Russian Chemical Reviews **77** (8) 683 – 708 (2008) © 2008 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2008v077n08ABEH003794

Highly concentrated emulsions. Physicochemical principles of the preparation and stability

V G Babak

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Abstract. Theoretical and experimental studies on highly concentrated emulsions are critically analysed. The views on the relationship between the stability of surfactant-stabilised emulsions and the properties of microemulsion phases formed in surfactant – water – oil ternary systems are considered. The empirical criteria and rules that can be used to predict the type and stability of emulsions are presented. The physicochemical factors determining the rupture stability of emulsion films are discussed. The bibliography includes 186 references.

I. Introduction

Highly concentrated emulsions (HCEs), or high-internal-phase content emulsions (HIPCEs),[1 – 12] are widely used in practice, especially in food industry, cosmetology and medicine.[7, 8, 13 – 20] They are also employed for extraction of antibiotics and pollutants;[21] in synthesis of meso- and microporous inorganic materials,[22] microscopic particles of inorganic oxide materials,[23] microcellular materials,[24] explosives,[25] highly porous polymeric materials and foamed plastics[10, 26 – 28] and as alternative reaction media in chemical and enzymatic catalytic synthesis of various compounds.[29 – 31]

Unlike dilute or simple concentrated emulsions in which microscopic (or submicroscopic) droplets of the liquid disperse phase execute Brownian motion, in HCEs liquid droplets are immobilised and form microscopic emulsion films in the contact region (Fig. 1). The content (by volume) of the liquid disperse phase (φ) in such emulsions exceeds 75% – 80%, which corresponds to random close packing of particles in globular polydisperse systems,[9, 32] and can be as high as 99% for rupture-stable emulsions. The continuous liquid phase in HCEs has the form of liquid films and Plateau borders in the space between highly deformed droplets and occupies only a few per cent (by volume). This allows HCEs to be treated as 'biliquid foams'.[33 – 35]

Under particular conditions HCEs can exhibit viscoelastic and plastic properties characteristic of physical gels; that is why they are also called 'gel emulsions'.[36 – 39] The onset of the gel properties in such emulsions is due to the so-called sol – gel transition occurring upon a change in physicochemical conditions (temperature, surfactant or salt concentration, *etc.*). This results in abrupt increase in adhesive forces acting between liquid droplets and, as a consequence, in bulk compression and manifestation of syneresis of emulsions.[40] In this connection gel-like emulsions are called 'compressible',[41 – 43] or 'adhesive',[44, 45] in contrast to fluid-like 'non-compressible', or 'non-adhesive' ones. In Russian literature, this type of emulsions are called 'structured' and 'non-structured', respectively.[46, 47] Other terms used in the literature include 'hydrocarbon gels',[48] 'aphrons',[21, 33] or, simply, 'highly concentrated emulsions'.[5, 16, 49 – 54] Information on the properties of HCE can be found in reviews.[40, 55 – 57]

Stable HCEs are prepared using surfactants chosen based on various criteria. Among them, the most widely used is Bancroft's rule,[58] Griffin – Davis hydrophilic-lipophilic balance (HLB) rule,[59 – 62] the phase inversion temperature (PIT) criterion proposed by Shinoda[63, 64] and other relations.[65] According to the Bancroft rule,[58] in oil-in-water (O/W) emulsions the surfactant is mainly dissolved in continuous aqueous phase, whereas in reverse (water-in-oil, W/O) emulsions it is mainly dissolved in continuous oil phase. A necessary condition for long-term stability of HCEs is the formation, by surfactant molecules, of saturated adsorption monolayers at water/oil interface. In this case microscopic emulsion films formed in the region of contact between droplets of the disperse phase have the structure of bilayer lipid membranes characterised by high rupture stability (see Fig. 1 *c*).

Usually, the concentrations of surfactants in the continuous phase of HCEs are much higher than corresponding critical micelle concentrations (CMCs). The continuous phase of a HCE represents a solubilised O/W micellar solution (microemulsion phase L_1) for emulsions or a solubilised W/O micellar solution (microemulsion phase L_2) for reverse emulsions.[36, 66 – 72] In the course of emulsification a noticeable quantity of surfactant molecules is consumed to form saturated

V G Babak A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-499) 135 50 85, tel. (7-499) 135 07 32, e-mail: babak@ineos.ac.ru

Received 31 March 2008
Uspekhi Khimii **77** (8) 729 – 756 (2008); translated by A M Raevskiy

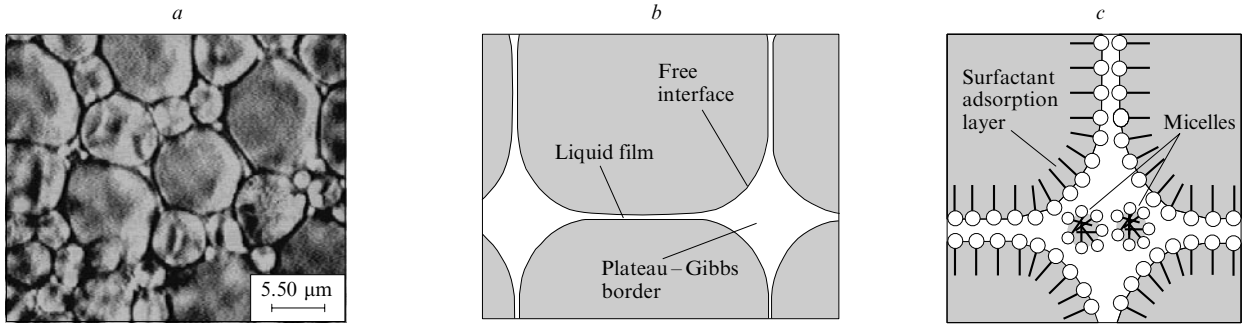


Figure 1. Micrograph of O/W highly concentrated emulsion (*a*) and schemes of its structure (*b*, *c*).

adsorption layers at the inner interface. The specific surface area of this interface is given by

$$A_{sp} \approx \frac{3}{\overline{R}}$$

($\overline{R}$ is the average radius of droplets), being of the order of $10^6 - 10^7$ m^2 m^{-3} for highly disperse HCEs. This relation is used for estimating the effective surfactant concentration in the continuous phase of HCE after emulsification provided that the total surfactant concentration in the system is known.

In the presence of an efficient surfactant, HCEs with moderate degree of dispersion can be prepared by simply shaking and mixing two phases taken in a specified ratio (*e.g.*, aqueous phase : oil phase = 90 vol.% : 10 vol.% in the case of W/O emulsions).[36, 67, 73] Surprisingly, the type of the emulsion formed is exactly the same as that predicted by known stability criteria, *e.g.*, the Bancroft rule [58] irrespective of the ratio (by volume) of both phases (within reason). Highly disperse stable HCE with a droplet size of about 1 μm (and smaller) are prepared by slowly adding the disperse phase to the dispersion microemulsion medium until a necessary value φ (by volume) with vigorous mechanical dispersion of the resulting emulsion.[74, 75]

Among other methods of preparation of HCEs, mention may be made of concentrating pre-prepared moderately concentrated emulsion by simple sedimentation, weak centrifugation [42, 50, 76] or ultracentrifugation [34] and by dialysis.[77] Highly concentrated emulsions stabilised with nonionic ethoxylated surfactants can be prepared using phase inversion technique from solubilised micellar solutions by rapidly changing the temperature.[64] For instance, O/W HCEs are formed by rapid cooling of W/O micellar solutions,[78, 79] whereas reverse (W/O) HCEs are formed by rapid heating of O/W micellar solutions.[22] In the case of ionic surfactants, reverse HCEs are prepared by rapidly increasing the salt concentration in the aqueous phase.[57] The mechanism of this phenomenon was substantiated in Ref. 40.

Undoubtedly, HCEs are of considerable interest for fundamental research in colloid science. In some sense they have been a stumbling block to the development of the theories of stability of disperse systems, based on the Derjaguin–Landay–Verwey–Overbeek (DLVO) theory and on thermodynamics of thin liquid films, because they failed to explain critical (threshold) dependences of the stability and rheological properties of such emulsions on physicochemical parameters (temperature, pH value, salt and surfactant concentrations, droplet size, oil type, *etc.*).

The critical temperature also called the phase inversion temperature (PIT) [63, 68, 80] corresponding to the onset of destruction of O/W emulsions (further heating leads to stabilisation of reverse emulsions) cannot be explained from the standpoint of the 'classical' DLVO theory. Based on this theory, one fails to explain asymmetric character of the rupture stability of liquid films, namely, why the oil–water–oil (O/W/O) liquid films rather than water–oil–water (W/O/W) films with bilayer lipid membrane structures are stable at temperatures below PIT in spite of nearly equal thicknesses (h_f) of these films and approximately equal complex Hamaker constant (A_H). According to the DLVO theory, the molecular component of the disjoining pressure

$$\Pi_{mol} = -\frac{A_H}{6\pi h_f^3}$$

is similar for stable O/W/O films and unstable W/O/W films. The surface tension

$$\gamma_f = 2\gamma + \Pi_{mol} h_f$$

for both types of films is also nearly equal (γ is the interfacial tension of free surfaces, which is equal for water and oil droplets with allowance for the relatively large radii of curvature of these particles).[3, 81–83] The lifetime of the first type of films can be as long as a few hours (and even days), whereas that of the second type of films is only a few seconds. At temperatures above the PIT, the character of film stability reverses, *i.e.*, the W/O/W films become stable while the O/W/O films become unstable.

Considerable progress in understanding of interrelations between the type of the microemulsion phases forming the continuous phase in HCEs and the stability of HCEs was made in the last decade only.[1, 40, 84–89] These advances are due to the development of various theories of microemulsions.[90–92] In particular, a theory of the effect of intrinsic local curvature of ordered anisotropic monolayers comprised of biphilic surfactant molecules separating the aqueous and organic microphases in such microemulsions on the free energy of microemulsion systems was developed.[90] The mechanism of the effect of intrinsic curvature of surfactant monolayers in microemulsion phases on the rupture stability of microscopic emulsion films (*i.e.*, HCE stability) [40, 89] was substantiated with allowance for (i) correlations between the types of microemulsion phases and the intrinsic local curvature of such monolayers [84, 86, 88] and (ii) results of studies of ultralow interfacial tension and its relation to the intrinsic curvature of surfactant monolayers.[85, 93]

In this review we present a survey of theoretical and experimental research on HCEs based on the concept of interrelation between the macroscopic properties of surfactant-stabilised emulsions and the properties of the microemulsion phases formed in surfactant – water – oil ternary systems.[1] This concept is a development and generalisation of the fundamental principle of physicochemical mechanics,[2] according to which the functional macroscopic properties of HCEs are determined by the properties of microscopic emulsion films formed in the contact region between liquid emulsion droplets.[3–6]

II. Empirical rules to predict emulsion type and stability

Generally, mechanical dispersion of a mixture of polar (aqueous) and nonpolar (organic, or oil) phases taken in 1 : 1 ratio (by volume) in the presence of a surfactant produces an unstable structure with highly developed mechanical internal surface whose surface area is determined by the power supplied. Switching off dispersion causes unstable structures to disappear and the system is separated into the starting macroscopic phases or undergoes transformation to a direct emulsion or reverse emulsion (Fig. 2). The formation of relatively stable complex (multiple) emulsions is also possible.[94]

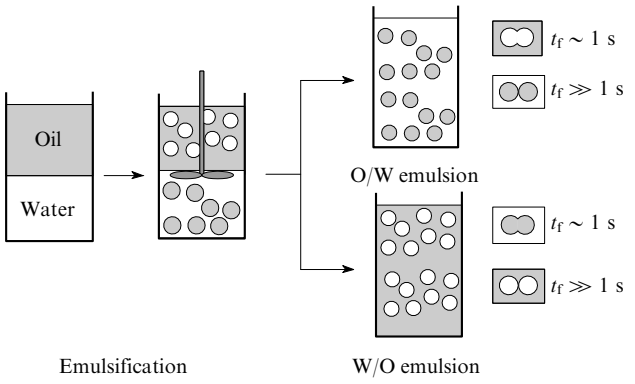


Figure 2. Scheme of formation of intermediate unstable multiple emulsion and its transformation into O/W or W/O emulsion depending on the type of surfactant and other physicochemical factors.
t_f is the characteristic lifetime of droplets before coalescence, which is equal to the emulsion 'lifetime' before destruction.

It was established experimentally that the types of the multiple and final emulsions depend only slightly on the starting volumes of water and oil in the mixture, namely, the water/oil ratio can vary over a wide range from 0.1 to more than 0.9, but the emulsion type will not change. The main factors affecting the type of emulsion include the molecular structure of surfactant and a number of physicochemical parameters, such as temperature, type of the oil phase (saturated or unsaturated hydrocarbons, fluorinated, chrorine-substituted compounds), the carbon number for 'classical' alkane-based oils, electrolyte concentration (mainly for ionic surfactants), hydrostatic pressure (when using, *e.g.*, supercritical pentane or CO_2) as the oil phase, *etc.*

1. The Bancroft rule

Among the empirical rules used to predict the type of emulsions, the Bancroft rule[58,95] is best known. According to this rule, 'a hydrophilic colloid will tend to make water the dispersion medium, while a hydrophobic colloid will tend to make water the disperse phase'. Formulated in terms of surfactant solubility in the aqueous and oil phases, Bancroft's rule predicts that emulsification of water and oil taken in nearly equal amounts (by volume) should produce a direct O/W emulsion if the surfactant is better dissolved in water than in oil and a reverse emulsion otherwise.

Surprisingly, there are no exceptions to this rule in spite of its simplicity. Bancroft's rule is valid for all compositions provided that the surfactant concentration is sufficiently high to form a saturated adsorption monolayer of surfactant molecules on the surface of emulsion droplets. The necessity of meeting this condition was reported by Binks[87] who studied the types of emulsions formed in the heptane – aqueous 0.01 M solution of $NaCl - C_{12}H_{25}O(C_2H_4O)_5H$ (n-dodecylpolyglycol ether, or C_iE_j, $i = 12$, $j = 5$) system. At temperatures above the PIT (PIT = $\sim$30 °C for this system), the molecular solubility of $C_{12}E_5$ in heptane is higher than in the aqueous phase and, according to the Bancroft rule, a water-in-heptane reverse emulsion should form. Nevertheless, heptane-in-water emulsions formed at $T = 50$ °C if the surfactant concentration (c_s) in heptane was lower than the CMC (60.4 mmol litre^{-1}) at this temperature. At the same time, if the surfactant concentration was sufficiently high to form saturated adsorption monolayers of surfactant molecules at the interface ($c_s >$ CMC), the reverse emulsions formed, as predicted by Bancroft's rule.

Note that the Bancroft rule predicts the type of an emulsion, leaving the emulsion stability out of consideration. However, it is high stability of HCEs that is of interest for practical applications. In some cases, *e.g.*, when HCEs are prepared by the phase inversion technique, one should know the regions of lowest emulsion stability and whether the types of multiple unstable emulsions can be controlled by varying the temperature, the salt or surfactant concentration, *etc.*

2. Griffin – Davis hydrophilic-lipophilic balance

Analysis and systematisation of results of the use of surfactants in emulsification technology (in particular, in the preparation of HCEs for cosmetology) showed that the emulsion type and stability depend on the ratio (balance) of hydrophilic and hydrophobic (or lipophilic) functional groups in the surfactant molecules.

a. The Griffin hydrophilic-lipophilic balance

The concept of hydrophilic-lipophilic balance (HLB) was first introduced by Griffin[59] to classify surfactants with respect to their functional properties, in particular, the ability to stabilise emulsions. Griffin proposed the following expression for calculating the HLB of nonionic ethoxylated surfactants:[60]

$$HLB_G = \frac{M_h}{5}, \quad (1)$$

where M_h is the proportion of hydrophilic groups (mol %) in the surfactant molecule. For instance, the HLB_G of the molecule of n-dodecylpolyglycol ether $C_{12}E_2$ is

$$HLB_G(C_{12}E_2) = \frac{M_{E_2}}{5} = \frac{1}{5}\frac{M_{E_2}}{M_{C_{12}E_2}}100\% =$$
$$= \frac{1}{5}\frac{2\times 44+1}{258}100\% = 6.9.$$

The HLB_G of other molecules [*e.g.*, $HLB_G(C_{12}E_{30}) = 17.7$] can be calculated by analogy.

Thus, nonionic surfactants can be systematised using the scale of their HLB values. The parameter HLB_G, also known as 'the characteristic HLB',[72] is used for calculating the PITs of nonionic ethoxylated surfactants.

b. The Davis hydrophilic-lipophilic balance. Group number calculation technique

Davis [62] extended the HLB concept to ionic surfactants and to surfactants having hydrophilic and hydrophobic substituents with more complex structure (*e.g.*, having double bonds and branchings, fluorinated surfactants, soaps with different counterions, *etc.*). The HLB_D scale is based on the inclusion of the relative solubility of surfactants in the oil (c_o) and aqueous (c_w) phases at room temperature, *i.e.*, on the partition coefficient of surfactants between these phases

$$K_p = \frac{c_o}{c_w},$$

and is determined by the linear dependence

$$HLB_D = 7 - 0.33\ln K_p, \quad (2)$$

in which the numbers, 7 and 0.33, were chosen by Davis seemingly in such a way that the interval of changes in HLB values of various surfactants span from 0 to 40, *i.e.*, be the same as the HLB_G value determined from relation (1).

