History and Status of the Emulsion Morphology Diagram for Two- and Three-Phase Emulsions

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Abstract: Emulsions are used in many important fields such as liquid-liquid extraction, wastewater treatment, emulsion polymerization, fine chemicals, foods, cosmetics, drugs, energy processing, liquid-membrane separations, microelectronics, electronic printing, magnetic recording material, advanced battery technology, novel separation technology, biotechnology, and hydrocarbon emission control processes. In the applications of emulsions in these fields it is essential to understand how to determine and control emulsion morphologies because they affect significantly physico-chemical properties of emulsions. Emulsion morphology is described on the basis of equilibrium conjugate phases. Hence, a more complete understanding of emulsion morphology requires a substantial knowledge of the phase behavior. In the emulsion morphology studies, emulsions have been formed by mixing various components (a surfactant, cosurfactant, oil, water, inorganic salt, etc) and therefore the phase diagrams have been of five or more dimensions and excessively complex. Hence, it is very difficult to establish fundamental relationships between phase behavior and emulsion morphologies for these systems. Experience has confirmed that it is valuable to use systems of two and three thermodynamic dimensions with inclusion of a fourth dimension (usually temperature). Hence, in this article mainly two- and three-phase emulsion morphologies and their relation to phase behavior are reviewed.

Keywords: emulsion, emulsion morphology, emulsion (morphology) inversion, emulsion morphology diagram.

1. Introduction

Emulsions are used in research and processes of many important fields such as liquid-liquid extraction, wastewater treatment, emulsion polymerization, fine chemicals, foods, cosmetics, drugs, energy processing, and liquid-membrane separations. During the last decade the areas of emulsion applications have been extended to microelectronics, electronic printing, magnetic recording material, advanced battery technology, novel separation technology, biotechnology, and hydrocarbon emission control process [1].

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In these research and processes, understanding how to determine and control emulsion morphology is of prime importance. By emulsion morphology it is meant which phase is continuous or which phase is dispersed. Thus, emulsion morphology refers to a topological property of the emulsion, which is best explained by example. Examples of emulsion morphologies that might be formed by two or three phases (A, B, C) include the familiar "A-in-B" (A/B) and "B-in-A" (B/A) morphologies and "multiple emulsions" (e.g., "A-in-B-in-A, A/B/A), but also three-phase morphologies such as "A-in-B-in-C" (A/B/C) or "A-and-B-in-C" (A+B/C) (see Figure 15). Hence, a commonly called O/W emulsion is the emulsion in which droplets of oleic phase are
dispersed in continuous aqueous phase. Likewise, W/O is the emulsion in which droplets of aqueous phase are dispersed in continuous oleic phase. Here, it should be noted that the symbols in the descriptions of emulsion morphologies denote the equilibrium conjugate phases. For example, in O/W and W/O emulsions O and W denote for oleic or oil-rich phase and aqueous or water-rich phase, respectively, but not the component "oil" and "water".

An emulsion is officially defined by the International Union of Pure and Applied Chemistry to be a dispersion of droplets of a liquid or liquid crystalline phase in a continuous phase of another liquid [2]. However, systems of three (or more) components often form three coexisting liquid or liquid crystalline phases, and these three-phase systems may also form dispersions. Systems in which all three phases are liquids and one phase is a microemulsion are of particular interest and are the only combination of three phases whose dispersion morphologies have been systematically studied. Hence, this paper discusses dispersions of two or three liquid phases (one of which is a microemulsion); and it defines "emulsion" to include all dispersions formed by liquid phases, whether their numbers be two or three. The emulsion morphology diagram of these systems demonstrates the logic of this terminology.

Emulsion morphologies affect significantly physicochemical properties of emulsion products. For this reason, in many cases a particular morphology is required and this morphology should be maintained for a certain period of time. Although one morphology is desired, emulsions experience an abrupt transition, for example, from O/W to W/O or vice versa at a certain condition. This transition is called emulsion (morphology) inversion and this inversion displays a hysteresis depending on the relative amounts of equilibrium conjugate phases (Figure 1). Hence, it is imperative to understand how a desired morphology is obtained and at what conditions this morphology inverts, and there have been a lot of studies on this issue.

