

does not increase with time, unlike emulsions stabilized by only SDS.

Chebil *et al.*[130] investigated the OR stability of O/W emulsions with the dispersed phase of hexane, octane or dodecane. The emulsions stabilized by only dextran with a covalently grafted hydrocarbon substituent were highly unstable to OR. When a mixture of dextran and $\overline{C}_{12}\overline{E}_4$ was used to stabilize the emulsion, the time dependence of the droplet size had a region corresponding to an almost constant size. The duration of the OR inhibition (t_{inh}) varied from 3 h to several months as the dispersed phase was changed from hexane to dodecane. The rate of OR sharply decreased.

Dispersed phase	Hexane	Octane	Dodecane
ω_{exp}, $m^3\,s^{-1}$	5.1×10^{-24}	3.9×10^{-25}	2.1×10^{-27}
t_{inh}, h	3	51	>1500

It was shown[23] that the OR stability considerably increased when emulsions were stabilized by a mixture of sodium polyacrylate with grafted azobenzene groups and a surfactant ($\overline{C}_{12}\overline{E}_4$). This fact was attributed by the authors to the adsorption of a surfactant – polymer complex at the interface in the emulsion, giving rise to a viscoelastic film, which prevented OR.

Oil-in-water emulsions of silicone oil with a droplet of < 500 nm were stable, in particular, to OR when stabilized with amphiphilic triblock copolymers — poly(2-methacryloyloxyethyl phosphorylcholine)-*b*-poly(ε-caprolactone)-*b*-poly(2-methacryloyloxyethyl phosphorylcholine) and poly(2-aminoethyl methacrylate)-*b*-poly(ε-caprolactone)-*b*-poly(2-aminoethyl methacrylate).[131]

Balaj *et al.*[132] found that OR did not take place in emulsions with a hydrocarbon and perfluorohydrocarbon mixture as the dispersed phase when a calcium alginate shell was formed on the droplet surface. The authors reasonably emphasized that no surfactant was present in the dispersion medium; therefore, micellar solubilization did not occur and OR was suppressed. However, it should be noted that the droplet size was relatively large: < 50 μm.

Zeeb *et al.*[133] stabilized emulsions with fish gelatin and sugar beet pectin cross-linked with fish gelatin. The OR rate of fish gelatin-stabilized emulsions was $(7.3\pm0.2)\times10^{-26}$ $m^3\,s^{-1}$. In emulsions stabilized by cross-linked pectin and gelatin, the OR rate was two times lower — $(3.1\pm0.2)\times10^{-26}$ $m^3\,s^{-1}$, which was attributed to the formation of a polymer film on the droplet surface.

A similar result was obtained in another study:[134] O/W emulsions stabilized by transglutaminase-cross-linked sodium caseinate were more stable than sodium caseinate-stabilized emulsions. The cross-linking was performed prior to emulsification. In this case, emulsions were stable during long-term storage. If β-lactoglobulin was used instead of non-cross-linked sodium caseinate, the emulsion stability to OR also increased due to the formation of mechanically stronger gel-like β-lactoglobulin adsorption layer on the droplet surface.

Stabilization by hydrophobically modified inulin (polyfructose) markedly decreased the OR rate in nanoemulsions by increasing the Gibbs elasticity of the adsorption layer.[135]

Upon the formation of an interfacial film of cinnamaldehyde, chitosan and glycerol monocaprylate, emulsions of eugenol in water were stable to OR for three months and the size of droplets almost did not increase.[136]

An exceptionally high OR stability was found for droplets of glyceryl triacetate with dissolved doxorubicin surrounded by a polymerized diacelylene lipid shell.[137]

The stability of paraffin oil in water emulsions stabilized by a mixture of Span 20 and Tween 20 increased upon the addition of hydrophobically modified polyacrylamide.[138] The authors explained this result assuming that polyacrylamide was adsorbed at the water/oil interface forming a solid film that prevented OR.

Pluronic F68-stabilized emulsions of soybean oil in water remained stable, in particular to OR, for long periods of time. The size of dispersed phase droplets was 0.3 μm and barely changed during 6 months.[139]

In nanoemulsions stabilized by a mixture of lecithin and PEG stearates (Myrj s40, Myrj s50 and Myrj s100), the OR rate was shown to decrease several-fold when the lecithin : PEG stearate ratio was 0.15 – 0.60.[8]

A nonaqueous nanoemulsion of PEG-400 in Miglyol 812 medium-chain triglycerides was more stable, in particular to OR, when stabilized by the poly(2-vinylpyridine) block copolymer with polybutadiene than when stabilized by low-molecular-mass nonionic surfactants — Tween 80 and Span 80.[140]

In water-in-chloroform emulsions stabilized by dextran with grafted hydroxy-2-n-dodecyl groups, the OR process played a crucial role in the emulsion degradation when the

fraction of the dispersed phase in the emulsion was < 10%. The rate of droplet growth decreased as the polymer concentration increased.[141]

Alzobaidi *et al.*[142] demonstrated that a CO_2 foam in oil can be stabilized using a polymeric surfactant. The surfactant used for this purpose was polydimethylsiloxane with grafted hydrocarbon chains. It was assumed that the adsorption layer formed by this surfactant stabilizes the foam, in particular, to OR.

The surfactant molecular mass and, hence, its diffusion coefficient in the dispersion medium influence the rate of OR. If the emulsion is stabilized by a high-molecular-mass surfactant, then diminishing small droplets as a result of OR leads to an increase in the concentration of surfactant molecules in the interfacial layer due to their slow diffusion towards larger droplets. It was shown that the OR rate is lower when high-molecular-mass surfactants are used for foam stabilization.[143, 144]

The interfacial tension was higher in protein-stabilized emulsions than in emulsions stabilized by low-molecular-mass surfactants; therefore, in these systems, the OR rate was higher in the early period. During OR, small droplets decreased, and the protein adsorption layer became more dense, as its desorption from the interface was slow. This reduced the interfacial tension and, correspondingly, the rate of OR.[145]

A study of interfacial layers formed by amphiphilic polydimethylsiloxane – polyoxyalkylene graft copolymers showed that they stabilized emulsions of water in silicone oil, similarly to Pickering stabilization. These copolymers were soluble in silicone oil and, on contact with water, small particles of a concentrated solution of the copolymer in silicone oil spontaneously formed and these particles were adsorbed at the interface.[146]

An opposite effect was found for an O/W emulsion of silicone oil. When the macromolecular stabilizer was deposited at the interface, the emulsion stability decreased, their stabilization being attained only upon film formation on a droplet surface.[147]

It was not always possible to stabilize emulsions to OR using interfacial polymer films. If O/W emulsions are stabilized by a triblock copolymer, Pluronic PE9400 or Levenol C201 (polyoxyethylene glycerol fatty acid esters), the major degradation mechanism is OR in the case of Pluronic PE9400 and coalescence in the case of Levenol C201.[148] In nanoemulsions stabilized by amphiphilic block copolymers with poly(2-oxazolines), the lowest stability to OR was found for propyl-2-oxazoline-containing systems. After 60 days, the droplet size increased by >300%. More hydrophobic nonyl-2-oxazolines stabilized nanoemulsions much better.[149]

When phenoxy-substituted dextran with different substitution degrees was used to stabilize emulsions with dodecane or hexadecane as the dispersed phase, the OR rate was approximately the same as in emulsions stabilized by other surfactants (see Table 1).[150]

In nanoemulsions of isopropyl myristate in water stabilized by PEG-60 hydrogenated castor oil, the OR made the major contribution to the phase separation. The OR rate linearly increased with increasing concentration of ethanol in the dispersion medium due to the increase in the solubility of isopropyl myristate.[151]

In emulsions stabilized by SDS or proxanol P-268 (polymeric surfactant with a molecular mass of ~13 000), the formation of a polymer film on the droplet surface did not decrease the rate of alkane mass transfer irrespective of the hydrocarbon chain.[47]

The rate and direction of OR can be affected by not only a polymer film at the interface, but also a gel-like network formed by macromolecules. It was shown[152] that if liquid droplets appeared and grew in a polymer gel network, compressive stresses might markedly increase the internal pressure to far exceed the Laplace pressure. Experiments using a gel network with a stiffness gradient demonstrated that droplets in stiffer network areas dissolved, while droplets in softer network areas were enlarged. In this ripening, which was called elastic ripening by the authors, the direction of OR can be reversed: larger droplets would decrease in size, while smaller droplets would grow.

8.2. Solid and liquid-crystalline films at the interface

Koroleva *et al.*[153] studied O/W nanoemulsions stabilized by nonionic surfactants with different melting points — Tween 80 (T_m < 20 °C), Tween 60 (T_m = 24° C), Span 80 (T_m < 20 °C) and Span 60 (T_m = 55 °C). The nanoemulsion stability to OR at 20 °C sharply increased upon the formation of a solid adsorption film of Tween 60 and Span 60 on the droplet surface (Fig. 21).