The HLB_D values are determined in the framework of thermodynamics of surfactant solutions based on a simplified concept of additive contributions of various functional groups to the relative solubility of surfactants in the aqueous and oil phases.[46] Taking into account the condition for equality of the chemical potentials of surfactant molecules in water and in oil

$$\mu_w = \mu_w^* + kT\ln a_w,$$
$$\mu_o = \mu_o^* + kT\ln a_o$$

(μ_o^* and μ_w^* are the standard chemical potentials of oil and water, respectively) and assuming the possibility of replacing the activities a_w and a_o by corresponding concentration c_w and c_o (this holds for surfactants because their CMCs $\ll 1$ mol litre^{-1}), one can write

$$K_p = \frac{c_o}{c_w} = exp\left(-\frac{\Delta\mu^*}{kT}\right). \quad (3)$$

The difference

$$\Delta\mu^* = \mu_o^* - \mu_w^*$$

equals the work of transfer of the surfactant molecule from the aqueous to the oil phase.

For instance, a C_iE_j-type molecule contains a hydrophobic alkyl chain comprised of i carbon atoms and a hydrophilic fragment comprised of j E = CH_2-CH_2-O groups. Then one can write

$$\Delta\mu^* = -kT\ln K_p = i\Delta\mu_C^* + j\Delta\mu_E^*. \quad (4)$$

Substituting expression (4) into relationship (2), one gets

$$HLB_D = 7 + i\frac{0.33\Delta\mu_C^*}{kT} + j\frac{0.33\Delta\mu_E^*}{kT}, \quad (5)$$

or, in the Davis notation,

$$HLB_D = 7 + \sum_\alpha n_\alpha. \quad (6)$$

The parameters $n_\alpha = 0.33\Delta\mu_\alpha^*/kT$ are called 'group numbers' and represent the contributions of various functional groups to the HLB of surfactant molecule. The group numbers of different functional groups in surfactant molecules, necessary for HLB calculations from the Davis equation (6) are given below

Functional group	Group number
$-CH_2-$; $-CH_3$; $=CH-$	−0.475
$-O-CH_2-CH_2-$	0.33
$-O-CH_2-CH_2-CH_2-$	−0.15
$-O-$	1.3
$-OH$	1.9
$-CO_2H$	2.1
$-N^+(CH_3)_3Cl^-$	9.4
$-CO_2^-Na^+$	19.1
$-SO_3^-Na^+$	38.7

The Davis group numbers are calculated using the known $\Delta\mu_\alpha^*$ values determined under normal conditions. A hypothetical liquid saturated hydrocarbon whose chain length does not affect the solubility of surfactant in this hydrocarbon, *i.e.*, the $\Delta\mu_\alpha^*$ value (generally, this assumption is incorrect, see below) is treated as the oil phase. According to Tanford,[96] the free energy gain on transfer of a hydrophobic group ($-CH_2-$ or $-CH_3$) from water to oil is

$$\Delta\mu_C^* \approx -1.4kT \div -1.45kT,$$

which, on the average, corresponds to the group number

$$n_{CH_2} = \frac{0.33\Delta\mu_C^*}{kT} \approx -0.475.$$

Transfer of one hydrophilic OE group from water to oil at room temperature is accompanied by negative free energy gain [97]

$$\Delta\mu_E^* \approx 1kT,$$

which corresponds to a group number

$$n_E = \frac{0.33\Delta\mu_E^*}{kT} \approx 0.33.$$

The group numbers of other functional groups (see above) were determined analogously.

Based on the known n_α values, one can calculate the HLB_D of surfactant molecules of any structure assuming additive contributions of different functional groups. For instance, for *n*-dodecylpolyglycol ether $C_{12}E_2$ one has

$$HLB_D = 7 + 12(-0.475) + 2(+0.33) \approx 2.$$

The HLB values of other surfactants are determined in a similar manner [*e.g.*, $HLB_D(C_{12}E_{30}) = 11.2$].

c. The Griffin – Davis empirical rule

According to an empirical rule known as the Griffin – Davis rule,[97] stable W/O emulsions can be prepared using hydrophobic ethoxylated surfactants (HLB = 3 – 8) characterised by relatively high solubility in oil. Hydrophilic surfactants with HLB = 12 – 18 show high solubility in water and form stable O/W emulsions. Surfactants characterised by HLB > 13 form micelles in the aqueous phase, while those characterised by HLB ≈ 8 – 12 are inefficient for preparation of both O/W and W/O emulsions.

One should keep in mind that the two HLB scales (Griffin's and Davis' ones) differ from each other. This should be borne in mind when using the HLB values reported in the literature. Indeed, the HLB_G values of $C_{12}E_2$ and $C_{12}E_{30}$ determined from relation (1) are 6.9 and 17.7, respectively, whereas the HLB_D values of these surfactants calculated from expression (6) are respectively equal to 2 and 11.2.

However, different HLB values are not the major drawback of the Griffin – Davis empirical rule, which is based on the HLB concept. A more serious disadvantage precluding practical use of the HLB approach to predict the type and stability of emulsions consists in that the Davis group numbers are strongly dependent on the temperature (this especially concerns epoxy groups), on the polarity (dielectric permittivity) and molecular mass (carbon number) of the organic phase, salt concentration in the aqueous phase, *etc*. In particular, on raising the temperature, the 'solubility' of epoxy groups in the aqueous phase decreases due to dehydration. As a result, the 'true' HLB of ethoxylated nonionic surfactants decreases. Although there is a possibility of taking into account the effect of physicochemical parameters on the solubility of surfactants in both phases and, therefore, on the group numbers, but the HLB scale thus constructed will be cumbersome and inconvenient for use.

Empirical rules based on the HLB approach (Griffin and Davis rules) and on the solubility of surfactants in adjacent phases (Bancroft rule) and proposed to predict the stability of HCEs have a fundamental common disadvantage. Namely, this is the lack of a commonly accepted physical theory that can explain how does the relative solubility of surfactants in adjacent phases (or the partition coefficient) determine the asymmetry of the coalescence rate of liquid droplets in O/W and W/O emulsions. In particular, it is unclear how instantaneous coalescence of water droplets in oil and long-term coexistence of two oil droplets in contact with the aqueous phase are related to the higher solubility of surfactants in water than in oil. *Vice versa*, if the solubility of a surfactant in oil is higher than in water, what is the reason for stabilisation of water – oil – water films, whereas oil – water – oil films break almost instantaneously?

The mechanisms based on different rates of thinning of both types of films[98 – 101] or on the Gibbs – Marangoni effect[102 – 104] are inapplicable to HCEs. Indeed, the relaxation and diffusion effects mentioned above have characteristic times of the order of tens or hundreds of seconds, whereas the lifetime of liquid films in stable HCEs can be as long as 10^6 s and even longer.

3. The concept of phase inversion temperature

Shinoda *et al.*[63, 64, 105, 106] developed a concept of phase inversion temperature applicable to nonionic ethoxylated surfactants. According to this approach, stability of emulsions is governed by the phase state of water – oil – nonionic surfactant mixtures. This concept was of great importance for systematisation and prediction of emulsion stability depending on the type of surfactant and physicochemical conditions.

a. Phase transitions in water – oil – surfactant ternary system

The constitutive diagram of a ternary system containing a nonionic (ethoxylated) surfactant, water and oil is shown in Fig. 3. Such a system is characterised by the upper and lower critical temperatures (T_u and T_l, respectively). Cross-section of the ternary phase diagram 'pyramid' (Fig. 3 *b*) by the plane corresponding to a '50% of water + 50% of oil' composition gives a 'Kahlweit fish'-type diagram (Fig. 3 *c*).[107] At $T < T_l$, the solubility of the nonionic surfactant in water is higher than in oil. *Vice versa*, at $T > T_u$, the solubility of the surfactant in oil is higher than in water. At low surfactant concentrations ($c_s < c_{min}$), raising the temperature does not cause the system to change its binary character in the whole temperature interval, the surfactant partition coefficients being gradually varied from very low to high.

If surfactant concentrations are higher than c_{min} ($c_s > c_{min}$), one deals with a binary system, the surfactant molecules form micelles in the aqueous phase (lower sample in Fig. 3 *a*). In the equilibrium state, the aqueous micellar solution is solubilised with oil and the so-called microemulsion phase L_1 is formed, which is enriched with the surfactant. The oil phase contains a negligible amount of surfactant. According to Winsor's classification,[108, 109] this system is classified as $\underline{2}$.† Mechanical dispersion of such a system gives direct O/W emulsions (lower sample in Fig. 3 *d*).

As temperature increases, the poly(ethylene oxide) (PEO) fragment of the nonionic surfactant undergoes dehydration and acquires hydrophobic properties, which reduces its solubility in water. Under particular conditions, raising the temperature to T_l causes separation of the microemulsion phase L_1 into two phases, the surfactant-enriched middle phase L_3 and the lower aqueous phase W containing a small amount of the surfactant. As a result, the binary system becomes a ternary one. According to Winsor, this is called system 3. The middle phase is a random bicontinuous structure,[109, 110] which ensures a good mixability of water and oil (middle sample in Fig. 3 *a*). In the vicinity of T_l (temperature range $T_l < T < T_u$) this phase is enriched with water. Raising the temperature from T_l to T_u causes the relative content of oil, $c_o/(c_o + c_w)$, to increase from ~ 0 to ~ 1. The middle phase containing equal amounts of water and oil is called 'balanced microemulsion' and the corresponding temperature is called the mean temperature (see Fig. 3 *c*)

$$T_m = \frac{T_l + T_u}{2}.$$

† Two types of notations of the Winsor systems can be found in the literature, $\underline{2}$ or Winsor I, $\overline{2}$ or Winsor II, 3 or Winsor III. They are shown in Fig. 3 *a* and *c*, respectively.

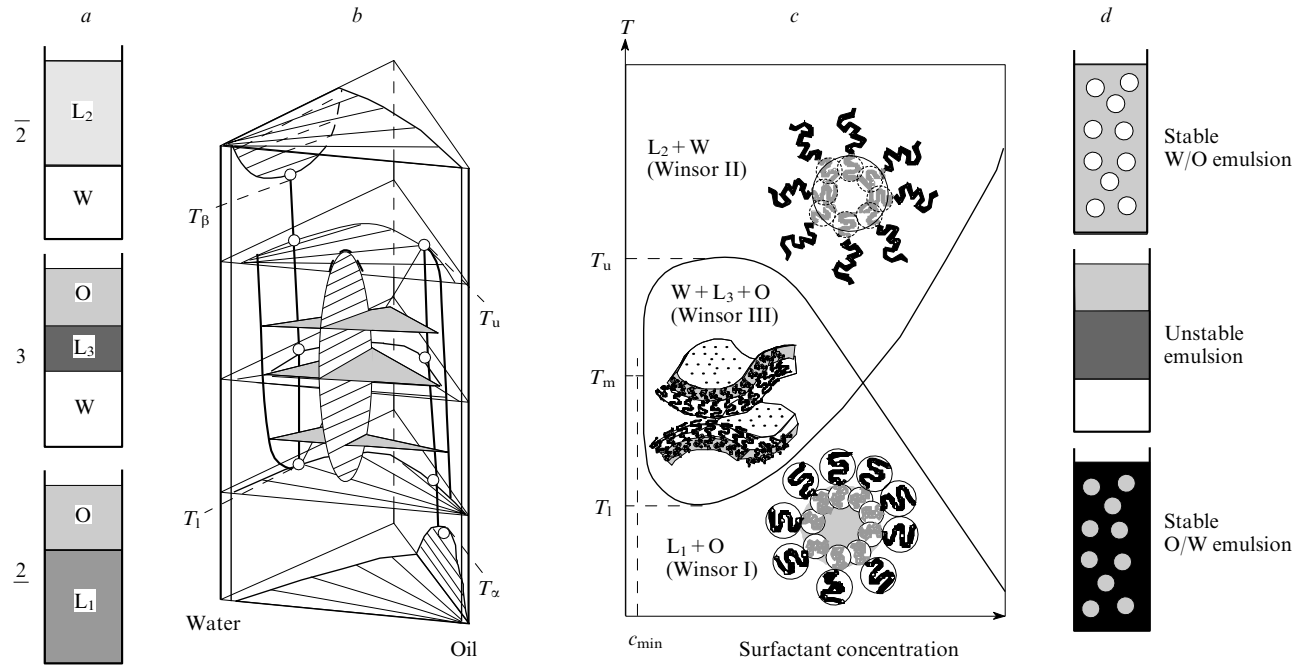


Figure 3. Schematic representation of Winsor systems (*a*), phase diagrams (*b*, *c*) and stable and unstable emulsions (*d*) for water – oil – C_iE_j surfactant ternary system.
T_α and T_β are the upper and lower critical temperatures for the surfactant solutions in oil and water, respectively; for notations T_u, T_l and T_m, see text.

Dispersion of system 3 leads to formation of very unstable emulsions (middle sample in Fig. 3 *d*).

At $T = T_u$, the L_3 and O phases merge and a new phase L_2 appears, which is in equilibrium with the aqueous phase W in the binary system $\underline{2}$. The microemulsion phase L_2 represents a solution of swollen (water-solubilised) reverse micelles in oil. Mechanical dispersion of such a binary system causes the formation of a reverse (W/O) emulsion (upper sample in Fig. 3 *d*).

b. Interfacial tension at Winsor phase boundaries

Owing to phase transitions the interfacial tension (γ) in Winsor systems decreases from 1 – 10 mN m^{-1} (these values are characteristic of the L_1/O and W/L_2 interfaces corresponding to the systems $\underline{2}$ and $\overline{2}$) to low and ultralow values corresponding to the W/L_3 and L_3/O interfaces in the region of 'balanced' microemulsion system 3 (Fig. 4). At temperature T_m, which equals the phase inversion temperature, the interfacial tension is minimum ($\gamma_{min} = 10^{-3} - 10^{-4}$ mN m^{-1}) and for the partition coefficient one has

$$K_p = \left(\frac{c_o}{c_w}\right)_{PIT} = 1,$$

which corresponds to equal molecular solubility of the surfactant in both phases, *i.e.*, to 'true' HLB of the surfactant molecules. Deviation of temperature from the PIT value causes the HLB value of surfactant molecules to deviate from the 'true' balance value and the partition coefficient changes in a fashion shown in Fig. 4 *b*.

Tensimetric method of determination of the PIT was first proposed in Ref. 106. It involves determination of the intersection point of the temperature dependences of the interfacial tension γ_{L_1O} and γ_{WL_2} at the L_1 and L_2 phase boundaries. This technique is also used to determine the temperatures of phase transitions in microemulsion systems occurring upon changes

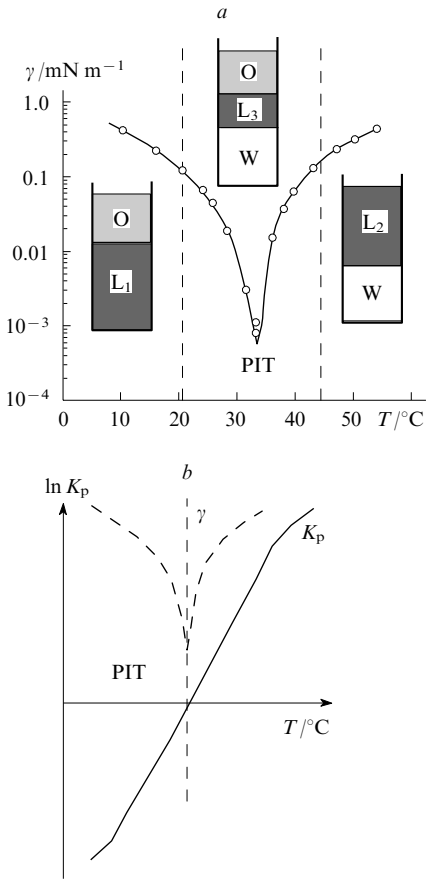


Figure 4. Temperature dependences of γ (*a*) and ln K_p (*b*) for water – octane – $C_{12}E_5$ ternary system.[93]

in other parameters, *e.g.*, salt concentration, content of alcohols, carbon number of the oil phase, *etc.*[65,69]

To determine the interfacial tension at the temperature of formation of a 'balanced' microemulsion (by, *e.g.*, the rotating droplet technique[93]), the sum of the interfacial tensions at the W/L_3 (γ_{WL_3}) and L_3/O (γ_{L_3O}) interfaces,

$$\gamma_{min} = \gamma_{WL_3} + \gamma_{L_3O}\,.$$

is measured. Generally, the middle phase can be removed and the system will contain only the W/O interface. This will not cause the equal concentrations in the two remaining phases ($c_o = c_w$) and the γ_{min} values to change. The temperature ranges of existence of Winsor binary systems $\underline{2}$ and $\overline{2}$ will be characterised by the partition coefficients $K_p < 1$ and $K_p > 1$, respectively.

At a specified temperature T corresponding to, *e.g.*, the binary system $\underline{2}$, one can to some extent increase the amount of surfactant dissolved in the system and still remain in the existence region of the L_1 phase, which represents a solution of oil-solubilised micelles (see Fig. 3 *c*). In this case the surfactant concentration in the oil phase will remain negligible, because the whole amount of surfactant added is consumed to form micelles whose concentration thus increases. *Vice versa*, the amount of surfactant dissolved in the system can be reduced down to the CMC value corresponding to disappearance of micelles n the aqueous phase. As the surfactant concentration changes, the interfacial tension at the L_1/O interface in the binary system $\underline{2}$ remains almost constant and corresponds to the given temperature T. (Small change in the interfacial tension at the L_1/O interface upon a change in the surfactant concentration in the aqueous phase is due to the change in the aggregation number and shape of micelles in the L_1 phase owing to the change in polarity of their environment, which affects the chemical potential of surfactant molecules.)