Once the phase behavior has been specified, the emulsion morphology is perhaps one of the most fundamental properties of the system. Attempts to determine and describe what factors control emulsion morphologies were made by Ostwald [3,4] and Bancroft [5]. Later the phase inversion temperature (PIT) idea was advanced to predict correlations of emulsion morphology with temperature and with the occurrence of middle-phase microemulsions [6]. Also, it has been reviewed how catastrophe theory [7-10] and critical-scaling theory [9,10] might be used with experimental determinations of emulsion morphologies. However, neither Bancroft’s rule (which is almost always misquoted [11]), the PIT concept [11], Ostwald’s stereometric model [12], nor catastrophe theory [9,10] has proven to be fully satisfactory for correlating and predicting emulsion morphologies. A fundamental problem common to all of these approaches is that they originally were formulated and/or applied without adequate knowledge of the phase behavior of the system of interest.

As previously mentioned, emulsion morphology is described on the basis of equilibrium conjugate phases. Hence, a more complete understanding of emulsion morphology requires a substantial knowledge of the phase behavior. In early studies of emulsion morphologies, emulsions were formed by mixing various components (a surfactant, cosurfactant, oil, water, inorganic salt, etc). For these early systems, the phase diagrams were of five or more dimensions and excessively complex, and therefore the relative amounts of the equilibrium conjugate phases were hardly known. Hence, it was very difficult to establish fundamental relationships between phase behavior and emulsion morphologies. Experience has confirmed the value of using systems of two and three thermodynamic dimensions with inclusion of a fourth dimension (usually temperature) only as required for actual approaches to a tricritical point. Emulsions comprising phases more than three can be formed. However, because they may have to be described in dimensions higher than four, mainly two- and three-phase emulsion morphologies and their relation to phase behavior will be dealt with in this article.

2. History of Emulsion Morphology Diagrams

Antecedents. Forerunners of the emulsion morphology diagram may be traced back to at least 1910, when Ostwald [3] described a hypothetical model for monodisperse, hard-core droplets of

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one phase in another, packed in a regular geometric structure. For each ordered packing, straightforward geometrical proofs give the maximum volume fraction of the dispersed phase; these fractions are all greater than 0.5. Emulsion inversion, that is, the abrupt change between A/B and B/A, occurs when the volume fraction of the dispersed phase exceeds the hard-sphere limit. These volume fractions range from 0.524 for regular cubic to 0.74 for cubic close packing (for a table of hard-sphere and measured values see [12]).

Real emulsion droplets are never hard spheres, and only recently have (essentially) monodisperse emulsions been prepared [13]. The model does not predict which packing the droplets should have. Moreover, Ostwald did not use the term "morphology diagram."

Nevertheless, as illustrated by Figure 1, one-dimensional morphology diagrams can be drawn for the Ostwald model. Because the dispersed-phase volume fractions at which inversion occurs are greater than 0.5, the emulsion morphology dia
gram has three regions: a region in which the morphology is A/B; a region in which the morphology is B/A; and a "hysteresis" region, in which the morphology may be either B/A or A/B, depending on which phase is added to the other.

In 1913 Bancroft [5] surveyed the scattered, unsystematic experiments and observations on emulsion morphologies that were available at that time. He inferred that the phase of the greater surfactant concentration was somewhat favored as the continuous phase. Although it is impossible to derive any specific model from this qualitative inference, it suggests that in Figure 1,

\[
I_{A/B} > I_{B/A} \quad (1)
\]

if B is chosen as the phase of greater surfactant concentration. Unfortunately, only a very few of the writers who have cited Bancroft's paper seem to ever have read it. His innocuous inference is ubiquitously misquoted as the totally erroneous "Bancroft's Rule," namely, "that the phase of the greater surfactant concentration is [always] the continuous phase."

\[
I_{B/A} = 0 \quad (2a)
\]
\[
I_{A/B} = 1 \quad (2b)
\]

This simple mis-statement seems to have led many researchers to believe that the morphology which may (or may not) be encountered slightly more often is the only one that can ever occur.