Emulsions stabilized to OR by a semisolid polymer film formed on the droplet surface were prepared. The amphiphilic polyethylene oxide-*b*-poly(ε-caprolactone) diblock copolymer was mixed with various oils (phenyl trimethicone, polydimethylsiloxane, cetyl ethylhexanoate, dioctanoyl-decanoyl-glycerol, isopropyl myristate and paraffin oil) at 80 °C. This mixture was used as the dispersed phase in O/W emulsions. As the emulsions were cooled down to ambient temperature, polymer separation took place to give an interfacial film. The droplet size distribution of the resulting emulsions remained almost constant for 4 months.[154]

When limonene- and xylene-in-water emulsions were stabilized by hydrophobin HFBII, the adsorption layer on the droplet surface became solid. The solid shell prevented the transfer of oil molecules even in emulsions of xylene, which is more than 10 times water-soluble than limonene.[155]

The formation of a lamellar liquid-crystalline phase in the dispersion medium was detected in nanoemulsions stabilized by Aerosol OT [sodium bis(2-ethylhexyl)sulfosuccinate] at high electrolyte concentration. These nanoemulsions were stable to OR.[33]

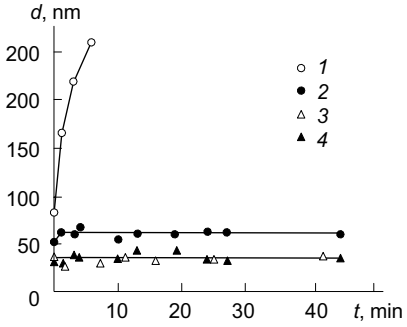


Figure 21. Time dependences of the average droplet diameter in O/W nanoemulsions stabilized by various combinations of nonionic surfactants.[153]
Surfactant: (*1*) Tween 80 + Span 80, (*2*) Tween 60 + Span 80, (*3*) Tween 80 + Span 60, (*4*) Tween 60 + Span 60.

8.3. Nano- and microparticles at the interface

A film can be formed on the droplet surface upon adsorption of solid nano- and microparticles. In this case, Pickering emulsions are formed. These emulsions can be stabilized by non-modified and surfactant-modified nanoparticles. Considering the rate of OR in these emulsions, one should take into account the droplet size of the dispersed phase. Pickering emulsions with droplets several tens of micrometres in size are formed most often. In these emulsions, the OR process does not take place due to small curvature of the interface and, hence, low Laplace pressure. Nevertheless, OR can take place between micrometre (and smaller) droplets.

Some researchers (see, *e.g.*, Refs 70, 145, 156) noted that adsorption of particles on the droplet surface may considerably retard and even stop OR.

If the droplet is not completely coated by adsorbed particles, the interfacial tension in the gaps corresponds to the interfacial tension at the water/oil interface. In the absence of a surfactant, the interfacial tension in the system is rather high and the interface is curved; therefore, OR takes place (Fig. 22 *a*). If the droplet surface is coated with a dense adsorption layer, the interface becomes saddle-shaped with local curvature radii r_1 and r_2 (Fig. 22 *b*). The local curvature radii of the menisci between the adsorbed particles become equal in magnitude and opposite in sign ($r_1 = -r_2$), and their effects are counterbalanced. Therefore, it can be assumed that OR is almost absent in such emulsions,[145] as the Laplace pressure in droplets is nearly zero

$$\Delta P_{\mathrm{Lp}} = \gamma(1/r_1 + 1/r_2) \approx 0 \qquad (19)$$

The polyhedral structures were formed in foams stabilized by polystyrene nanoparticles with a narrow size distribution; the particle radius to gas bubble radius ratio was ~0.1. The Laplace pressure was very low due to the absence of curvature and the foams were stabilized to OR.[157]

The OR rate considerably decreased when emulsions of 4-cyano-4′-pentylbiphenyl in water were stabilized by microparticles of the poly(*N*-isopropylacrylamide) gel at 4 : 1 mass ratio of the dispersed phase to the microparticles (Fig. 23).[156]

Persson *et al.*[158] showed that in O/W nanoemulsions stabilized by silica nanoparticles and containing hexadecane or squalene as the dispersed phase, the OR almost did not take place for 1.5 months and three years, respectively. In

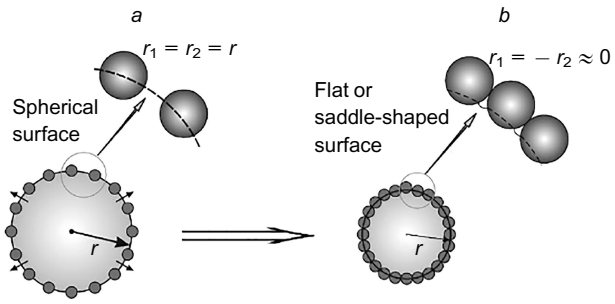


Figure 22. Schematic drawing of the droplet surface not completely covered by adsorbed particles (*a*) and completely coated with a dense adsorption layer of particles (*b*).[145] r_1 and r_2 are the local meniscus radii at the water/oil interface.

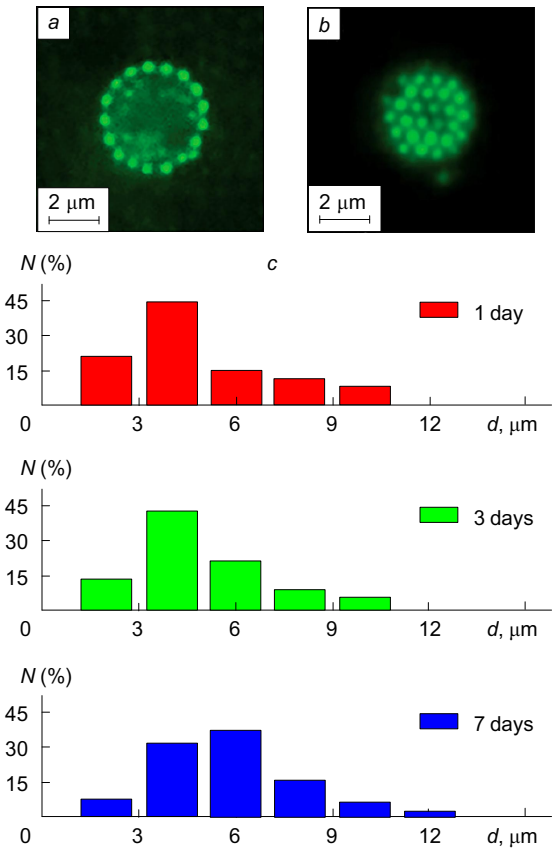


Figure 23. Spinning disk confocal microscopy images of the emulsion droplets (*a*, *b*) and size distributions of emulsion droplets (*c*).[156] (*a*) droplet cross-section, (*b*) lateral view.

the case of Pickering nanoemulsions with dispersed phase of shorter hydrocarbon chain alkanes, OR did proceed due to insufficiently low solubility of these compounds in the dispersion medium of nanoemulsions.

In Pickering emulsions stabilized by poly(glycerol monomethacrylate-*b*-2,2,2-trifluoroethyl methacrylate) nanoparticles of ~8.4 nm size, OR was detected if the dispersed phase droplets consisted of octane or decane. In emulsions containing dodecane and tetradecane, the average droplet size barely changed during six months, as the solubility of these alkanes in the aqueous phase was markedly lower.[159]

In W/O emulsions with perfluorocarbon dispersion medium stabilized by silica nanoparticles, the OR was almost absent.[160] As indicated by the authors, the nanoparticles did not form micelles; therefore, the major mass transfer route between the droplets was eliminated.

The cyclohexane droplets stabilized by lignin nanoparticles with grafted polyacrylamide chains were stable to OR and almost did not increase in size for a month (and more).[161]

Binks *et al.*[99] described the results obtained for compositional ripening that took place upon mixing of two emulsions containing β-ionone and squalane as the dispersed phases and stabilized by silica nanoparticles or $\overline{C}_{12}\overline{E}_8$ ethoxylated surfactant. β-Ionone (smaller droplets in Fig. 24 *a*) migrated to squalane droplets (larger droplets in Fig. 24 *a*). As time went on, the size of β-ionone droplets decreased, whereas the size of squalane droplets increased

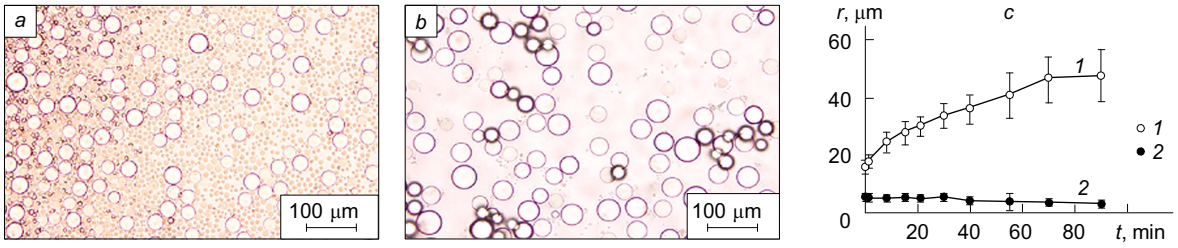


Figure 24. Micrographs of a mixture of emulsions with β-ionone and squalane stabilized by silica nanoparticles in the initial stage (*a*) and after complete dissolution of β-ionone droplets (*b*) and kinetic curves for variation of the average droplet radius of squalane (*1*) and β-ionone (*2*) (*c*).[99]

(Fig. 24 *c*). If an excess of nanoparticles was added to the emulsion, they were adsorbed on the growing squalane droplets, and the system was stable to coalescence. A linear time dependence of the cube of the average radius was observed for emulsions stabilized by the surfactant and for emulsions stabilized by excess nanoparticles.

Trujillo-Cayado *et al.*[70] prepared stable emulsions containing thyme oil in the dispersed phase and stabilized by the Kolliphor EL surfactant (Cremophor EL, polyoxyethylated castor oil) and by Aerosil®COK 84 nanoparticles, which are a 5 : 1 mixture of Aerosil®200 silica nanoparticles and AEROXIDE®Alu C alumina nanoparticles. As shown by the authors,[70] nanoparticles were adsorbed on the droplet surface and formed a gel-like network in the emulsion dispersion medium. As a result of nanoparticle adsorption, the rate of OR in these emulsions sharply decreased.