Complexity of experimental measurements of partition coefficient K_p deserves particular attention in connection with the fact that usually hydrophilic surfactants are very poorly soluble in the oil phase at the interface with the L_1 phase and, correspondingly, hydrophobic surfactants are very poorly soluble in the aqueous phase at the interface with the L_2 phase. This influences the accuracy of determination of the difference, $\Delta\mu^*$, between the standard chemical potentials and the HLB values of surfactant molecules, which are calculated using the experimental K_p values.

c. Empirical relationships for calculations of the phase inversion temperature

At the temperature T_m, a balanced microemulsion (Winsor 3 system) 'uptakes' equal amounts of water and oil, *i.e.*, the hydrophilicity and lipophilicity of the surfactant molecule are balanced. Therefore, it is assumed that at the phase inversion temperature we deal with a 'true' HLB of the surfactant molecule. This temperature is called the 'HLB temperature' and denoted as T_{HLB}. This is the critical temperature for emulsions because they have the lowest separation stabilities near the T_{HLB}. Numerous experiments[63,64,105,106] showed that stable O/W emulsions are formed at temperatures that are about 5 to 10 °C lower than the PIT, while reverse emulsions are formed at temperatures 5 to 10 °C higher than the PIT. The temperature of range 10–20 °C including the PIT is the most 'dangerous' because in this range emulsion droplets rapidly coalesce and the emulsion undergoes separation into two macroscopic phases. Thus, the PIT of the nonionic surfactant–water–oil ternary system unambiguously determines the temperature interval of emulsion stability.

The PITs of C_iE_j nonionic ethoxylated surfactants depend on the molecular structure of the surfactant and oil. An empirical relation[111] for calculating the PIT values (in Celsius degrees) has the form

$$\mathrm{PIT} \approx 15.5\,\mathrm{HLB_G} + 18\sqrt{6 + \mathrm{ECN}} - 215, \qquad (7)$$

where the HLB_G is determined from expression (1) and ECN is the so-called equivalent carbon number of the molecules constituting the oil phase. For saturated hydrocarbons, the ECN is equal to the number of carbon atoms, while for unsaturated, cyclic and other hydrocarbons, particular optimal empirical values independent of the type of surfactants used are ascribed to it (*e.g.*, benzene is characterised by ECN = 1).

For instance, a $C_{10}E_4$–water–decane ternary system is characterised by a PIT value of about 30 °C [calculated using expression (7) at ECN = 10 and $HLB_G \approx 11$]. According to Shinoda's empirical rule, stable decane-in-water direct HCEs are formed at temperatures below 20–25 °C, whereas water-in-decane (reverse) HCEs are formed at temperatures above ~35–40 °C. Near the PIT, in the temperature range from 25 to 35 °C, HCEs become unstable. At the same time, the HCE stabilities increase as the temperature mover away from the 'dangerous' temperature region. It should be noted that replacement of an oil by another one causes the 'dangerous' temperature range (HCE instability region) to shift. For instance, the $C_{10}E_4$–water–hexane system is characterised by PIT ≈ 20 °C, *i.e.*, the temperature range shifted by 10 °C towards the lower-temperature region compared to the temperature range for the decane-containing system. Thus, hexane-based emulsions are unstable in the range 15–25 °C, while the decane-based emulsions are quite stable in this temperature range.

Other empirical relations for PIT calculations are also available, *e.g.*, this one[112]

$$\mathrm{PIT} \approx 15.5\,\mathrm{HLB_G} + 1.8\,\mathrm{ECN} - 160, \qquad (8)$$

which can be applied to hydrocarbon surfactants and oils at $8 < \mathrm{ECN} < 16$ and $10 < \mathrm{HLB_G} < 14$. An empirical relationship proposed[72] for fluorinated surfactant and fluorocarbon oils has the form

$$\mathrm{PIT} \approx 31\,\mathrm{HLB_G} + 16\sqrt{6 + \mathrm{ECN}} - 270, \qquad (9)$$

where ECN is the number of carbon atoms in saturated fluorocarbon fluids and takes the following values for unsaturated, cyclic and fluorinated hydrocarbons: 7 for perfluorodecalin, 5 for methylfluorocyclohexane, 1 for $C_8F_{17}CH{=}CH_2$ and 6 for $C_4F_9CH{=}CHC_4F_9$.

It should be emphasised that replacement of a hydrogen atom by a fluorine atom in the alkyl chains of nonionic ethoxylated surfactants considerably enhances their hydrophobicity. For instance, replacement of a CH_2 group by a CF_2 one causes T_m to decrease by about 10 °C.[72] At the same time the addition of additional OH groups to the hydrophilic substituent significantly decreases the lipophilicity (solubility in the oil phase) of surfactant molecules.[113,114] For instance, the solubilities of polyglyceryl dodecyl ethers $R_{12}(OC_2H_4CH(OH)CH_2)_2OH$ in decane are 70–80 times lower than those of $R_{12}(OC_2H_4)_2OH$, 'classical' nonionic oxyethylated surfactants.[114]

Sottmann and Strey carried out a systematic experimental investigation of the dependence of the properties of microemulsion phases in model C_iE_j–water–n-alkane ternary systems on the molecular structure of the surfactant and oil.[93] The dependences of the PIT and the T_l and T_u temperatures on the chain length of hydrophobic (n_i) and hydrophilic (n_j) groups, as well as on the chain length of n-alkanes in the oil phase (n_k) are presented in Fig. 5. In particular, it was shown that chain elongation of the hydrophilic group E_j by an oxyethyl (OE) group causes the PIT to increase by about 20 °C (Fig. 5*a*) on the average; chain elongation of the C_i substituent by two CH_2 groups causes the PIT to decrease by nearly 16 °C on the average. As the chain length of the oil-phase n-alkane increases by two CH_2 groups, the PIT shifts by about 5 °C only (Fig. 5*b*).

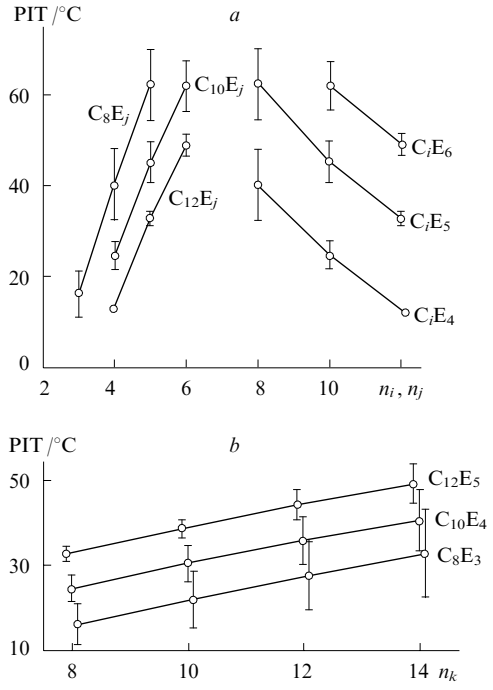


Figure 5. Dependences illustrating the effect of the molecular structure of C_iE_j-type nonionic surfactants [alkylpoly(ethylene glycol) ethers] in octane (*a*) and oil (*b*) on the phase inversion temperature in the water–oil–surfactant system.

The dependence of the PIT on the 'optimal' parameters n_i^*, n_j^* and n_k^* can be described by the function

$$\mathrm{PIT} = F(n_i^*, n_j^*, n_k^*).$$

Being written in the form

$$\mathrm{PIT} \approx \alpha + \delta_{CH_2} n_i^* + \delta_{EO} n_j^* + \delta_o n_k^* = \alpha + \sum_\beta n_\beta, \qquad (10)$$

this function is used for rather accurate determination of the 'dangerous' temperature range of emulsion instability. Here α is a constant; n_β are the 'group' numbers which, by analogy with the Davis empirical equation (6), formally describe additive contributions of various functional groups present in the surfactant molecule and in the oil phase to the PIT ignoring possible correlations between these parameters; and δ_{CH_2}, δ_{EO} and δ_o are the contributions to the PIT calculated per functional group in the alkyl chain of the surfactant molecule, in the poly(ethylene oxide) chain, and in the oil-phase molecule. For instance, for water–n-alkane–C_iE_j ternary systems (see Fig. 5) in the temperature range from 10 to 70 °C the function (10) can be represented in the form

$$\mathrm{PIT} \approx -2 - 6 n_i^* + 16 n_j^* + 2.5 n_k^*. \qquad (11)$$

If hydrophilic surfactants in water–octane–surfactant systems have a relatively long poly(ethylene oxide) chain and short alkyl chains (*e.g.*, C_8E_{12}), the PIT is higher than the boiling point of water and therefore physically unattainable. In this case the whole interval of available temperatures is below the PIT; such surfactants are good emulsifiers for preparing O/W emulsions at all temperatures. At the same time in the case of hydrophobic surfactants with long alkyl chains and short PEO chains (*e.g.*, $C_{12}E_2$) the PIT of the water–octane–surfactant system is in the region of negative temperatures. The region of available temperatures is above the PIT; such surfactants are good emulsifiers for preparing reverse emulsions at all temperatures.

d. Generalisaton of the concept of phase inversion in surfactant–water–oil system to other variables

It is of crucial importance that phase transformations in Winsor systems can be induced not only by varying the temperature, but also by changing the hydrophilic and hydrophobic chain length in (or HLB of) surfactant molecules, the carbon number of oil, as well as the alcohol and electrolyte concentrations (c_{al} and c_{el}, respectively), pressure (p), *etc.* These parameters are treated as 'equal partners' with respect to their effects on phase transformations.

Effect of the molecular structure of surfactant and type of the oil phase on phase transformations in ternary systems. A number of examples illustrating the effect of the PEO and n-alkane chain length on the type of microemulsion phases formed and on interfacial tension are presented in Fig. 6. For a series of $C_{10}E_j$ surfactants in octane at a constant temperature of 45.5 °C the interfacial tension depends on the parameter n_j as shown in Fig. 6*a*. The ternary system including a balanced microemulsion with ultralow interfacial tension ($\gamma \approx 5 \times 10^{-3}$ mN m^{-1}) can be prepared under these conditions using the surfactant with the PEO chain length $n_j = 5$. As n_j increases by unity, the ternary system undergoes separation into two phases (transition from the Winsor 3 to the Winsor $\underline{2}$ system occurs) and the interfacial tension increases by a factor of nearly 100. As the parameter n_j decreases by unity, the interfacial tension increases to the same extent; now this corresponds to transition from the Winsor 3 to the Winsor $\bar{2}$ system. Thus, emulsification at $T \sim 45$ °C results in the formation of a stable O/W emulsion in the water–octane–$C_{10}E_6$ system, a stable reverse (W/O) emulsion in the water–octane–$C_{10}E_4$ system and an unstable emulsion in the water–octane–$C_{10}E_5$ system (the last-mentioned emulsion undergoes rapid separation).

The nature of the oil phase has an equally pronounced effect on the phase state and interfacial tension (Fig. 6*b*). If decane is used as the oil phase, a balanced microemulsion characterised by ultralow interfacial tension is formed in the ternary system based on $C_{12}E_5$ at a temperature of 39.4 °C; here, the stability of macroscopic emulsion is minimum. When dodecane or tetradecane are used instead of decane, Winsor $\underline{2}$ binary system is formed at the same temperature and the interfacial tension increases by a factor of about 10 and 100 for dodecane and tetradecane, respectively. In these cases,

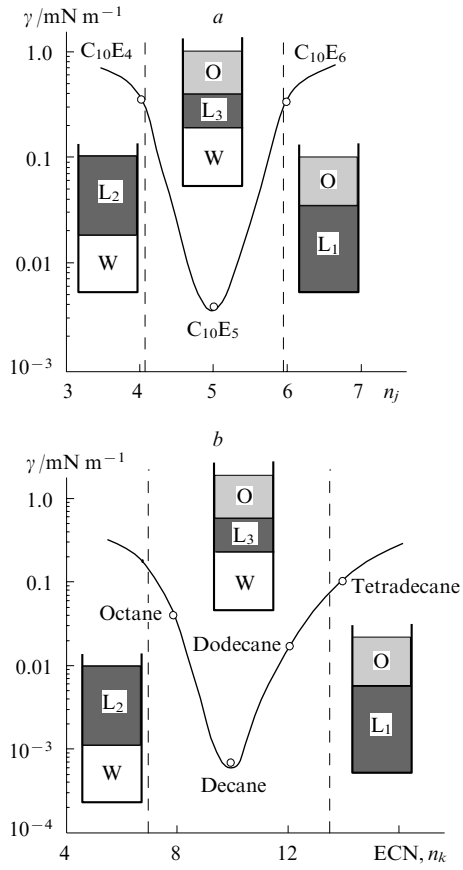


Figure 6. Dependences illustrating the effect of the molecular structure of surfactant (*a*) and oil (*b*) molecules on phase formation and interfacial tension in water – oil – C_iE_j microemulsion ternary systems.
Water – octane – $C_{10}E_j$ system at $T = 45.5$ °C (see Table 1 in Ref. 93) and water – oil – $C_{12}E_5$ system at $T = 39.4$ °C (see Table 2 in Ref. 93).

O/W emulsions are formed and their stabilities increase as follows: dodecane – tetradecane – hexadecane. Replacement of decane by octane or hexane at the same temperature causes the formation of Winsor $\overline{2}$ binary system with high interfacial tension. Emulsification of this system leads to formation of reverse emulsions whose stabilities increase on going from octane to hexane. This illustrates a pronounced effect of the nature of the oil phase on the stability of macroscopic emulsions.

Influence of salt and alcohols on phase transitions in surfactant – water – oil system. Phase transitions in multicomponent systems containing alcohols and salts can be induced by changing the concentrations of these components at fixed temperature and content of surfactant and oil. In particular, variation of the electrolyte concentration has the strongest effect on the phase state of systems based on ionic surfactants (Fig. 7).[115] These parameters are sometimes called the 'formulation variables'.[87, 116]

In the early studies on oil recovery by forced displacement from underground reservoirs using salt solutions of surfactants, the formulation variables corresponding to balanced microemulsions were called 'optimal', because microemulsions prepared under the 'optimal' conditions led to the maximum oil recovery.[65, 69, 117] This field of technology has accumulated a large body of experimental data on the properties of microemulsion systems in various physicochemical conditions, which is systematised on the basis of various empirical rules

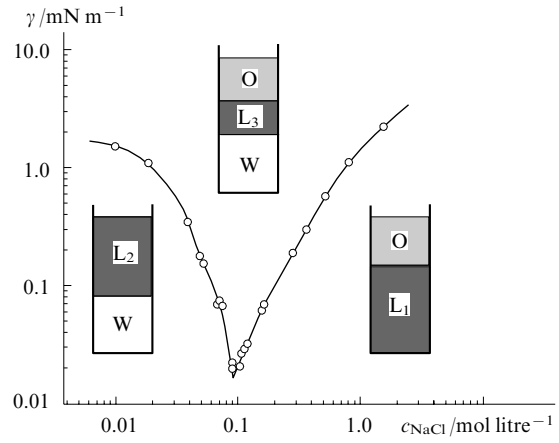


Figure 7. Effect of electrolyte (NaCl) concentration on the phase state of water – silicone oil – AOT microemulsion ternary system ($c_{AOT} = 3$ mM, $T = 25$ °C; data taken from Ref. 115).
AOT is sodium bis(2-ethylhexyl) sulfosuccinate.

and dependences.[65, 69, 118 – 120] Here we will present a number of dependences and relevant terminology.

An empirical expression for the PIT of multicomponent systems containing salts and alcohols can be written in the form

$$\mathrm{PIT} \approx \alpha(c_{el}, c_{al}) + \sum_{\beta} n_{\beta}(c_{el}, c_{al}) \approx \approx \alpha + \sum_{\beta} n_{\beta} + f(c_{el}) + f(c_{al}), \quad (12)$$

where $f(c_{el})$ and $f(c_{al})$ are empirical functions that take into account the effect of the salt and alcohol concentrations on the PIT. It is assumed that salt is mainly dissolved in the aqueous phase and that the partition coefficient of the alcohol between the oil and aqueous phases is known. If the reference state of the system is defined at $c_{el} = 1$ N (in water) and $c_{al} = 1$ M (in oil), the functions $f(c_{el})$ and $f(c_{al})$ can to a first approximation be written as follows:

$$f(c_{el}) = \delta_{el} c_{el},$$

$$f(c_{al}) = \delta_{al} c_{al}.$$

Then, Eqn (12) can be re-written in the form

$$\mathrm{PIT} \approx \alpha + \sum_{\beta} n_{\beta} + \sum_{m} \delta_m c_m, \quad (13)$$

where m stands for the salt and alcohol.

Correlations between the 'optimal' variables of some practically valuable balanced microemulsions were proposed in an early study by Bourrel *et al.*[65] Using these correlations, one can predict and control the effects of these variables on the PIT shift. The equation for the systems based on nonionic ethoxylated surfactant and alkanes written in terms of Ref. 65 is as follows

$$a - \mathrm{EON}^* = k\,\mathrm{ACN} - \sum_i m_i A_i - bS - \mathrm{c}(T - 28), \quad (14)$$

where a and k are constants for the given surfactant; EON* is the optimal average number of ethylene oxide units in the surfactant molecule [this parameter is similar to the parameter n_j^* in Eqn (10)]; ACN is the alkane carbon number identical to

Shinoda's ECN in Eqn (7); m and b are the experimentally determined constants of alcohols and salt, respectively; A and S are the concentrations (in mass %) of the alcohol and salt, respectively; and c is the experimentally determined temperature coefficient for the temperature range of 28 – 60 °C.

