Phase and emulsion morphology diagrams of nonionic amphiphile/oil/water systems and their interrelationships

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Abstract - For two-phase, non-multiple emulsions, the emulsion morphology diagram
shows, as a function of temperature and phase or component concentration, which
phase is dispersed and which is the continuous one, as well as the temperatures and
compositions at which inversions occur. The emulsion morphology diagram plays for
emulsions a role that is similar to the role played by phase diagrams for phases.

INTRODUCTION

An emulsion has been defined as a system in which "liquid droplets and/or liquid crystals are dispersed in a liquid" (ref. 1). For conjugate phases A and B two such emulsion morphologies are possible: A-in-B (A/B) and B-in-A (B/A). Other, multiple morphologies also have long been known, such as A/B/A and B/A/B/A (ref. 2), but multiple emulsions and emulsions of more than two conjugate phases (ref. 3) fall outside the scope of this article.

Once its phases have been specified, the morphology of an emulsion is perhaps its most fundamental property. Attempts to determine and describe what factors control emulsion morphologies were made by Ostwald (ref. 4, 5) and Bancroft (ref. 6). 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 (ref. 7). Recently Salager reviewed how catastrophe theory might be used with experimental determinations of emulsion morphologies (ref. 8). However, neither Bancroft's rule [which is almost always misquoted (ref. 9)], the PIT concept, (ref. 9) Ostwald's hard-sphere model (ref. 10), nor catastrophe theory (ref. 11, 12) 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 amphiphile/oil/water systems.
A more-complete understanding of the relationships between emulsion morphologies and the phases from which they are formed requires a fuller knowledge of the phase behavior including, in particular, knowledge of the phase diagrams of systems that form triconjugate top, middle, and bottom phases. Many of the chemical systems used in early studies of such "middle-phase microemulsion" systems contained a nonionic amphiphile (i.e, "cosurfactant"), organic salt (i.e., surfactant), oil, water, and one or more inorganic electrolytes (ref. 15), Temperature is also an important thermodynamic variable. The phase diagrams of such systems require five or more dimensions and are excessively complex for establishing fundamental

relationships between phase behavior and emulsion morphologies. Experience (ref. 9-12, 16-19) has confirmed the value of using systems of two and three thermodynamic dimensions (by the phase rule, the minimum required for formation of biconjugate and triconjuate phases, respectively) with inclusion of a fourth dimension (required for a non-virtual tricritcal point) only as required for actual approaches to a tricritical point. In fact, even in single-temperature, amphiphile/oil/water phase diagrams the fact that the tielines are not parallel creates difficulties in theoretical interpretations (ref. 12). For experimental tests of catastrophe and scaling theories of emulsion inversion it initially proved preferable to limit the chemical system to two components (e.g., amphilphile/water) that have a consolute point and to use temperature as the second dimension to vary the distance from a critical point (ref. 11).

PHASE DIAGRAMS
Amphiphile/water

The smallest number of components that can form an emulsion is two. Figure 1 illustrates the type of miscibility gap that is exhibited by many nonionic amphiphiles with water (and by other pairs of liquid components as well). At temperatures between the lower consolute solution temperature, T_{lcst}, and the upper consolute solution temperature, T_{ucst}, the system can form a water-rich aqueous phase in equilibrium with an "amphiphilic phase," which has a greater concentration of amphiphile. (In a real system one of the two critical points may not be observable; e.g., T_{lcst} may be below the freezing point.)
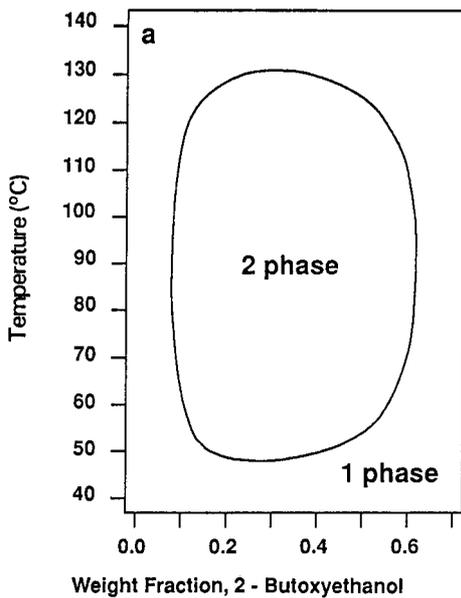

