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Phase Equilibria

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I. INTRODUCTION

All liquid detergents contain at least one surfactant in the presence of other materials, such as electrolytes, oily materials, and other impurities. Unlike the academic researcher, the formulator must work with industrial-grade raw materials containing significant amounts of different molecules, the properties of which may significantly differ from those of the main material. The understanding of how a given property of a “pure” system is affected by “impurities” is accordingly of essential practical importance. Understanding the principles by which a given product behaves (as is or under use conditions) allows us to replace counterproductive trial-and-error by more efficient methods with a broader range of potential applications. Phase diagrams are very useful tools to achieve this understanding.

II. WHAT IS A PHASE DIAGRAM?

A phase diagram is a graphic representation of the phase behavior of a system under study. The behavior of a single component as a function of temperature and pressure can be represented on a phase diagram, which will show the conditions under which a material is a solid, liquid, or gas. More complex phase diagrams may involve several components. Phase diagrams are very useful tools for formulation, as they allow one to define not only the acceptable composition range of a product but also enable one to optimize the order of addition of the different raw materials.

A. Two-Component Phase Diagrams

1. Temperature and Composition

Whether a given proportion of two (liquid) ingredients will mix is defined by thermodynamics. Although in regular systems the entropy of mixing is always positive and accordingly favorable to mixing, the enthalpy of mixing can be positive or negative depending on the energy of formation of heterocontacts at the expense of homocontacts.

An exothermic mixture usually leads to mixing in all proportions. This is the case for water and ethanol. If the mixing is endothermic, the number of coexisting phases and their composition depend on temperature. Increasing the temperature usually results in an increase in the mutual solubility of the two compounds, eventually leading to complete miscibility above a critical temperature, the upper consolute temperature (UCT). Note that some abnormal systems can also have a lower consolute temperature (LCT). Both UCT and LCT are thermodynamic *critical points*. At a critical point, the compositions of the two phases in equilibrium become identical.

Figure 3.1 shows a schematic representation of a two-component phase diagram characterized by a UCT. The left axis corresponds to pure component A and the right axis to pure component B. The abscissa corresponds to different A–B compositions. It is very common to express the compositions in weight fraction. Mole fraction or volume fraction can also be used. The central, shaded area corresponds to the two-phase domain, also referred to as the *miscibility gap*. The clear zone surrounding it represents a single phase.

2. Tie Lines and Lever Rule

When a mixture separates into two phases, it is important to know the compositions and the amounts of the two phases in equilibrium. A *tie line* links the two conjugated compositions in equilibrium. This means that any composition located on the same tie line will separate in the same two phases, the compositions of which are defined by the points of contact of the tie line with the phase boundary.

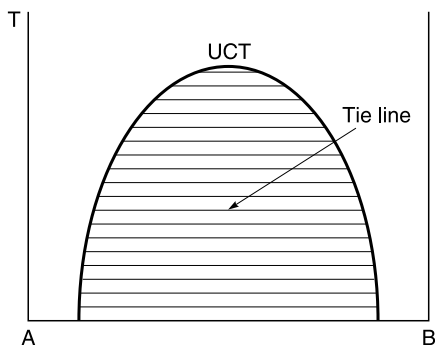


FIG. 3.1 Phase diagram of two components (A and B) that are only partly miscible at low temperature and become fully miscible above the upper consolute temperature (UCT).

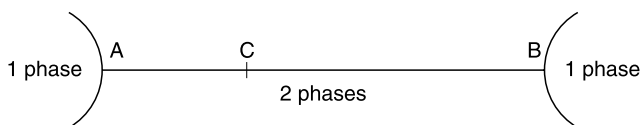


FIG. 3.2 Lever rule allowing quantification of the proportion of two coexisting phases in a two-phase domain of a phase diagram.

The relative amounts of the two phases are determined according to the lever rule (Figure 3.2). If the compositions are expressed in weight fractions, the weight fraction of phase A is CB/AB and the weight fraction of phase B is AC/AB .

B. Three-Component Phase Diagrams

Practical systems involve more than two components. A three-component system can be represented by an equilateral triangle (Figure 3.3). A corner of the triangle represents a pure component, a side represents the binary mixture of the components represented by the adjacent corners, and any point in the triangle represents one and only one three-component composition.

The weight fraction of component A in the composition represented by P in the triangle is given by the ratio of the lengths of the segments perpendicular to the sides: $P_a/(P_a + P_b + P_c)$. Similarly, the amount of B is given by $P_b/(P_a + P_b + P_c)$ and the amount of C by $P_c/(P_a + P_b + P_c)$.

Such a phase diagram is valid at one temperature. The effect of temperature on a three-component phase diagram can be visualized in three dimensions, with temperature on the elevation axis. The phase diagram looks like a triangular prism, with every horizontal slice corresponding to one temperature.

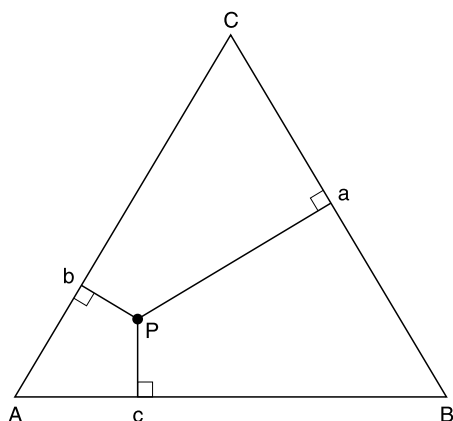


FIG. 3.3 Method of determining the composition of a three-component mixture.

1. Fields and Densities

There is an important difference among the thermodynamic functions of state as far as phase equilibria are concerned. Some thermodynamic functions of state, such as temperature and pressure, have the same value in all the phases of a system under equilibrium conditions. They are actually the “forces” driving a system to its equilibrium. Such functions are referred to as *fields* [1].

The other thermodynamic functions of state generally have different values in the different phases of a system at equilibrium. Typical examples are the phase volumes, composition, enthalpy, etc. Such functions are known as *densities*.

A thermodynamic expression of functions of state can be expressed as a sum of field variables multiplied by their conjugated density. For example

$$G = U + PV - TS + \sum \mu_i n_i$$

where U is the internal energy, PV is the product of the field variable *pressure* and the density variable *volume*, TS is the product of the field variable *temperature* and the density variable *entropy*; and $\mu_i n_i$ is the product of the field variable *chemical potential* of component i and the density variable *number of moles* of component i . The chemical potentials are the field functions conjugated with the concentrations.

2. Phase Rule

For a multicomponent system, the phase rule [2] allows us to know the number of independent variables necessary to define completely (from a compositional point of view) a system. This number is called the *number of degrees of freedom* or the

variance of the system. The variance f is given by

$$f = C - \Phi + 2$$

where C is the number of chemically independent components in the system, Φ is the number of coexisting phases at equilibrium, and the last term takes care of temperature and pressure. Note that this definition of the variance supposes that the components do not react with each other. For systems at constant pressure, such as all systems under atmospheric pressure, the last term should be 1. Similarly, systems studied at constant temperature and pressure have 0 as the last term.

A direct implication of the phase rule is that a three-component system in one phase at atmospheric pressure and at 25°C has a variance equal to 2. This means that two dimensions are necessary to describe fully such a system. Another implication is that such a system could show a maximum of three coexisting phases. Indeed, a negative variance does not have any physical meaning.

A system based on five components will need, according to the phase rule, a four-dimension hyperspace to be completely described. To represent such a system, some variables are usually grouped. The accuracy of such a representation is, of course, imperfect.

A more accurate procedure is to set a variable to a constant value. This is impossible with a composition because it is a density and is usually different in each of the coexisting phases. The phase rule determines the number of independent variables a system needs to be represented but does not introduce any restriction on the choice of the independent variables. It is accordingly much better, whenever possible, to fix a field variable to reduce a system of one dimension. Instead of using concentrations (density variables), a representation as a function of the chemical potentials is easier to read and is more accurate. The problem is that, in practice, it is very complicated to work at defined chemical potentials.

3. Tie Lines and Critical Points

Let us consider two liquids A and B that are not very soluble in each other. Addition of liquid C increases the miscibility of B in A and of A in B. The addition of C has the same effect as increasing the temperature in the binary phase diagram. The major difference is that the tie lines are no longer necessarily parallel to the baseline, and the critical end point is no longer at the maximum of the miscibility gap (Figure 3.4). This is because C does not partition evenly between the two coexisting phases. In the present case, C goes preferably into B. The critical end point is located near the A corner. An isothermal critical end point is usually referred to as a *plait point*.

4. Three-Phase Domain

In some cases a three-phase region occurs (Figure 3.5). The coexistence of three phases in equilibrium in an isothermal three-component phase diagram is

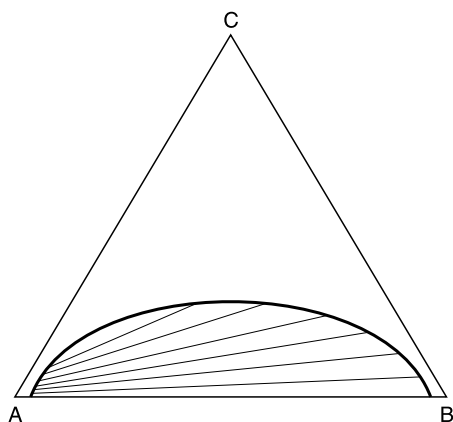


FIG. 3.4 A Winsor II ternary phase diagram.

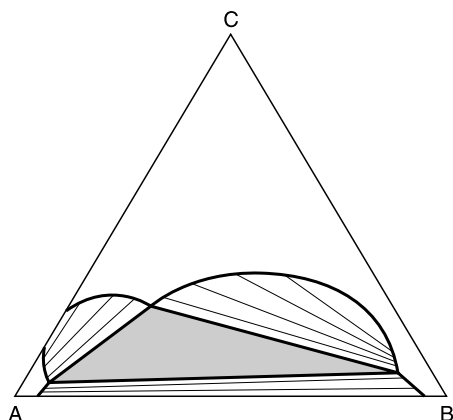


FIG. 3.5 A Winsor III ternary phase diagram.

a zero-variant situation. Of course, an infinity of different compositions fall inside the three-phase triangle, but the compositions of the three coexisting phases are the same for all the initial compositions falling in the three-phase triangle. They are represented by the three corners of the three-phase triangle. What changes are their respective amounts.