Figure 2. Emulsion morphology diagram of Sasaki [14] for the system acetic acid/ethyl ether/water (right corner: water, left corner, ethyl ether).

Additional well-planned series of modern, systematic tests of the validity of Bancroft's Rule are needed; for the few systems of simple amphiphiles that have been systematically studied, equations (2) are never true.

Early emulsion morphology diagrams. The earliest known emulsion morphology diagram was published by Sasaki in 1939 [14]. He made emulsions by shaking mixtures of acetic acid, ethyl ether, and water by hand. As illustrated by Figure 2, his experiments and diagram divided the compositions that formed two liquid regions into three regions: a region in which the emulsions were always "oil-in-water," a region in which they were always "water-in-oil," and an intermediate region in which the emulsion morphology depended on the method of shaking. Sasaki was familiar with the papers of Ostwald and Bancroft, and showed that "oil-in-water" emulsions were somewhat "more favored" in the sense that the hysteresis region lay to the aqueous side of the tie line midpoints (which divide the tie lines into equal volumes of aqueous and oleic phases). Sasaki even investigated three-phase dispersion morphologies composed of two liquids and gas.

Compared to present day knowledge of emulsion morphologies, Sasaki's work was incomplete or in error in only three significant ways: (1) he incorrectly drew the critical point for emulsion inversion as being different from the phase critical point (although his measurements clearly allow the two points to be at identical compositions, (2) he did not study temperature effects, and (3) he did not study either two-phase or three-phase emulsions in systems that form three conjugate liquid phases.

Following Sasaki's seminal study, Ross and Kornbrekke performed similar measurements on the ethanol/benzene/water system [15]. Figure 3 illustrates the findings of Ross and Kornbrekke, as redrawn by Smith and Lim [9]. As suggested by Figure 3, the conclusions of Ross and Kornbrekke largely agreed with Sasaki's, but differed in two ways: (1) Ross and Kornbrekke understood that at
the critical point of phases A and B. The boundary between A/B and B/A morphologies must fall on the phase critical point, and (2) in the intermediate "hysteresis" region either the A/B or B/A morphology might be formed by (what seemed to be) a single method of shaking. That is, they found the "choice" of morphology to be a stochastic process. The morphology probability depended only on the tie line and the position of the sample composition along the tie line (i.e., the phase volume fractions). Thus, in Figure 3 the two inversion hysteresis lines represent the loci of 90% probabilities of morphologies A/B and B/A, respectively.

3. Recent Emulsion Morphology Diagrams

Two-component systems with a consolute critical point. In 1990 Smith and Lim reported the first measurements of the emulsion morphology diagram of a two-component system with a consolute critical point [10]. For this study they chose the n- butoxyethanol"water" system, C₈H₁₇OC₂H₄OH(C₂E₅)/0.01 M NaCl-in-water. (The small concentration of salt was added to enhance the electrical conductivity differences between conjugate phases, but has little effect on the phase diagram [16,17]). Figure 4 illustrates the phase diagram of C₂E₅/water. In addition to testing several more-fundamental questions, this oil-free system illustrates the limitations of models and terminologies that describe emulsions as droplets of oil in water, or vice versa.