The equation proposed [121] for ionic surfactants (alkyl sulfonates) has another form (in the notations of Ref. 65):

$$\ln S^* = k\,\mathrm{ACN} + f(A) - \sigma. \tag{15}$$

Here S^* is the salt concentration at the PIT, $k = 0.16$ for all alkyl sulfonates, $f(A)$ and σ are the experimentally determined functions depending on the type of alcohol and surfactant, respectively. The values of the σ/k ratio denoted as EPACNUS (Extrapolated Alkane Carbon Number at Unit Salinity and no Alcohol) for a number of microemulsion systems were reported in the literature.[120]

More recently, a modified empirical correlation between the 'optimal' variables for nonionic surfactants was proposed [120, 122]

$$\frac{\mathrm{SAD}}{RT} = \alpha - \mathrm{EON} - k\,\mathrm{ACN} + bS - \phi(A) - c_T(T-25) + \mathrm{const}, \tag{16}$$

where

$$\mathrm{SAD} = \mu_\mathrm{w}^* - \mu_\mathrm{o}^* = -RT\ln K_\mathrm{p} \tag{17}$$

(surfactant affinity difference) is the quantity equal to the standard work of transfer of a surfactant molecule from oil to water; α is a constant [identical to the parameter a in Eqn (14)] characterising the type of surfactant; b and c_T are constants; $\phi(A)$ is an empirical function depending on the type and concentration of the alcohol; const is a parameter equal to $-\ln K_\mathrm{p}^*$ and determined for the so-called reference system corresponding to the 'optimal' microemulsion system. Taking into account the equality $K_\mathrm{p} = K_\mathrm{p}^*$ expression (16) proposed for characterisation of 'optimal' microemulsions can be rewritten as follows (parameters corresponding to the PIT are asterisked):

$$c_T(\mathrm{PIT} - 25) = \alpha - \mathrm{EON}^* - k\,\mathrm{ACN}^* + b\mathrm{S} - \phi(A), \tag{18}$$

which is quite similar to Eqn (14).

Thus, empirical expression (18) can be treated as an example of extension of the 'group' number technique of calculations of the Davis HLB of surfactant molecules to the case of variable physicochemical parameters in the medium (salt and alcohol concentrations, *etc.*). However, unlike the Griffin – Davis empirical rule the expression (18) is cumbersome and inconvenient for using in systematisation of experimental results. In addition, unclear physical meaning of the empirical parameters precludes application of this expression to new microemulsion systems with unknown empirical parameters. This reduces the heuristic value of expression (18).

Effect of pressure on the type of microemulsion phases for supercritical fluids and stability of highly concentrated emulsions. An increase in hydrostatic pressure causes intensification of the transitions Winsor $\overline{2}$ → Winsor 3 → Winsor $\underline{2}$.[123, 124] As the pressure increases, the PIT changes by 1 – 2 °C per 100 bar for the systems containing conventional liquid hydrocarbons.[123] This dependence can be more pronounced under supercritical conditions (P_c, T_c) for liquefied gases used for preparation of microemulsions and macroscopic emulsions.[125, 126] For instance, the effect of pressure on the phase transitions in the '$C_{12}E_6$ – propane – aqueous salt solution' microemulsion systems was studied.[125] Most studies in this field are devoted to carbon dioxide (T_c = 31 °C, P_c = 73.8 bar), a non-toxic, inflammable and relatively cheap compound treated as promising substitute of organic solvents. Owing to low dielectric permittivity ($\varepsilon = 1.0 - 1.6$) and weak van der Waals intermolecular interaction (small molecular polarisability-to-volume ratio equal to 0.012 – 0.032) supercritical CO_2 is (similarly to fluorinated oils) a poor solvent for both polar and nonpolar liquids.[127] This allows preparation of both O/W and reverse (W/O) emulsions based on supercritical CO_2.[128]

By analogy with traditional water – oil systems, the concept 'hydrophilic-CO_2-philic balance' (HCB) was introduced for characterisation of the emulsifying properties of the surfactant in 'water – supercritical CO_2' system. For instance, the Davis HCB of some surfactants was determined [127] from the relation

$$\mathrm{HCB} = 7 - b\ln K_\mathrm{p}, \tag{19}$$

where $K_\mathrm{p} = c_{\mathrm{CO_2}}/c_\mathrm{w}$. At the same time the authors of Ref. 127 pointed out that the relative solubilities of surfactants in water and in supercritical CO_2 depend on the hydrostatic pressure, CO_2 density and temperature. In particular, the study of a series of $CF_3[OCF_2CF(CF_3)]_n(OCF_2)CO_2^-NH_4^+$ fluorinated surfactants revealed a transition from CO_2/water emulsions to water/CO_2 reverse emulsions with an increase in the pressure (CO_2 density) at constant temperature. The CO_2 density at which phase inversion occurs corresponds to unstable emulsions or balanced microemulsions. This is due to the fact that an increase in the CO_2 density causes an increase in the surfactant solubility in CO_2 and subsequent decrease in the HCB. At the same time it was established that an increase in the molecular mass of the surfactant leads to phase inversion from O/W emulsions for surfactants with $n \approx 2$ to reverse emulsions for surfactants with $n > 4$. These results are in agreement with the increase in the surfactant solubility in supercritical CO_2 upon chain elongation in the fluorocarbon substituent.

The pressure and temperature dependences of interfacial tension of various surfactants at the CO_2/water interface were measured.[127, 129 – 131] It was shown that in the region of balanced emulsions the interfacial tension γ tends to ultralow values;[128, 132] in particular, it was established that the PITs of

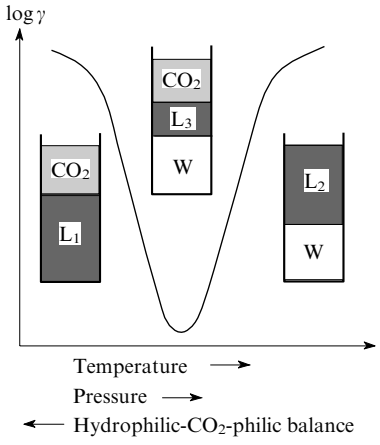


Figure 8. Phase behaviour of and interfacial tension in water – CO_2 – surfactant system as function of physicochemical parameters: a schematic draw.
L_1 and L_2 are the CO_2- and water-solubilised micellar phases, respectively.

highly concentrated emulsions prepared in the supercritical CO_2 – water system decrease as the hydrostatic pressure (CO_2 density) increases (Fig. 8). The pressure dependence of the PIT in supercritical CO_2 – water systems can be included in the empirical equation of the type (13) and represented in the form

$$\text{PIT} \approx \alpha + \sum_{\beta} n_{\beta} + \sum_{m} \delta_m c_m + f(P), \qquad (20)$$

where $f(P)$ is an empirical function of pressure.

e. Deviations from hydrophilic-lipophilic balance

The examples of the effect of various parameters on the phase inversion temperature of the water – oil – surfactant system (see above) show that this system can reach the state of a balanced microemulsion by varying the temperature at constant pressure and 'compounding' parameters (n_i, n_j, n_k, c_{el} and c_{al}) or by varying the 'compounding' parameters ('equal partners' with respect to temperature) at constant temperature. The region of 'optimal' values of these parameters (including temperature) corresponds to the lowest interfacial tension, being 'dangerous' for macroscopic emulsions.

As mentioned above, the region of balanced microemulsion corresponds to the hydrophilic-lipophilic balance temperature T_{HLB} at which the surfactant molecules in the Winsor 3 system solubilise equal amounts of oil and water. Clearly, other parameters in the region of balanced microemulsion correspond to the 'true' HLB of surfactant molecules. In this connection Eqn (20) can formally be treated as the equation of a hypersurface in the multidimensional space of these variable parameters. In the vicinity of this hypersurface macroscopic emulsions are characterised by very low stability, which increases with the distance from the hypersurface.

As an example, Fig. 9 presents the 'dangerous' surface (plane) in the three-dimensional system of coordinates for a series of C_iE_j surfactants (surfactant – water – octane system). On this surface the T, n_i and n_j values (at constant values of other parameters) correspond to a balanced microemulsion. The regions 'above' and 'below' the plane correspond to Winsor $\overline{2}$ and Winsor $\underline{2}$ binary systems. Stable emulsions and reverse emulsions are formed in the regions 'below' and 'above' the plane, respectively, separated by a 'distance ' of about 5 to 10 °C from the plane along the temperature axis. To a first approximation, one can admit that for other variables the widths of the 'dangerous' intervals for macroscopic emulsions are

$$\Delta n_i \approx \pm 1,$$

$$\Delta n_j \approx \pm 2,$$

$$\Delta n_k \approx \pm 4.$$

The surfaces corresponding to balanced microemulsions can also be constructed for different-type oil phases. In particular, for tetradecane Eqn (11) predicts a shift of the 'dangerous' plane by ~15 °C towards higher temperatures. Graphical schemes similar to Fig. 9 simplify the search for optimal process parameters for preparation of HCEs.

Having written Eqn (20) in the form

$$\Delta_{HLB} = T - \alpha - \sum_{\beta} n_{\beta}, \qquad (21)$$

the 'formulation' variables (temperature, type of surfactant (HLB) and oil (carbon number), *etc*., see below) are reduced to a single variable Δ_{HLB}, namely, the deviation from the HLB, *i.e*., from the hypersurface corresponding to the minimum interfacial tension or balanced microemulsion. In the $\Delta_{HLB} > 0$ ($\Delta_{HLB} < 0$) region the surfactant has a higher solubility in oil (water) and, therefore forms stable W/O (reverse) emulsions or stable O/W emulsions, respectively, in accordance with Bancroft's rule. Thus, the Δ_{HLB} value can be utilised for prediction of emulsion type and evaluation of emulsion stability.

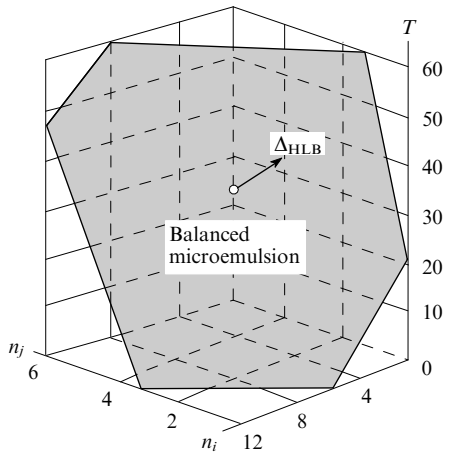


Figure 9. Balanced microemulsion plane of surfactant – water – octane system plotted in the T, n_i and n_j coordinates.
Δ_{HLB} is the deviation from hydrophilic-lipophilic balance.

III. Physicochemical factors determinimg the rupture stability of emulsion films

Breaking of HCEs, *i.e*., their separation into macroscopic phases (water and oil), is a result of rupture of microscopic emulsion films between emulsion droplets, which leads to coalescence of droplets (Fig. 10 *a*).

Spontaneous formation of a HCE in a chosen surfactant – water – oil ternary system is possible under particular physicochemical conditions (component concentrations, temperature, pressure, presence of salt and alcohols, *etc*.). The HCE type can be predicted using, *e.g*., Bancroft's rule. If the physicochemical conditions are chosen in optimal manner, the HCE lifetime can be as long as a few weeks and even months, which points to high rupture stability of microscopic emulsion films that are structurally similar to bilayer lipid membranes. As an illustration, Fig. 10 *a* presents a micrograph of a reverse HCE in which water droplets form stable surfactant-stabilised thin films in the contact region.

High stability of membrane-like liquid films (black Newton films) is well known. It was explained based on the thermal fluctuation mechanism of rupture in such systems.[133–136] However, the most interesting is the asymmetry in their stability, *i.e*., very low stability of O/W/O films accompanied by high stability of W/O/W reverse films and *vice versa*. Mechanical dispersion of oil and water taken in nearly 1 : 1 ratio causes simultaneous formation of both types of emulsions, that is, an O/W emulsion and a W/O reverse emulsion. However, one of them undergoes nearly instantaneous destruction after switching off the dispersion and the system eventually contains only the stable emulsion. Taking into account the fact that both types of liquid films are characterised by similar thickness h_f and tension γ_f (indeed, they are stabilised with the same surfactant), 'classical' concepts of rupture

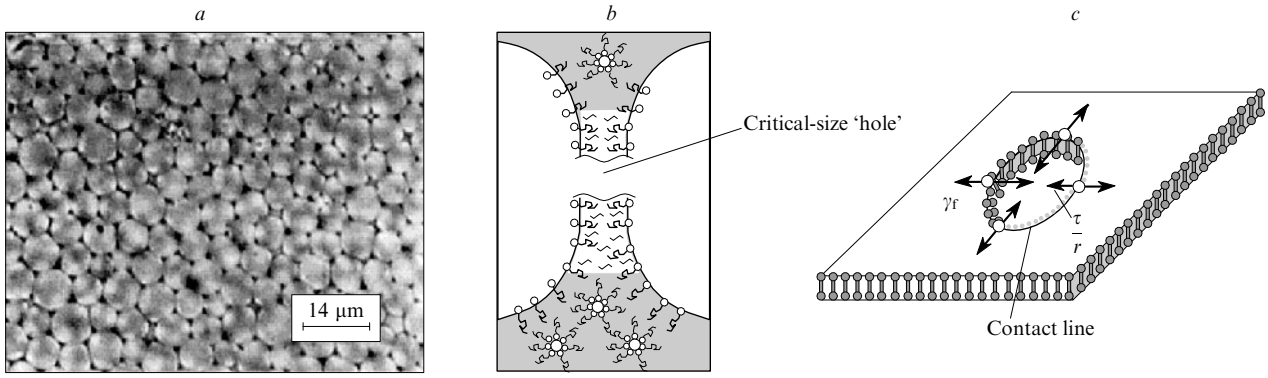


Figure 10. A micrograph of highly concentrated W/O emulsion (*a*) and schematic illustrations of rupture of an emulsion film due to fluctuation-induced formation of a 'hole' (*b*) and 'hole' equilibrium under the action of film tension forces and linear pressure (*c*).

mechanisms provide no explanation for the asymmetry in film stability.

1. Thermal fluctuation mechanism of rupture of emulsion films

The classical 'hole' theories assume that destruction of a thin liquid film is due to the formation of a critical-size 'hole' by thermal fluctuation mechanism (see Fig. 10 *b*). The destruction probability of such a film is proportional to the Boltzmann factor $\exp(-E_a/kT)$, where E_a is the activation energy equal to the work of creation of a 'dangerous hole'. If $E_a > kT$, one deals with rupture-stable emulsion films; otherwise ($E_a < kT$), films are rapidly destroyed. Derjaguin *et al.*[133, 136] developed a version of the 'hole' theory for calculating E_a values, which uses a membrane model for a thin liquid film of (conventionally) zero thickness (detailed treatment of thermodynamic models for liquid thin films is available in Refs 83 and 137).

The action of forces on a 'hole' of radius r in an emulsion film is schematically shown in Fig. 10 *c*. The membrane tension γ_f is a specific quantity (force per unit length) that acts as two-dimensional pressure normal to the 'hole' boundary and tends to make the 'hole' bigger. A positive line tension τ is responsible for two-dimensional capillary pressure τ/r that precludes an increase in the 'hole' size. The formation of a 'hole' of very small radius, such as $\gamma_f \ll \tau/r$, by the fluctuation mechanism is followed by its 'collapse' under the action of line tension. If the radius of a 'hole' formed exceeds the critical value $r_{max} = \tau/\gamma_f$, the 'hole' size increases irreversibly and eventually one deals with rupture of the film.

The critical radius r_{max} and the work, E_a, of the formation of a critical-size 'hole' can be determined from the condition for maximum free energy of the system

$$\Delta\Omega = -\pi r^2\gamma_f + 2\pi r\tau, \tag{22}$$

i.e., from the condition

$$\frac{\partial\Delta\Omega}{\partial r} = 0.$$

The first negative term in expression (22) corresponds to the gain in free energy as a result of the increase in the hole surface area $A = \pi r^2$ and the second positive term is the work of the force of linear tension τ for the formation of a contact line with the perimeter $L = 2\pi r$. The final expression for the activation energy has the form

$$E_a = \frac{\pi\tau^2}{\gamma_f}. \tag{23}$$

Note an analogy between homogeneous nucleation of a new phase in the bulk and 'homogeneous' two-dimensional formation of a 'hole'.[138, 139] In the former case the activation energy for the formation of a bubble (droplet) with the critical radius r_{max} and the surface area $A^* = 4\pi r_{max}^2$ is

$$E_a = \frac{1}{3}A^*\gamma,$$

whereas in the latter case ($r_{max} = \tau/\gamma_f$ and the perimeter $l^* = 2\pi r_{max}$) one gets for the activation energy

$$E_a = \frac{1}{2}l^*\tau.$$

In the framework of the 'hole' theories the effect of the thickness of a liquid film on E_a can be included using the thermodynamic model for a liquid film based on the concept of the interacting dividing surfaces.[83, 137] According to this model, the interfacial tension at one surface of the film is expressed through the parameters γ_f, h_f and the disjoining pressure (Π) [140]

$$\gamma = \frac{1}{2}(\gamma_f + \Pi h_f).$$

In this case [141] one has

$$\tau \approx \frac{1}{2}\pi h_f\gamma.$$

Taking account of the condition $\Pi h_f \ll \gamma_f$, which is usually valid for emulsion films, one can write [40]

$$\tau \approx \frac{1}{4}\pi h_f\gamma_f. \tag{23a}$$

Thus, the expression for the activation energy for film destruction (23) takes the form

$$E_a \approx \frac{1}{16}\pi^3 h_f^2\gamma_f \approx \frac{1}{8}\pi^3 h_f^2\gamma. \tag{24}$$

For instance, at $\gamma \approx 1-10$ mN m^{-1} for emulsion films of thickness $h_f \approx 10$ nm one gets $E_a \approx (10^2-10^3)kT$ or $E_a \approx (4-40)\times 10^{-19}$ J, which corresponds to high rupture stability of these films. In the near-PIT region characterised by low and ultralow ($\gamma \approx 10^{-3}-10^{-2}$ mN m^{-1} and lower) interfacial tension the activation energy for destruction is $\sim(0.1-1)kT$ and lower, which leads to rapid rupture of the films and coalescence of droplets.

