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Mechanistic Aspects of Phase Reactions in Aqueous Surfactant Systems

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Abstract: Phase transformations which accompany changes of state in binary systems can be expressed using a reaction equation format, which greatly facilitates analysis of the event. Some phase reactions occur simply, while others (those in which disproportionation occurs) display "reaction mechanisms" which are analogous to those long known in molecular chemistry. In surfactant systems the peritectic thermal decomposition of crystal hydrates invariably leads initially to metastable lamellar liquid crystal phases, from which the equilibrium products arise. Similar mechanisms likely apply to nonsurfactant systems, except that the intermediate state is a liquid phase. Phase reaction products may be determined by either thermodynamic or kinetic factors.

1. INTRODUCTION.

Physical organic chemists are keenly aware that the mechanism by means of which chemical reactions actually occur usually differs from the stoichiometric equation which describes the reactants and products. The rate equation may even include species which do not exist in the stoichiometric reaction equation. A classic example is the acid-catalyzed halogenation of acetone, in which the rate of enolization governs the overall reaction rate and the reaction is first order in acetone and hydrogen ion. The concentration of halogen does not influence the rate, and all the halogens react at similar rates [1].

2. STOICHIOMETRIC PHASE REACTIONS.

The physical reaction processes that occur during changes of state can be described using reaction equations which are entirely analogous to those used for molecular reactions [2]. The information required to construct these equations is implicitly contained within phase diagrams; the diagram of an important and familiar system (sodium chloride-water, shown in Figure 1) may be used to illustrate these ideas [3].

It will be recalled that the x,y-coordinates at any point within a phase diagram depict the concentration and temperature of the mixture of interest. For example, the point at (23.3,25) in Figure 1 depicts graphically the location of a 23.3% salt solution that is held at a temperature of 25 °C. The process of cooling this mixture may be visualized by following downward the vertical dashed line which passes through this point. Vertical lines in such diagrams are termed "isopleths". Isopleths depict graphically those physical processes during which mixtures are heated or cooled at fixed composition - surely the most commonly performed process in all of science. When superimposed upon a particular phase diagram, such process paths allow one to infer, by inspection, the state of a system at any temperature and the discontinuous changes of state which may occur at specific temperatures. The complementary process of isothermal mixing (varying composition at constant temperature) is depicted using "isotherms", which are horizontal lines.

The phase behavior of this 23.3% mixture can be perceived from this diagram. "Phase behavior" is defined by stating the number, composition, and nature of the phases which exist. The diagram indicates that a

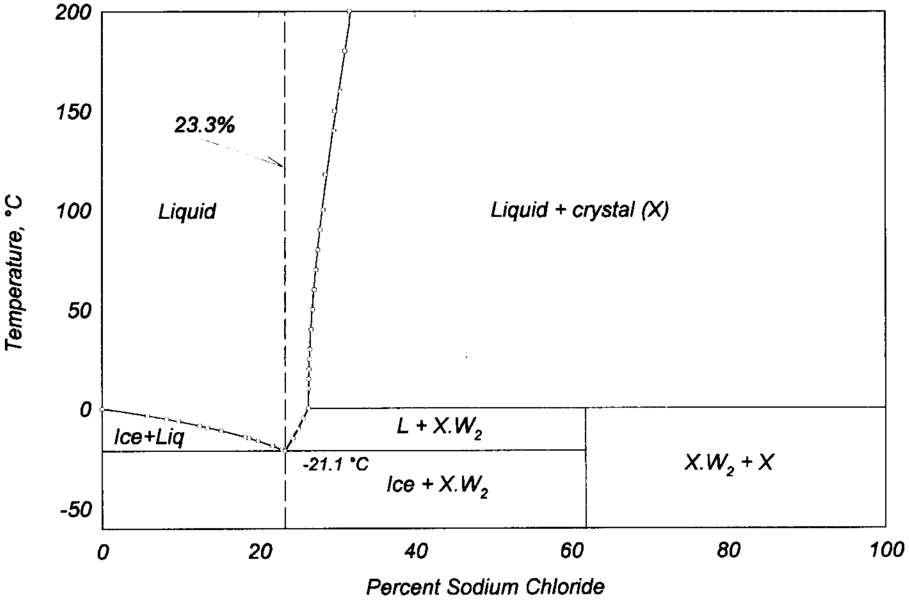


Figure 1. The sodium chloride-water phase diagram [3], with the eutectic isopleth at 23.3% indicated by the dashed line.

23.3% solution of sodium chloride is at 25 °C a single liquid phase. This phase persists down to -21.1 °C - at which temperature profound changes of state occur. The physical process which occurs as heat is removed isothermally from this mixture at this temperature is disproportionation of the liquid phase, to form as reaction products two crystal phases. One is more dilute than the original liquid (ice), while the other is more concentrated (a crystal dihydrate $X{\cdot}W_2$ containing two water molecules per sodium chloride ion pair). The isothermal (horizontal) line which touches the ice, liquid, and $X{\cdot}W_2$ phase regions (at unique points) is termed a "eutectic discontinuity" [4]. Below the eutectic line the liquid phase vanishes, and the equilibrium state of the mixture consists of the two crystals. It is very important to keep in mind that phase diagrams are intended to depict equilibrium states; metastable phases should not be misrepresented as equilibrium phases in these diagrams. In this system the eutectic liquid may easily be cooled to well below the eutectic temperature as a metastable phase, because crystals are slow to form.