Foam stabilization by solid particles of LamemuL®K 2000 K surfactant (a mixture of mono- and diglycerides) in vegetable oils were also stabilized to OR.[162]

In O/W emulsions with polychlorinated biphenyl stabilized by bentonite, iron oxide or magnesium oxide, OR was not stopped. The OR rate was 2.7×10^{-25} m^3 s^{-1} (Ref. 163).

In nonaqueous Pickering emulsions of glycerol in dodecanol, the OR rate was relatively high — 1.17×10^{-21} m^3 s^{-1} (Ref. 164). However, the authors emphasized that, more probably, OR was not the predominant process, and flocculation could also make a certain contribution to enlargement of the droplets.

The use of nano- and microparticles of hydrocolloids does not always result in stabilization of emulsions. Most hydrocolloids are deformable particles; therefore, they cannot completely prevent OR.[165]

Thus, the fabrication of strong interfacial films on the droplet surface in emulsions can retard OR; however, this method is not always effective.

9. Effect of surfactant type and concentration on the Ostwald ripening rate

The LSW theory was originally developed for solid solutions with one-component dispersed phase. These systems are different from emulsions because no surfactant molecules are present either at the interface or in the dispersion medium. If the surfactant concentration in the dispersion medium of an emulsion exceeds the CMC, substances of the dispersed phase droplets can be solubilized in the surfactant micelles. In this case, micelles can participate in the mass transfer from smaller droplets to larger ones, especially if the solubility of the diffusing substances in the dispersion medium is very low.

Analysis of publications dealt with experimental studies of OR in O/W emulsions makes it possible to identify three ranges of surfactant concentrations affecting the OR rate in different ways:

— if the concentration of the surfactant in the dispersion medium is lower than CMC, the OR rate decreases with increasing surfactant concentration due to a decrease in the interfacial tension on the droplet surface;

— if the surfactant concentration in the dispersion medium exceeds the CMC, the OR rate increases with increasing surfactant concentration; in most publications, the experimental rates of OR were higher than those calculated by Eqn (6) with allowance for molecular solubility, but were considerably lower than those calculated with allowance for micellar solubilization of the dispersed phase substance in micelles;

— at high concentrations of the surfactant in the dispersion medium, the rate of OR either increased, but to a lesser extent, or decreased.

The surfactant effect on the OR rate in emulsions with alkanes in the dispersed phase was studied most comprehensively for SDS. Taylor and Ottewill[48,166] studied OR in emulsions of dodecane in water stabilized by SDS with some pentanol added. In the concentration range below CMC, the OR rate and the interfacial tension at the oil/water interface decreased almost linearly with increasing log$C$ (Fig. 25). This pattern is in line with the LSW equation, which shows a linear dependence of the OR rate on γ. At higher concentrations above CMC, the rate of OR sharply increased, despite the fact that the interfacial tension remained almost constant.

A similar dependence was obtained by Djerdjev and Beattie[35] (see Fig. 25). The increase in the OR rate at SDS concentrations above CMC was attributed to the fact that in the early period OR took place and the droplet diameter increased from the initial ~200 nm to ~300 nm. When the droplets became larger ($d > 300$ nm), the OR rate increased. This was attributed to depletion flocculation of decane droplets; however, increase in the rate as a result of higher solubilization in micelles was not ruled out.

Taylor[16] reported data on the OR in SDS-stabilized emulsions of decane in water. Initially, emulsions with a dispersed phase fraction of 0.3 and an SDS concentration of 0.174 mol L^{-1} were prepared. Then the emulsions were diluted with water, and the SDS concentration in dilute emulsions varied from 0.0078 to 0.174 mol L^{-1}.

The critical micelle concentration of SDS in water is 8.2×10^{-3} mol L^{-1} (Ref. 167). Thus, the surfactant con-

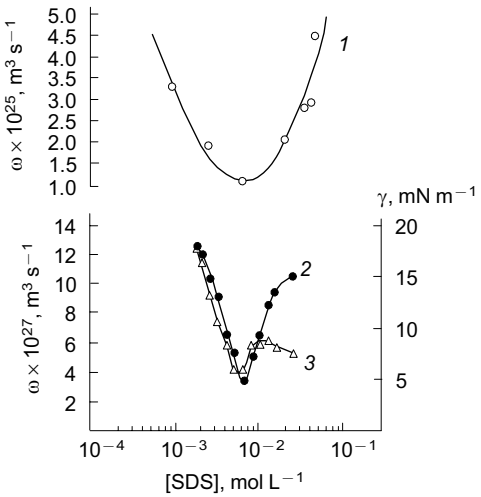


Figure 25. Ostwald ripening rate (*1*, *2*) and interfacial tension (*3*) *vs.* SDS concentration in dodecane [35] and decane [166] emulsions. Dodecane emulsions also contained 0.071% pentanol.

centration in these emulsions was either slightly below or considerably above the CMC. As the SDS concentration increased, the OR rate increased (Fig. 26). At higher substance concentrations, the difference in the OR rate was within the measurement error.

Kabalnov *et al.*[168] investigated the OR rate in O/W emulsions of saturated hydrocarbons with different chain lengths ranging from decane to hexadecane. The authors studied emulsions with a dispersed phase fraction of 3.3×10^{-5} and SDS concentration below the CMC (3.3×10^{-5} mol L^{-1}) or a dispersed phase fraction of 0.1 and SDS concentration above the CMC (0.1 mol L^{-1}). If the surfuctant concentration was above the CMC, the experimental OR rates decreased by a factor of $3.8 \cdot 10^4$ as the hydrocarbon chain was elongated from C_{10} to C_{16} (Table 6); however, the rates were still several-fold higher than the theoretical values calculated taking account of the molecular solubility.

The same authors [168] reported the OR rates in emulsions of decane in water stabilized by a 0.1 M SDS solution at various temperatures. According to the presented results, the OR rate at a temperature above the Krafft point was ~3 times higher than the OR rate at temperatures below the Krafft point. Despite the considerable difference of the OR rates in the emulsions containing surfactant micelles in the dispersion medium (at temperatures above the Krafft point), the authors [168] held to the opinion that solubilization in the surfactant micelles did nor make a considerable contribution to the OR kinetics.

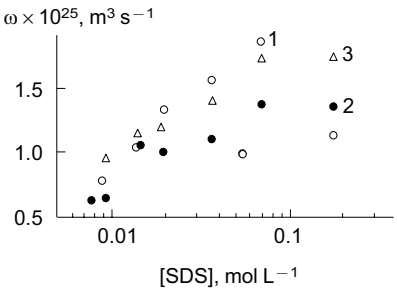


Figure 26. Ostwald ripening rates *vs.* SDS concentration in emulsions of decane in water. Different points correspond to the results of three series of independent measurements.[16]

Soma and Papadopaulos [169] investigated SDS-stabilized emulsions of decane in water, with SDS concentration being varied in the range of 0.0001 – 0.05 mol L^{-1}. The fraction of the dispersed phase was 0 – 0.002. The data on the OR rates in emulsions with a dispersed phase fraction of 0.002 and various SDS concentrations are summarized in Table 7.

Table 7. Experimental and theoretical OR rates in SDS-stabilized emulsions of decane in water.[169]

Concentration of SDS, mol L^{-1}	ω_{theor}, m^3 s^{-1}	ω_{exp}, m^3 s^{-1}	$\omega_{exp}/\omega_{theor}$
0	1.62×10^{-25}	2.50×10^{-24}	15.43
1.0×10^{-4}	1.59×10^{-25}	4.62×10^{-25}	2.91
5.0×10^{-4}	1.35×10^{-25}	4.17×10^{-25}	3.09
1.0×10^{-3}	1.17×10^{-25}	3.68×10^{-25}	3.15
5.0×10^{-3}	5.41×10^{-26}	2.13×10^{-25}	3.94
1.0×10^{-2}	2.82×10^{-26}	2.06×10^{-25}	7.31
2.5×10^{-2}	2.82×10^{-26}	2.87×10^{-25}	10.18
5.0×10^{-2}	2.82×10^{-26}	3.64×10^{-25}	12.91

At surfactant concentrations below CMC, the rate of OR decreased with increasing SDS concentration. According to the LSW theory, this is due to the decrease in the water/oil interfacial tension in the emulsion. If the concentrations were above the CMC, the OR rate increased with increasing SDS concentration. The theoretical OR rates were calculated using the following characteristics of decane: water solubility, 5.1×10^{-5} kg m^{-3}; and diffusion coefficient, 6.79×10^{-10} m^2 s^{-1}. The interfacial tensions were determined previously.[167] The experimental OR rates were more than two times higher than the calculated values. This difference was attributed to the Brownian motion of the dispersed phase droplets in the emulsion, which is neglected by the LSW theory.

Llamas *et al.*[170] determined the OR rate in an SDS-stabilized emulsion of dodecane in water. The OR rate was 3.2×10^{-26} m^3 s^{-1} at the surfactant concentration of 7×10^{-4} mol L^{-1}.

Kabalnov [12] determined the OR rates in emulsions of $C_{11}H_{24}$ in water with a dispersed phase fraction of 0.1 over a wider range of SDS concentrations. The obtained results were used to plot the dependences of the OR rate and micellar solubilization of undecane as functions of the SDS concentration (Fig. 27).