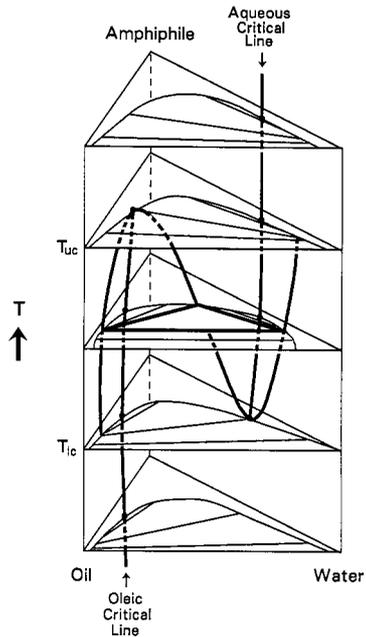Fig. 1. Miscibility gap with two critical points in a two-component system.

Fig. 2. Trigonal prismatic phase diagram for an amphiphile/oil/water system.

Amphiphile/oil/water

Figure 2 illustrates binodal gaps and plait points of the types that are often observed in systems of three components, including the amphiphile/oil/water systems of many emulsions. The amphiphile may peferentially partition into the aqueous phase ($T < T_{lc}$) or into the oleic phase ($T > T_{uc}$).

As illustrated by Fig. 2 and in greater detail by Fig. 3, for nonionic-amphiphile/oil/"water" systems (including those with inorganic electrolytes) there often exists an intermediate range of temperatures ($T_{lc} < T < T_{uc}$) throughout which three liquid phases simultaneously form. These triconjugate phases are the Top phase (T), Middle phase (microemulsion, M), and Bottom phase (B). The composition of M changes with temperature,

ranging from that of the bottom phase at the lower critical endpoint temperature (T_{lc}) to the composition of the top phase at the upper critical endpoint temperature (T_{uc}).

For many purposes, particularly for "PIT" experiments in which the temperature is changed, it is necessary to use the three-dimensional diagram (ref. 16) to plan and interpret experiments (ref. 9). Even in the absence of any measurements, Figs. 2 and 3 illustrate the utility of phase diagrams for the understanding of emulsion morphologies : From Fig. 3 one immediately sees that there are three two-phase regions (A-B, C-D, and E-F) and thus six different possible morphologies of non-multiple, two phase emulsions: A/B, B/A; C/D, D/C; and E/F, F/E (ref. 20). Thus, attempts to determine, correlate, and predict whether emulsions are "oil-in-water" or "water-in-oil" are doomed to frustration, since they fail to acknowledge four classes of emulsions that belong to neither morphology.
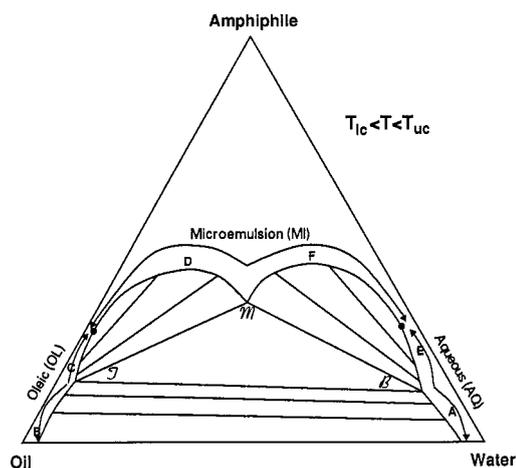

