Status of Aqueous Surfactant Phase Science

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Recent phase studies of several surfactant-water systems, using new or refined methods, have revealed significant errors in earlier phase diagrams. These diagrams had been determined largely using methods based on the isoplethal phase studies principle. This principle has inherent limitations which do not exist in isothermal methods.

Isothermal nuclear magnetic resonance and refined calorimetric methods have been extensively used in recent surfactant phase studies. Methods based on the new lyotrope gradient (swelling) principle show great promise as a means of improving the efficiency and quality of surfactant phase studies.

KEY WORDS: Gradient methods, isoplethal, isothermal, liquid crystal phases, phase science, phase study methods, surfactants, swelling.

The aqueous phase behavior of surfactants is academically interesting and industrially useful. The earliest investigations of this subject were undertaken to describe "soap-boiling"—the process by means of which refined soap is isolated after the saponification of fat. Soap boiling had been developed empirically to a high art by the beginning of the 20th century, but in the 1920's, McBain, at Bristol University, initiated pioneering physical studies of soap-water-salt systems. These studies had the explicit objective of transforming the art of soap-boiling into a science and improving the process (1).

McBain's work was initiated during the heyday of phase science. The Gibbs Phase Rule was relatively new, but it was firmly established and was being applied to virtually every kind of chemical system. The breadth and depth of phase research during this era is evident from the encyclopedic treatise edited by Roozeboom and Schreinemakers (2).

Phase study principles and methods. Two principles for doing phase studies were known to McBain (3). One class of methods was based on the isothermal analytic principle, in which coexisting phases are separated and analyzed. Other methods followed the isoplethal principle, in which mixtures are heated or cooled and the temperatures of phase discontinuities noted.

Where applicable, isothermal methods are preferred for locating phase boundaries. The isothermal analytic method is the method of choice for accurately determining critical exponents (4). Practically, however, this method is restricted almost entirely to investigations of two coexisting liquids of low viscosity; it cannot even be used to fully define crystal-liquid equilibria. While the liquid phase may be cleanly separated, occlusion of liquid within the crystal mass precludes isolation of the pure crystal phase. The "wet-residues" method of Schreinemakers was developed to address this problem (5).

The isothermal method has limited value for surfactant systems because of the high viscosities of liquid crystal phases. An exceptional case where it has been applied is the $C_{10}E_4$-water system (6). The method was usable in this instance because phase equilibrium is rapidly attained, and involves the coexistence of low viscosity liquid or liquid crystal phases.

Because of these problems most surfactant phase studies have been based on isoplethal methods, which were first utilized in 1882 by Alexejew (7). Isoplethal studies are executed by heating or cooling mixtures and noting the temperatures at which discontinuities occur in the number of phases present. Isoplethal methods are simple, and the response to temperature changes can be followed using a wide range of parameters. Besides direct observation and microscopic texture, dilatometry (volume measurements), calorimetry, and x-ray data were the principal kinds of data utilized (8).

The fact that composition is known during an isoplethal experiment is an important strength of this principle, as minimal analytical determinations are required. Isoplethal methods are also well suited for determining isothermal discontinuities. They are less than ideal for locating other boundaries, however, because inherent limitations exist.

One limitation results from the fact that temperature changes often dictate extensive mass transport—both within phases and across interfaces. Sufficient time for equilibrium to be maintained may not be allowed, thus compromising the data (9-11). Another limitation lies with the difficulties which result from the fact that when isothermal discontinuities are crossed, new phases which typically differ in structure from the original phases must be created. Particularly when the temperature change dictates the formation of crystal phases, nucleation and growth of the phase may be so slow that the discontinuity is not observed (8). Further, temperature changes may induce the generation of colloidal structure, and if the solubility is small this structure may be kinetically stable. These phenomena may be misinterpreted as an equilibrium phase discontinuity (12).