Thus, the classical 'hole' theories of film rupture correctly describe the abrupt decrease in the breakage stability of emulsions in the vicinity of the PIT, where the interfacial tension is low and ultralow ($\gamma \approx 10^{-2}-10^{-4}$ mN m^{-1}).

2. Asymmetry of rupture stability of emulsion films

As mentuioned above, the 'hole' theories provide no explanation for the observed asymmetry of the rupture stability of different types of liquid films. For instance, a stable heptane-in-water HCE is formed in the surfactant–water–heptane ternary system at 25 °C using a nonionic surfactant polyglycol n-dodecyl ether ($C_{12}E_5$).[116] The lifetime of this emulsion can be as long as a few days and even weeks, which is schematically shown in Fig. 11 as the plot of the integrated probability, $P(t_f)$, of destruction of W/O/W emulsion films *vs*. time. The lifetime of O/W/O reverse emulsion film is a few seconds.

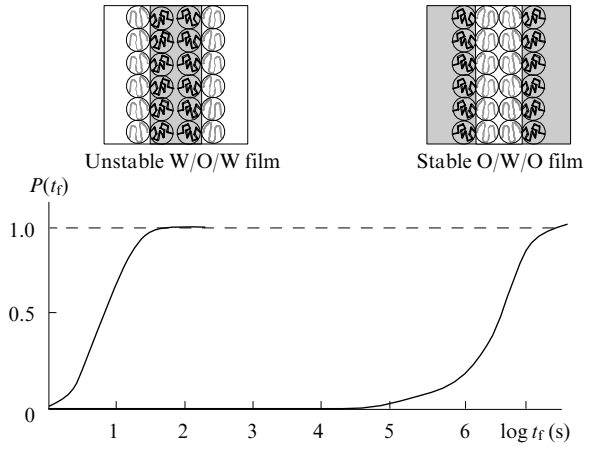


Figure 11. Dependences illustrating pronounced asymmetry of the rupture stability of emulsion films.

This great difference between the rupture stabilities of different types of films has no explanation in the framework of the DLVO theory and the classical 'hole' theories of rupture of emulsion films. Indeed, on the one hand, the interfacial tension in plane-parallel films is assumed to be nearly equal for both types of films. On the other hand, the thicknesses of water-in-oil (O/W/O) films and oil-in-water (W/O/W) films should not differ appreciably taking into account nearly equal volumes of the hydrophilic and hydrophobic moieties in the $C_{12}E_5$ molecule. One can admit that owing to higher solubility of this ether in water at 25 °C the water film will be somewhat thicker than the heptane film. However, taking into account expression (24), this provides no explanation for the so large difference (about 6 decimal orders of magnitude) between the lifetimes (t_f) of different types of films (see Fig. 11).

a. Dependence of interfacial tension on surface curvature

The asymmetry in emulsion film stability can be explained in the framework of the 'hole' mechanism of film destruction assuming that absolute values of positive linear tension τ for the W/O/W and O/W/O films in expression (23) are different. This assumption is equivalent to the idea that the interfacial tension depends on the surface curvature,[84–86,93] which was used in deriving expression (23a) relating the linear tension to the interfacial tension in the 'hole' region. The possibility for such a dependence to exist is due to the energy properties of saturated surfactant monolayers, in particular, lateral interaction between surfactant molecules.

According to the theory microemulsions,[91,92] saturated surfactant monolayers between the aqueous and oil phases in lyotropic microemulsion systems are characterised by the local curvature H_0 governed by the size of hydrophilic and hydrophobic fragments of the surfactant molecules in the monolayer. As the temperature rises, such systems exhibit successive mutual transformations of lyotropic mesophases, starting from swollen (oil-solubilised) micelles (L_1 phase in Winsor $\underline{2}$ binary system), to swollen (water-solubilised) reverse micelles (L_2 phase in Winsor $\overline{2}$ binary system) *via* the balanced bicontinuous L_3 phase in Winsor 3 ternary system. Depending on the molecular structure of the surfactant, hexagonal, cubic and lamellar intermediate phases are also possible.[142,143]

These phase transformations are due to the change in the local curvature of interfacial monolayers formed by nonionic surfactants[84,88] from convex to concave relatively to the aqueous phase as temperature increases (Fig. 12). The mean local curvature is given by

$$H_0 = \frac{1}{2}(H_1 + H_2)$$

(H_1 and H_2 are the principal surface curvatures) and changes from positive to negative, being equal to zero at the phase inversion temperature. The Gaussian curvature

$$K_0 = H_1 H_2$$

is negative for the Winsor 3 ternary system and positive for the $\underline{2}$ and $\overline{2}$ binary systems.

As temperature increases to the lower critical temperature T_l, the L_1 phase undergoes separation into two phases and a new interface between the middle phase L_3 and the aqueous phase (L_2 phase) is formed. Almost the whole amount of surfactant goes from the L_1 aqueous phase to the L_3 middle phase, the surfactant concentration in the L_1 phase decreases, which corresponds to its rather low molecular solubility in water. The curvature of surfactant monolayers in the microemulsion phases changes from spherical in the L_1 phase to almost zero in the L_3 bicontinuous phase. As the upper critical temperature T_u is attained, the L_3/L_2 interface disappears and molecules go from the surfactant phase, thus forming a swollen micellar phase L_2. The content of surfactant in the middle phase L_3 is maximum at the phase inversion temperature at which the mean local curvature is zero and the negative Gaussian curvature is minimum.

Raising the temperature initially causes the interfacial tension at the L_1/L_2 interface in the Winsor $\underline{2}$ system to reduce (see Fig. 12*b*) and take a minimum (ultralow) value $\gamma_{L_1L_2} \leqslant \gamma_{L_1L_3} + \gamma_{L_3L_2}$ in the temperature range from T_l to T_u

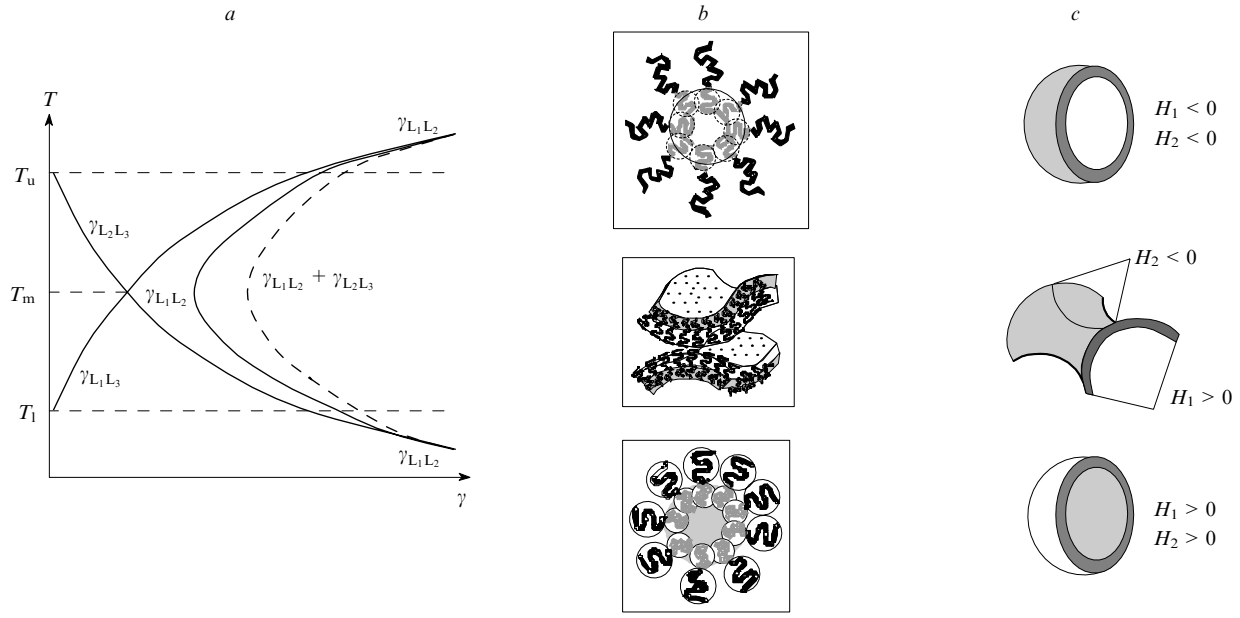


Figure 12. Temperature dependences of interfacial tension in Winsor systems (*a*), schematic representation of microemulsion phases (*b*) and changes in curvature of surfactant monolayers (*c*).

(the sign of this inequality is related to the condition for system stability).[144] At the instant of formation of the L_1/L_3 interface, the corresponding interfacial tension $\gamma_{L_1L_3}$ is zero; it increases with temperature and becomes $\gamma_{L_1L_2}$ after passing the T_u temperature. Correspondingly, the $\gamma_{L_3L_2}$ interfacial tension is a continuation of the $\gamma_{L_1L_2}$ interfacial tension in the intermediate temperature range $T_l < T < T_u$; it decreases as temperature decreases and becomes zero at T_u. It should be noted that interfacial tension at a flat L_1/L_2 interface is independent of the existence of the middle phase L_3, being solely governed by the curvature of surfactant monolayers in the L_3 phase. The surfactant can mechanically be removed from the L_3 phase as its formation develops, thus leaving only one interface (L_1/L_2); here the $\gamma_{L_1L_2}(T)$ dependence will remain unchanged.

According to the pioneering idea of Helfrich,[90] saturated surfactant monolayers are characterised by a kind of elasticity. This means that bending or saddle-splay deformation of this type of monolayers requires external forces to make a thermodynamically reversible work, which increases the interfacial free energy of the monolayers ($\Delta\gamma_c$). An undeformed surfactant monolayer with the local curvature H_0 has a minimum interfacial free energy. Deformation of such a layer will lead to an increase in the interfacial energy. To a first approximation, this can be described as follows:[90]

$$\Delta\gamma_c(H) = 2\kappa(H - H_0)^2 + \bar{\kappa}K, \qquad (25)$$

where H is the actual curvature at a given instant and κ and $\bar{\kappa}$ are respectively the bending and saddle-splay moduli of the monolayers.

If a swollen spherical micelle of radius r_{mic} is chosen as a reference state and the surfactant monolayer is considered as undeformed monolayer with the local curvature $H_0 = 1/r_{mic}$, in the Helfrich approximation from Eqn (25), ignoring the contribution of saddle-splay deformation $\bar{\kappa}$, one gets the expression for the interfacial tension of a flat monolayer ($H = 0$)

$$\gamma_0 = \Delta\gamma_c(0) + \Delta\gamma_c(H_0) = H_0^2(2\kappa - \bar{\kappa}) \approx \gamma_{min} + 2\kappa H_0^2. \qquad (26)$$

where γ_{min} is the minimum interfacial tension corresponding to the local curvature of the monolayer.

Equation (25) was derived taking account of the fact that the mean and Gaussian curvatures of a spherical surface of radius R are respectively given by

$$H = H_1 = H_2 = \frac{1}{R},$$

$$K = H^2 = \frac{1}{R^2}.$$

Assuming the value $r_{mic} \approx 2-3$ nm for the radius of swollen micelles and using the estimate of the bending modulus $\kappa = 0.6kT$ (Ref. 84), one gets for the following local curvature and interfacial tension of a flat surface $H_0 \approx (0.5-0.3) \times 10^9$ m^{-1} and $\gamma \approx (0.5-1)$ mN m^{-1}, respectively. The estimate of interfacial tension ($\gamma \approx 1$ mN m^{-1}) agrees with the results of experimental measurements of interfacial tension in surfactant–water–oil ternary systems forming stable HCEs.[84–86, 93, 143–147]

If a flat interface is chosen as the reference state, the expression for the interfacial tension of the curved surface has the form[40]

$$\gamma_c(H) = \Delta\gamma_c(H) - \Delta\gamma_c(0) = 2\kappa\left(H^2 - 2HH_0\right) + \bar{\kappa}K. \qquad (27)$$

It should be noted that the major contribution to interfacial tension is made by those components of surface forces that are due to elastic deformation of surfactant monolayers; the interfacial tension of undeformed monolayers, γ_{min}, is very low and can be neglected. The mechanism of formation of the Helfrich's elasticity of surfactant monolayers based on the so-called 'wedge' model is illustrated in Fig. 13.[68, 91] According to this model, the hydrophilic (PEO) and hydrophobic (alkyl) fragments of the surfactant molecule have different proper volumes that are conditionally placed in a truncated cone. In the undeformed state (swollen micelle) the cones form a monolayer with the closest packing, which determines the radius r_{mic}^{g} of a swollen micelle; the cohesive energy between

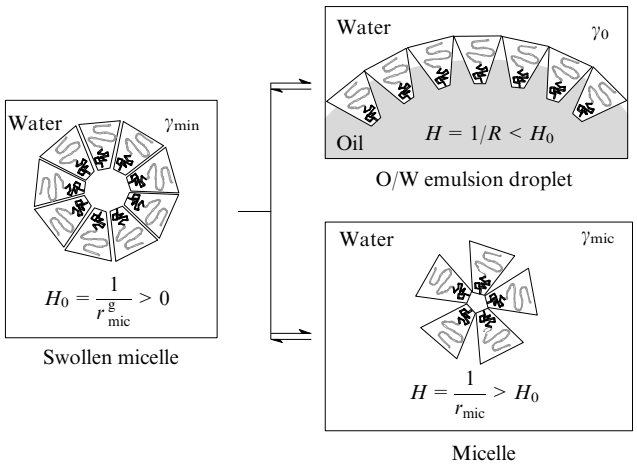


Figure 13. Schematic illustration of the effect of lateral interaction between surfactant molecules in a monolayer on interfacial tension.

lateral fragments of the molecules is maximum. This state corresponds to a minimum of the free energy of the monolayer, *i.e.*, to the minimum interfacial tension γ_{min}. As the radius of curvature increases to the value $R \gg r^g_{mic}$ corresponding to an O/W emulsion droplet, lateral interaction between the alkyl chains of the surfactant molecules weakens, thus causing the free interfacial energy of the monolayer to increase to γ_0; this value can be measured experimentally. The interfacial tension of the emulsion droplets of radius $R = 1-10$ μm is almost equal to the γ_0 value because the condition $H \ll H_0$ is valid.

In the case of unswollen micelles of radius $r_{mic} < r^g_{mic}$, which are, *e.g.*, formed in the absence of the oil phase, the surfactant molecules will not form close-packed monolayers on the micelle surface. The curvature of such micelles is greater than that of swollen micelles and therefore the lateral interaction between hydrophilic chains of surfactant molecules weakens and the free energy of the system increases. This also causes the interfacial tension to increase to the value γ_{mic}, which is assumed to be much higher than γ_{min}, but is not determined experimentally. If this system is placed in contact with the oil phase, solubilisation of the oil molecules within micelles (*i.e.*, swelling of micelles) will occur and the surfactant monolayers will go from the deformed state to a state corresponding to the local curvature of close-packed molecules. Thus, the solubilisation of micelles is driven by the gain in free energy of the system during transition from the deformed to undeformed state of surfactant monolayers.

b. Stable O/W emulsion films at temperatures below the phase inversion temperature

In the case of a stable O/W/O film between oil droplets of an O/W emulsion in water (Fig. 14 *a*), which corresponds to hydrophilic surfactant molecules that form swollen micelles in the aqueous phase, creation of a 'hole' requires an energy expenditure. In the framework of the film model based on the idea of two interacting dividing surfaces,[81, 83] the formation of a 'hole' of radius r_h in a film of thickness h_f is accompanied by the formation of a new interface characterised by a constant curvature

$$H = \frac{1}{2}\left[\left(\frac{1}{r_h} - \frac{2}{h_f}\right)\right]$$

and the surface area

$$A \approx \pi^2 h_f r_h .$$

Within the limits of applicability of this simplified geometric description of the 'hole' surface its curvature in the early stage of formation at $r_h = h_f/2$ is zero ($H = 0$, as for the flat surface); as r_h further increases, the curvature becomes negative ($H < 0$). Since in the whole range of variation of the radius r_h the interfacial tension remains approximately equal to γ_0, the conditions of the classical 'hole' theories of rupture of liquid films are ful filled. Using the arguments used in deriving

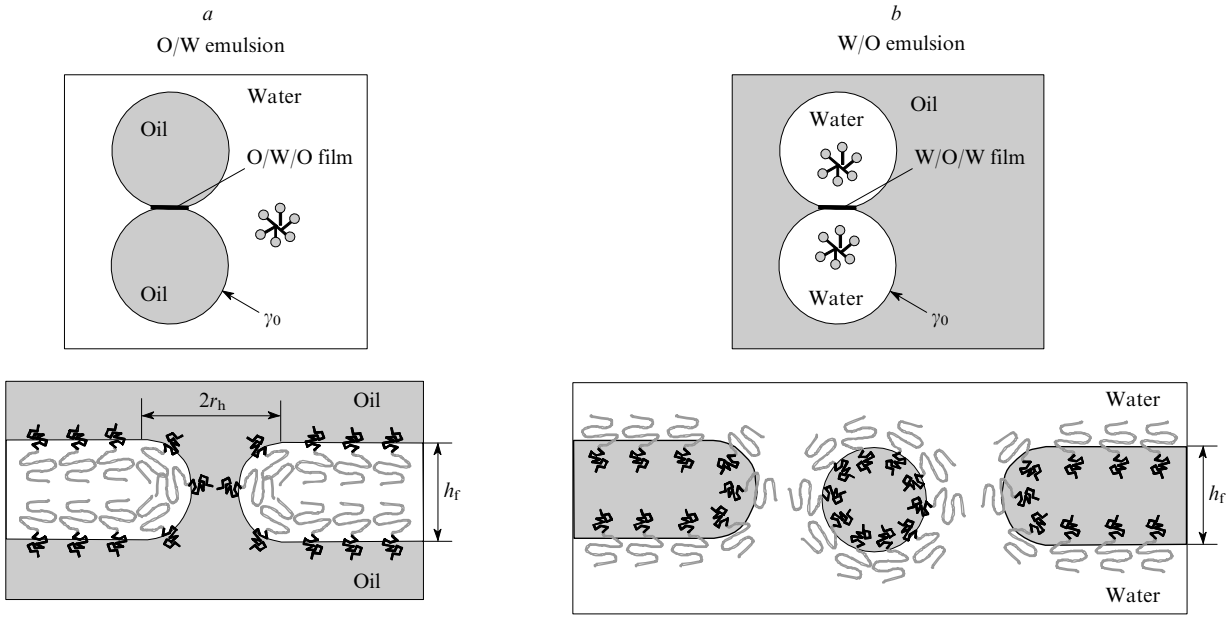


Figure 14. Schematic illustration of destruction of O/W/O (*a*) and W/O/W (*b*) emulsion films.