Table 6. Ostwald ripening rate in SDS-stabilized emulsions of saturated hydrocarbons in water; solubilities of hydrocarbons in water and solubilization in SDS micelles.[168]

Hydrocarbon	Solubility in water, mL mL^{-1}	Solubilization in 0.1 M SDS solution, mL mL^{-1}	ω_{theor}, m^3 s^{-1}	ω_{exp}, m^3 s^{-1}	$\omega_{exp}/\omega_{theor}$
Decane	7.1×10^{-8}	4.0×10^{-3}	0.7×10^{-25}	2.3×10^{-25}	3.3
Tridecane	1.4×10^{-9}	2.0×10^{-3}	1.6×10^{-27}	4.1×10^{-27}	2.6
Hexadecane	2.7×10^{-11}	0.5×10^{-3}	2.2×10^{-29}	8.7×10^{-29}	4.0

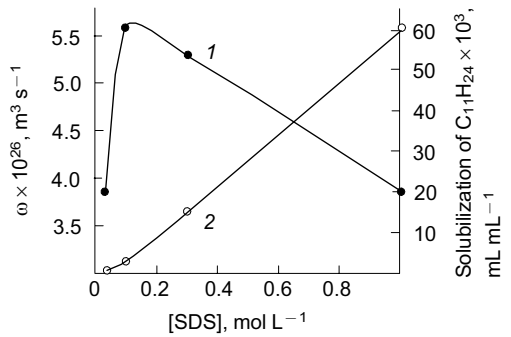


Figure 27. Ostwald ripening rate (*1*) and solubilization (*2*) of undecane in micelles *vs*. SDS concentration plotted by the authors using data of Kabalnov.[12]

As the concentration of the surfactant was above CMC, solubilization of undecane in SDS micelles sharply increased. The OR rate did not increase in proportion to solubilization. In view of this fact, the author concluded that micelles cannot serve as undecane carriers in these emulsions.

The results reported in the cited publication were obtained for only four widely different concentrations of the surfactant. Higher studied concentrations of SDS were above the CMC_2, that is, the concentration above which the surfactant micelles were non-spherical. In the studied emulsion, the dispersion medium could contain non-spherical micelles and other surfactant structures with diffusion coefficients lower than those of spherical micelles; therefore, the OR mechanism could considerably differ from the mechanism described by the LSW theory.

De Smet *et al.*[13] presented comparative analysis of the OR rates in SDS-stabilized emulsions reported by various authors. It was noted that differences between the results could be due to the difference in purity of the surfactants used and to partial SDS hydrolysis to form dodecanol. In order to eliminate the influence of the products of surfactant hydrolysis, OR was studied in emulsions stabilized by sodium dodecylbenzenesulfonate, which was not hydrolyzed in water. The dispersed phase fraction in undecane-in-water emulsions was 0.01. The surfactant concentration in the emulsions was markedly higher than the CMC ($\sim$0.002 mol L^{-1}), being in the range from 0.033 to 0.15 mol L^{-1}. An increase in the surfactant concentration in these emulsions resulted in some decrease in OR. This finding was attributed to the fact that the average droplet diameter increased and the specific interfacial area decreased and, hence, the amount of the adsorbed surfactant diminished during OR. An excess amount of the surfactant dissolved in the dispersion medium and formed micelles. The concentration of micelles in the dispersion medium of the emulsions increased during OR. As time went on, the amount of oil solubilized in micelles increased and, hence, the OR rate might be decreased.

Investigation of emulsions stabilized by other surfactants showed that the rate of OR depends on the type of surfactant.[171] In emulsions of octane in water stabilized by cationic surfactants such as dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide and trimethylcetylammonium bromide and by nonionic n-dodecyl-β-maltoside surfactant ($C_{12}G_2$), the OR rates were 1.3×10^{-21}, 3.3×10^{-22}, 3.1×10^{-22} and 7.8×10^{-23} m^3 s^{-1}, respectively.

In nanoemulsions with cinnamon essential oil stabilized with a 9 : 1 mixture of nonionic Tween 80 and cationic lauric arginate or anionic lysolecithin, the OR was lower than the OR rate in nanoemulsions stabilized by only Tween 80.[172] Mixed surfactant micelles had a higher surface charge; therefore, the OR rate in these emulsions was lower.

If the dispersed phase contained a substance with low water solubility, *e.g.*, hexadecane, and was stabilized with either Tween 20 or arabic gum, these emulsions were stable to OR. Emulsions with decane in the dispersed phase with the same surfactants were unstable to OR.[173]

In paraffin oil-in-water emulsions stabilized by a mixture of Tween 80 and Span 80, the OR rate decreased from 7.1×10^{-29} to 0.9×10^{-29} m^3 s^{-1} as the total surfactant concentration increased from 4 mass % to 8 mass %.[174] The authors emphasized that at these surfactant concentrations, the monolayer adsorption on the droplet surface was achieved, and the excess amount of surfactants was present in the dispersion medium as micelles. Mei *et al.*[175] also observed a decrease in the OR rate with increasing surfactant concentration in paraffin oil nanoemulsions stabilized by a mixture of Tween 80 and Span 80.

The rate of OR in nanoemulsions of ethyl oleate in water stabilized by Cremophor EL and containing butan-1-ol decreased with increasing surfactant concentration.[176]

When the concentration of a surfactant such as polyethylene glycol monolaurate with a molecular mass of $\sim$600 was increased, the OR rate in decane- and undecane-in-water emulsions decreased and was lower than the theoretical value calculated by the LSW equation.[177] The decrease in the OR rate was attributed to hydrocarbon solubilization in micelles that decreased the rate of hydrocarbon transport from smaller droplets to larger ones.

Weiss *et al.*[178] reported the results of studying OR in tetradecane-in-water emulsions stabilized by Tween 20, Tween 40, Tween 60 and Tween 80. The OR rate in these emulsions first increased and then decreased with increasing surfactant concentration. The authors assumed that the decrease in the OR rate could be due to the following factors:

— decrease in the diffusion coefficient of micelles at higher surfactant concentrations caused by increasing viscosity;

— formation of other self-associated structures of the surfactant that transport the oil at a lower rate than spherical micelles;

— formation of a surfactant multilayer film on the droplet surface in the emulsions, which retarded the diffusion of oil molecules from the droplets.

It should be noted that publications dealing with the effect of surfactant concentration on the OR rate do not consider the concentration ranges of various surfactant structures. As a rule, only the CMC_1 (critical concentration above which spherical micelles are formed) is indicated, and even this value is not always present. The published results on the OR rate could be obtained for emulsions with various self-associated surfactant structures in the dispersion medium, such as lamellar, cubic, hexagonal and others; therefore, it is impossible to draw an unambiguous conclusion about the effect of relatively high surfactant concentrations on the rate of OR.

10. Possible mechanisms of mass transfer between droplets of the dispersed phase in the Ostwald ripening

The mechanism of mass transfer between the dispersed phase droplets in emulsions during OR is currently a debated issue. Certainly, different mechanisms can be implemented in various emulsions depending on the composition and solubility of components.

If the solubility of the dispersed phase substance in the dispersion medium is not infinitely low, the great contribution to the OR rate is made by molecular diffusion. In addition, surfactant molecules can also participate in the mass transfer from smaller to larger droplets. The transfer can occur upon hydration of the polar groups of surfactant molecules in the case of water diffusion or by association between molecules of the dispersed phase substance and the surfactant. The dispersed phase substance can also be transported through the dispersion medium as solubilized into the core of micelles or nanoemulsion droplets. The most controversial issue is still the mechanism of transfer of the dispersed phase substance that has a very low solubility in the dispersion medium.

Oil-in-water emulsions. Many authors who studied the rate of OR in O/W emulsions supposed that the mass transfer from smaller droplets to larger ones occurs by molecular diffusion, as there is no sharp increase in the OR rate following the increase in the surfactant concentration in the emulsion.[12, 17, 168, 179, 180] However, the rate of OR depends on the nature of the surfactant.[29] In addition, solubilization of the dispersed phase substance in surfactant micelles resulted in increasing OR rate.[98, 106, 145, 181] This gave reason to assume that the organic phase is transported through the aqueous dispersion medium of emulsions by means of micelles[15, 100, 101, 169] or microemulsion droplets.[182] However, it was often emphasized that if surfactant concentrations exceeded the CMC, the rate of OR increased but to a lesser extent than it could be expected take into account the solubilizing capacity of micelles.

The role of micelles in the mass transfer between droplets was most actively debated in the scientific literature in the 1990s. For example, one article was entitled 'Can Micelles Mediate a Mass Transfer between Oil Droplets?'.[12] That paper considered the following mechanisms for the transport of substances between droplets in emulsions and the possible role of micelles in this process:

(1) micelles can collide with the dispersed phase droplets; therefore, they take up the substance from smaller droplets and exchange it with larger droplets as this is a fusion – fission process;

(2) micelles cannot collide with the dispersed phase droplets; therefore, they solubilize the dispersed phase substance from a molecular solution in the dispersion medium; solubilization is a relatively fast process, and micelles occur in a local equilibrium with the dispersion medium;

(3) micelles cannot collide with emulsion droplets; they solubilize the substance dissolved in the dispersion medium; solubilization is a slow process; therefore, micelles are not in local equilibrium with the dispersion medium.