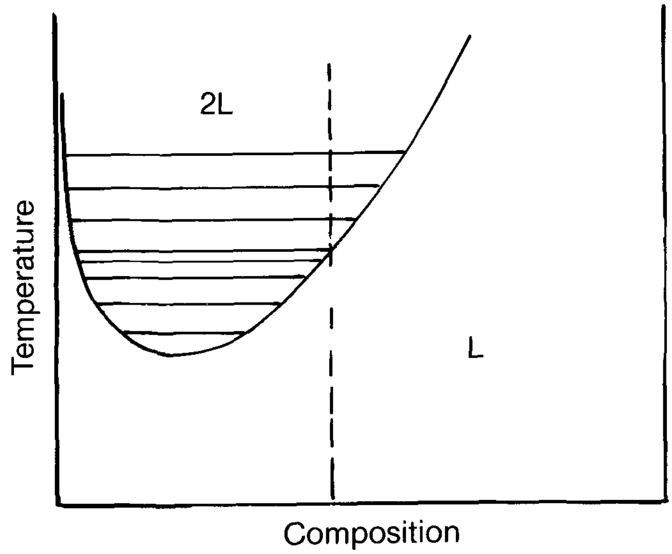

FIG. 1. Typical form of the lower consolute ("cloud point") boundary in aqueous surfactant systems. The dashed line represents a particular isopleth which crosses the boundary.

Other limitations are the critical opalescence which exists near critical points, [which may be confused with phase separation (13)], the fact that composition is varied in discrete increments and narrow one- or two-phase regions may be missed (9,14), and the existence of an inherent lever rule problem.

This lever rule problem is the most serious limitation of the isoplethal phase studies principle. It may be illustrated using the diagram of a system which displays a lower consolute boundary, the particular boundary which is responsible for "cloud points" (15) in aqueous nonionic surfactant and polymer systems (Fig. 1). During an isoplethal study one passes from the one- to the two-phase region as the temperature is increased, and the objective is to define the temperature of the boundary.

The lever rule problem exists because precisely at the boundary temperature, the fraction of the coexisting phase is precisely zero. Typically the liquid phase at the boundary temperature is crystal clear (except near the critical composition). Therefore, in order to perceive the boundary one must pass the boundary temperature into the biphasic region, so that a detectable quantity of the coexisting phase is formed. It is the clouding of the mixture due to the separation of this phase, typically at first as an emulsion, which gives this boundary its name.

The net effect of these various problems is to render data collected using isoplethal methods inherently subjective and uncertain (16). With careful work and for selected boundaries the uncertainty may not be large, but it does exist. This subjectivity and uncertainty exist irrespective of whether or not instruments are used.

Recent developments in methodology. In recent years there have been three major developments in phase study methodologies for surfactant systems. One is the use of deuterium (or phosphorus) nuclear magnetic resonance to recognize the existence of multiphase regions (17,18). This is feasible if a nuclear magnetic resonance (NMR) parameter (e.g., the splitting of the deuterium signal) is significantly different in the two phases. (It is also essential that rapid exchange or other motions do not compromise the result). This method has provided otherwise inaccessible insight into the phase behavior of polar