Smith and Lim [10] equilibrated a mixture of butoxyethanol and brine at a carefully controlled temperature, separated the two phases, then successively added known volumes of one of the phases to a known volume of the other phase. After each addition they emulsified the system by means of reproducible mechanical agitation and measured the electrical conductivity of the resulting emulsion like in their previous work [18]. Figure 5 illustrates the measured conductivity vs. volume fraction of the amphiphile-rich phase, when the amphiphilic phase (AM) was successively added to the aqueous phase (AQ). For aqueous-continuous (AM/AQ) emulsions, emulsion conductivity was predicted (with no adjustable parameters) from the measured conductivities and volume fractions of the two phases, by means of the Maxwell equation. The close agreement between the measured and predicted conductivities provided quantitative evidence for the morphology AM/AQ [19]. (For AQ/AM emulsions, the conductivity is so small that the percentage difference between measurement and prediction can be relatively large.) The volume
fraction at which the conductivity underwent a large drop provided the volume fraction at which inversion of the emulsion occurred. The experiment was repeated (at the same temperature) by addition of aqueous phase to amphiphilic phase; the phase volume fractions for the two different experimental directions along the tie line were different; that is, inversion hysteresis was observed.

The entire process of phase equilibration and separation, "titrations," and measurement of the two different volume fractions at which emulsion inversion occurred was repeated for other temperatures in the vicinity of the lower consolute solution temperature. Figure 6 is a plot of each pair of emulsion inversion points (T vs. phase volume fraction).

Because the phase diagram of the system also was known (measurement of the phase densities also is desirable), the phase volume fractions of Figure 6 could be converted to component concentrations (i.e., the units of a phase diagram), so that the emulsion inversion points could be plotted on the phase diagram. The resulting plot is shown in Figure 7.

The qualitative similarities between Figure 7 and the single-temperature, ternary emulsion morphology diagrams of figures. 2 and 3 are immediately obvious. In each diagram there is a region, adjacent to the B ends of the tie lines, in which only the A/B morphology is observed, and a region adjacent to the A ends of the tie lines, in which only the B/A morphology is detected. These two regions are separated by a hysteresis region, in which, depending on the previous conditions, either morphology may be found. Starting at the thermodynamic critical point, the emulsion inversion lines diverge from other. But both lines curve towards the phase of greater amphiphile concentration. Thus, at the critical point inversion occurs at equal volumes of the conjugate phases. However, contrary to Bancroft's early qualitative deduction--the phase of greater amphiphile concentration is actually less likely to be encountered when the experimental composition is randomly chosen without reference to the emulsion morphology diagram! Apparent violations of Bancroft's rule were observed also in other works [20-22].

Figure 8 [24] illustrates the phase diagram of an amphiphile/oil/water system [25] that forms a middle-phase microemulsion, M. Examples of such systems include C12H25OC(OH)2 decane/water [26] or C12H25(OH)2/C12H25OH ("CaEz")/tetradecane/water [27]. (For a "real" surfactant, such as C12Ez, the diagram would be more complicated, because of the occurrence of liquid crystalline phases [28].)

Samples whose compositions fall within the tie
Figure 8. Phase diagram of an amphiphile/oil/water system that forms a middle-phase microemulsion: A = aqueous phases (in equilibrium with oleic phases B), C = oleic phases (in equilibrium with microemulsions phases D), E = aqueous phases (in equilibrium with microemulsion phases F); middle phase microemulsion, M, is at intersection of lines D and E; top phase, T, is at intersection of lines B and C; bottom phase, B, is at intersection of lines A and E.

triangle of Figure 8 form three liquid phases, of compositions T, M, and B (corners of the tie triangle). Each pair of adjacent corners of the tie triangle is connected by a binodal curve (as well as by a side of the tie triangle). Compositions between a side of the tie triangle and the adjacent binodal curve form two conjugate phases in equilibrium with each other; each such pair of phases is connected by a tie line. For two of the binodals the compositions of the conjugate phases can become closer and closer and their connecting tie line shorter and shorter, until the phase compositions and the endpoints of the tie lines become identical at a plait point. The compositions on the binodals between these two critical points (including M) are "limiting microemulsions." Each limiting microemulsion is in equilibrium with either an aqueous or an oleic phase (M is in equilibrium with one of each). On the low-ampiphil-concentration side of the tie triangle, aqueous and oleic phases occur in conjugate pairs. Most compositions outside of the tie triangle and the three binodal curves form only a single liquid phase. (For simplicity, the two-phase region illustrated by Figure 4 has been omitted from figures 8-10.)