C. Recording Phase Diagrams

There are basically two methods for recording phase diagrams: the titration method and the constant composition method. Both have advantages and drawbacks.

1. Titration Method

In the titration method a mixture is titrated by another. Typically, a mixture of two of the components is titrated by the third. The weight of titrant to reach a phase boundary is carefully recorded and plotted on the phase diagram. The process is then repeated to cover the whole domain to be investigated. Such a method is relatively fast and can give a good idea of the phase boundaries.

There are two major drawbacks to this method. First, this method gives the phase diagram at one temperature only. To determine the phase diagram at another temperature, the process must be repeated. The temperature domain available with the titration method is limited for practical reasons, as all the components must be kept at the same temperature.

The second drawback is that the method is usually used in out-of-equilibrium conditions. In some systems, such as those involving lyotropic liquid crystals, the time required to reach equilibrium can be very long; metastable phases can also be encountered.

A phase diagram recorded by the titration method should be used as a guide only and should never be applied for long-term stability prediction.

2. Constant Composition Method

In the constant composition method a series of compositions covering the composition range to be studied are prepared in test tubes, which are sealed. The test tubes are shaken thoroughly and allowed to stand in a thermostatic bath. The test tubes containing turbid solutions are allowed to stand until they separate into two or more completely clear phases. The number of clear phases can be reported on the phase diagram, and the phase domains can be mapped.

This method is very time consuming, but it allows one to approach true equilibrium conditions, and the tubes can be used at other temperatures. Another advantage of this method is that, when a system gives more than one phase, it is possible to analyze the phases and accordingly know exactly where the phase boundaries are, as well as the orientation of the tie lines.

III. PHASE DIAGRAMS FOR IONIC SURFACTANT-CONTAINING SYSTEMS

A. Ionic Surfactant and Water

1. Krafft Point

The Krafft point can be defined as the temperature T_k above which the amphiphile (surfactant) solubility in water greatly increases [3]. The reason is that the water solubility of the amphiphile, which increases with temperature, reaches the amphiphile critical micelle concentration (C_M in [Figure 3.6](#)). When the solubility curve is above C_M the dissolved amphiphile forms micelles and the amphiphile

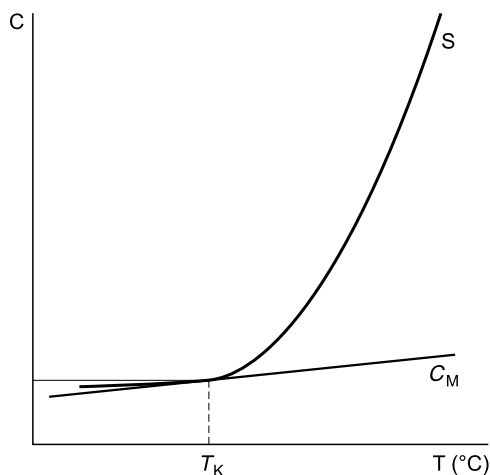


FIG. 3.6 The Krafft point is the temperature at which the solubility of the amphiphile becomes higher than its critical micelle concentration (C_M).

activity in water solution no longer increases. There is accordingly no longer a limitation to solubilization.

The Krafft point is a triple point because at this temperature three “phases” coexist [4]: hydrated solid amphiphile, individual amphiphile molecules in solution (unimers), and amphiphile molecules involved in micelles.

The value of T_K increases as the amphiphile hydrophobic chain length increases. The Krafft points of the sodium salts of the classic amphiphiles (alkyl sulfates, sulfonates, and benzenesulfonates) are usually below room temperature. The Krafft point is a function of the counter-ion. Alkaline earth cations give higher Krafft points: for sodium laurylsulfate, $T_K = 9^\circ\text{C}$; the values for the calcium, strontium, and barium salts are 50, 64, and 105°C , respectively.

Because the Krafft point imposes a limitation in formulation, the following rules to reduce T_K are of interest:

- Chain branching and polydispersity reduce T_K .
- Complexation of Mg and Ca reduces T_K .
- The presence of unsaturation decreases T_K .

A very efficient way to reduce T_K is to incorporate two or three oxyethylene monomers between the amphiphile hydrophobic chain and the polar head group (alcohol ethoxy sulfates). In each case other properties of the amphiphile, such as the surface activity, can be consequently modified.

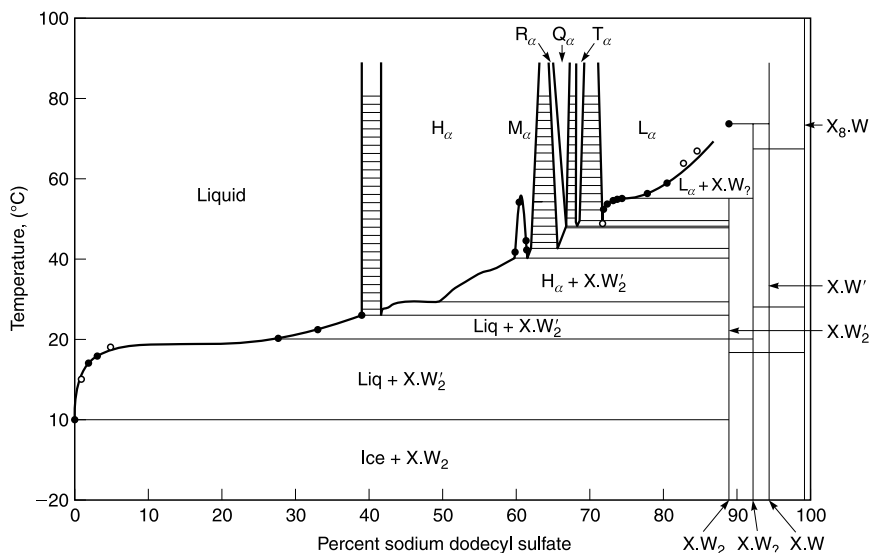


FIG. 3.7 Typical phase diagram of a water–anionic surfactant system.

2. Phase Diagram

The phase diagram of sodium dodecyl sulfate–water is representative of many ionic systems (Figure 3.7) [5]. In Figure 3.7 “Liquid” is the aqueous micellar phase; H_α is the hexagonal lyotropic liquid crystal, sometimes called the middle phase; and L_α is the lamellar lyotropic liquid crystal, sometimes called the neat phase. On the surfactant-rich side, several hydrated solid phases are present.

As a general rule, in any (real) phase diagram, at any point representative of a region and on its boundaries, the number of phases and their nature are similar.

A tie line is the line joining the points representing two coexisting phases. If the total composition of a mixture falls in a two-phase region, it separates into the two phases located at both sides of the tie line that passes the formulation point. The weight distribution of the two phases is given by the lever rule.

B. Ionic Surfactant, Water, and Organic Material Ternary Systems

1. Organic Material: Hydrocarbon

Let us consider an isotherm of a water–ionic amphiphile binary mixture above the Krafft point (for example, water–sodium octanoate) [6]. At an amphiphile concentration of 7% (the critical micellar concentration), the micellar isotropic solution L_1 appears and lasts up to 41%. Between 41 and 46% is the miscibility

gap between L1 and H1, the hexagonal phase, which lasts up to 52%. Above 52% is the miscibility gap between H1 and the hydrated crystal.

If a nonpolar component (aliphatic hydrocarbon or tetrachloromethane) is added, almost nothing happens (Figure 3.8a). The solubility of octane in either the micellar solution or the liquid crystal is very limited. This is true of any molecule exhibiting only dispersion cohesive forces (induced dipole–induced dipole van der Waals forces).

2. Organic Material: Polar but Not Proton Donating

The solubility of a molecule exhibiting dipole–dipole cohesive forces and low H-bonding cohesive forces, such as methyl octanoate, is greater than that of a hydrocarbon, but nothing particular happens in the center of the phase diagram.

3. Organic Material: Proton Donating

If the third component is a water-insoluble alcohol (five carbons or more), amine, carboxylic acid, or amide, the phase topography is profoundly modified. The phase diagram shown in Figure 3.8b [7] shows in addition to L1 and H1 a very large lamellar phase, a narrow reverse hexagonal phase H2, and, even more important, a “sector-like” area of reverse micelles L2. This means that the solubility of *n*-decanol in a sodium octanoate–water mixture containing between 25 and 62% amphiphile is far more important (30 to 36%) than pure water (4%) and pure sodium octanoate (almost zero). This phase is essential to obtain water-in-oil (w/o) microemulsions.

The solubility of *n*-decanol in the L1 phase is also important (up to 12% at the “end” of the L1 phase). The L1 phase is accountable for the observation of oil-in-water (o/w) microemulsions. The L_{α} domain, generally located in the middle of the diagram, points toward the water side for a critical surfactant-to-cosurfactant ratio. (A 1:2 sodium octanoate to *n*-decanol ratio leads to a lamellar phase with as little as 17% surfactant–cosurfactant mixture.) In some cases, such as for octyl trimethylammonium bromide (OTAB)–hexanol–water, the lamellar phase already exists for 3% hexanol + 3% OTAB!

The practical interest of a lamellar liquid crystal lies in its suspending capability. A lyotropic liquid crystal exhibits a viscoelastic behavior that allows suspension of solid particles for a very long time. The lamellar phase is additionally characterized by an ideal critical strain to provide the suspension with good resistance to vibrations and convections, without impairing its flowability with too great a viscosity.