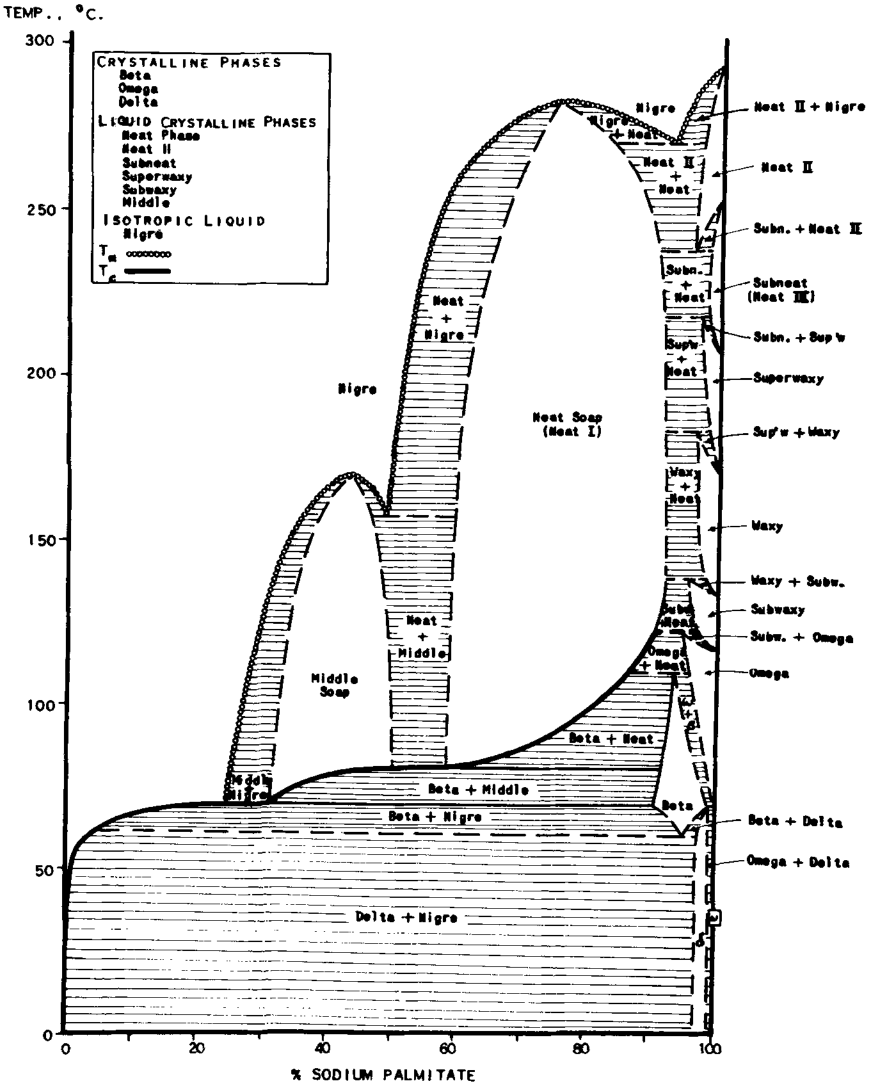

FIG. 2. A sodium palmitate-water phase diagram, which represented the best available information until the work of Madelmont and Perron (20).

lipids and numerous other surfactants (17). If phase ratios could be determined from such data without physically separating the phases, this method could be regarded as an extension of the isothermal analytic method. Since line shapes (using deuterium NMR) depend on sample history and colloidal structure, this is not presently a straightforward analysis (A. Kahn, personal communication).

A second important development stems from an improved understanding of the factors which influence calorimetric lineshapes, and refinements in the analysis of thermograms which result (19).

Finally, an entirely new principle for executing phase studies, the "lyotrope gradient" principle (20), has been developed. This is based on the generation and direct analysis of phases formed by swelling. Gradient or swelling methods amount to quantitative refinements of qualitative flooding or penetration experiments, which have been used for many years by some investigators (16) and are being extensively used currently (21). The "diffusive interfacial transport" (DIT) method (16), in which phases are quantitatively analyzed using refractive index data, is based on this principle.

A reexamination of existing phase data. Several classical aqueous surfactant systems have recently been reexamined using these new methods. The results have been most unsettling, because in every instance so far qualitative errors in the previously accepted phase diagrams