Fig. 3. Isothermal cross section for $T_{lc} < T$
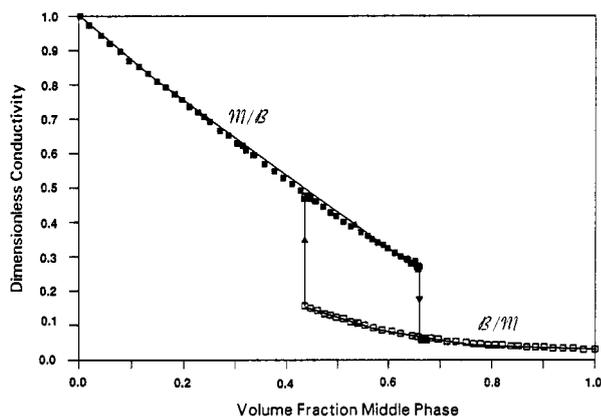$< T_{uc}$ for the phase diagram of Fig. 2.

Fig. 4. Emulsion electrical conductivities:
points: measured; line: predicted.

EXPERIMENTAL DETERMINATIONS OF MORPHOLOGIES

Although earlier researchers (ref. 13,14) often assigned emulsion morphologies on the basis of visual examination of their creaming behavior, it should be emphasized that the morphology of a steady-state emulsion and the morphology of an emulsion formed during creaming of that steady-state emulsion are not necessarily the same (ref. 19). Most recent determinations (ref. 8-11, 16-19) of emulsion morphology diagrams have employed electrical conductivity measurements on steady-state emulsions. This practice is favored by the demonstration that, when the more conductive phase is the continuous phase, the electrical conductivity of an emulsion can be accurately predicted from the measured volume fractions and electrical conductivities of the two phases *without any adjustable parameters*, even for very concentrated emulsions in which the fraction of the dispersed phase exceeds 60 volume percent (ref. 21). In these cases the electrical conductivity is an *absolute*, rather than just a *qualitative*, indicator of the morphology.

Figure 4 shows a typical set of conductivity data, measured for both directions along the tieline, for steady-state emulsions prepared from a pair of pre-equilibrated phases where the phase concentrations range from one end of the tieline to the other. [Experimental details have been given elsewhere (ref. 9-11, 16-19, 21).] Also shown are the conductivities predicted by an effective-medium model (ref. 21) from the phase conductivities and volume fractions. The data show that two different morphologies occurred along the tieline, that the inversions from one to the other were discontinuous, and that the inversion phase concentrations differed slightly for the two directions along the tieline (i.e., inversion hysteresis was observed). By repeating such measurements for various tielines at different, known distances from the critical point, one can plot (Figs. 5-8) each pair of inversion points as a function of that distance and then determine the shapes of the two resulting inversion lines and the dependence of the inversion hysteresis

width on the distance from the critical point (ref. 11). This experimental design is suggested by catastrophe theory, which predicts how the inversion lines and the distance between them should vary with distance from the critical point (ref. 8,11,12). The ability of these plots to show how emulsion morphologies depend on composition, experimental path, and temperature is similar to the way in which phase diagrams show how the numbers and compositions of phases depend on system composition and temperature (ref. 11).