C. Ionic Surfactant, Water, Proton-Donating Material, and Hydrocarbon Quaternary Systems

The “solubility” of an oil such as decane in the micellar isotropic solution L1 or in the reverse micellar isotropic solution L2 can be very important. L1 leads to w/o

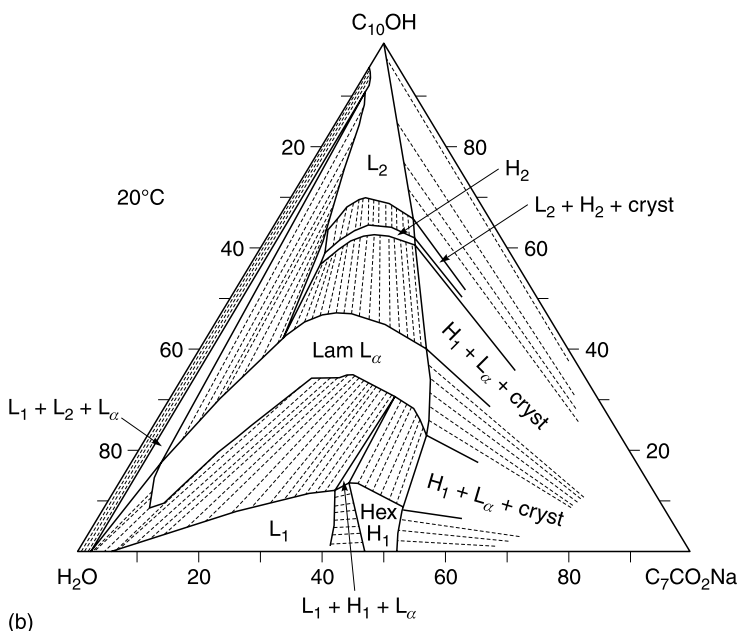
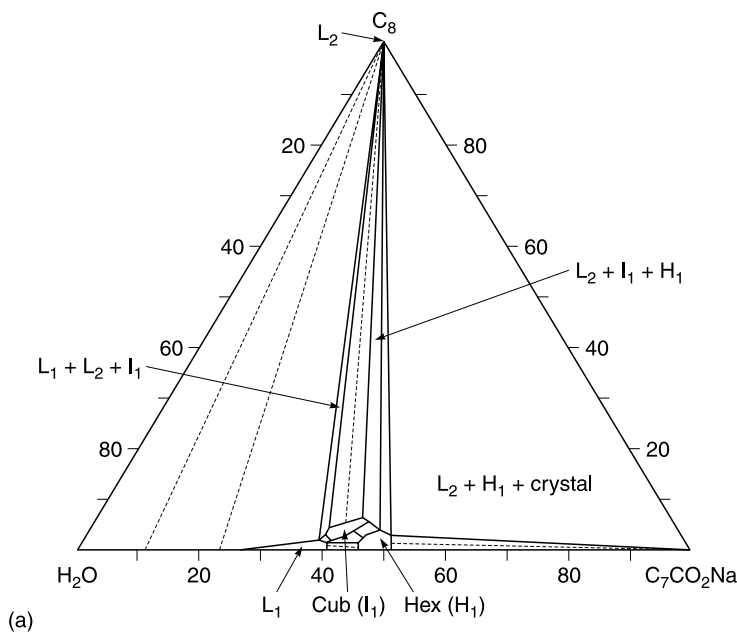


FIG. 3.8 (a) Typical ternary phase diagram of water, an amphiphile (sodium octanoate), and a hydrocarbon (octane). (b) Typical ternary phase diagram of water, an amphiphile (sodium octanoate), and a co-amphiphile (decanol). This phase diagram was established by Ekwall in 1975.

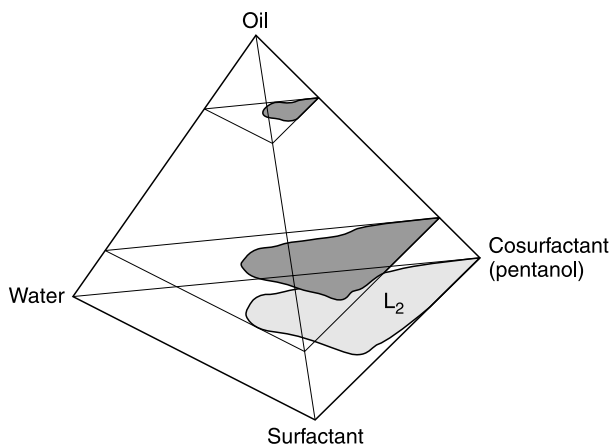


FIG. 3.9 Phase diagram of a water-in-oil microemulsion.

microemulsions and L2 to o/w microemulsions. Note that the cosurfactant is an amphiphile with (generally) a lower molecular weight than the main amphiphile, the surfactant.

1. Water-in-Oil Systems

As shown in Figure 3.9, the L2 phase is able to solubilize a very large amount of a hydrocarbon such as decane or hexadecane. In fact, a composition containing up to 75% decane and water/surfactant/cosurfactant proportions corresponding to the L2 phase is still clear, fluid and isotropic, forms spontaneously, and is thermodynamically stable. The structure of this microemulsion can be (to some extent) regarded as a dispersion of tiny water droplets (reverse micelles) in a continuous phase of the hydrocarbon. The surfactant and cosurfactant are mainly located at the water/oil interface. This type of system is often referred to as a w/o microemulsion.

The term “microemulsion” to describe such systems is not well chosen: it conveys the idea of an actual emulsion characterized by submicrometer (below 0.1 μm) droplets. As is well known, an emulsion is not thermodynamically stable and cannot be represented by a single-phase domain in a thermodynamic phase diagram. The so-called microemulsions must be considered as real micellar solutions containing oil in addition to water and surfactants. These solutions, although very far from ideal in the thermodynamic sense, are nevertheless always real in the thermodynamic sense. Another important difference between microemulsions and emulsions is that, in general, a microemulsion requires significantly more surfactant than an emulsion.

These w/o microemulsions exhibit other important characteristics:

- The domain of existence is large. Significant compositional changes can occur without crossing a phase boundary. Such behavior is particularly important for manufacturing processes, because it provides robustness to the formulation.
- They are very stable in a large temperature range, usually from the Krafft point up to the boiling point. Moreover, the phase boundaries are almost insensitive to temperature.
- The phase topography remains almost unchanged even if up to 75% of the ionic amphiphile is replaced by a nonionic amphiphile.

To obtain a wide w/o microemulsion phase it is essential to adjust carefully the cosurfactant structure (usually its chain length) and its relative amount. Although trial and error is still the most commonly used method for obtaining microemulsions, a tentative rule is to combine a very hydrophobic cosurfactant (*n*-decanol) with a very hydrophilic ionic surfactant (alcohol sulfate) and a less hydrophobic cosurfactant (hexanol) with a less hydrophilic ionic surfactant (OTAB). For very hydrophobic ionic surfactants, such as dialkyl dimethylammonium chloride, a water-soluble cosurfactant, such as butanol or isopropanol, is adequate (this rule derives at least partially from the fact that an important feature of the cosurfactant consists of readjusting the surfactant packing at the solvent/oil interface).

2. Oil-in-Water Systems

It was stated earlier that the solubility of decane in the L1 phase is almost zero. For a well-defined surfactant-to-cosurfactant ratio, very large quantities of decane (or any hydrocarbon) can be solubilized in the L1 phase. A thin, snake-like single-phase domain develops toward the oil vertex of the phase diagram (Figure 3.10). This phase can be regarded as amphiphile micelles swollen with oil.

Generally, the o/w microemulsion phases are only metastable systems. As with any metastable system, o/w microemulsions need an activation energy to separate; sometimes this activation energy is so large that the separation almost never occurs. Such systems are not thermodynamically stable and should accordingly not be considered in a phase diagram. However, they form spontaneously and are stable (because of the high activation energy for separation) for a very long time.

A typical example of a very stable metastable system is a mixture of one volume of oxygen with two volumes of hydrogen. The mixture is spontaneous and stable for a very long time, without being thermodynamically stable. The final thermodynamically stable state is obtained by adding a catalyst (platinum foam) or a flame to the mixture.

Although not thermodynamically stable, o/w microemulsions form spontaneously and are accordingly useful (ease of manufacture).

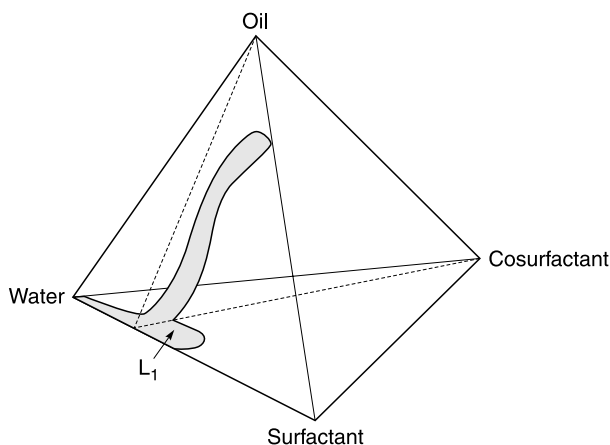


FIG. 3.10 Phase diagram of an oil-in-water microemulsion.

Thermodynamic instability implies some constraints on o/w microemulsions:

- Their position may depend on the order of addition of the raw materials and on the shear imposed on the system.
- Their domain of existence is generally narrow.
- They can be sensitive to freeze and thaw cycles.

IV. PHASE DIAGRAMS FOR NONIONIC SURFACTANT-CONTAINING SYSTEMS

The phase topography of a ternary system involving water, a hydrocarbon, and a polyethoxylated fatty alcohol depends on the hydrocarbon chain length, branching, degree of unsaturation, aromaticity, etc., on the amphiphile structure (hydrophobic and hydrophilic chain length), and also on temperature, which exerts a very strong influence on the configuration (and accordingly on the solubility) of the polyoxyethylene segments in water solution. A review has been presented in a series of papers [8–11].

The phase topography is strongly influenced by the more elementary behaviors of the binary amphiphile–oil and amphiphile–water systems.