Eqn (24), the expression for the linear tension and activation energy for film destruction take the form

$$\tau \approx \frac{1}{2}\pi h_f \gamma_0 , \tag{28}$$

$$E_a \approx \frac{1}{8}\pi^3 h_f^2 \gamma_0 . \tag{29}$$

Numerical estimation of the activation energy with $h_f \sim 10$ nm and $\gamma_0 \sim 1$ mN m^{-1} gives $E_a \sim 200\,kT$, which corresponds to rupture-stable films.

c. Unstable reverse emulsion films at temperatures below the phase inversion temperature

In the case of 'hole' formation in a W/O/W film between two water droplets in oil (Fig. 14 *b*), the curvature of the 'hole' surface

$$H = \frac{1}{2}\left(\frac{2}{h_f} - \frac{1}{r_h}\right)$$

will increase with r_h from zero at $r_h = h_f/2$; this positive quantity (the 'hole surface' is convex towards the aqueous phase) tends to the value $H_f = 1/h_f$, which is similar to the local curvature of swollen micelles, H_0. The interfacial tension of the curved 'hole surface' tends to the minimum value γ_{min}. In this case the expressions for the linear tension and the activation energy for film destruction have the form

$$\tau \approx \frac{1}{2}\pi h_f \gamma_{min} , \tag{30}$$

$$E_a \approx \frac{1}{8}\pi^3 \frac{h_f^2 \gamma_{min}^2}{\gamma_0} . \tag{31}$$

Evaluation of the activation energy with $h_f \approx 10$ nm and $\gamma_0 \approx 10^{-3}$ mN m^{-1} gives $E_a \approx 10^{-3}\,kT$, which corresponds to films that are very unstable towards destruction. Moreover, one can assume that a W/O/W liquid film will undergo spontaneous dispersion into swollen micelles, because this process, similarly to the 'hole' formation, almost does not require any energy expenditure.

The stability of reverse emulsions towards destruction and respective instability of O/W emulsions at temperatures above the PIT can be explained in a similar manner.

3. Formation of emulsions from micellar solutions by phase inversion technique

Highly concentrated emulsions can be prepared not only by the 'classical' mechanical dispersion of the internal phase in a dispersion medium followed by concentration of the disperse phase by centrifugation, sedimentation or dialysis, but also by intense heating or cooling of solubilised micellar solutions of surfactants [38, 78, 79, 148–151] or by changing other parameters (*e.g.*, electrolyte or surfactant concentration) with no mechanical dispersion.[57, 152, 153] In particular, O/W HCEs stabilised with nonionic polyoxyethylated surfactants are formed upon abrupt cooling of the reverse (O/W) micellar phase L_2, whereas reverse (W/O) HCEs are spontaneously formed from the L_1 (O/W) micellar phase upon abrupt heating.

a. Empirical temperature dependence of interfacial tension

Raising the temperature causes a sequence of interconversions of lyotropic mesophases, starting from swollen (oil-solubilised) micelles (L_1 phase in the Winsor $\underline{2}$ binary system, see Fig. 3) to swollen (water-solubilised) reverse micelles (L_2 phase in the Winsor $\overline{2}$ binary system) through a balanced bicontinuous L_3 phase in the Winsor 3 ternary system.

A semiempirical scaling dependence of the tension between two phases (*a* and *b*) on temperature has the form [85, 93, 154]

$$\gamma^* = (\tau^*)^2 + 1, \tag{32}$$

where γ^* is the reduced interfacial tension and τ^* is the reduced temperature

$$\gamma^* = \frac{\gamma_{ab}}{\bar{\gamma}_{ab}}, \tag{33}$$

$$\tau^* = \tau\sqrt{-\frac{2\kappa + \bar{\kappa}}{\bar{\kappa}}} .$$

The minimum interfacial tension $\bar{\gamma}_{ab}$ is expressed through a scaling length

$$\bar{\xi} = \frac{2}{H_l - H_u}$$

(H_l and H_u are the curvatures at the temperatures T_l and T_u, respectively) in the form

$$\bar{\gamma}_{ab} = -\frac{\bar{\kappa}}{\bar{\xi}^2}, \tag{34}$$

and the characteristic scale length for temperature is defined by

$$t = 2\,\frac{T - T_m}{T_u - T_l} \tag{35}$$

assuming that

$$H_l - H_u = \alpha(T_u - T_l),$$

α is the empirical temperature coefficient equal to $\sim 10^7$ m^{-1} K^{-1}. Using relationship (32), several tens of surfactant–water–oil ternary systems containing C_iE_j nonionic surfactants were described.[85, 93, 154] In particular, it was established that all systems meet the condition $\kappa \approx -2\bar{\kappa}$, the average bending and saddle-splay moduli being equal to $\sim 1\,kT$ and $\sim 0.5\,kT$, respectively.

The experimentally determined temperature dependences of the interfacial tension for a number of ternary systems are shown in Fig. 15. All the dependences have narrow deep minima corresponding to balanced microemulsions, the minima $\gamma_{min} = \bar{\gamma}_{ab}$ corresponding to different phase inversion temperatures. Noteworthy is the deepest minimum for the $C_{12}E_4$–octane–water system at $T_m = 12$ °C, which becomes more shallow and shifts towards higher temperatures with an increase in the oil carbon number and in hydrophilicity of the surfactant molecule (elongation of the PEO chain or shortening of alkyl chain) and with the overall shortening of the chain in the surfactant molecule. For some systems [*e.g.*, a fluorinated surfactant $R_8^FE_2 = C_8F_{17}C_2H_4SC_2H_4(OC_2H_4)_2OH$ with a long fluoroalkyl chain including eight carbon atoms and perfluorodecalin as the oil phase] the PITs are in the region of negative temperatures.[147, 155]

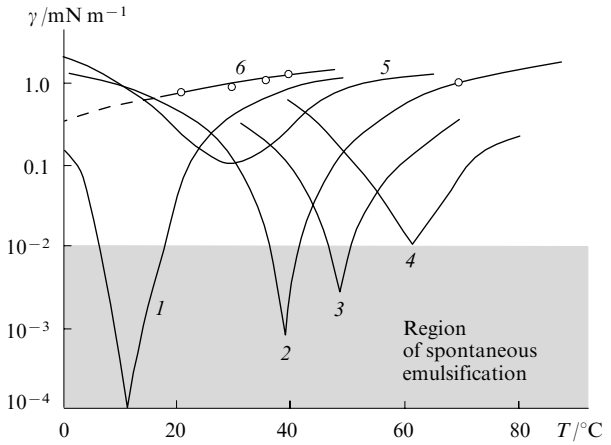


Figure 15. Temperature dependences of interfacial tension for surfactant – water – oil ternary systems.
Surfactant: $C_{12}E_5$ (*1*–*3*), $C_{10}E_5$ (*4*), C_8F_3 (*5*) and $R_8^FE_2$ (*6*); oil phase: octane (*1*, *4*), decane (*2*), tetradecane (*3*, *5*) and perfluorodecalin (*6*). The spontaneous emulsification region (shown conventionally) includes systems promising for preparation of gel emulsions by PI technique.

b. Mechanism of HCE formation from solutions of swollen micelles

It was shown [8, 37] that the size of gel emulsion droplets is highly sensitive to the rate at which the temperature changes during the phase inversion. The longer the residence time of the system in the 'dangerous' temperature range characterised by low and ultralow interfacial tension the larger the mean size of emulsion droplets. This correlation can be used for controlling the size of gel emulsion droplets. Note that phase inversion can also be attained by rapidly varying 'formulation' parameters, *e.g.*, the salt and co-surfactant concentrations, *etc.*[122, 123] Temperature changes should take a relatively short time in the whole bulk of the system; this is necessary to prevent the emulsion from destruction at ultralow interfacial tension.

In the zero curvature region the temperature dependence of interfacial tension exhibits a deep narrow minimum; in this region γ takes ultralow values (see Fig. 15). According to modern concepts, this mimimum is due to the effect of lateral interaction between surfactant molecules on the free surface energy of the system. In terms of thermodynamics of interfaces this can be treated as the dependence of interfacial tension on the elasticity of curved surfactant monolayers.[84–86, 93]

As mentioned above, if a flat surface is in thermodynamic equilibrium with a micellar solution, the major contribution to the interfacial tension γ_0 comes from the work of bending of the spherical surface of the surfactant monolayer in a swollen micelle upon its transformation to the flat surface.[84] The local curvature, H_0, of the monolayer is determined by the packing parameter of the surfactant molecules in the monolayer,[91] which in turn is due to the relative volumes and the shape of the hydrophilic and hydrophobic molecular fragments, which depends on the physicochemical parameters ('formulation variables'), such as T, P, c_{el}, ECN, *etc.*

For instance, the temperature dependence of the mean local curvature H_0 of the monolayer of a C_iE_j nonionic surfactant can be written as follows [84]

$$H_0(T) = \alpha(T_0 - T),$$

where $\alpha \approx 1.22 \times 10^7$ m^{-1} K^{-1} for the water – n-octane – $C_{12}E_5$ ternary system and T_0 is the PIT (32 °C for this system). At T_0, the local curvature H_0 of the monolayer is zero; at $T < T_0$, it is positive, being negative at $T > T_0$. Using the Helfrich expression for interfacial tension

$$\Delta\gamma_c(H) = 2\kappa(H - H_0)^2 + \bar{\kappa}K$$

minimisation of the free energy of spherical droplets ($d\Delta\gamma_c/dH = 0$) leads to the expression

$$H_0 = H\left(1 + \frac{1}{2}\frac{\bar{\kappa}}{\kappa}\right),$$

relating H_0 to the experimentally determined curvature H. Assuming that the interfacial tension γ_0 equals the free energy spent for deformation of the curved monolayer in the swollen micelle to a flat monolayer on a flat surface, one gets the expression for interfacial tension

$$\gamma_0 = \Delta\gamma_c(H) - \Delta\gamma_c(0) = \gamma_{min} + 2H^2(\kappa + \bar{\kappa}) - \bar{\kappa}K, \qquad (36)$$

where

$$\gamma_{min} = \frac{kT}{2\pi\xi^2}\ln\frac{\xi}{c},$$

the parameters ξ and c are the characteristic scaling lengths determined from the electromagnetic radiation and neutron scattering experiments. Assuming for the elasticity moduli the values $\kappa = 0.6\,kT$ and $\bar{\kappa} = 0.3\,kT$, Strey [84] showed that Eqn (36) correctly describes the experimental dependence $\gamma_0(T)$ for the water – n-octane – $C_{12}E_5$ system. More recently,[85] about twenty systems containing C_iE_j surfactants were described using a theoretical model based on the Landau theory of tricritical systems, Eqn (32) and only one fitting parameter $\kappa/\bar{\kappa}$. This approach allows one to relate the interfacial tension in ternary systems to structural parameters of micellar phases and then to describe the properties of HCEs.

A mechanism of formation of gel emulsions from solutions of swollen micelles was proposed.[40] It is practically implemented in the phase inversion technique. Figure 16 illustrates structural changes within the L_1 micellar phase formed by the C_iE_j surfactant on heating. For instance, a system containing 0.1 M NaCl solution, decane and $C_{12}E_4$ was used;[38] the concentration of $C_{12}E_4$ in the L_1 phase was $c_s = 3\%$ and the volume fraction of decane solubilised in micelles was in the range 5% – 10%. Under these conditions the specific internal surface area corresponding to swollen micelles was of the order of $A_{sp} \approx a_1 c_s \approx 10^2$ m^2 m^{-3}, where $a_1 \approx 0.5$ nm^2 is the surface area per molecule in the interfacial layer assuming spherical oil droplets (swollen micelles) of about 10-nm mean radius. This corresponds to the average aggregation number of the surfactant in micelles of about 100 and an about 30-nm mean distance between droplets. Thus, initially (before heating) the system contained swollen micelles and free surfactant molecules whose concentration was equal to the CMC of the surfactant (see Fig. 16 *a*).

Heating causes the HLB of surfactant molecules to decrease due to dehydration of OE groups and the spontaneous curvature of interfacial layers of O/W micelles to change from convex to concave relative to the aqueous phase, which favours the formation of reverse micelles. This is accompanied by a decrease in the surfactant solubility in water and an increase in its solubility in oil. As a consequence, a diffusion flow of surfactant molecules across the surface of swollen micelles is created. The interfacial tension becomes ultralow; this diffusion flow creates convective flows in the aqueous phase, which flow towards the interior of the swollen micelles, thus increasing their volume and causing the formation of

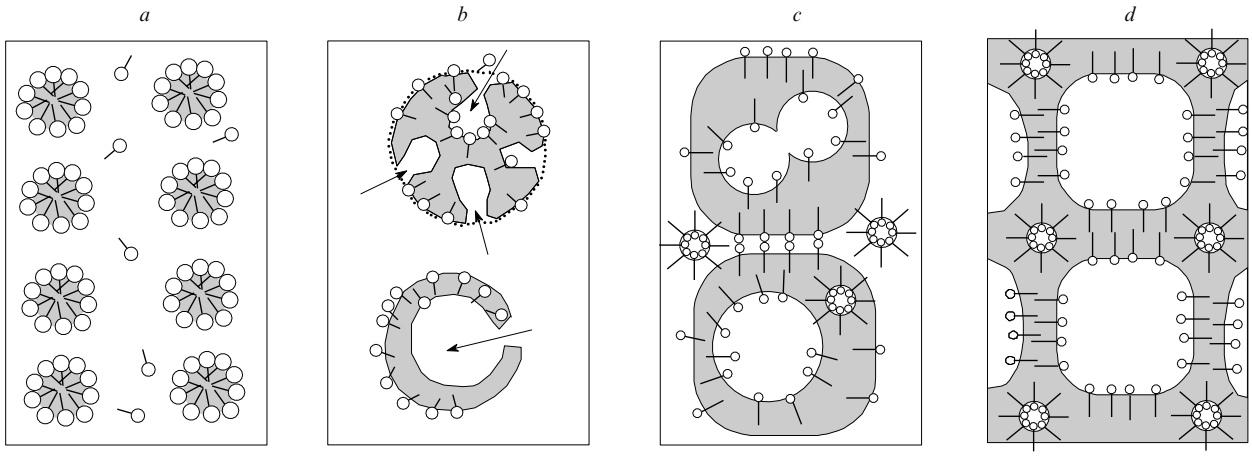


Figure 16. Preparation of reverse gel emulsion from a solution of swollen micelles (L_1 phase) by phase inversion technique.
Swollen O/W micelles (*a*), spontaneous formation of W/O microdroplets within swollen O/W micelles by diffusion and convection mechanisms (*b*), growth of W/O nanodroplets by Ostvald ripening mechanism or by coalescence (*c*) and coalescence of O/W droplets and formation of W/O gel emulsion (*d*).

microscopic water droplets encapsulated in the oil droplets (Fig. 16 *b*). Owing to ultralow interfacial tension in the temperature region near the PIT both microscopic water droplets in the swollen micelles and the swollen micelles in the aqueous phase rapidly coalesce. However, if the residence time of the system in the 'dangerous' temperature region near the PIT under heating is short, then the coalescence of microscopic water droplets does not develop to a very high extent. At temperatures above the PIT, microscopic water droplets formed become stable to coalescence, whereas the oil droplets (swollen micelles) rapidly coalesce (temperature region in which O/W emulsions are unstable) (Fig. 16 *c*). As a result, a reverse emulsion containing relatively small water droplets is formed (Fig. 16 *d*). At the same time if the system resides a too long time in the 'dangerous' region with low interfacial tension, the average radius of water droplets will increase owing to coalescence and Ostwald ripening.[38]

c. Criterion for spontaneous formation of emulsions from solutions of swollen micelles

The proposed mechanism of spontaneous formation of gel emulsions upon phase inversion makes it possible to outline some limitations to its practical implementation. Indeed, the formation of emulsions with the droplet radius R from solutions of swollen micelles requires that the minimum interfacial tension γ_{min} corresponding to the PIT be rather low. The characteristic radius of water droplets formed by the thermal fluctuation mechanism inside swollen micelles (see Fig. 16 *b*) can be estimated using the relation[40]

$$4\pi R^2\gamma^* \approx kT, \tag{37}$$

where γ^* is the critical (minimum) interfacial tension (at higher γ values the formation of water droplets with the radius R is unlikely). For instance, spontaneous formation of droplets with $R = 10$ μm requires $\gamma^* \leqslant 10^{-2}$ mN m^{-1} (in Fig. 15 the region of spontaneous emulsification for this particular case is shown by dashed line).