If the first mechanism is implemented, the rate of mass transfer should be proportional to the number of collisions between the droplets and micelles, *i.e.*, it should be proportional to the numerical concentration of micelles, which is not always confirmed by experimental data. If the emulsion is stabilized by an ionic surfactant, droplets and micelles are like-charged and that prevents them from colliding. Thus, if the second mechanism is valid, the OR rate is expected to increase in the presence of micelles by the factor β

$$\beta = 1 + \frac{SD_m}{C_b^{\infty} D} \tag{20}$$

Here S is the solubilizing capacity of the micelles, C_b^{∞} is the concentration of a saturated solution of the dispersed phase substance in the dispersion medium, D_m and D are the diffusion coefficients of micelles and molecules, respectively.

Kabalnov[12] showed that for decane-in-water emulsions stabilized by a 0.1 M SDS solution at $D_m : D = 0.01$ and $S : C_b^{\infty} = 10^5$, one should expect a $\geqslant$1000-fold increase in the OR rate due to the presence of micelles in the emulsion dispersion medium. However, this was not confirmed experimentally. According to rough estimates, the time required to establish the equilibrium between a micelle and the dispersion medium was 0.1 s; the time a micelle existence near a droplet was $\sim$0.001 s. Since the micelle velocity was rather high and solubilization was slow, it was concluded that micelles were not in a local equilibrium with the dispersion medium.

Carroll[190] studied the rate of dissolution of microscopic oil droplets, which were adhered to fibres immersed into an aqueous solution of a nonionic surfactant — tetraethylene glycol octyl ether ($\overline{C}_8\overline{E}_4$). The oil solubility in water was very low ($<10^{-9}$ mass %). The dissolution rate of oil droplets at a temperature below the Krafft point was $\sim$100 times lower than that at temperatures above the Krafft point, *i.e.*, when surfactant micelles were present in the aqueous solution. Relying on these data, the author suggested that in the case of poorly soluble substances, the solubilization of the dissolved substance in micelles is unlikely. Therefore, the following solubilization mechanism took place in the presence of nonionic surfactants: diffusion of a micelle towards a droplet, disintegration of the micelle, adsorption of surfactant molecules on the droplet surface and the subsequent desorption giving a swollen micelle containing the solubilized substance.[183]

The time of micelle existence is determined by the duration of the residence of individual molecules in a micelle and the duration of complete disintegration and rearrangement of micelles. The time of disintegration and rearrangement of SDS micelles at the CMC is 1.8×10^{-3} s (Ref. 184), and it is almost not changeed if the SDS concentration increases to 5×10^{-2} mol L^{-1} (Ref. 185). Similar results were obtained by Ward and Quigley.[186] The average disintegration time of SDS micelles, adsorption of molecules at the oil/water interface and desorption giving micelles with oil molecules amounted to 10^{-3} s.

The fact that the time of micelle existence near a droplet[12] was comparable with micelle disintegration and rearrangement time confirmed a rather high probability of the solubilization mechanism including micelle disintegration, adsorption and desorption.[169]

Weiss *et al.*[14] considered the following possible mechanisms of solubilization in micelles:

— the uptake of oil molecules dissolved in the aqueous phase by micelles (Fig. 28 *a*);

— collision of micelles with the surface of emulsion droplets (Fig. 28 *b*);

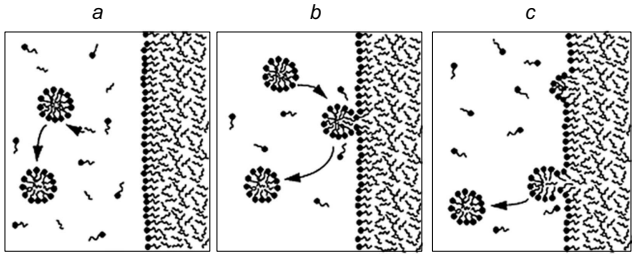


Figure 28. Schematic drawing of the solubilization mechanisms in O/W micelles: uptake of oil molecules dissolved in the aqueous phase (*a*), collision of micelles with the emulsion droplet surface (*b*), spontaneous desorption of the oil and surfactant molecules from the droplet surface as swollen micelles with oil (*c*).[14]

— desorption of oil and surfactant molecules from the droplet surface to give swollen micelles with oil (Fig. 28 *c*).

In the case of the first mechanism, the solubilization rate was proportional to the oil solubility in the aqueous phase. Molecular dynamics calculations demonstrated that this mechanism is valid only for solubilization of hydrocarbons with a chain length of a few carbon atoms. Therefore, the most likely mechanism of oil solubilization in micelles is simultaneous desorption of oil and surfactant molecules from the interface.[187, 188]

Weiss *et al.*[14] considered the micelle formation as a result of simultaneous detachment of oil and surfactant molecules from the droplet surface and assumed that the mass transfer between the droplets mainly takes place on collisions of micelles with the droplet surface.

In homologous series, the adsorption rate is lower for surfactants with a longer hydrocarbon chain than for short-chain surfactants.[189] In many experiments dealing with studying OR in emulsions, the rate of surfactant adsorption showed an exponential dependence on the CMC value; therefore, it was concluded that, first, disintegration of micelles takes place and then single surfactant molecules are adsorbed at the interface.[97]

Analysis of experimental data showed that both micellar solubilization mechanisms are possible, that is, incorporation of oil molecules dissolved in the aqueous medium into micelles, and collisions of micelles with the surface of the dispersed phase droplets.[14, 190, 191] If the surfactant has a high hydrophilic – lipophilic balance (HLB), the major solubilization mechanism is the transfer of dissolved oil molecules into the micelle core. In this case, solubilization is slow and depends on the oil solubility in the aqueous dispersion medium.[97] In the case of surfactants with a lower HLB of 9 – 12, the solubilization rate is high, and the more likely mechanism is that implemented upon micelle collisions with the interface in the emulsion.

It was shown[14] that the rate of increase in the average droplet diameter in an O/W emulsion depends on not only the hydrocarbon chain length, but also on the chemical structure of the oil molecule. If the dispersed phase was composed of a saturated hydrocarbon, the OR rate was lower than in emulsions of an unsaturated hydrocarbon with the same chain length. The solubilization of unsaturated hydrocarbons in Tween 20 micelles was several orders of magnitude faster than that of saturated hydrocarbons. Despite this considerable difference between the rates of oil solubilization in micelles, the OR rates for emulsions with saturated and unsaturated hydrocarbons differed by a factor of only 2 – 3.

For O/W emulsions stabilized by nonionic surfactants, it was shown[178] that the OR rate decreased in the following order of surfactants: Tween 80 > Tween 20 > Tween 40 > Tween 60 > Triton SP 190 > Triton SR 175. The OR rate was inversely correlated with the solubilizing capacity of micelles. This was attributed to the fact that a large amount of oil was rapidly solubilized in micelles formed by more hydrophobic surfactants. The oil desolubilization rate was much lower; therefore, the oil transfer to micelles prevailed.

Ariyaprakai and Dungan[192] studied the influence of nonionic surfactants on the OR rate. It was shown that the rate increases with increasing concentration of the surfactant. However, no correlation with the solubilizing capacity of the surfactant micelles was identified.

A higher OR rate was observed for Tween 20-stabilized emulsions of decane in water than for similar emulsions stabilized by Tween 80.[193] A more than 10-fold increase in the OR with increasing concentration of the surfactant was attributed to the fact that the transport by surfactant micelles is the predominant mechanism of decane transfer from smaller droplets to larger ones.

De Smet *et al.*[13] suggested that the major role of surfactant micelles is not to carry oil molecules between the oil droplets in O/W emulsions, but to enhance the oil solubility in the aqueous medium, which is higher in the presence of micelles. Therefore, micelles were treated as small oil droplets. In this case, the molecular solubility of oil in the aqueous phase was calculated by the equation

$$\frac{C_{\mathrm{m}}^{\infty}}{C_{\mathrm{b}}^{\infty}} = \exp\left(\frac{2\gamma V_{\mathrm{m}}}{RTr_{\mathrm{m}}}\right) \qquad (21)$$

where C_{m}^{∞} is the concentration of a saturated solution (solubility) of oil in water in the presence of oil droplets and micelles, r_{m} is the micelle radius. If the radius of the micelles of 2 – 5 nm is substituted into this equation, this will give

$$\frac{C_{\mathrm{m}}^{\infty}}{C_{\mathrm{b}}^{\infty}} \approx 1.4 - 2.4 \qquad (21a)$$

In the authors' opinion,[13] in the presence of micelles in the dispersion medium of the emulsion, the OR rate should increase by the same factor. Indeed, exactly this increase in the OR rate was observed in SDS-stabilized O/W emulsions (for example, see [12, 13, 166, 169]).

If emulsions were stabilized by nonionic surfactants, the presence of micelles in the dispersion medium resulted in a somewhat more pronounced (approximately 4-fold) increase in the OR rate. Weiss *et al.*[178] also held the opinion that micelles can transport the oil during OR both *via* solubilization of molecules dissolved in the aqueous medium and upon micelle collisions with dispersed phase droplets. The oil solubility is higher near droplets due to curvature of their surface; therefore, when micelles approach droplets, oil solubilization takes place. In this case, the OR rate increases depending on the amount of solubilized oil and on the diffusion coefficient.