A. Nonionic Surfactant and Oil

Polyethylene oxide is not soluble in hydrocarbons such as hexane or decane. If a fatty chain is attached to a short segment of polyethylene oxide (4 to 8 ethylene oxide units), the nonionic amphiphile obtained exhibits a solubility profile in oil

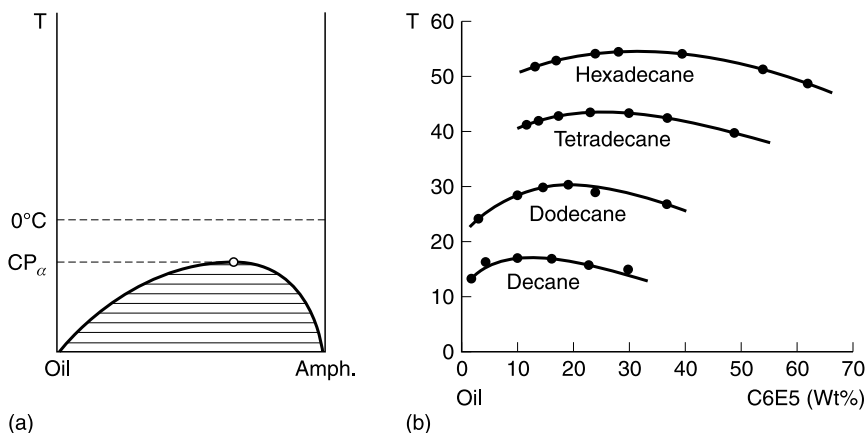


FIG. 3.11 (a) Haze point temperature (CP, critical point; amph, amphiphile). (b) Haze point temperature dependence on oil structure.

depending on temperature. At low temperatures a miscibility gap is obtained, translating to the insolubility of the polyethylene oxide chain in the oil. At high temperatures the effect of the entropy is predominant and the amphiphile is soluble in all proportions in the oil.

As predicted by the Flory–Huggins theory, such a system shows a lower miscibility gap characterized by an upper critical point, at temperature T_α , which depends on both the oil and the amphiphile structure (Figure 3.11a). The critical composition is usually not far from the pure oil side.

Figure 3.11b shows the lower miscibility gap between some *n*-alkanes and C6E5 (pentaethylene glycol monohexyl ether). The upper critical temperature T_α increases with increasing hydrocarbon chain length (hydrophobicity).

The critical temperature T_α is often referred to as the haze point temperature, and the miscibility gap between oil and amphiphile plays an essential role in the ternary phase diagram.

B. Nonionic Surfactant and Water Cloud Point

The phase diagram of a nonionic amphiphile–water binary system is more complicated (see Figure 3.12). A “classic” upper critical point exists, but it is usually located below 0°C . At higher temperatures most nonionic amphiphiles show a miscibility gap, which is actually a closed loop with an upper as well as a lower critical point. The lower critical point CP_β is often referred to as the cloud point temperature. The upper critical point often lies above the boiling temperature of the mixture (at 0.1 MPa). The position and the shape of the loop depend on

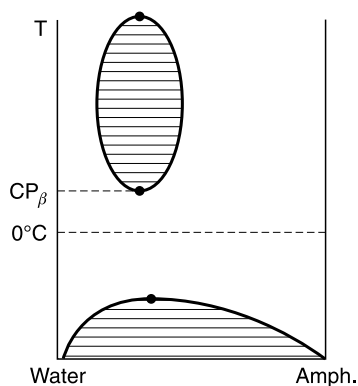


FIG. 3.12 Phase behavior of a water–nonionic amphiphile system (CP, critical point; amph, amphiphile).

the chemical structure of the amphiphile. The cloud point temperature plays an essential role in three-component phase diagram topography.

The closed loop can be regarded as a vertical section through a “nose” in the concentration–temperature–pressure space at constant pressure (see Figure 3.13a). When the pressure increases, the surface covered in the temperature–concentration phase by the phase separation loop decreases and vanishes at a critical pressure P^* .

The shrinking of the loop of the water–ethylene glycol butyl ether (C4E1) system with increasing pressure is shown in Figure 3.13b. The critical conditions for the loop to vanish are $T^* = 95^\circ\text{C}$, $P^* = 80\text{ MPa}$, and $C^* = 28\text{ wt}\%$.

To show the multidimensional nature of these phenomena, note that similar effects (shrinking of the loop, f.i.) can be achieved by the addition of “hydrotropic” electrolytes at constant pressure or by increasing the hydrophilicity of the amphiphile. Figure 3.13c shows the loop areas of butanol (C4E0), ethylene glycol butyl ether (C4E1), and diethylene glycol butyl ether (C4E2). The last does not exhibit a loop at 0.1 MPa (1 atm), but the system behaves actually as if the nose were “lurking.”

Although no phase separation occurs in water, the lurking nose exerts some influence on the three-component phase diagram. Another way to look at the same phenomenon is to consider that, in conditions close to $T = 90^\circ\text{C}$ and $C = 30\text{ wt}\%$, the C4E2–water system is such that the mixing entropy is just high enough to maintain the molecules in a single phase, the enthalpic term being positive (endothermic). As soon as a third incompatible component (the oil f.i.) is incorporated, the entropy is no longer able to maintain the molecules in a single phase, and phase separation occurs.

In Table 3.1, the hydrophilic/lipophilic balance (HLB) is calculated according to the empirical equation $\text{HLB} = 20M_{\text{H}}/M$, where M_{H} is the molar mass of the

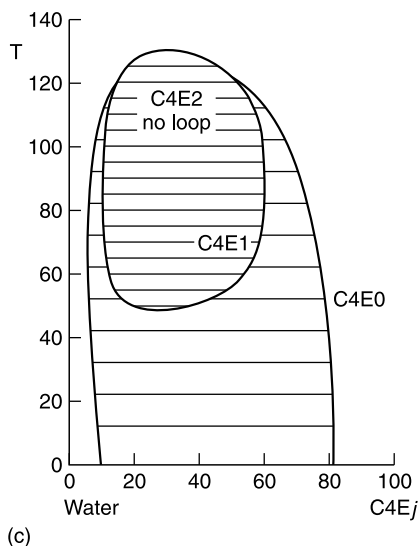
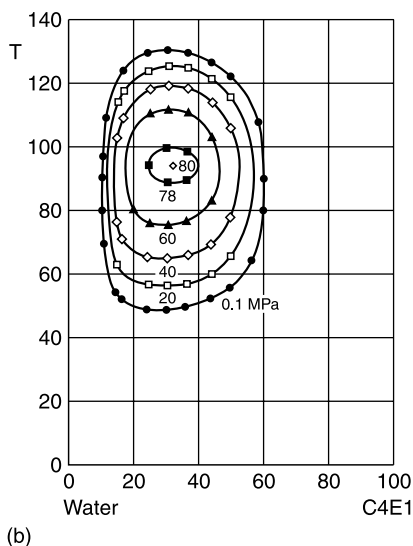
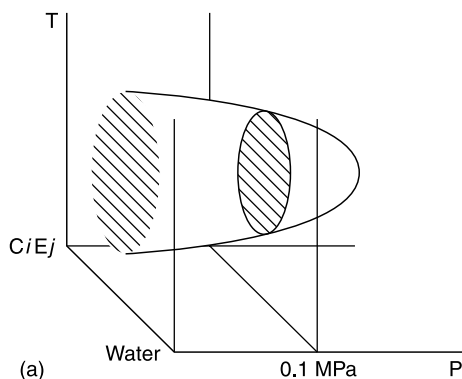
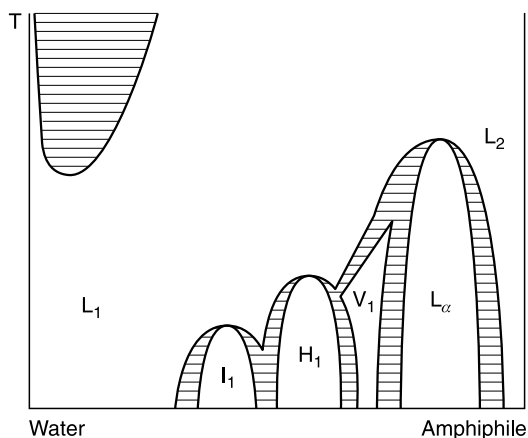


FIG. 3.13 (a) Effect of pressure on the size of the closed loop. (b) Closed loop of the water–ethylene glycol butyl ether system at different pressures. (c) Effect of the hydrophilic group of the amphiphile on the shape of the closed loop. (From Schneider, G., *J. Phys. Chem. (Munich)*, 37, 333, 1963. With permission.)

hydrophilic group and M the total molar mass of the ethoxylated amphiphile. The parameter γ_{\min} is the minimum amphiphile concentration required for the homogenization of a 1:1 (wt%) mixture of water and n -decane at around 40°C and T_{β} and C_{β} are the coordinates of the lower critical points (cloud point). Although the HLB seems to be correlated with the cloud point, it cannot give any information on

TABLE 3.1 Values of HLB, γ_{\min} , T_{β} and C_{β} for Selected Amphiphiles

Amphiphile	HLB	γ_{\min} (wt%)	T_{β} ($^{\circ}\text{C}$)	C_{β} (wt%)
C4E1	10.3	58.9	48.7	29.0
C6E3	12.7	47.4	45.4	13.5
C8E4	12.6	29.6	39.6	6.9
C10E5	12.5	19.7	40.3	3.5
C12E6	12.4	10.6	48.0	2.2

**FIG. 3.14** Binary phase diagram of a water–ethoxylated nonionic amphiphile system, including lyotropic liquid crystal domains. (From Kalhweit, M. and Strey, R., *Angew. Chem. Int. Ed. Engl.*, 24, 654, 1985. With permission.)

the amphiphile efficacy (γ_{\min}). Even if the HLB remains constant, increasing both the polar and the nonpolar parts of a surfactant molecule significantly improves its efficacy (at least its water–oil coupling efficacy).

The closed loop is not the only characteristic of the nonionic surfactant–water binary phase diagram. Like the ionic surfactant–water mixture, nonionic surfactants, at higher concentration in water, exhibit lyotropic mesophases. Figure 3.14 shows a typical binary phase diagram exhibiting the full lyotropic mesophase sequence: I1, cubic isotropic phase; H1, direct hexagonal phase (middle phase); V1, special cubic (“viscous” phase); L_{α} , lamellar phase (neat phase). Note the presence of the two-phase domains surrounding each mesophase, the critical point on top of each, and the zero-variant three-phase feature.