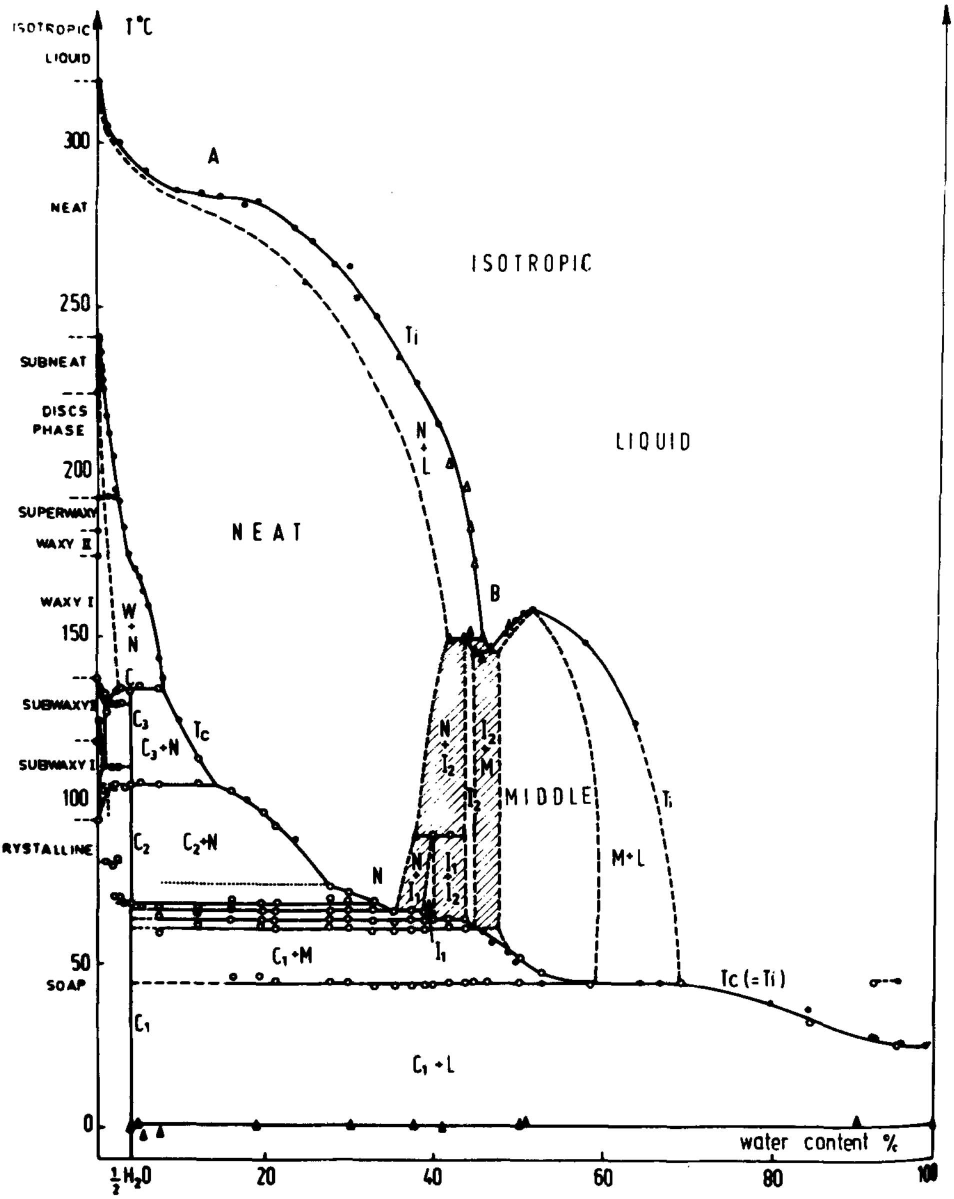

FIG. 3. The sodium laurate-water phase diagram of Madelmont and Perron (20; reproduced with permission of Colloid & Polymer Science). The small phase regions I_1 and I_2 are the intermediate phases. "Neat", lamellar; and "middle", normal hexagonal liquid crystal phases. Sodium palmitate is qualitatively similar.