Ionic surfactant micelles cannot directly approach the droplet surface because of electrostatic repulsion; therefore, they take up less oil. Micelles of nonionic surfactants take up more oil, as electrostatic repulsion is almost absent. Hence, they increase the OR rate to a higher extent. Therefore, Eqn (20) was supplemented by the factor α, which

depends on the energy barrier that hampers collisions of micelles with dispersed phase droplets,

$$\beta = 1 + \alpha \frac{SD_m}{C_b^{\infty} D} \quad (22)$$

If there is no energy barrier, micelles can collide with droplets and, in this case, the OR rate is expected to increase according to Eqn (20).[178] However, in real experiments, the OR rate increased, but to a lesser extent. The α value that was calculated by the authors from their experimental data was $3 \times 10^{-5} - 4 \times 10^{-4}$. The authors concluded that either micelles are not in local equilibrium with droplets or there is a very high energy barrier.

In the presence of an energy barrier, the OR rate is reasonably lower than without a barrier. If an SDS-stabilized emulsion is diluted with an SDS solution with concentration exceeding the surfactant concentration in the dispersion medium, the rate of OR increases, but to a lesser extent. When a Tween 20 solution with a concentration higher than the surfactant concentration in the dispersion medium is added to a nanoemulsion stabilized by nonionic Tween 20, the OR rate increases with increasing the surfactant concentration. The experimental OR rates exceeded those calculated by the LSW equation by factors of 2.4 – 19.0.[194] Meanwhile, the results of mathematical modelling using the molar ratio of the oil and surfactant that participate in the oil transfer between the droplets demonstrated that experimental results are described most adequately if this parameter is taken to be twice higher than oil solubilization in micelles.[195]

Weiss and McClements[191] investigated the escape of tetradecane from dispersed phase droplets to the aqueous dispersion medium and solubilization in various surfactant micelles. The coefficient of tetradecane mass transfer through the droplet surface increased with decreasing HLB of the surfactant (Fig. 29 *a*). The same trend was observed for the solubilizing capacity of micelles, which increased with decreasing surfactant HLB (Fig. 29 *b*). In the authors' opinion, on moving away from HLB equal to 7, the optimal curvature radius of the surfactant layer increased, and this resulted in the formation of smaller micelles.

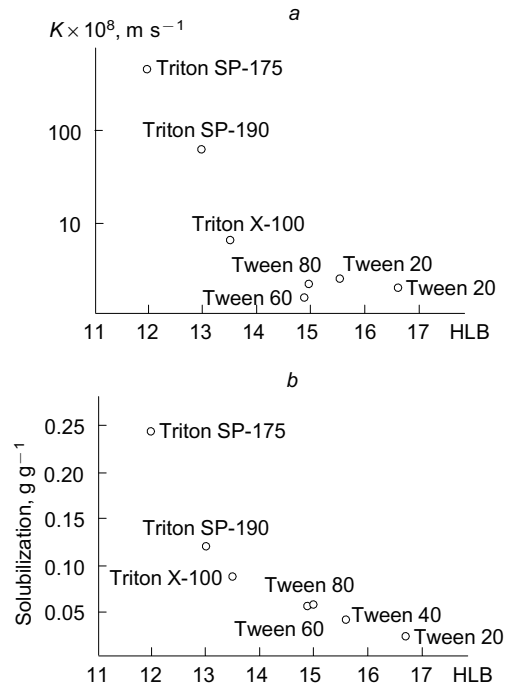


Figure 29. Mass transfer coefficients (K) for the organic phase across the droplet surface in an O/W emulsion (*a*) and solubilizing capacity of micelles (*b*) depending on the hydrophilic – lipophilic balance of the surfactant.[191]

Pulse-field gradient NMR spectroscopy[181] showed that the dispersion medium of alkane – Triton X-100 – water emulsions contained micelles with the solubilized alkane. The size of these micelles (microemulsion droplets) was 20 nm. In the authors' opinion, micelles mediated the alkane transfer between the droplets, which increased the OR rate.

Investigation of emulsions with hydrocarbons in the dispersed phase in the absence of surfactants showed the occurrence of mass transfer between small and large droplets.[30] The OR rates were comparable with the rates of hydrocarbon transfer in surfactant-stabilized emulsions. No micelles were present in these emulsions. However, the micrographs obtained with freeze – fracture electron microscopy some period after the emulsion preparation contained droplets 20 – 50 nm in diameter (Fig. 30). The number of large droplets was much lower than the number of nanodroplets; therefore, the latter can be assumed to be responsible for the mass transfer in the system. It cannot be ruled out, however, that some of these nanodroplets are small droplets that have decreased to the nanometre size due to oil transfer to larger droplets.

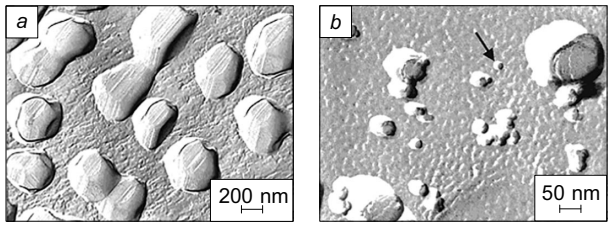


Figure 30. Freeze – fracture electron microscopy images of a cyclohexane-in-water emulsion: (*a*) emulsion immediately after the preparation, (*b*) emulsion after some period of time. The arrow shows one of the nanodroplets.[30]

The mathematical modelling of OR in emulsions studied experimentally by Llamas *et al.*[170] was performed using the Brownian dynamics method.[196] According to the results, in emulsions of octane in water stabilized by dodecyl-β-maltoside ($C_{12}G_2$), the unimodal size distribution of droplets was transformed with time into a bimodal distribution. As can be seen from dependences shown in Fig. 31, smaller droplets were relatively large (~400 nm). The position of the first maximum almost was not shifted and the height of the peak was not decreased in the time range of 3300 – 8300 s, while the peak width reduced with time.

Otero *et al.*[197] studied the mass transfer between two droplets placed in a mixture of toluene and ethanol in 9 : 1 volume ratio. One droplet consisted of distilled water, while the other one was composed of a 1 : 1 mixture of water and ethanol. Within several minutes, a channel between a water droplet and a water + ethanol droplet was formed by smaller droplets (2 – 20 μm) (Fig. 32). In the authors' opin-

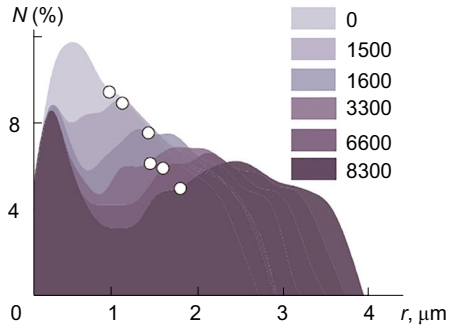


Figure 31. Time variations of the droplet size distribution in a dodecyl-β-maltoside-stabilized emulsion of octane in water derived by Brownian dynamics modelling.[196] The dots correspond to the average droplet size in the emulsion at a definite time point; the OR time (s) is indicated in the plot.

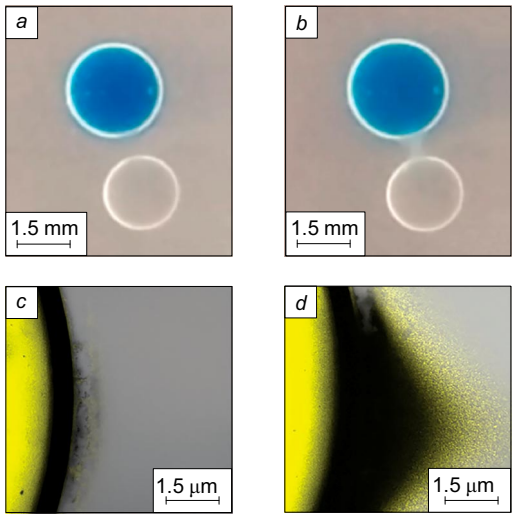


Figure 32. Formation of a turbid flow between a water droplet and a water + ethanol droplet immediately after injection (*a*) and after 10 min (*b*). At higher magnification: a water droplet immediately after injection (*c*) and after 5 min (*d*). The water droplet is stained with Nile blue. Images *a* and *b* were video recorded; *c* and *d* were obtained by confocal microscopy.[197]

ion, emulsification on the surface of a water droplet was due to the Marangoni effect, *i.e.*, a local decrease in the interfacial tension.

When two droplets were injected into a system consisting of toluene, ethanol and 0.2 vol.% silica nanoparticles, the nanoparticles were adsorbed almost instantaneously on the droplet surface. In this case, spontaneous emulsification took place and a flow from a water droplet to a water and ethanol droplet appeared, with no silica nanoparticles being present on the surface of the spontaneously formed smaller droplets. Apparently, mass transfer occurred in opposite directions during compositional ripening of the studied systems. Ethanol diffused from the droplets of water and ethanol to water droplets due to molecular diffusion. Due to lower solubility, water migrated in smaller droplets formed spontaneously on the surface of larger water droplets.

The mechanism of mass transfer between droplets may differ for concentrated and dilute emulsions. It can be reasonably assumed that oil mass transfer between the flocculated droplets would be faster than that between the droplets located at some distance from each other.[100]

Schmitt *et al.*[31, 198] investigated emulsions of alkanes in water stabilized by oxyethylated surfactants. The fraction of the dispersed phase in the emulsion reached 75%. In an early period, the droplet size distribution in the emulsions narrowed down; therefore, it was concluded that the droplet growth was caused by the OR process. It was suggested that the mass transfer from smaller droplets to larger ones in concentrated emulsions occurs *via* penetration of single oil molecules across the adsorption layer of the surfactant upon the contact of droplets rather than *via* substance diffusion in the continuous phase of the emulsion.[97, 198]

In emulsions of alkanes in water stabilized by Triton X-100 with a dispersed phase fraction from 0.54 to 0.78, the rate of OR varied from 3.1×10^{-16} to 3.6×10^{-20} m^3 s^{-1} on going from hexane to tetradecane.[181] These values were several orders of magnitude higher than the OR rates in dilute emulsions (see Table 1). A certain contribution to the increase in the droplet size in these emulsions may be made by coalescence.