EMULSION MORPHOLOGY DIAGRAMS

From the phase rule and the definition of two-phase, non-multiple emulsions, it follows that one should be able to map onto Figs. 1-3 the following: (a) which system compositions of conjugate phases I and J are I-in-J emulsions, (b) which have the J-in-I morphology, (c) which compositions may have either morphology (i.e, hysteresis), (d) which compositions are a mixture of both morphologies, and (e) which compositions (if any) have neither morphology. We call such a diagram a "dispersion morphology diagram," or somewhat more precisely for emulsions, an "emulsion morphology diagram" (ref. 16). In fact, one can choose either the component concentrations or phase concentrations as independent variables. The latter choice is somewhat more precise, since steady-state emulsions are fundamentally viewed as functions of phase concentrations, while the former choice is often more concise in that it allows the phase diagram and the dispersion morphology diagram to be combined into one.
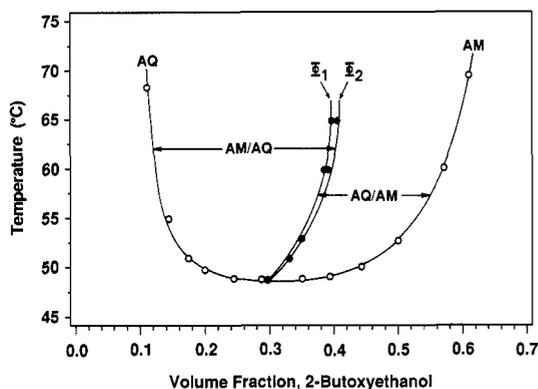

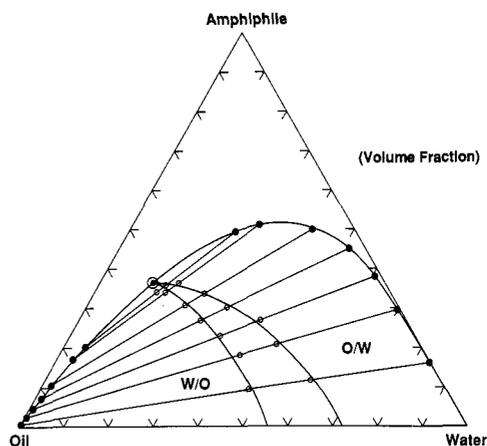Fig. 5. Dispersion morphology and phase diagrams (ref. 11,12) for the system $C_4H_9OC_2H_4OH$/aqueous 10 mM NaCl.

Fig. 6. Dispersion morphology and phase diagrams for the system ethanol/ benzene/water (ref. 12,14).

Amphiphile/water

Figure 5 (ref. 12) shows the phase and emulsion morphology diagrams measured (ref. 11) for a system ($C_4H_9OC_2H_4OH$/aqueous 10 mM NaCl) that exhibits the type of phase behavior illustrated by Fig. 1. The line of aqueous-phase compositions, AQ, meets the line of amphiphilic phases, AM, at the lower consolute point, which is a critical point for the two phases. Emulsion inversion lines Φ_1 and Φ_2, which curve towards the phase of greater amphiphile concentration, meet at this same point, which is also a critical point for the emulsion morphologies. As indicated by the double-headed arrows <--AM/AQ--> and <--AQ/AM-->, between lines AQ and Φ_1 the observed morphologies were always AM/AQ and between lines AM and Φ_2 the observed morphologies were always AQ/AM. Between lines Φ_1 and Φ_2 the observed morphology depended on the experimental path: when phase AM was added to AM/AQ emulsions the inversion to AQ/AM did not occur until line Φ_2 was reached and when phase AQ was added to AQ/AM emulsions the inversion to AM/AQ occurred when line Φ_1 was reached. The width of the hysteresis region, $\Phi_2 - \Phi_1$, went to zero at the critical point. When the phase volume fraction was chosen as a "control" variable, catastrophe theory was successful at fitting $\Phi_2 - \Phi_1$, but not the individual curvatures of Φ_1 or Φ_2 (ref. 11).

Amphiphile/oil/water: $T<T_{lc}$ and $T>T_{uc}$

Figure 6 illustrates the type of dispersion morphology diagram found (ref. 12,16) for the type of phase behavior ($T < T_{lc}$) illustrated by Fig. 2. Emulsions of the system C_2H_5OH/benzene/water were originally studied by Ross and Kornbrekke (ref. 14). As in Fig. 5, inversion lines Φ_1 and Φ_2 meet at the critical point (ref. 14) and curve toward the phase of greater amphiphile concentration. Between Φ_1 and Φ_2 either emulsion morphology might be observed, but as indicated by Fig. 6, in the other two-phase regions of the diagram the morphology was always either "oil-in-water," O/W, or "water-in-oil," W/O.