Changes of temperature cause the phase diagram to evolve through the sequence illustrated by Figure 9. As the temperature is decreased from some temperature between T_{tc} and T_{tc}, the aqueous phase-

microemulsion binodal shrinks until it becomes a single point, the "lower critical endpoint." Simultaneously, the tie triangle shrinks in "height," becoming a "lower critical tie line" of zero height at T = T_{tc}. Conversely, when the temperature is raised, the oleic phase-microemulsion binodal shrinks, until it becomes an "upper critical endpoint" at T_{te}. Below T_{tc} and above T_{te} the respective binodal curves and plait points disappear, leaving only a single two-phase region.

Of all the characteristic points in the phase diagram, the composition of the middle phase is most sensitive to temperature. Point M moves in an arc between the composition of the bottom phase (point B) at T_{tc} and the composition of the top phase (point T) at T_{te}, reaching its maximum surfactant concentration near T = (T_{tc} + T_{te})/2. (Points B and T move by much smaller amounts, also.) The complete nonionic-ampiphile/oil/water-temperature
Two-phase morphology diagram is illustrated by Figure 10, including the S-shaped curve of $T$, $M$, and $B$ compositions; the two lines of plait points, which terminate at the lower and upper critical endpoints; and the lower and upper critical tie lines (at $T_c$ and $T_{uc}$ respectively).

Two-phase emulsion morphology diagram in triangular prismatic coordinates. There have been progresses in understanding how the emulsion morphology is related to the phase behavior of the ternary surfactant/oil/water systems [18,29-32]. Until recently [33], it was thought that all non-multiple emulsions were either "oil-in-water" (O/W) or "water-in-oil" (W/O) and this terminology persists today. However, in the phase diagram of figures. 8-10 there are three kinds of conjugate phases—microemulsion (MI), aqueous (AQ), and oleic (OL). All pairwise combinations of these phases occur—MI-AQ, MI-OL, and AQ-OL—one for each two-phase region. It is plausible to assume that for each phase pair both A/B and B/A morphologies should exist. Hence, as Figure 8 makes clear, hypothetically there should be six non-multiple, two-phase "morphologies," of which four contain a microemulsion phase. These six two-phase morphologies are oleic-in-aqueous (OL/AQ) and aqueous-in-oleic (AQ/OL), but also, oleic-in-microemulsion (OL/MI), microemulsion-in-oleic (MI/OL), aqueous-in-microemulsion (AQ/MI), and microemulsion-in-aqueous (MI/AQ) [33]. The terminology "O/W" for OL/AQ emulsions or "W/O" for the AQ/OL morphology might plausibly be used. But the O/W and W/O terminology cannot possibly be valid for emulsions that contain a microemulsion phase.

In fact, the existence of all six emulsion morphologies has been confirmed experimentally by experiments similar to those described above for the C$_{16}$E$_{11}$/brine system [11,12].

The MI-AQ and MI-OL binodals have all of the essential thermodynamic features (tie lines and plait point) of the single-binodal systems (figures. 2 and 3) studied by Sasaki [14] and Ross and Kornbrekke [15]. In fact, as illustrated by Figure 10, above the upper critical endpoint temperature or below the lower critical endpoint temperature the phase diagram has only a single binodal, continuous with the AQ-MI or OL-MI binodal, respectively. Hence, it is plausible to expect that the emulsion morphology diagram for AQ-MI and OL-MI binodals should resemble the emulsion morphology diagram of Figure 3. The resultant diagram is plotted in Figure 11 [18]. The existence of OL/MI and MI/OL emulsions and the inversion hysteresis lines meeting at the critical point subsequently was demonstrated for the C$_{16}$E$_{11}$/decane/brine system [11].

Measurements along the three sides of the tie triangles of various chemical systems confirmed the existence of all six of the MI/AQ, AQ/MI; MI/OL, OL/MI; and AQ/OL, OL/AQ morphologies [12,34-36].