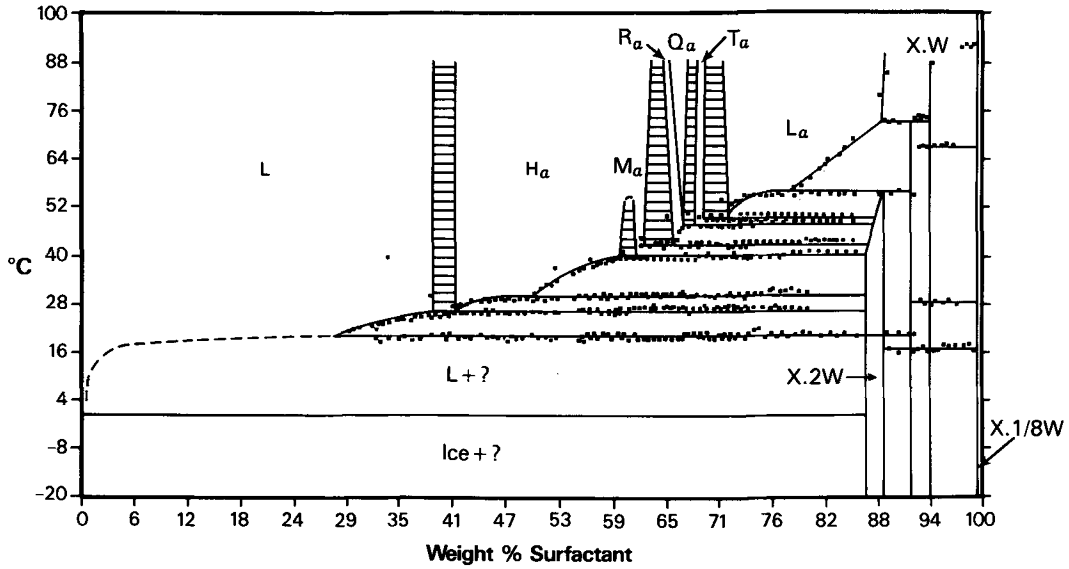

FIG. 4. The sodium dodecyl sulfate-water system, after Kekicheff *et al.* (9). The original studies were performed in D_2O. To produce the above Figure the data coordinates were extracted from the original publication using a digitizing tablet. Each composition was converted to the composition in H_2O corresponding to the same mole fraction as in D_2O, and the Figure was redrawn by computer. Transition temperatures were assumed to be the same in H_2O as in D_2O.

have been disclosed. These problems exist in the diagrams of surfactants whose water solubilities range from very high to exceedingly small.

The first indication of a problem stemmed from the redetermination of several soap-water diagrams, using calorimetry, by Madelmont and Perron (22-28). Figure 2 shows a sodium palmitate diagram which was considered by Rosevear to include the best available information on the sodium palmitate-water system as of 1951 (29). This diagram resulted from extensive studies by McBain, the Volds, Ferguson, Nordsieck, Rosevear and others. It shows the classical liquid crystal phase sequence of hexagonal and lamellar phases. (Cubic phases are commonly found in potassium, but not sodium, soaps).

Madelmont and Perron discovered that two previously unrecognized phases exist between the lamellar and the hexagonal phases. These have been termed "intermediate" phases, and are shown in the revised diagram of the sodium laurate-water system (Fig. 3). They are present in other soap-water systems as well. The existence of these phases has since been confirmed by Tiddy and others using swelling, X-ray, and NMR methods (30,31), and models for their structures were proposed.

The phase diagram of the sodium dodecyl sulfate (SDS)-water system has also been revised (Fig. 4). In recent studies the phases present were produced by swelling, their structures determined using synchrotron x-radiation data, and their compositions defined using calorimetry (9). Several important features exist in this diagram.

First, there are six structurally different liquid crystal phases present, as well as at least three stoichiometric crystal hydrates. It is suggested that some of these liquid crystals, such as the T_α phase, structurally resemble the intermediate soap phases (above). Second, both first- and second-order phase transitions are claimed to exist. An example of the latter is the boundary between the R_α and the Q_α phases. Surfactant phase transitions are typically first-order transitions. Finally, a highly unusual miscibility gap is suggested to exist within the hexagonal phase region. At high temperatures this H_α phase is transformed smoothly with increasing concentration into the monoclinic (M_α) phase. At low temperatures, however, the transformation is discontinuous and a miscibility gap exists. The existence of a critical point within a liquid crystal phase—a new and very important discovery, if true—is implied.

Uncertainties remain in this SDS-water diagram as to crystal phase coexistence relationships and other details, but this nevertheless is work of exceptional quality and significance.

Finally, it appears that even the $C_{10}E_4$-water diagram, which was investigated by Lang (6) with great care and using a variety of techniques (except for swelling methods), has been found to be in error. The existence of all the phases suggested by Lang could be confirmed using the DIT technique, but discrepancies from the published diagram include both qualitative differences in the phase behavior at the limit of existence of the central liquid (L_2) region and quantitative differences in the boundaries of the liquid crystal region (14). Specifically, the L_2 region intrudes into the liquid crystal (D) region, and terminates at an azeotropic point. As a result, the D phase is found on both the dilute and the concentrated side of the L_2 phase just below the azeotropic temperature. Index data suggests that the D phase composition extends to about 12-15% $C_{10}E_4$, instead of the 35% suggested earlier. Otherwise these studies confirmed the earlier diagram.