Although very difficult to determine with accuracy, the miscibility gaps always exist, as well as the three-phase situations. Of course, the critical temperatures and

concentrations corresponding to each mesophase depend on the chemical nature of the amphiphile, the pressure, and the optional presence of an electrolyte.

Figure 3.15 shows some examples of real nonionic amphiphile–water binary phase diagrams [10,12]. As a rule, amphiphiles with a hydrocarbon chain length of eight or fewer carbon atoms exhibit only the loop (in a domain depending on the ethoxylation) and no mesophase.

Longer chain amphiphiles show one or more mesophases (usually one). The type of the main mesophase (the one having the highest critical temperature) depends on the relative volumes of the ethoxylate and hydrocarbon chains. If the volumes are similar, the lamellar phase is predominant. This is the case for C12E6. If the volume of the ethoxylate chain is significantly higher than that of the hydrocarbon chain, the hexagonal phase will melt at higher temperature (C12E7); if the volume of the ethoxylate chain is much higher than that of the hydrocarbon chain, the cubic phase I1 may appear.

In some cases, such as for C12E5, the lamellar phase L_α (or the H1 phase) interferes with the loop (with the cloud point curve) and induces the so-called critical phase L3. L3 is an isotropic, often bluish phase, exhibiting a zero-variant three-phase critical point at its lowest temperature of existence. The three phases present at the critical conditions are W (water with a minute amount of amphiphile), L3, and L_α . The L3 phase seems to have a beneficial action on cleaning performance, maybe because of the presence of the critical point.

C. Nonionic Surfactant, Water, and Oil

From the phase behavior of both binary mixtures (water–amphiphile and oil–amphiphile), it is now possible to account, at least qualitatively, for the three-component phase diagram as a function of temperature. The presence of a haze point on the oil–amphiphile phase diagram (critical point α) at temperature T_α shows that the surfactant is more compatible with the oil at high than at low temperature. The presence of a cloud point on the water–amphiphile phase diagram (the lower critical point β) at temperature T_β shows that (at least in the neighborhood of the temperature domain) the amphiphile is less compatible with water at high than at low temperature. As a consequence (the other parameters being kept constant), the amphiphile behavior depends on temperature.

At low temperature the amphiphile is more compatible with water than with oil. The phase diagram corresponding to this situation is shown in Figure 3.16 (a1 or a2). The tie line orientation is directly deduced from the partitioning of the amphiphile between water and oil: because under the current conditions the surfactant is more compatible with water than with oil, the majority of the amphiphile is in the water phase and only a limited amount of amphiphile is present in the oil. Accordingly, the tie lines point in the direction of the oil vertex. The phase diagrams a1 and a2 of Figure 3.16 are referred to as Winsor I (WI).

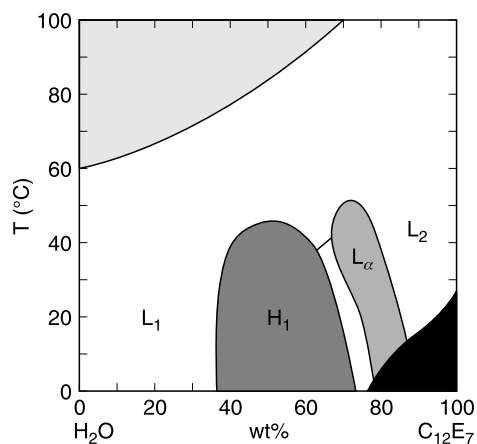
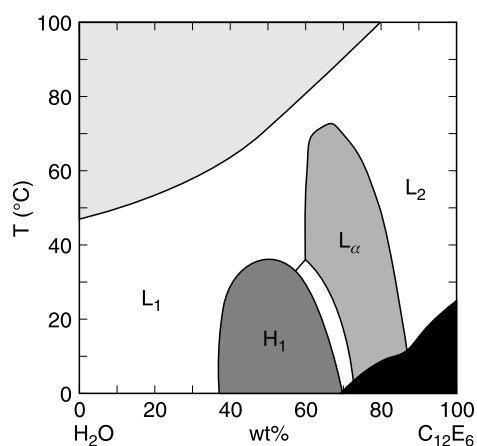
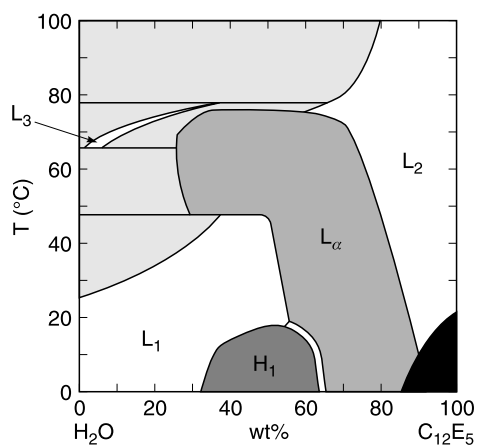


FIG. 3.15 Examples of water–ethoxylated nonionic amphiphile binary phase diagrams. (From Broze, G., *Comm. J. Com. Esp. Deterg., Barcelona*, 20, 133, 1989. With permission.)

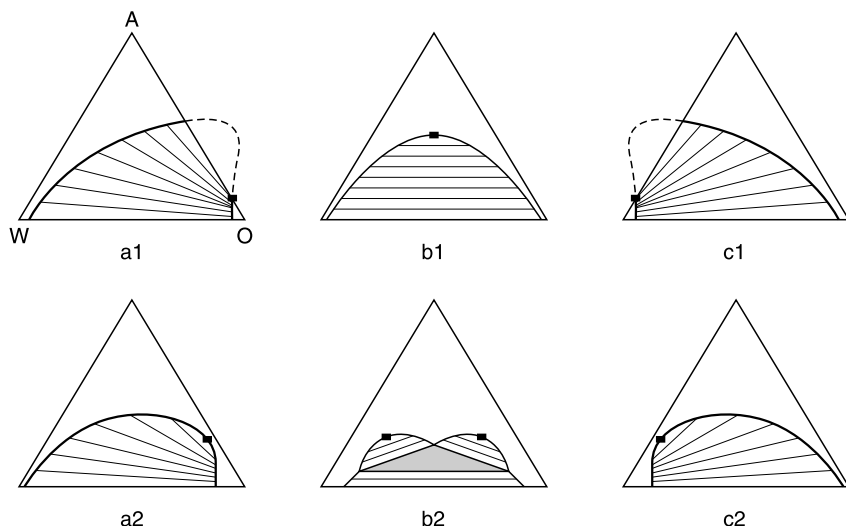


FIG. 3.16 Evolution of water–ethoxylated nonionic amphiphile–oil ternary phase diagrams with temperature (temperature increasing from a to c).

If the temperature at which the phase diagram is recorded is above T_α (the haze point), a critical point CP_α is present near the oil vertex (although pure amphiphile and pure oil are miscible, the presence of a small amount of water “recalls” the lack of compatibility between amphiphile and oil). If the temperature is below T_α , no critical point appears in the three-component phase diagram (it would be positioned at a negative water concentration).

At high temperatures these mixtures are more compatible with oil than with water. The phase diagram corresponding to this situation is shown in Figure 3.16 (c1 or c2). The amphiphile partitioning now favors the oil, and the tie lines point in the direction of the water vertex. Phase diagrams c1 and c2 of Figure 3.16 are referred to as Winsor II (WII). A critical point CP_β occurs if the temperature is below the cloud point T_β , but more often the critical point lies outside the Gibbs triangle ($T > T_\beta$).

In WI and WII representations, the critical points CP_β and CP_α are called plait points. If the difference between the temperature T at which the phase diagram is recorded and the critical point of the binary mixture, T_β or T_α , increases, the distance from the plait point to the oil–amphiphile axis for CP_β and the water–amphiphile axis for CP_α also increases. An important characteristic of a ternary system is the line that links the plait points as a function of temperature. The plait point curve is really the trace of the partitioning of the amphiphile between oil and water. The closer the plait point is to the oil, the more water soluble the amphiphile, and vice versa.

At low temperatures the amphiphile is more compatible with water because water interacts strongly with the hydrophilic head group. Accordingly, the hydrodynamic volume of the head group is greater than that of the hydrocarbon tail. At high temperatures head group hydration is reduced and so is the hydrodynamic volume, which becomes smaller than the hydrodynamic volume of the hydrocarbon tail. There is necessarily a temperature at which the hydrodynamic volumes of the two antagonistic parts of the amphiphile molecule are equal. This particular temperature, represented by \tilde{T} , is the phase inversion temperature (also called the HLB temperature). The phase inversion temperature is a characteristic (and is accordingly a function) of the nature of the oil, the amphiphile, and the water solution (if electrolytes are present). If the pressure can vary (as in oil recovery), this also changes \tilde{T} . It is important to realize that \tilde{T} can be higher than both CP_β and CP_α when the amphiphile solubility is very small in water and oil.

The topography of the phase diagram at the phase inversion temperature depends on the mutual incompatibilities among oil–amphiphile, water–amphiphile, and water–oil. Even with a polar oil and water containing a chaotropic (hydrotropic) electrolyte, the water–oil incompatibility is enough to guarantee a miscibility gap from 0 to 100°C.

For the amphiphile the situation is not as simple. At \tilde{T} the amphiphile is equally compatible with water and oil, but no assumption is made about the degree of compatibility. Two limiting cases can occur:

1. The amphiphile is very compatible with both water and oil. The phase diagram will look like diagram b1 of Figure 3.16, with a plait point only for an equal amount of oil and water and with the lines parallel to the water–oil axis (equal partitioning). This plait point corresponds to the merging of the CP_α and CP_β lines, and the projection of the plait point curves on the oil–water–temperature phase diagram should look like those shown in Figure 3.17a or Figure 3.17b.