Higher rates of OR compared with theoretically calculated ones were obtained for concentrated foams. In glycerol tristearate and propylene glycol foams, the experimental OR rates were 2 – 10 times higher than the theoretical ones.[143]

The mechanism of transfer of the dispersed phase substance upon the contact of nanoemulsion droplets has been explored.[199, 200] According to the authors, there were dilute nanoemulsions of hexadecane, which were stable to coalescence. Small-angle scattering showed that the composition of the droplets was averaged approximately 4 min after mixing of a $C_{16}H_{34}$ nanoemulsion with a $C_{16}D_{34}$ nanoemulsion. The authors attributed this to the fact that collision of droplets was accompanied by a decrease in the thickness of the adsorption layer, and the surfactant molecules moved apart to let molecules of the organic phase to penetrate from one droplet to another.

Water-in-oil emulsion. In emulsions and nanoemulsions with squalene as the dispersion medium and distilled water as the dispersed phase stabilized by dipalmitoylphosphatidylcholine, reverse micelles were the carriers of water from smaller droplets to larger ones. The conclusion about the micellar transfer was drawn from experimental data on stabilization of emulsions by mono- and multiple phospholipid layers taking account of the fact that water is almost insoluble in squalene.[201]

The water transfer between dispersed phase droplets by reverse micelles and nanodroplets has been studied by Koroleva and Yurtov.[108] The water diffusion coefficient in the dispersion medium of water-in-hydrocarbon oil emulsions was 0.3×10^{-14} m^2 s^{-1}, which was almost four orders of magnitude lower than the molecular diffusion coefficient. Therefore, it was suggested that nanoscale droplets were the carriers of water. The water diffusion across the interface brought about interfacial instability, which resulted in spontaneous emulsification to give nanoemulsion droplets.

The micrographs of a W/O emulsion with distilled water as the dispersed phase are shown in Fig. 33. After 2 h, the dispersion medium of this emulsion was filled by nanodroplets ~20 nm in diameter; after 15 days, the nanodroplets were still present in the dispersion medium of the W/O emulsion, but in a substantially lower amount. The authors concluded that water diffusion in nanoemulsion droplets or in reverse micelles is the most probable mecha-

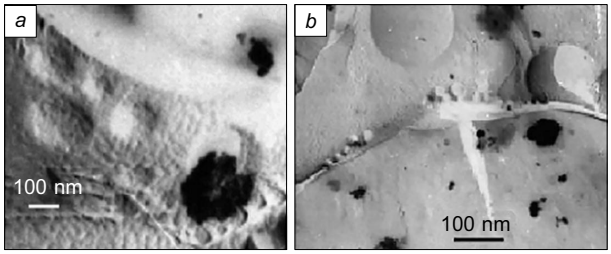


Figure 33. Freeze – fracture electron microscopy images of a W/O emulsion with distilled water as the dispersed phase.[108]
(*a*) The space between smaller droplets of the dispersed phase is filled by nanodroplets; (*b*) several nanodroplets are located on the surface of a large droplet. The micrographs were obtained within 2 h after the preparation of the W/O emulsion.

nism of water transfer through the organic phase in the studied W/O emulsions.

Multiple emulsions. The mechanism of water transfer through the organic phase was studied in water – oil – water multiple emulsions. There is no common opinion about the water transfer mechanism in such systems. Wen and Papadopoulos[202] concluded that water can be transported in nonpolar medium *via* hydration of single surfactant molecules and solubilization in reverse micelles.

A study of a multiple emulsion of distilled water – 0.1 M Span 80 solution in a hexadecane – aqueous NaCl solution revealed spontaneous emulsification around a distilled water droplet[203] (Fig. 34). The nanodroplets migrated towards the aqueous phase containing a NaCl solution. It was concluded that under these conditions, mass transfer was controlled by phase transfer processes to a larger extent than by diffusion in the organic phase.

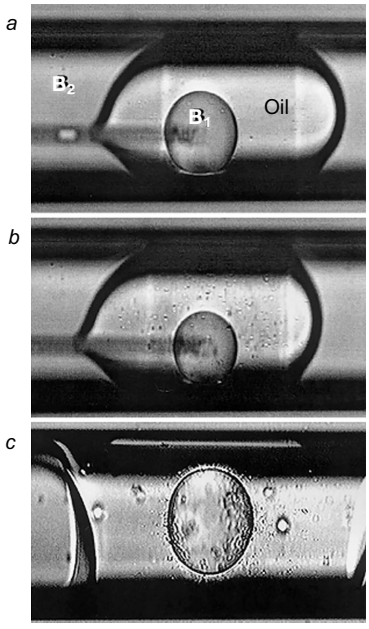


Figure 34. Micrographs of the system simulating a multiple emulsion obtained by capillary microscopy.[203]
(*a*) Initial point of time; (*b*, *c*) after 10 min at a NaCl concentration in the external water phase of 1 and 5 mol L^{-1}, spontaneous emulsification on the surface of distilled water droplet takes place. Oil is organic phase, B_1 and B_2 are the internal and external aqueous phases; the capillary diameter is 200 nm.

The mass transfer in an oil – water – oil multiple emulsion was studied by Stambouli *et al.*[204] The tetradecane droplets were dispersed in an aqueous phase containing Tween 20 to form an O/W emulsion and then this emulsion was dispersed in hexadecane. The peak corresponding to hexadecane in the thermograms shifted with time towards lower temperature (Fig. 35), which was indicative of the tetradecane transport from the internal phase droplets into the external hexadecane phase. The peak corresponding to tetradecane decreased, which is indicative of decreasing droplet size as a result of decreasing amount of tetradecane in them. Some shift of the first maximum towards lower temperatures indicates that hexadecane also migrated from the external organic phase to tetradecane droplets although to a lesser extent.

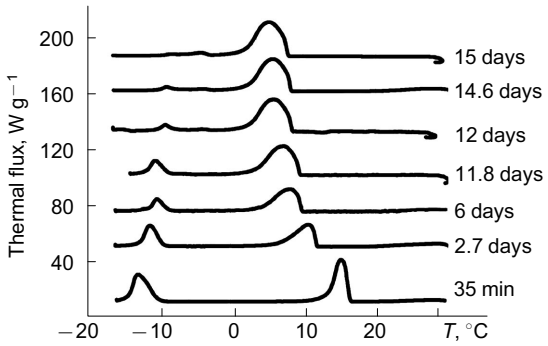


Figure 35. Thermograms of the tetradecane – water – hexadecane multiple emulsion. The concentration of Tween 20 is 4 mass % with respect to the aqueous phase.[204]

An increase in the concentration of Tween 20 led to increasing rate of tetradecane mass transfer. Indeed, the transfer of ~27% of tetradecane took place in 100 h if the concentration of Tween 20 was 2 mass %; the percentage of transferred tetradecane was ~48 mass % for concentration of 4 mass %; and the percentage was ~60 mass % for concentration of 7 mass %, that is, the rate of tetradecane transfer increased almost linearly as a function of surfactant concentration. On the basis of the model describing the rate of diminution of the tetradecane droplets, Stambouli *et al.*[204] concluded that the micellar rather than molecular diffusion of tetradecane is the major mechanism of mass transfer in the given system.

Pickering emulsions. The effect of micelles on the mass transfer of alkanes between the droplets was demonstrated most clearly by Drelich *et al.*[106] in O/W. Pickering emulsions stabilized by a mixture of silica nanoparticles and surfactants — Tween 20, SDS and polymeric oxyethylated Synperonic F127 surfactant (polyoxyethylene – polyoxypropylene – polyoxyethylene triblock copolymer). Two sorts of emulsions were prepared, one with tetradecane and one with hexadecane as the dispersed phase, stabilized only by nanoparticles. The emulsions were mixed with each other and, in order to prevent creaming, the mixture was stirred at 3 rpm for 14 days. As can be seen in Fig. 36, the size distribution of the droplets in the mixed emulsion almost did not change during 14 days, which attests to the absence of mass transfer between the droplets.

It is also seen in the thermograms that in the absence of surfactants, no mass transfer took place between the droplets (Fig. 37 *a*). When Tween 20 was added to the emulsions,

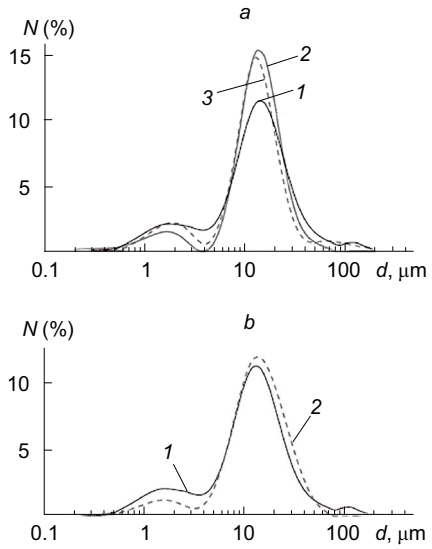


Figure 36. Droplet size distributions in tetradecane and hexadecane in water emulsions (*a*) and in a mixture of these emulsions at the initial time point and after 14 days (*b*).[106]
(*a*) $t = 0$ days, (*1*) mixture of two emulsions; (*2*) tetradecane emulsion, (*3*) hexadecane emulsion; (*b*) (*1*) mixture of two emulsions, $t = 0$ days, (*2*) mixture of two emulsions, $t = 14$ days.

the mass transfer of tetradecane to hexadecane droplets proceeded rather rapidly; hence, the peak corresponding to hexadecane shifted to lower temperature (Fig. 37 *b*). Upon the addition of anionic SDS, the mass transfer also took place, but at a lower rate (Fig. 37 *c*). In the case of addition of Synperonic F127 polymer, no mass transfer was detected in the system (Fig. 37 *d*). It was shown experimentally that no droplet coalescence occurred in the emulsion mixture.