Analysis of the experimental curves $\gamma(T)$ presented in Fig. 15 showed that gel emulsions wit this droplet size can be prepared by the phase inversion technique from ternary systems characterised by ultralow minimum interfacial tension (less than 10^{-2} mN m^{-1}). These are, *e.g.*, the water–decane–$C_{12}E_5$ and water–tetradecane–$C_{12}E_5$ systems. The former was used by Kunieda *et al.*[38] for the preparation of W/O gel emulsions from solutions of swollen micelles (L_1 phase) on heating from 20 to 50 °C. The second system was used[78] to prepare O/W emulsions from reverse micellar solutions (L_2 phase) on cooling from 70 to 20 °C. It was assumed[40] that the water–octane–$C_{12}E_5$ ternary system characterised by $\gamma_{min} \sim 10^{-4}$ mN m^{-1} (see Fig. 15) should be more efficient than the first two systems and that gel emulsions cannot be prepared by the phase inversion technique using the water–tetradecane–C_8E_3 system because in this case $\gamma_{min} \sim 10^{-1}$ mN m^{-1}. A negative result is also expected for the water–octane–$C_{10}E_5$ system until appreciable reduction of the interfacial tension γ_{min} in some way (by, *e.g.*, adding lyotropic NaCl-type electrolytes, see Refs 107 and 156).

d. Preparation of highly disperse emulsions

The fact that gel emulsions cannot be prepared by the phase inversion technique does not preclude the use of other methods to this end. For instance, a stable reverse gel emulsion was prepared by mechanically dispersing the water–perfluorodecalin–$R_8^FE_2$ system.[51,157] These fluorinated gel emulsions are formed at room temperature, because their PITs are at negative temperatures (~ -80 °C).[71,72,158]

At the same time by dispersion of the internal phase at temperatures near the PIT (provided that the PIT is in accessible temperature region) one can appreciably reduce the energy expenditure for emulsification owing to a decrease in the interfacial tension in the vicinity of the PIT. This method of preparation of submicrometre emulsions (or miniemulsions) was first reported by Shinoda[159,160] and is widely used at present.[40] Emulsification in the 'dangerous' instability region is followed by the transition to the emulsion stability region by raising (or lowering) the temperature by $\sim 10-20$ °C for the reverse (or O/W) emulsions.

4. Size effect of surfactant molecules and lateral interaction in monolayers on stability of emulsions

As mentioned above, changes in the physicochemical parameters (temperature; salt, surfactant and co-surfactant concentrations, *etc.*) of a ternary system can be followed by phase transitions accompanied by changes in the curvature of surfactant monolayers. For instance, an $L_1 \rightarrow L_3 \rightarrow L_2$ phase

transition occurs in the ternary system containing a nonionic oxyethylated surfactant with moderately long hydrophilic and hydrophobic chains (see Fig. 3) at relatively low surfactant concentrations as temperature increases. During this transition the mean curvature of surfactant monolayers changes from positive for direct micelles to negative for reverse micelles upon transition through the L_3 bicontinuous phase (balanced microemulsion, or Winsor 3 system), which corresponds to zero mean curvature of monolayers and is formed at the phase inversion temperature. A balanced microemulsion can also be prepared by changing other physicochemical parameters of the system.

a. Effect of rigidity of monolayers on rupture stability of emulsion films

Monolayers of surfactants with moderately long hydrophilic and hydrophobic chains that are formed far from the balanced microemulsion region are characterised by low bending modulus $\kappa \approx 1\,kT$; these are flexible monolayers.[84] According to Eqn (27), the interfacial tension is relatively low ($0.1-1$ mN m^{-1}, see Refs 85, 93, 154) even far from the balanced microemulsion region.

Simultaneous elongation of both hydrophilic and hydrophobic fragments of surfactant molecules in such a manner that a preset HLB remains unchanged, all other factors being the same, will enhance the lateral interaction between surfactant molecules in the monolayers. As a consequence the trend towards formation of the L_α lamellar phase instead of the L_3 labile bicontinuous phase characteristic of short-chain surfactants (Fig. 17 *a*) becomes more pronounced in the vicinity of the PIT. In the lamellar phase the lateral interaction between nearly equal-volume hydrophilic and hydrophobic fragments of surfactant molecules in the monolayer causes the formation of plane-parallel bilayers separated by alternating water and oil layers. Monolayers of the L_α lamellar phase and the L_3 phase have a zero curvature in the PIT region, but their bending moduli are much higher ($\kappa \approx 10-100\,kT$) and correspond to rigid monolayers. Therefore, the minima in the $\gamma(T)$ curves become less pronounced, the minimal interfacial tension for the lamellar phases considerably increases compared to the corresponding value for the L_3 phase and takes value in the interval from 0.1 to 1 mN m^{-1} (Fig. 17 *b*).[161]

For instance, fluorinated surfactants characterised by stronger lateral hydrophobic and dipole-dipole interactions between fluoroalkyl chains have higher interfacial tension and form the lamellar phase at lower concentrations compared to non-fluoriinated hydrocarbon surfactants.[39, 72, 158, 162] The formation of hydrogen bonds between hydrophilic groups of polyglycol ethers [114, 163–165] also causes strengthening of lateral interaction between hydrophilic groups, which favours the formation of the lamellar phase of surfactant molecules.

b. The emulsifying ability of phospholipids

Amphiphilic phospholipid molecules containing two alkyl chains can form bilayer lipid membranes and liposomes. When in aqueous solutions, they can be involved in the formation of the L_α or L_β lamellar phases. Flexible membranes of the L_α type with liquid-crystalline ('molten') hydrocarbon core are formed above the critical temperature T_c [*e.g.*, 58 °C for distearylphosphatidylcholine (DSPC)].[46] Near this temperature, DSPC monolayers with relatively low bending modulus of the order of $1\,kT$ are formed. At temperatures below T_c, L_β-type membranes with crystalline ('frozen') hydrocarbon core are formed. The bending modulus of corresponding monolayers increase to $\sim 10\,kT$ and more. As a result, emulsions stabilised with phospholipids in this temperature range [7, 166] are much more stable near the PIT compared to the emulsions stabilised with short-chain surfactants because the formation of 'holes' in the emulsion films having the structure of rigid bilayer lipid membranes requires a large energy expenditure [see Eqn (31)]. This property of phospholipids is used for preparation of multiple emulsions [57, 153] characterised by relatively high rupture stability of both types of liquid films (Fig. 17 *a*).

The spontaneous curvature of monolayers is almost zero and therefore rather sensitive to changes in the physicochemical parameters, such as the molecular structure of phospholipids, the type of the oil phase, temperature and the water/oil

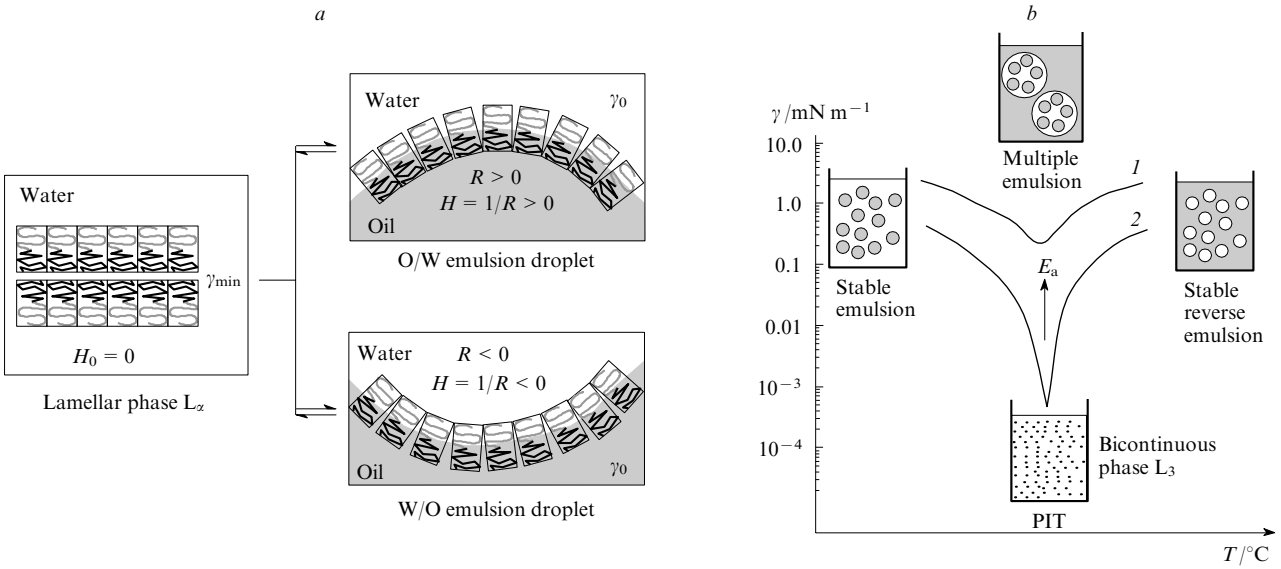


Figure 17. Schematic illustration of the effect of lateral interaction between surfactant molecules in monolayers on emulsion stability (*a*) and semiquantitative temperature dependences of interfacial tension in the surfactant monolayers (*b*).
Long-chain surfactants (*1*) and short-chain surfactants (*2*).

ratio (by volume) in the ternary system. Changes in these parameters are followed by noticeable (positive or negative) deviation of the spontaneous curvature from zero and, correspondingly, by changes in the emulsifying ability of phospholipids. For instance, a Winsor 3 system, in which the L_β lamellar phase is in equilibrium with almost pure water and octane, is formed in the water – octane – DSPC ternary system at room temperature and at moderate concentrations of DSPC. In this case the local curvature of the DSPC monolayers at the water/octane interface is almost zero and the O/W and W/O emulsions (or multiple emulsions) formed in the system are of moderate stability. However, at temperatures above 58 °C DSPC becomes a good emulsifier of octane-in-water reverse emulsions because of transition to the Winsor $\overline{2}$ system (the L_α lamellar phase is in equilibrium with water and with the surfactant solution in octane), in which the DSPC monolayers have a negative spontaneous curvature. A similar result (formation of the Winsor $\overline{2}$ system and the ability to stabilise the reverse emulsions) can be attained upon replacement of DSPC by dioleylphosphatidylcholine (DOPC), which forms the L_α-type bilayer lipid membranes (phase transition temperature of DOPC with unsaturated oleic fatty-acid residues is −22 °C).

Taking into account the interrelation between the emulsion stability and the curvature of phospholipid monolayers, one can predict how these physicochemical factors influence the emulsifying ability of phospholipids. For instance, the well-known enhancement of stability of reverse emulsions upon replacement of phosphatidylcholines by phosphatidylethanolamines [167] can be explained by an increase in the negative curvature of phospholipid monolayers upon replacement of bulky choline group $[-CH_2-CH_2-N^+(CH_3)_3]$ by a more compact ethylamine group $(-CH_2-CH_2-N^+H_3)$.[97] The experimentally observed enhancement of stability of reverse emulsions with a decrease in the carbon number (molecular chain length) of the oil [167] can be a result of better 'impregnation' of the hydrocarbon fragments of the phospholipid monolayer with the oil molecules having a lower molecular mass; this leads to greater 'swelling' of the hydrophobic fragment of the monolayer and to a greater negative curvature. The observed [7] abrupt decrease in the stability of DOPC-stabilised water-in-octane reverse emulsions upon replacement of n-octane by n-fluoroalkane can be explained by the oleophobic character of the fluorinated oil. n-C_8F_{18} molecules are no longer soluble in the hydrocarbon region of the DOPC monolayer, which leads to an increase in the monolayer curvature (in this case, to a change in the curvature from a negative value to zero).

5. Stabilisation of emulsions with liquid-crystalline phases and nanoparticles

An increase in the surfactant concentration in the bulk of the disperse medium is accompanied by phase transformations and formation of lyotropic mesophases (Fig. 18). Highly concentrated emulsions prepared by emulsification of the oil or aqueous phases in the disperse medium exhibit the properties of gels and are widely used in cosmetology for preparation of sprays, lotions, creams and foams.[14, 16, 152, 168–174] Such emulsions are also used in production of solid foams.[22, 26]

a. Lamellar emulsions

In the vicinity of the PIT an increase in the concentration of the long-chain surfactant (*e.g.*, phospholipids) causes the formation of the L_α (or L_β) lamellar phase. If the surfactant concentration is sufficiently high to form lamellar polylayers on the surface of droplets (Fig. 19), the corresponding type of

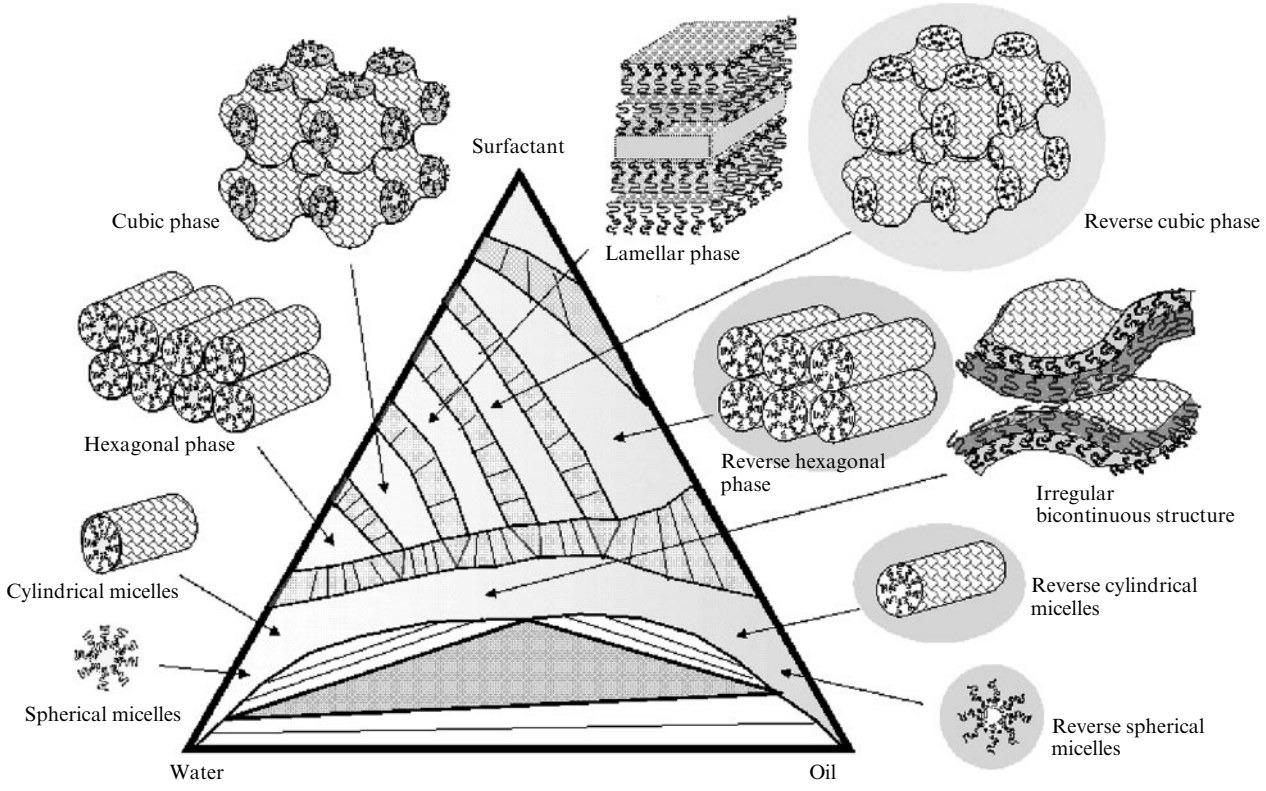


Figure 18. Schematic view of possible microemulsion structures on the constitutive diagram of a hypothetical surfactant – water – oil ternary system.