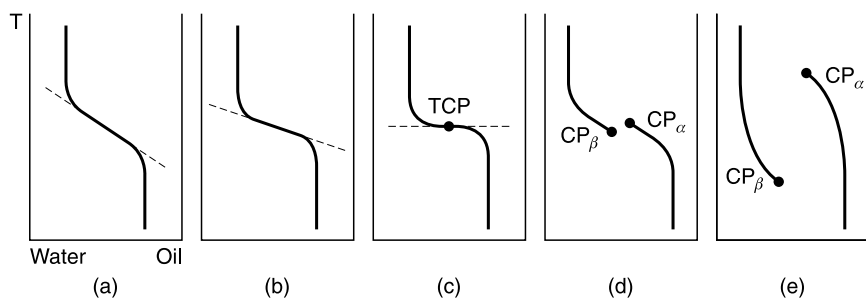


FIG. 3.17 Transition from an infracritical situation (a and b) to a supercritical situation (d and e) through a tricritical point (TCP) (c). (From Kahlweit, M. and Strey, R., *Angew. Chem. Int. Ed. Engl.*, 24, 654, 1985. With permission.)

2. The amphiphile is equally (and significantly) incompatible with both water and oil. The phase diagram will now look like diagram b2 of Figure 3.16. A three-phase triangle (3PT) appears.

Three phases are now in equilibrium:

1. A water-rich phase (W)
2. An oil-rich phase (O)
3. An amphiphile-rich phase (S)

The amphiphile-rich phase is also called the surfactant phase or the middle phase. These terms, due to Shinoda, result from the physical appearance of a three-phase system:

1. A dense, water-rich phase at the bottom
2. A light, oil-rich phase at the top
3. A phase containing most of the amphiphile in the middle

It is worth noting that with higher molar volume amphiphiles, such as C12E4, a significant amount of the amphiphile can be present in the oil phase, even at \tilde{T} . Here, too, the plait points CP_α and CP_β will be inside or not be inside the Gibbs triangle depending on the relative positions of \tilde{T} , T_α , and T_β .

If the phase diagram exhibits a 3PT it is called a Winsor III (WIII) system. In such a situation, the plait point curves do not merge but “cross” each other and stop at two terminal critical points (see Figure 3.17d or Figure 3.17e).

The sequence of the evolution of a three-component system when temperature is increased can be summarized as follows. If the amphiphile is strongly incompatible with oil and water the sequence is WI \rightarrow WIII \rightarrow WII. If the amphiphile is compatible or is weakly incompatible with oil and water the sequence is WI \rightarrow WII.

A way to modify amphiphile compatibility with oil and water is to change the amphiphile molecular mass, keeping the appropriate balance between lipophobicity and hydrophobicity. A high-molecular-weight amphiphile like C12E6 will show a WI–WII–WII sequence; a low-molecular-mass amphiphile like C4E2 will show (with decanol acetate as the oil) a WI–WII sequence. By varying the amphiphile compatibility through the molecular mass, it is possible to pass from a WI–WII to a WI–WIII–WII sequence. At a certain point a situation as shown in Figure 3.17c will occur: the plait point curves just merge critically and the 3PT collapses. This situation corresponds to a *tricritical point*, an essential concept in theoretical thermodynamics.

When the system is such that a 3PT appears (by far the most common case), the 3PT is present from a temperature T_l lower than \tilde{T} to a temperature T_u above \tilde{T} . To some extent the difference between T_l and T_u is a measure of how far the system is from the tricritical conditions. (Note that \tilde{T} is not necessarily the mathematical average of T_l and T_u , but it is close to it.)

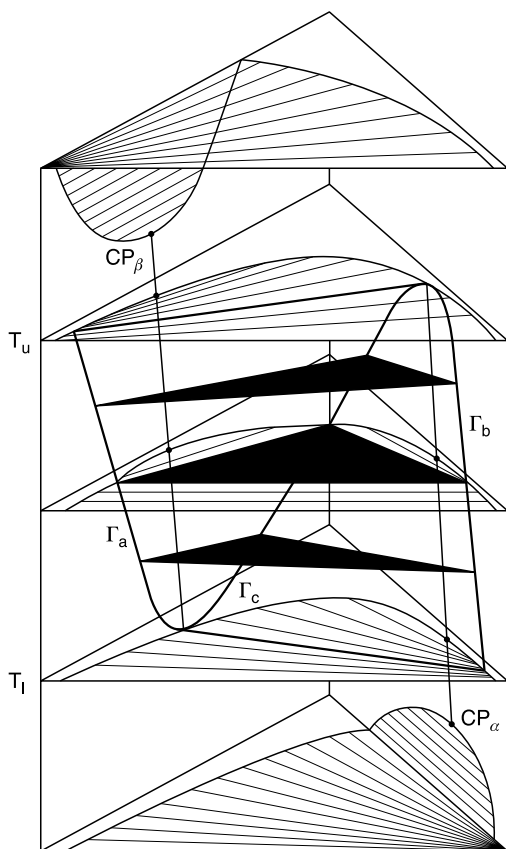


FIG. 3.18 Detailed evolution of the phase diagram of a water–oil–ethoxylated nonionic amphiphile (low molecular weight) with temperature. (From Kalhweit, M. and Strey, R., *Angew. Chem. Int. Ed. Engl.*, 24, 654, 1985. With permission.)

The thermal evolution of a typical system, with broken critical lines (see Figure 3.18), can be summarized as follows:

For $T < T_l$, the phase diagram is a typical WI.

T_l is the temperature of the critical end point of the CP_β curve. At $T = T_l$, the phase diagram is still a WI, but with a critical tie line from which the 3PT will appear with the slightest increase in temperature.

For $T_l < T < \tilde{T}$, the corner of the 3PT corresponding to the amphiphile phase remains close to the water side but moves “clockwise” in the Gibbs triangle.

For $T = \tilde{T}$, the amphiphile corner of the 3PT reaches “12 o’clock” (phase inversion temperature).

For $\tilde{T} < T < T_u$, the corner of the 3PT corresponding to the amphiphile phase keeps on “moving clockwise” to the oil phase.

T_u is the temperature of the critical end point of the CP_α curve. At $T = T_u$, the amphiphile corner of the 3PT merges with the oil corner and the 3PT collapses in a critical tie line of a WII phase topography.

At $T > T_u$, the phase diagram is a typical WII.

It is important to remark on the shape of the line joining the three corners of the 3PT triangle (Γ lines). It is a single, continuous gauche line, with a minimum at T_l on the water side of the critical tie line and a maximum at T_u on the oil side of the critical tie line. The branches can be identified (Γ_a , Γ_b , and Γ_c), each corresponding to the compositions of each corner of the 3PT. It is important to note that Γ_a has nothing to do with CP_α and that Γ_b has nothing to do with CP_β . Γ_i are composition curves, and CP_i are critical point curves. At a critical end point, however, the critical point curve meets the extreme of the composition curve (CP_α meets Γ_a at T_u and CP_β meets Γ_b at T_l).

Another important characteristic of these systems is that the best compatibility capacity is achieved at $T = \tilde{T}$, when the hydrodynamic volumes of both parts of the surfactant are equal. Under phase inversion conditions, the amount of amphiphile needed to make compatible a mixture of equal amounts of oil and water is minimal. The phase inversion conditions are accordingly looked for to minimize the amphiphile quantity needed to achieve a given task.

Winsor behavior is not the only characteristic of water–oil–nonionic amphiphile systems. The lyotropic mesophases appearing on the water–amphiphile binary phase diagrams expand to some extent in the Gibbs triangle (Figure 3.19).

Amphiphiles based on alcohols lower than C8 do not generate liquid crystals at all (amphiphiles based on alcohols of C4 and less do not even give micelles). Alcohol-based nonionic amphiphiles of C10 and above give lyotropic liquid crystals, at least usually up to T_u . Figure 3.19 shows the typical and general behavior of a ternary system with an amphiphile giving liquid crystals. At a temperature below T_l each lyotropic mesophase appearing on the water–amphiphile binary phase diagram expands in the Gibbs triangle. At a temperature close to \tilde{T} generally only the lamellar liquid crystal phase is present, and points toward the amphiphile corner of the 3PT. Above T_u all the liquid crystals are molten.

D. Effects of System Parameters on Phase Behavior

1. Nonionic Surfactant Structure

The parameters T_u , T_l , and \tilde{T} increase if more hydrophilic amphiphiles are used. This is easily explained by the HLB concept: a more hydrophilic amphiphile will remain in water up to a higher temperature.

Another fundamental effect of the amphiphile is a result of its molecular mass (or molar volume): increasing the molecular mass of an amphiphile at constant HLB

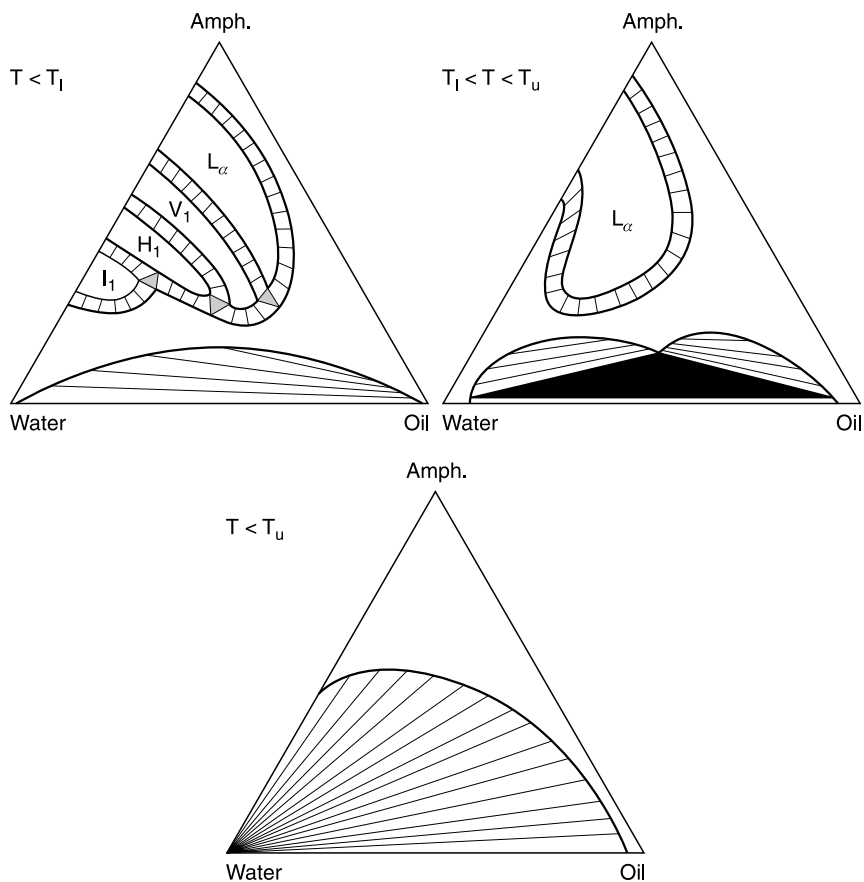


FIG. 3.19 Ternary phase diagrams involving nonionic amphiphiles (amph) generating lyotropic liquid crystals with water. (From Kallweit, M. and Strey, R., *Angew. Chem. Int. Ed. Engl.*, 24, 654, 1985. With permission.)

results in much less amphiphile being required to compatibilize equal amounts of water and oil, as illustrated in [Figure 3.20](#).