The rate of tetradecane solubilization in Tween 20 and SDS micelles was ~15 times higher than the hexadecane solubilization rate.[192] In view of this fact, Drelich *et al.*[106] suggested that a larger number of micelles took part in the transport of tetradecane molecules compared to hexadecane molecules.

A study of the effect of the surfactant concentration on the mass transfer showed that at a Tween 20 concentration of 8.8×10^{-4} mol L^{-1}, no mass transfer took place. This concentration of the surfactant was lower than that required for monolayer adsorption at the emulsion interface with allowance for the surface of silica nanoparticles. At this concentration, Tween 20 micelles did not exist and, hence, the mass transfer of tetradecane did not take place either. When the Tween 20 concentration exceeded the concentration needed for the monolayer adsorption, the rate of tetradecane mass transfer increased with increasing surfactant content. Relying on these results, the authors[106] concluded that micellar transfer of tetradecane takes place between droplets in the emulsion.

11. Conclusion

Ostwald ripening, the transfer of the dispersed phase substance from smaller droplets to larger ones, proceeds in emulsions almost in all cases, but has a higher or lower intensity. Even when the degree of polydispersity of the emulsion is very low, *i.e.*, if the emulsion is almost monodisperse, there are differences (although minor) in the droplet sizes. Hence, a difference arises between the chemical potentials of the substance inside different droplets, which gives rise to OR. This process is especially relevant for O/W nanoemulsions, since the difference between the chemical potentials of the dispersed phase substance sharply depends on the droplet size within this range.

Among methods used to retard OR, the most efficient one is incorporation into the dispersed phase of a component with a very low solubility in the dispersion medium. This enables kinetic stabilization of the emulsion to OR. Coating of elastic polymeric films on the droplet surface does not always reduce the OR rate. There are publications reporting both a high and low efficiency of this method.

The most debatable topic in the OR theory is what is the mechanism of mass transfer between droplets of the dispersed phase? If the solubility of the dispersed phase substance in the dispersion medium is not extremely low, then evidently, the mass transfer between the droplets occurs *via* molecular diffusion in the dispersion medium. In the case of very low solubility of the dispersed phase substance in the dispersion medium, there is no common opinion on the transfer mechanism among the researchers engaged in this field. The exact determination of the solubility of these compounds is difficult. Therefore, it cannot be unambiguously stated that in this case, OR also

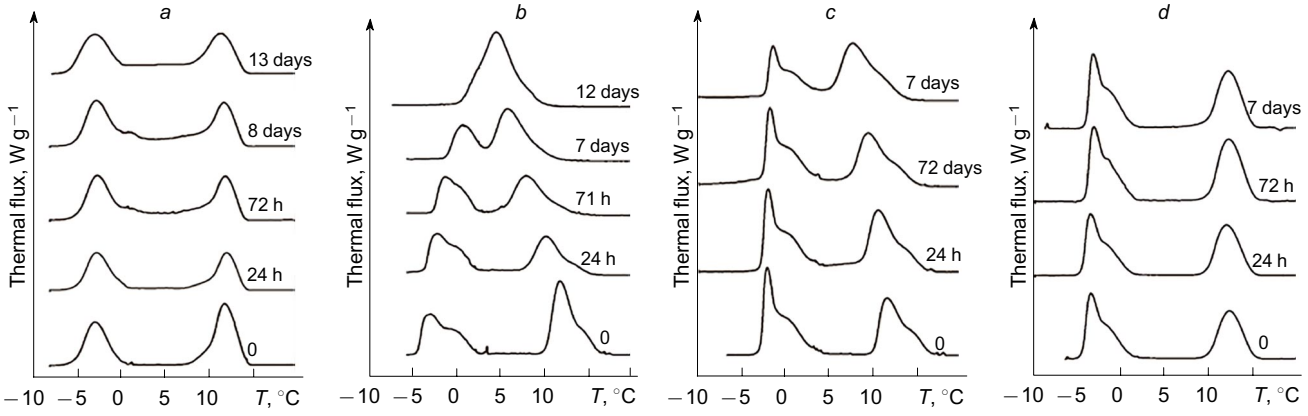


Figure 37. Thermograms of a mixture of tetradecane and hexadecane emulsions in water.[106] Emulsions are stabilized only by silica nanoparticles (*a*), silica nanoparticles and Tween 20 (*b*), sodium dodecyl sulfate (*c*), Synperonic F127 (*d*). Surfactant concentration is: 1.6×10^{-2} mol L^{-1}.

proceeds by a molecular diffusion mechanism and obeys the LSW equation, but the OR rate is very low. Critical analysis of the published experimental data makes it possible to state the following specific features of OR in these systems:

— if emulsion stabilizers do not form micelles, OR most often does not take place; if macromolecules that form micelle-like globules are used as surfactants, it should be borne in mind that they have very low diffusion coefficients; therefore, the OR process can be unnoticed;

— Ostwald ripening takes place; in most cases, the formation of droplets of either nanometre or micrometre size was detected; droplets are formed during mass transfer upon spontaneous emulsification caused by the interfacial tension gradient on the droplet surface and interfacial instability (Marangoni effect).

The foregoing provides the conclusion that micelles and nanodroplets are the carries of the dispersed phase substance with very low solubility in the dispersion medium. If the emulsion is stabilized by nonionic surfactants, there are no steric restrictions for the adsorption and desorption of micelles at the droplet surface; therefore, the mass transfer is faster. If the emulsion is stabilized by ionic surfactants such as SDS, which is traditionally used and has been most comprehensively studied, the mass transfer is slower.

These conclusions are confirmed most clearly in the paper of Drelich *et al.*[106] The presented results not only unambiguously attest to a micellar mechanism of mass transfer between dispersed phase droplets, but also explain the data obtained by other authors. Tween 20 is a nonionic surfactant; therefore, there are no electrostatic restrictions for the diffusion of Tween 20 micelles towards the droplet surface in the emulsion. Micelles are adsorbed on the surface, disintegrated and rearranged, capturing solubilized substance of the dispersed phase, and diffuse to the surface of other droplets with higher chemical potential of the dispersed phase substance.

In emulsions stabilized by an anionic surfactant such as SDS, micelles are repelled from the droplet surface, since both are negatively charged. In this case, the most probable mechanism is solubilization of molecules of the dispersed phase dissolved in the dispersion medium. This process is slower than the previous one, and the mass transfer in these systems proceeds more slowly.

If emulsions are stabilized by polymers, the mass transfer of the dispersed phase substance is, in some cases, very slow (barely noticeable). Most likely, the main reasons for the decrease in the mass transfer rate in these emulsions is not only the formation of interfacial elastic films, but, first of all, the absence of micelles able to transport the dispersed phase substance.

The understanding of the OR mechanism for systems with different solubilities of the dispersed phase substance in the dispersion medium is necessary for the control over the OR rate. The use of known methods of slowing down this process or development of new methods would enable the preparation of highly stable emulsions and nanoemulsions, which are in demand in various industry branches: medical, pharmaceutical, food and polymeric industries, *etc*.

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12. List of acronyms and designations

A — area,
C — concentration,
C^0 — initial concentration,
C^∞ — concentration of a saturated solution (solubility),
C_b^∞ — concentration of a saturated solution (solubility) of the dispersed phase substance in the bulk of dispersion medium,
CMC — critical micelle concentration,
Cryo-SEM — cryo-scanning electron microscopy,
d — droplet diameter,
D — diffusion coefficient of molecules,
D_m — diffusion coefficient of micelles,
e — Euler number,
E — elastic modulus,
f — volume fraction,
h — interfacial film thickness,
HLB — hydrophilic – lipophilic balance,
$k(\varphi)$ — coefficient depending on the fraction of the dispersed phase in the emulsion,
LSW — Lifshitz – Slezov – Wagner theory,
M — molecular mass,
N — fraction of droplets,
O/W —oil-in-water emulsion,
OR — Ostwald ripening,
ΔP_{Lp} — Laplace pressure,
P_{os} — osmotic pressure,
P^∞ — equilibrium pressure,
r — droplet radius,
$\bar{r}_{cr}$— critical droplet radius,
R — universal gas constant,
S — solubilizing capacity of micelles,
SDS — sodium dodecyl sulfate,
t — time,
T — temperature,
u — normalized radius $r/\bar{r}_{cr}$,
V_m — molar volume,
x — mole fraction,
W/O — water-in-oil emulsion,
α and β — coefficients,
γ — interfacial tension,
ε — elasticity,
μ_d and μ_b — chemical potentials of the dispersed phase substance in the disperse state and in the bulk;
μ_C — chemical potentials of the dispersed phase substance dissolved in the dispersion medium,
ρ — density,
σ — root-mean-square deviation,
φ — fraction of the dispersed phase in the emulsion,
ω — OR rate,
ϕ — osmotic coefficient.

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