Amphiphile/oil/water: $T_{lc}<T<T_{uc}$

The dispersion morphology diagram predicted for the phase diagram of Fig. 3 is illustrated by Fig. 7 (ref. 16). Most of the behavior predicted by Fig. 7 has been confirmed by experiments on systems of the type amphiphile/n-alkane/water (ref. 9,10,16) although the somewhat more complicated behavior of multiple emulsions or of mixtures of A/B and B/A morphologies is sometimes observed.
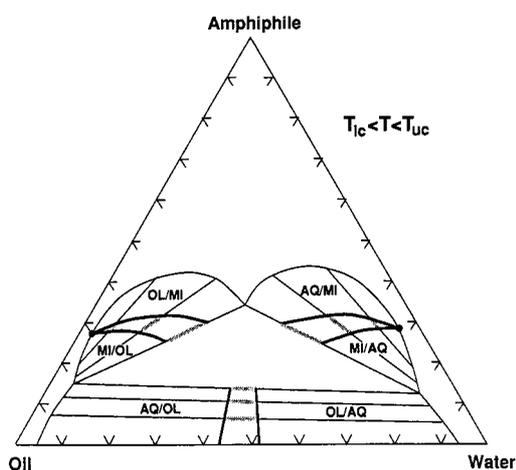

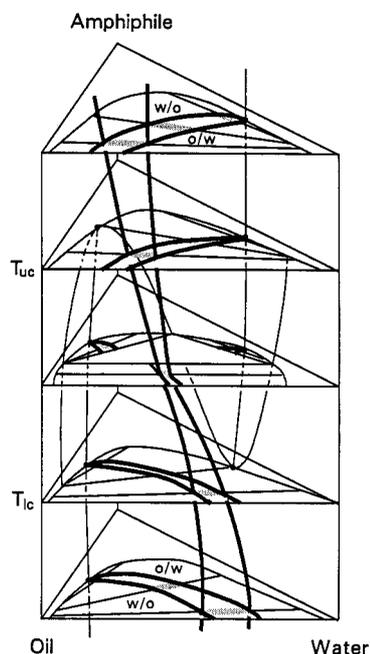Fig. 7. Dispersion morphology diagram (ref. 16) for the phase diagram of Fig. 3.

Fig. 8. Dispersion morphology diagram (ref. 16) for the phase diagram of Fig. 2.

Amphiphile/oil/water: trigonal prismatic diagram

Figure 8 shows the dispersion morphology diagram that results when isothermal cross sections such as Figs. 6 and 7 (for the same chemical system) are combined into a trigonal prismatic diagram that fully illustrates the composition and temperature dependence of the morphologies. Once the various boundaries in the emulsion morphology diagram of Fig. 8 have been measured for a particular chemical system, the diagram can be used to predict the morphologies that will occur and the points at which the morphologies will change for any particular sequence of composition and/or temperature changes that are of interest.

As an example of the use of Fig. 8 we may consider the following. As usually presented, (ref. 7) the PIT concept seems to imply (ref. 20) that above the phase inversion temperature all emulsions are "W/O," whereas below that temperature all emulsions are "O/W". Hence, an emulsion must invert when the temperature passes through the PIT. However, Fig. 8 predicts that no morphology change need occur if the

amphiphile concentration is sufficiently small that the number of phases never changes from two to three. Experiments (ref.16) in which the temperature was cycled up and down through the PIT while the system composition remained fixed and the number of phases always remained two have confirmed the prediction of the dispersion morphology diagram shown by Fig. 8 that a system can pass through the PIT without the ocurrence of any change of emulsion morphology.

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