2. Effect of Oil

(a) *Molar Volume.* Increasing the oil molar volume results in an increase in T_u , T_1 (if they exist), and \tilde{T} . This is illustrated in [Figure 3.21](#) for aliphatic hydrocarbon, alkyl benzene, and alkanol acetate mixtures with water and diethylene glycol monobutyl ether (C4E2). Increasing the oil molar volume corresponds to increasing the oil–water incompatibility. Another result is an increase in the difference

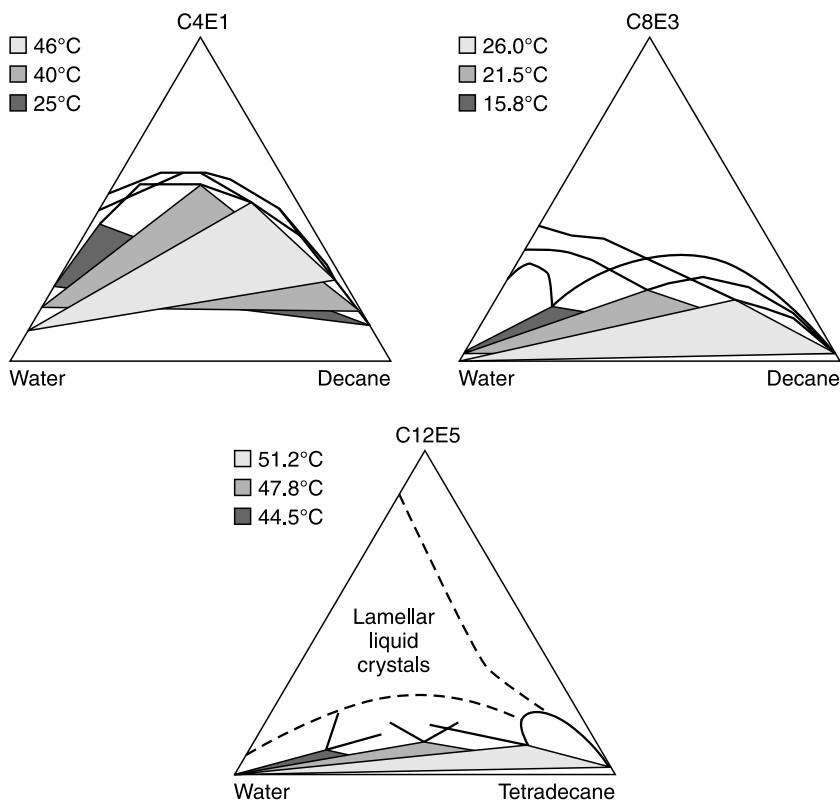


FIG. 3.20 Effect of the molecular weight of an amphiphile on the shape of the ternary phase diagram. (From Kahlweit, M., Strey, R., and Haase, D., *J. Phys. Chem.*, 89, 163, 1985. With permission.)

between T_u and T_l . This is illustrated by the alkyl benzene series in Figure 3.21, which presents a tricritical point for an alkyl chain length between six and seven.

(b) *Polarity.* Because increasing the oil polarity (by moving from aliphatic hydrocarbons to alkyl benzenes to alkanol acetates) decreases the water–oil incompatibility, it is not surprising that the Winsor transitions (T_u , T_l , and \tilde{T}) occur at lower temperatures and the supertricriticality decreases.

The polarity of the oil can be estimated from Hansen's three-dimensional solubility parameters. Hansen separated Hildebrand's solubility parameter into three independent components: δ_d for the dispersion contribution, δ_p for the polar contribution, and δ_h for the H-bonding contribution. As an estimation of the oil polarity, we define D_{ph} as the square root of the square of the polar component plus the

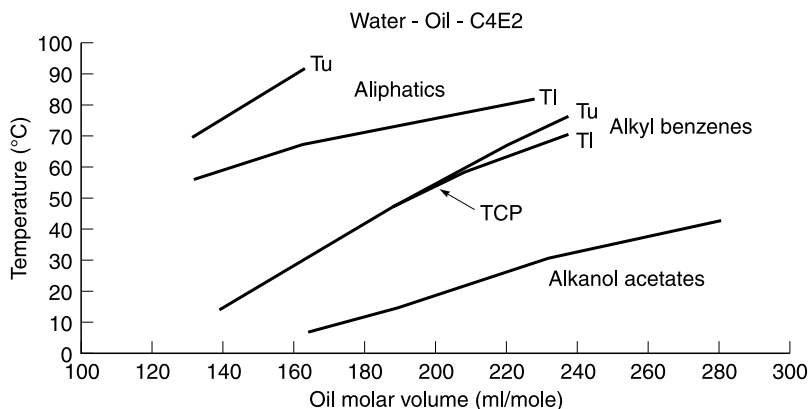


FIG. 3.21 Effects of oil molar volume and polarity on the characteristics of ternary phase diagrams obtained with water and diethylene glycol butyl ether.

square of the H-bonding component of the solubility parameter, using the table published by Barton [13].

For ternary mixtures of alkanes, alkyl benzenes, or alkanol acetates with water and C4E2, the phase inversion temperature can be satisfactorily expressed as

$$\tilde{T}(^{\circ}\text{C}) = 1.016V - 0.00121V^2 - 44.72D_{\text{ph}} + 4.747D_{\text{ph}}^2 - 2.74$$

where V is the oil molar volume in ml/mol and D_{ph} is the oil polar character in $\text{MPa}^{1/2}$. The effects of the molar volume and of the polarity appear to be independent, at least in this specific case.

3. Effect of Electrolytes

It is possible to modify the behavior of water by adding electrolytes. Electrolytes usually reduce the solubility of uncharged organic components in water. Although the great majority of electrolytes exert a salting-out action, several exceptions exist, such as perchlorates and thiocyanates, which have a salting-in action.

The salting-out or salting-in characteristics of electrolytes were discovered at the end of the nineteenth century by Hofmeister [14] and essentially remain a mystery. It has been established that this effect has nothing to do with ionic strength: different salts at the same ionic strength have different salting-out or salting-in characteristics. Besides, unlike a classic electrostatic effect, it is almost linear with salt concentration (at least in the low concentration range).

In water, the effects of anions are much more pronounced than the effects of cations. The sequence of anions for increasing salting-out character in aqueous solutions is as follows: nitrate < chloride < carbonate < chromate < sulfate.

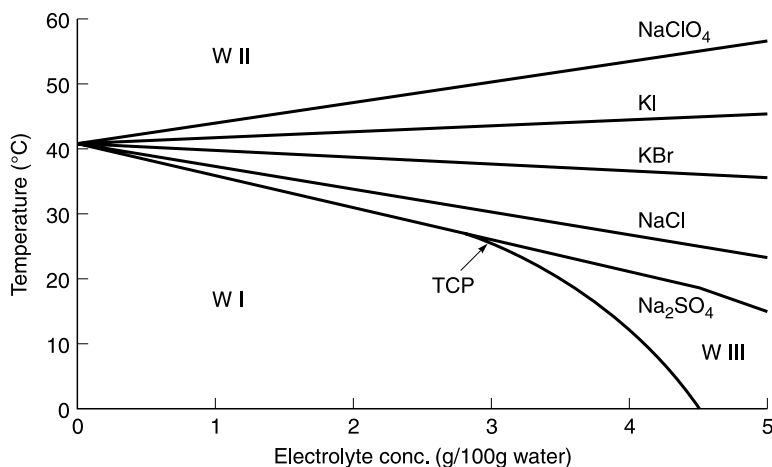


FIG. 3.22 Effect of the nature and concentration of electrolytes on the characteristics of ternary phase diagrams obtained with water, diethylene glycol butyl ether, and tridecanol acetate.

Perchlorates and thiocyanates are salting-in electrolytes. A salting-out electrolyte strengthens the structure of water and makes it less available to hydrate organic molecules; salting-in electrolytes disrupt the structure of water, creating “holes.” Salting-in electrolytes usually have a positive enthalpy of solubilization in water (endothermic solubilization).

In practice, salting-out electrolytes make water even more incompatible with oil. The result is a decrease in the Winsor transition temperatures and an increase in the supercritical character. The amount of amphiphile necessary to compatibilize water and oil generally increases in the presence of a salting-out electrolyte. All these tendencies are reversed with a salting-in electrolyte. Figure 3.22 illustrates the effects of different electrolytes on a C4E2–C13 acetate–water system.

4. Effect of Low-Molecular-Mass, Water-Soluble Organic Molecules

Water can be made less incompatible with oil by adding small, uncharged, water-soluble organic molecules, such as amides and substituted ureas [15].

High salting-in performance is obtained with organic molecules with the following characteristics:

- Amphiphilic structure
- Hydrophobic segment short enough to prevent aggregation
- Concentration well below the solubility limit

Typical examples are urea derivatives, especially butyl urea.