Soaps, SDS, and $C_{10}E_4$ are all highly water-soluble. In the case of monoglyceride surfactants the solubility is low, but measurable. Preliminary investigations of a representative monoglyceride-water system (monoolein) have been performed using the DIT method, and here too inconsistencies in the earlier data were disclosed (14).

Two cubic phases were found to exist instead of one, and the qualitative behavior at the limit of existence of the lamellar phase differs significantly from that suggested by the earlier diagram.

The most difficult kind of surfactant to investigate is the least soluble. Dilong-chain surfactants having eighteen carbons per chain typically display vanishingly small water solubilities, probably $< 10^{-15}$ M (12). Phase studies of these compounds are treacherous.

Dialkyldimethylammonium salts were first investigated by Kuneida and Shinoda (32). Their partial diagram of the dioctadecyldimethylammonium chloride (DODMAC)-water system placed the Krafft discontinuity temperature near 40°C, and the dilute boundary of the lamellar phase at 3.5%. This system was recently reexamined using swelling and other methods (12). The Krafft discontinuity temperature was found to be 47.5°C and the composition of the dilute liquid crystal boundary to be 31.5%—significantly different values. The existence of crystal mono- and dihydrates, whose chemistry constitutes an extremely important dimension of the physical science of this system, was also demonstrated.

Overview. It is clear from the above that problems and uncertainties exist in the phase diagrams of systems which not long ago were regarded as well established. This statement does not imply that the previous work is entirely wrong or of poor quality, and it is worthwhile to consider exactly where the problems lie.

Those aspects of earlier phase studies which have withstood reexamination include the boundaries defining the limits of liquid phases, the Krafft boundary location (excepting those in particularly difficult systems like DODMAC), and the approximate region of existence of liquid crystal phases which span large areas in the diagram.

The major problems which have been revealed include missed or overlooked phases. Besides the intermediate phases in soaps and the cubic phase in monoglycerides, uncertainties exist regarding the composition range and coexistence relationships of the lyotropic nematic phases which have been observed in some cationic surfactant-water systems (33). Phases are easily missed when two phases have similar optical textures (e.g., the hexagonal and biaxial rod phases, as noted by a referee). Occasionally, phase reactions involving nonequilibrium phenomena are misinterpreted as equilibrium phase transitions. An example is the dramatic reaction of the crystal monohydrate of DODMAC with water. This produces a biphasic "gel" that was regarded earlier as a liquid crystal phase (12). This problem will be most prevalent for highly insoluble surfactants which, because of their low solubility, form stable colloidal structure in biphasic mixtures.

This particular problem is basically one of correctly counting the number of phases present. An example of this problem in polar lipid-water systems is the controversy over whether or not mixtures displaying vesicular structure consist of one or two phases. It has been seriously proposed that vesicles may exist in solution, as reversibly formed structures, in systems such as didodecyldimethylammonium chloride-water. If true, the vesicle geometry constitutes a novel form of micellar aggregate (34).

Another example of this problem is the "gel" and "coagel" states of surfactants (35) and polar lipids (36). While often regarded as discrete phases, it seems likely that these states are instead colloidally structured biphasic mixtures of an ordered phase with a liquid phase. In the DODMAC-water system, the so-called "gel" and "coagel" states were shown to consist of the liquid phase and stoichiometric crystal hydrates (10).

A third problem is that of accurately defining the boundaries of liquid crystal phase regions. These boundaries are often represented as dotted lines, whose existence is inferred on the basis of the Phase Rule. Finally, there is the problem of reliably determining the qualitative aspects of phase behavior at isothermal discontinuities. Examples include the manner in which phases decompose in the $C_{10}E_4$ and monoolein systems at the upper temperature limit of their existence.

That these problems exist—in systems which were carefully studied by major investigators—suggests that the methods which have been available are inadequate for surfactant phase studies. The utilization of NMR data to supplement data obtained using classical methods has contributed significantly to recent investigations. The further development and widespread utilization of this principle and of swelling methods (both qualitative and quantitative) should improve both the quality of surfactant phase studies and the ease with which they are performed.

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