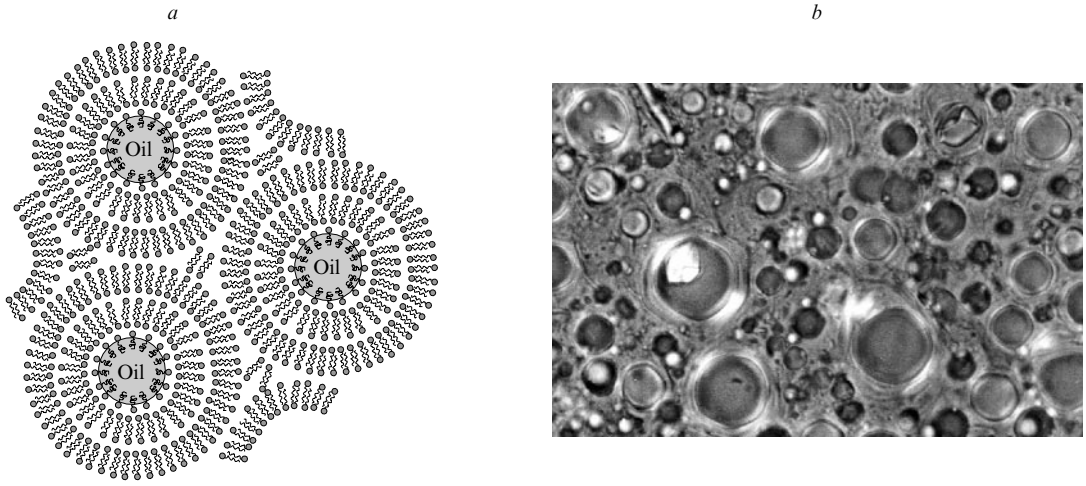


Figure 19. Lamellar emulsion: a sketch of the structure (*a*) and a photograph (*b*).

emulsions becomes considerably more stable.[169, 175] This is confirmed by an increase in the activation energy for 'hole' formation in the polylayer; the E_a value can be as high as $10^3\,kT$ and more. Such lamellar emulsions are prepared based on both phospholipids and polyglycol alkyl ethers having relatively long chains, *e.g.*, $C_{12}E_4$ (0.1 M NaCl – decane),[38] $C_{12}E_5$ (water – decane),[176] $C_{12}E_6$ (oleyl alcohol – n-hexadecane),[177] *etc.*[178]

b. Emulsions stabilised with cubic phase

Changes in the chemical composition of the surfactant – water – oil ternary system and in the temperature and other physicochemical parameters can be followed by the formation of other types of lyotropic mesophases, *e.g.*, hexagonal or cubic ones (see Fig. 18).

The cubic phase (Fig. 20) exhibits high viscoelastic properties (shear modulus is $\sim 10^5$ Pa and more).[147] This phase is formed from, for instance, the L_2 micellar phase upon increase in the surfactant concentration. The surfactant monolayers are organised in such a manner that aqueous nanotubes form two interpenetrating (but not intercrossing) structures with respective group symmetries *Ia*3*d* and *Pn*3*m* (see Fig. 20 *c*). Three nanotubes meet together in the lattice sites of the former structure that is basic to the cubic phase. Four nanotubes meet together in the lattice sites of the latter structure, which is only formed if the aqueous phase is present in excess. The specific internal surface area of the cubic phase is about 500 $m^2\,g^{-1}$.

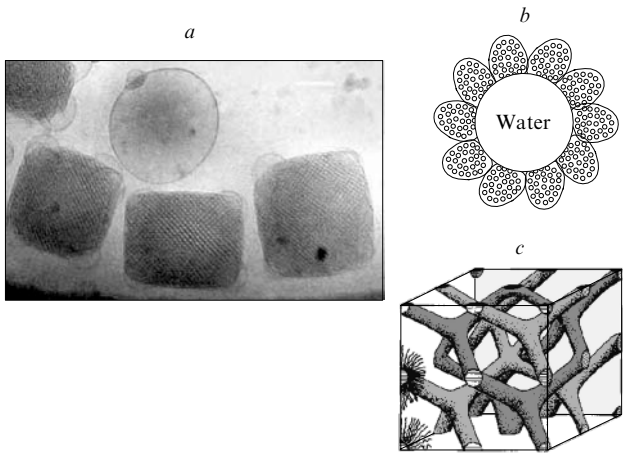


Figure 20. Micrograph of cubic-phase nanoparticles (*a*) that can stabilise emulsion droplets (*b*) and the structure of this phase (schematically) (*c*).

Both types of HCEs [147] stabilised with nanoparticles of the cubic phase (see Fig. 20 *b*) are of the greatest interest from the standpoint of practical application in, *e.g.*, cosmetology and medicine. The nanoparticles as well as droplets of nanoparticle-stabilised emulsions can contain encapsulated water-soluble pharmaceuticals,[146, 147, 179] which enables prolonged release by slow diffusion. Such emulsions form a layered three-dimensional porous structure, which protects human skin from being damaged with harmful aerosols (tobacco smoke, burnt gases, *etc.*).

c. Pickering emulsions

Stabilisation of emulsions with microparticles was discovered by Pickering [180] more than a hundred years ago. In the last decade this effect has attracted considerable attention of researchers in connection with the possibility of preparation of novel microporous materials with interesting functional properties.[181 – 184] Latexes,[185] aerosil (silica),[183] clay particles,[186] pH-sensitive microgel particles,[182] *etc.* are used as colloid particles. Stabilisation of Pickering emulsions does not require surfactants, which appreciably shortens the duration of biological tests and certification of corresponding formulations.

Pickering HCEs stabilised with polymer nanoparticles. Figure 21 presents a scheme of preparation of a Pickering O/W emulsion with the oil/water ratio $\varphi_0 = V_o : V_w = 1$, which is stabilised with nanoparticles of average size $R_p \approx 100$ nm prepared from a biocompatible polymer Eudragit RS (polymer/water ratio $\varphi_p = V_p : V_w = 0.05$). Owing to high energy of adhesion to the water/heptane interface almost all nanoparticles are contained in the interface and the average radius (R_d) of droplets formed is determined from the condition for the formation of interfacial monolayer comprised of these nanoparticles

$$R_d = \frac{kR_p\varphi_0}{\varphi_p},$$

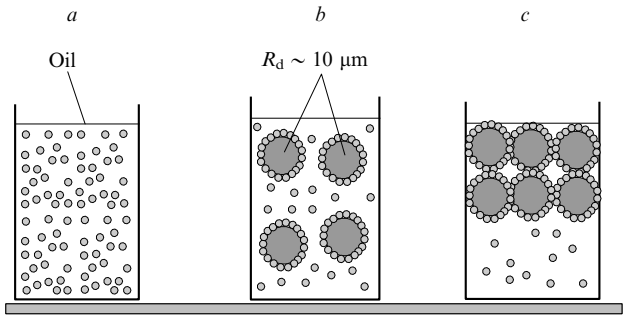


Figure 21. Scheme of preparation of a Pickering HCE stabilised by biocompatible polymer nanocapsules.
Colloid particles, $R_d = 0.1$ μm (*a*); oil droplets (*b*) and HCE (*c*).

where $k = 1-3$ is the packing parameter of the particles in the monolayer. After emulsification, oil droplets surface and form O/W highly concentrated emulsions.

A photograph of a concentrated emulsion and micrographs of HCE droplets are presented in Fig. 22. The high stability of Pickering emulsions is substantiated by the existence of a polyhedral structure in the HCE, which is characteristic of dry foams (Fig. 22 *c*). Evaporation of heptane from and subsequent drying of this HCE results in a macroporous

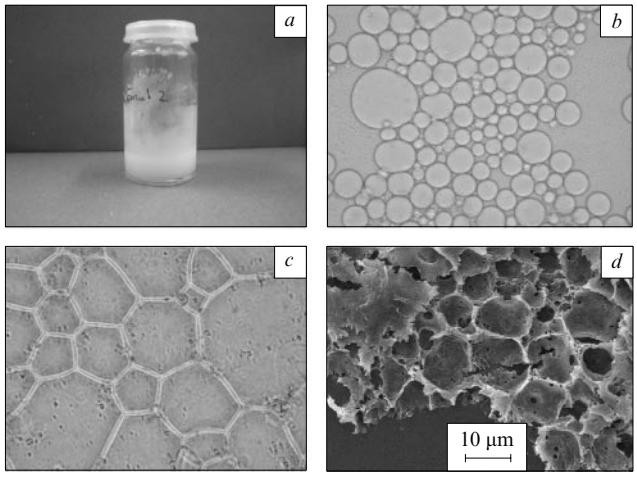


Figure 22. A photograph of concentrated emulsion (*a*) and micrographs (*b*–*d*) of highly concentrated emulsions stabilised by Eudragit RS nanoparticles (with permission of M-J Stébé).

structure in which the surface of cells is formed by nanoparticles (Fig. 22 *d*) (a detailed report of this study is prepared for publication).

Mechanism of stabilisation of emulsion films with nanoparticles. The ideas of the mechanism of emulsifying action of low-molecular-mass surfactant (see above) can also be applied to describe the stability of Pickering emulsions (Fig. 23). In this case, by analogy with the HLB of particles of radius R_p, one can introduce the ratio of the surface areas of the particles wetted by water and oil, namely,

$$\mathrm{HLB} = \frac{A_w}{A_o} = \frac{1+\cos\theta}{1-\cos\theta}, \tag{38}$$

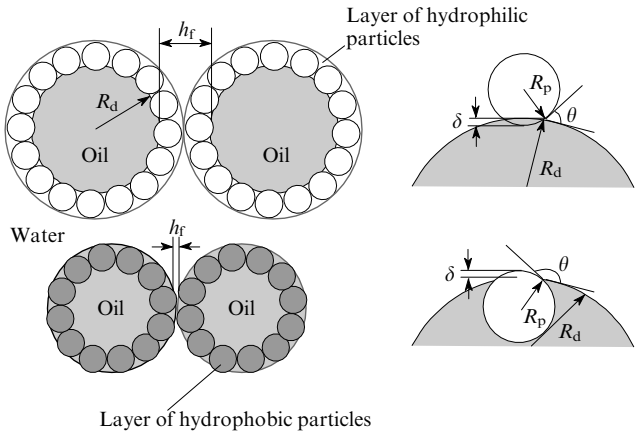


Figure 23. Scheme illustrating the principle of stabilisation of Pickering emulsions.

where θ is the contact angle (or wetting angle). The contact angle θ with the oil/water interface is acute for hydrophilic particles (they are better wetted with water than oil) and obtuse for hydrophobic particles. In the case of balanced wetting ($\theta = \pi/2$) the HLB is equal to unity, being greater than unity for hydrophilic particles ($\theta < \pi/2$) and lesser than unity for hydrophobic particles ($\theta > \pi/2$). These relationships are similar to those for hydrophilic and hydrophobic surfactants used for stabilisation of 'classical' emulsions.

This analogy can be extended by demonstrating the applicability of Bancroft's rule to the Pickering emulsions. According to this rule, 'hydrophilic surfactants stabilise O/W emulsions while hydrophobic surfactants stabilise reverse emulsions'. Indeed, in the case of emulsification of an oil in aqueous dispersion of hydrophilic particles a monolayer of hydrophilic particles on the surface of oil droplets of radius $R_d \gg R_p$ in water will be immersed in oil at a depth of

$$\delta \approx R_p(1-\cos\theta).$$

The thickness h_f of the water film stabilised with these particles approximately equals $4R_p$. Formal application of the 'hole' mechanism of rupture of liquid films to the Pickering films using Eqn (29) for particles of radius $R_p \approx 10-100$ nm taking account of the fact that the interfacial tension at the water/oil interface in the absence of surfactant is ~ 50 mN m^{-1} gives the following estimate of the activation energy for rupture of Pickering films:

$$E_a \approx \frac{1}{8}\pi^3 h_f^2 \gamma_0 \approx \left(1-10^2\right) \times 10^5 kT. \tag{39}$$

The high E_a value points to high stability of Pickering emulsions.

At the same time if O/W emulsions are stabilised with highly hydrophobic particles ($\theta \simeq 2\pi$), the thickness of the water film is

$$h_f \approx 2\delta \approx 2R_p(1+\cos\theta) \approx R_p \sin^2\psi,$$

where $\psi = 2\pi - \theta$.

The expression for the activation energy for rupture of this film with $R_p \approx 10-100$ nm and $\gamma_0 \approx 50$ mN m^{-1} has the form

$$E_a \approx \frac{1}{8}\pi^3 h_f^2 \gamma_0 \approx \frac{1}{2}(1 - 10^2) \times 10^4 \sin^2\psi \times kT. \quad (40)$$

For the contact angles $\theta \approx 1^\circ$ and $R_p \approx 10$ nm one gets $E_a \approx 1\,kT$, which corresponds to unstable emulsions. As the size of the solid particles increases, the activation energy also increases (analogy with the effect of stability enhancement of 'classical' emulsions with an increase in the size of surfactant molecules).

The reverse of the aforesaid is valid for emulsification of the aqueous phase in oil. Consider emulsification of water and oil taken in nearly 1 : 1 ratio (by volume). Hydrophilic particles adsorbed at the water/oil interface will tend to curve the interfacial layer in the positive direction (make it convex towards the aqueous phase). This corresponds to preferred formation of oil droplets in continuous aqueous medium. At the same time hydrophobic particles will tend to make the curvature of the interfacial layer negative, which favours the formation of reverse emulsions. This is a manifestation of yet another analogy between the Pickering emulsions and 'classical' emulsions. However, one should keep in mind that moderately hydrophobic particles, for which the contact angle is not too small, can stabilise O/W emulsions, just as the moderately hydrophilic particles can stabilise reverse (W/O) emulsions. This follows from Eqn (40). The activation energy for rupture of a water film stabilised with hydrophobic particles can be as high as $E_a \approx 10^3\,kT$ and more; these value are impossible in the case of water films stabilised with low-molecular-mass hydrophobic surfactants.

IV. Conclusion

The mechanism of rupture of microscopic liquid films stabilised with low-molecular-mass surfactants considered above provides an explanation for peculiarities of the effect of the molecular structure and physicochemical parameters of surfactants used on the rate of HCE destruction.

Intense destruction of HCEs as the surfactant – water – oil ternary system approaches the region of balanced microemulsions (for instance, the vicinity of the PIT) can be explained by the thermal fluctuation mechanism of rupture of liquid films. Ultralow interfacial tension ($\gamma_{min} \approx 10^{-2} - 10^{-4}$ mN m^{-1}) causes the activation energy for film rupture to decrease as a result of formation of critical-size 'holes'. Both types of stable HCEs can be prepared in the temperature ranges of existence of microemulsion systems that are 5 – 10 °C lower and higher than the PIT. These HCEs are characterised by relatively high interfacial tension of the order of 1 mN m^{-1}.

Asymmetry in stability of HCEs, *e.g.*, high stability of O/W emulstions and catastrophic destruction of reverse HCEs stabilised by water-soluble surfactants at $T <$ PIT and *vice versa* (HCEs stabilised with oil-soluble surfactants at $T >$ PIT) can be explained by the difference between the line tension of different types (O/W/O and W/O/W) of liquid films in different temperature ranges. This difference follows from the dependence of interfacial tension on the mean and Gaussian surface curvatures. In deriving expressions (27) and (29) it was established that the line tension of a film of thickness h_f is expressed through the interfacial tension γ_h of the 'hole' surface

$$\tau \approx \frac{1}{2}\pi h_f \gamma_h .$$

This gives different expressions for the rupture-stable and rupture-unstable films, respectively:

$$\tau \approx \frac{1}{2}\pi h_f \gamma_0 ,$$

$$\tau \approx \frac{1}{2}\pi h_f \gamma_{min},$$

As a result, the activation energies for film rupture are different.

For stable films one gets

$$E_a \approx 4h_f^2\gamma_0 \approx (10^2 - 10^3)kT,$$

while for unstable films one gets

$$E_a = \frac{4h_f^2\gamma_{min}^2}{\gamma_0} \approx (0.1 - 1)kT.$$

The well-known higher stability of emulsions stabilised with fluorocarbon nonionic surfactants [39, 72, 158, 162] compared to systems stabilised with non-fluorinated surfactants is due to higher rigidity of the fluorinated surfactant monolayers owing to higher lateral adhesion within these layers. Similarly, attachment of hydroxyl groups capable of forming hydrogen bonds within surfactant monolayers to the hydrophilic fragments of the surfactant molecules makes the monolayers more rigid, thus enhancing the stability of emulsions.[164]

At equal HLB_D values of surfactant molecules [namely, at equal partition coefficients K_p in the aqueous and oil phases, see Eqn (3)], an increase in the volumes of the hydrophilic and hydrophobic fragments leads to thickening of the liquid film, an increase in the activation energy for rupture [see Eqn (29)] and, therefore, to higher stability of emulsions all other factors being the same.

According to our concept, the effect of physicochemical factors, *e.g.*, temperature, HLB of surfactant molecules as well as electrolytes and nonionic additives on the stability of HCEs manifests itself indirectly as the influence on the local curvature of monolayers (*i.e.*, interfacial tension). For instance, in the temperature range of stability of reverse emulsions ($T >$ PIT + 10 °C) further heating enhances emulsion stability owing to an increase in γ_0. Contrary to this in the temperature region of stability of O/W emulsions ($T <$ PIT – 10 °C) cooling favours an increase in the emulsion lifetime. Correspondingly, enhancement of stability of O/W emulsions with chain elongation in the hydrophilic chains (with an increase in the HLB of surfactant molecule) at a specified temperature is due to an increase in interfacial tension (owing to an increase in the PIT, see Fig. 5). In the last-mentioned example one should account for the effect of the increase in the capillary pressure on the thinning of the liquid film and, therefore, on the increase in the rupture probability.

The effect of the increase in the surfactant concentration on the emulsion stability is related [40] to the increase in the non-compensated osmotic pressure of surfactant micelles in the continuous phase. As this pressure increases, the surface area of microscopic emulsion films between emulsion droplets increases. According to statistical theory of film rupture,[6] this leads to a decrease in the average lifetime following the relation $t \approx a_f^{-b}$ (scaling effect), where the parameter b varies from 1 to 2. However, the increase in the surfactant concentration in the bulk of the duspersion medium is followed by the formation of liquid-crystalline phases (*e.g.*, lamellar, hexagonal and cubic ones). Thin layers of these phases between emulsion droplets are more rupture stable than liquid films of bilayer membrane type. As a result, the separation stability of emulsions considerably enhances. Emulsions are even more stable when stabilised with nanoparticles.

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