V. EMULSIONS

Unlike microemulsions, emulsions are not thermodynamically stable. When a mixture of oil (such as decane) and water is shaken, oil molecules come into contact with water. The area of contact between oil and water increases. As the two liquids are not miscible, increasing the area of contact results in an increased energy. In the case of decane, creating 1 m^2 of contact with water requires 0.050 J . This does not appear to be very much; however, if one considers one liter of a 50:50 volume mixture, creating a dispersion of $10 \text{ }\mu\text{m}$ droplets requires 15 J . The net result is that water and oil will rapidly separate.

Adding a well-chosen surfactant can reduce the rate of separation between oil and water. Indeed, many of the surfactant molecules will be located at the oil/water interface, reducing significantly the interfacial tension to the order of 1 mN/m . The energy required to create the interface will be accordingly reduced. However, the role of surfactants is not limited to interfacial tension reduction. By adsorbing at the surface of the droplets, a surfactant will create a protecting barrier, which will significantly increase the droplet lifetime.

A. Emulsion Instability and Breakdown

One can distinguish two different types of instabilities. There are instabilities resulting from thermodynamics, such as flocculation, coalescence, and Ostwald ripening, and there are those resulting from gravity, such as sedimentation, creaming, and coacervation.

1. Flocculation and Coalescence

Let us consider an emulsion of an oil (e.g., decane) in water. The oil droplets are constantly in motion due to thermal agitation or convection. In the course of their movements they may collide with each other. The collision may be perfectly elastic, in which case only the velocities of the droplets change, but their size or number do not. The collision, however, may not be elastic. The droplets may stick together, leading to flocculation. In a flocculation process the number of droplets remains constant, but they are no longer independent: they move together. In fact, flocculation involves many droplets, leading to large structures named flocs, which may even create a three-dimensional network. This can result in a viscosity increase, which may lead to a paste or a gel state.

Flocculation, by itself, can be reversible. Agitation may be sufficient to redisperse the droplets. However, when in close contact, the wall separating two droplets may break, allowing the droplets to merge into a single, bigger droplet. This phenomenon is referred to as coalescence and is not reversible. It results in a drift of the particle size distribution toward larger values, and may even lead to total phase separation.

Flocculation and coalescence can be avoided by preventing droplets approaching each other. In fact, flocculation (which may lead to coalescence) is the result of the van der Waals forces between two droplets. These forces act at relatively short distances, and are always attractive. There are two ways to counteract these forces: electrostatic repulsion and steric repulsion.

(a) *Electrostatic Repulsion.* The creation of electrical charges on droplets induces electrostatic repulsion forces that act at a longer distance than van der Waals forces. If strong enough, the electrostatic repulsion can offset van der Waals attraction, which means that the particles will repel each other. Ionic surfactants or polymers are commonly used to achieve electrostatic repulsion.

Electrostatic repulsion has a limitation. It works only for systems that do not contain large quantities of electrolytes. Indeed, the presence of electrolytes reduces the so-called Debye length, which is basically the distance at which electrostatic repulsion is effective. Electrolytes also compress the electrical double layer. The result is a reduction of the electrostatic repulsion, which may become weaker than van der Waals attraction.

(b) *Steric Repulsion.* Rather than creating electrical charges at the surface of droplets, it is possible to adsorb a water-soluble polymer. This polymer will expand in the aqueous phase to a certain distance. When two particles covered with polymer approach each other the polymer chains are compressed. This compression results in loss of configurational entropy. Besides, in the area where the polymer shells overlap, due to compression the local polymer concentration is higher. Osmotic pressure will pull the particles apart.

The selection of polymer is critical. If too water soluble, the polymer will not adsorb very well on the droplet surface. If not hydrophilic enough, the polymer will lie flat on the surface, so that van der Waals attraction can again take place.

The molecular weight of the polymer is also important. A polymer of too low a molecular weight will not be efficient. The use of a high-molecular-weight polymer is better, but its concentration has to be high enough to cover the surface of all the droplets. If the amount of polymer is not high enough the same polymer molecule can anchor onto two different droplets, leading to the phenomenon known as bridging flocculation.

Properly selected nonionic surfactants can be good candidates to stabilize emulsions through steric repulsion.

2. Ostwald Ripening

Ostwald ripening also leads to a shift of particle size distribution toward higher values, but the mechanism is fundamentally different. Let us consider two droplets of different sizes located close together but not in contact. The Laplace pressure, which is equal to twice the interfacial tension divided by the droplet radius, is higher in the smaller particle. Now, if the oil has a nonzero solubility in water (which is the case for decane: its solubility in water is very small, but finite),

diffusion will occur from the smaller particle toward the larger one through the continuous aqueous phase. The result is a growth of the larger particle at the expense of the smaller one.

Ostwald ripening obviously depends on particle polydispersity. If all the particles have the same size, there is no reason for one to grow at the expense of another. Ostwald ripening is also a function of the solubility of the oil in water and of the diffusion coefficient. This provides an excellent means to reduce its effect. The addition of a moderate amount of a water-insoluble oil such as a triglyceride is usually enough to reduce the impact of this destabilization mechanism.

3. Concentration Depletion

It may be logical to think that the higher the surfactant concentration, the more stable the emulsion. This is not always true. Indeed, a surfactant in excess forms micelles, which are significantly smaller than the emulsion droplets. Droplets are of the order of a micrometer and micelles are 5 to 100 nm. Droplets are surrounded by numerous micelles which bombard them constantly due to Brownian motion. When two droplets happen to be close to each other the collisions of the micelles are no longer isotropic. There are fewer micelles between the two droplets. The result from the unbalanced collisions is that the droplets are actually brought into contact.

This phenomenon is highly sensitive to droplet size and it is sometimes used as a method to prepare homodisperse emulsions by fractionation.

4. Sedimentation and Creaming

Sedimentation or creaming, depending on the relative densities of the oil and water phases, results from the action of gravity on the droplets. Under a gravitational field a spherical droplet will accelerate until it reaches a velocity for which the friction force balances the gravitational force. At this point the particle will move at a constant velocity v predicted by Stokes' law:

$$v = \frac{\Delta\rho r^2}{6\pi\eta}$$

where $\Delta\rho$ is the density difference between the oil and water phases, r is the radius of the supposed spherical droplet, and η is the viscosity of the continuous phase.

Stability can be reached if the density of the dispersed phase exactly matches that of the continuous phase. This is difficult to achieve in practice as the volumic expansion coefficients are different for oil and water. Density matching accordingly holds only at one temperature. Decreasing the particle size reduces the separation rate but does not stop it. Moreover, particle size reduction commonly leads to a viscosity increase, and even to gelling. Increasing the viscosity contributes to separation reduction but it is not very easy to achieve in practice.

Good physical stability can, however, be obtained by developing a viscoelastic network in the continuous phase. The elastic component acts as a net that prevents the droplets from settling or creaming. Viscoelastic networks can be obtained with high-molecular-weight water-soluble polymers or lyotropic liquid crystals.

5. Coacervation

The electrostatic repulsion discussed above may be strong enough to prevent particles from coming into close contact but still be too weak to maintain the droplets far enough away from each other to counteract the effect of gravitation. The result is the sedimentation (or creaming) of some of the droplets. Unlike flocculation, coacervation is very easily reversible by simple agitation. Sometimes even convection currents are enough to redisperse the droplets.

Coacervation is usually observed in electrostatically stabilized systems in which the electrolyte concentration is slightly too high.

VI. NANOEMULSIONS

The term “nanoemulsion” naturally creates confusion with the term “microemulsion.” One may think that nanoemulsions have droplets smaller than microemulsions, since the prefix “nano” indicates a quantity three orders of magnitude smaller than a quantity indicated by the prefix “micro.” As mentioned earlier in the chapter, the term microemulsion is not well chosen, but it is too well established to change it.

Microemulsions are thermodynamically stable phases, which can be represented by clear areas in equilibrium phase diagrams. Nanoemulsions are really small emulsions, with the main characteristics of emulsions: they are not thermodynamically stable and the way they are prepared has a great impact on their physical stability. The only difference with common emulsions is their very small droplet size, which ranges from 10 to 500 nm. Accordingly, nanoemulsions may look bluish, due to light diffusion (brown/yellow by transmission), just like microemulsions close to a critical point.

In contrast to thermodynamically stable microemulsions, nanoemulsions can be highly efficient in releasing oily materials. Indeed, they are highly metastable: the droplet size is small, but the interfacial tension is not so small. This results in the Laplace pressure inside the droplets being very high. Metastability is due to the activation energy required for two droplets to merge.

There are essentially two ways to prepare nanoemulsions. These are the phase inversion temperature (PIT) process and the high-pressure homogenization (HPH) process.

A. PIT Process

A regular emulsion is prepared with a surfactant that is mainly water soluble, at a temperature lower than the PIT of the system. The emulsion is heated to the PIT.

At this temperature the interfacial tension is very small, and a very limited mechanical energy is required to mix thoroughly the ingredients. (Note that it is not necessary to add enough surfactant to reach the middle phase.) The temperature is then rapidly reduced to room temperature. The small droplets are accordingly “frozen” in their state before the rapid temperature reduction.

Unfortunately, the droplet size distribution of a nanoemulsion prepared by the PIT process is relatively large. Due to the high Laplace pressure, Ostwald ripening takes place rapidly, limiting the lifetime of the nanoemulsions to a few minutes to a few days. The addition of a water-insoluble component can significantly reduce the breakdown kinetics; however, long-term stability is rarely achieved with this process.

B. HPH Process

A high-pressure homogenizer is an instrument able to generate high-speed collisions between the droplets of a preformed emulsion. The result of these collisions is the production of very small (nanometric) droplets. If the process conditions are carefully optimized, narrow droplet size distributions can be obtained, and the addition of a water-insoluble oil can largely overcome Ostwald ripening.

The drawbacks of the HPH process are the expensive investment required, the constant attention of a highly skilled engineer during the operation, and the delicate cleaning and sanitization of the production line.

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