Figure 11. Postulated dispersion morphology diagram for the two-phase regions bounding a "microemulsion" tie triangle, subsequently confirmed by experiments (see reference [18]).

Three-phase emulsion morphology diagram in triangular prismatic coordinates. Once the two-phase morphology diagram of Figure 11 had been confirmed for several chemical systems, Smith and co-workers turned their attention to the morphologies of the three-phase emulsions formed by compositions inside the tie triangle. They first showed that the tie triangle is divided into three regions, each with a different continuous phase, \( M \), \( T \), or \( B \) [37]. The boundaries between the regions begin, approximately, at the midpoint of each side of the tie triangle and meet near the center of the tie triangle [37]. Hence, except possibly near the boundaries between the regions, the continuous phase is the phase of greatest volume fraction.

The division of the tie triangle into regions of three different continuous phases is hardly surprising, for the following reasons: As illustrated by Figure 8, in a ternary system of constant temperature and pressure, the middle-phase microemulsion (\( M \)) is simply one of an infinite number of microemulsion phases. The other limiting microemulsions lie on the binodals on either side of \( M \), stretching between the plait points of the two binodals. The composition and physical properties of \( M \) are fixed, but continuous with those of the limiting microemulsions in the two-phase regions on either side of it. Likewise, the bottom phase (\( B \)) is simply one, unique aqueous phase among many; and the top phase (\( T \)) is simply one oleic phase among all the rest. Thus, by changes of composition the system can pass from AQ/MI, to three-phase emulsion, and on to OL/MI emulsion, while the continuous phase remains a microemulsion along the entire path. Analogous two-phase, three-phase, two-phase paths exist for which the emulsion morphology is always an aqueous phase, or always an oleic phase. When a side of the tie triangle is crossed the emulsion morphology must change, because one of three phases either just begins to form or finally disappears; but there are no abrupt changes of continuous phase or other emulsion property. The properties of the boundaries between continuous phases are illustrated in greater detail by figures 12-14 [38].

Three-phase emulsions can have many more morphologies than the two allowed by the simple A/B and B/A morphologies of two-phase systems.
Figure 15. Cartoon illustration of the twelve theoretical morphologies of three-phase macroemulsions in which one of the phases is a middle-phase microemulsion

Although they have not yet all been reported, theoretically there are twelve three-phase emulsion morphologies formed by the top, middle, and bottom phases [39,40]. These twelve morphologies are "totally engulfing"--T/M/B, M/T/B, M/B/T, B/M/T, and B/T/M, T/B/M; "non-engulfing"--(T + M)/B, (B + M)/T, and (B + T)/M; and "partially engulfing"--(T + M)/B, (B + M)/T, and (B + T)/M. These twelve three-phase emulsion morphologies are illustrated by Figure 15.

Of particular note in Figure 15 is the property of what phases are in physical contact with each other: (1) For partially engulfing morphologies all three two-phase interfaces exist, and there is a line of three-phase contact; the three possible "choices" for the continuous phase allow three morphologies of this type, but only in partially engulfing morphologies are all three pairwise interfaces present. (2) For non-engulfing morphologies, no interface exists between the two dispersed phases; droplets of unlike phases always have continuous phase between them. Since there are three possible continuous phases, there are three possible non-engulfing morphologies. (3) In engulfing morphologies, as in non-engulfing morphologies, one of the two-phase interfaces is "missing"; however, the missing interface is between the continuous phase and one of the dispersed phases. Hypothetically, the two phases of the core and shell can be interchanged. Hence, mathematically, there are six engulfing morphologies, two for each choice of continuous phase. In the non-engulfing and partially engulfing morphologies the two dispersed phases are morphologically equivalent, but the core and shell are not.

In general, electrical conductivity measurements have proven to be an excellent way to identify continuous phases in three-phase emulsions, when well defined experimental paths of known volume fractions and the conductivities of the three phases are used. Moreover, theoretical equations exist for the electrical conductivities of some three-phase emulsion morphologies, in particular the engulfing core-and-shell structure A/B/C [41]. However, at present, electrical measurements do not provide a completely general method for determining the morphology of the two dispersed phases [39,40]. The emulsion conductivity depends primarily on the conductivity of the continuous phase, and the conductivities of different morphologies with the same continuous phase may not be greatly different. Hence, other experimental methods and additional theoretical ideas are needed to choose among the four morphologies that are hypothetically possible for each measurable continuous phase.

For bulk phases A, B, and C, phase B is said to be a wetting phase if it wets the A-C interface so that there is no physical contact between A and C; a wettability transition between these two conditions occurs when the interfacial tension between A and C equals the sum of the A-B and B-C tensions. If all three interfaces occur simultaneously, the system has no wetting phase. Smith postulated that, for any given continuous phase, the morphology of the two dispersed phases is determined by the wettability among the three phases [39]. If, in macroscopic experiments, one of the three phases wets the interface between the other two, it will do so also in their emulsions; if none of the three phases is wetting and all three two-phase interfaces occur for bulk phases, then the same condition will obtain in their emulsions. Differences between the morphologies of the bulk phases and their emulsions may occur very near wetting transitions. Interfacial tensions, and thus wetting transitions, depend on droplet radii; hence, there will be small differences of temperature or composition between bulk-phase wetting transitions and changes of emulsion-morphology.

Thus, when no phase is wetting, the emulsion morphology will be partially engulfing; depending on their volume fractions, A, B, or C may be the continuous phase. When phase C wets the A-B
interface, the morphology will be non-engulfing \((B + A)/C\) if \(C\) is the continuous phase, engulfing \(B/C/A\) if \(A\) is the continuous phase, and engulfing \(A/C/B\) if \(B\) is the continuous phase; interchange of the core and shell and the morphologies \(C/B/A\) and \(C/A/B\) cannot occur for this wetting condition, because \(C\) must be physically between \(A\) and \(B\). For \(C/B/A\) to occur, \(B\) must be a wetting phase; and for \(C/A/B\) to form, \(A\) must be a wetting phase.

Hence, the theoretical existence of twelve morphologies is actually the result of permuting three phases among four hypothetical wettabilities: \(A, B, C\) or none as the wetting phase.

In fact, of the four hypothetical wettabilities, two are definitely known, a third has been reported (but not independently confirmed), and the fourth never has been observed. Wetting microemulsion phase and no wetting phase are both relatively common; Smith and Covatch [42,43] were the first to observe a temperature-induced transition between them. Wetting by the bottom phase of the top phase-microemulsion phase has been reported [44]. Wetting by a top phase, if it can occur, remains to be observed.

Thus, we predict, six \([T/M/B, B/M/T, \text{non-engulfing } (B + T)/M; \text{and partially engulfing } (T + M)/B, (B + M)/T, \text{and } (B + T)/M]\) of the twelve three-phase emulsion morphologies definitely should be found; observation of the \(M/B/T, T/B/M, \text{or non-engulfing } (M + T)/B\) morphology would confirm the possibility of wetting by a bottom phase; and observation of either the \(M/T/B, B/T/M, \text{or non-engulfing } (M + B)/T\) morphology would constitute the first discovery of a wetting top phase. The existence of some of the six predicted morphologies has been "proven" by electrical conductivity measurements [35,39,40]. By freezing the emulsions, Lim has obtained direct visual proof for one of the predicted morphologies and non-conclusive support for another [45].

It is interesting to note that Sasaki's early work [14] indirectly supports the predictions. Although he did not study three-phase emulsions, Sasaki did do experiments on dispersions of a gas and a liquid in a second liquid. The morphologies he observed were in accord with the wetting hypothesis; whereas morphologies that did not meet the wettability hypothesis for morphologies of three-phase dispersions were not observed, or very quickly disappeared.

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