If one starts anew at the coordinates (61.9%, -20 °C) the diagram indicates that again only one phase exists. Its composition is that of the dihydrate of sodium chloride, and it has a crystalline phase structure [5]. Such phases are termed "phase compounds"; they have a rigidly defined stoichiometric composition and may be isolated as pure, thermodynamically homogeneous phases. As the temperature is raised no major change occurs until the temperature reaches 0.1 °C, at which point the crystal is transformed into two other phases. Just as at the eutectic (above), this transformation involves disproportionation in phase compositions to one product which is more dilute (a liquid phase of 26.30% composition) and another which is more concentrated (a crystal phase which is the 100% sodium chloride crystal). This kind of phase discontinuity is termed a "peritectic" [6]. Eutectics and peritectics are closely similar in all aspects save one: at a eutectic the phase of intermediate composition vanishes on cooling, while at a peritectic this phase vanishes on heating. A degenerate class of isothermal discontinuities also exists in which two of the three coexisting phases have identical compositions. The name "polytectic" has been given to this discontinuity [7], as it is commonly found within binary systems when a polymorphic transition occurs in a crystal phase.

Stoichiometric phase reactions at isothermal discontinuities. Although known since the turn of this century [8], it is not as widely appreciated at present that the physical transformations which occur at eutectic and peritectic discontinuities are as rigidly defined stoichiometrically as are molecular chemical reactions. It is very useful to express these transformations in a conventional reaction equation form, as this is familiar to all chemists. The reaction which occurs at the above eutectic is described qualitatively by the equation

$$Liquid \rightleftharpoons Ice + X.W_2 + q^{eu}$$

The term q^{eu} is the heat of the eutectic phase reaction. The form of this equation indicates that the transformation is driven to the right by the subtraction of heat from the liquid phase. This change of state occurs strictly isothermally in well-defined mixtures, just as do melting or boiling processes in well-defined one-component mixtures.

The reaction equation for the peritectic reaction of $X{\cdot}W_2$ is

$$X.W_2 + q^{peri} \rightleftharpoons Liq + X$$

This reaction is driven by the isothermal *addition* of heat to the $X{\cdot}W_2$ crystal, as indicated by fact that the q^{peri} term is on the left side of this equation. X symbolizes the dry sodium chloride crystal.

Application of the lever rule [9] allows one to calculate phase ratios at these discontinuities from the phase diagram and to assign stoichiometric mass (or mole) fraction coefficients to the reactants and products. When this is done, the complete balanced equations for the eutectic phase reaction becomes

$$1\ Liq \rightleftharpoons 0.624\ Ice + 0.376\ X.W_2 + q^{eu}$$

and for the peritectic reaction

$$1\ X.W_2 + q^{peri} \rightleftharpoons 0.517\ Liq + 0.483\ X$$

An important difference between phase reaction equations and chemical reaction equations is that the stoichiometric coefficients in the former are scalar parameters, whereas those in chemical equations are typically integers. Once the thermodynamic parameters are known, the isothermal heat effects that occur at the discontinuity temperature (*e.g.*, during a calorimetric scan) can be calculated along any isopleth which falls within the span of the discontinuity [9,10]. In comparing these calculated heat effects with actual calorimetric data, it is imperative to recognize that nonisothermal heat effects also exist along all isopleths except at the eutectic composition. Surprisingly, thermodynamic models for the analysis of these nonisothermal heat effects were first derived only in 1977 [11]. Their magnitude depends on both the form of the phase boundaries and the specific composition being studied [12,13].

Finally, it is worth noting that other important physical processes may be diagrammed and treated thermodynamically using closely analogous equations. Staying within the sodium chloride-water system, an example is the isothermal vaporization of water from a biphasic mixture of saturated salt solution and salt crystals. The reaction equation for this process at 25 °C may be written as

$$1\ Liq\ (26.43\%) + q^{vap} \rightleftharpoons 0.2643X + 0.7357H_2O\ (vap)$$

In a binary system the variance of a two-phase mixture is two, while that of a three-phase mixture is one. For this reason both temperature and pressure must be specified in order to render the system invariant during the vaporization reaction, while only one (either pressure or temperature) is required at three-phase discontinuities. Once the variance of the system is reduced to zero, however, the reaction equations governing peritectic and vaporization processes are closely parallel and may be treated similarly.

3. THE MECHANISMS OF PHASE REACTIONS.

Phase transformations have often not been expressed in terms of phase reactions. Relatively little attention has been paid to the paths or mechanisms by means of which they actually occur, but this issue arose during an in-depth study of the dioctadecyldimethylammonium chloride (DODMAC)-water system. The synthetic and reaction chemistry of quaternary ammonium salts dates from 1851, when Hoffmann's comprehensive investigations of quaternary ammonium halide synthesis and reactions were published [14]. The phase behavior of monolong-chain quaternary ammonium surfactant-water systems has been known for some time [15], but that of this dilong-chain surfactant (and related ones) remained virtually unknown until the late 1980's [7,16,17]. The evident simplicity of the molecular structure of DODMAC belies the considerable complexity of its physical behavior - a not uncommon phenomenon.

The equilibrium phase diagram of the DODMAC-water system is shown in Figure 2. Although this diagram has a different appearance from that of the sodium chloride-water system, it differs qualitatively in only one truly important respect: the existence of a lamellar liquid crystal phase. The existence of these fluid (but highly structured) phases constitute the most definitive feature of the aqueous phase behavior of surfactants [18]. During this study (whose primary focus was on documenting the equilibrium phase diagram), it was discovered that some - but not all - of the phase reactions which occur follow an indirect path to equilibrium. This was a source of considerable confusion during determination of the phase diagram. Further, it was found that these particular reactions display a "reaction mechanism" which is closely analogous to that found in molecular reactions. The principal information from which mechanistic information was inferred was that on phase reaction rates - just as in molecular reactions. Such data are typically not easily quantified, however, as the dilute solution approximations which render familiar kinetic data easily interpretable are invalid during most phase transformations.

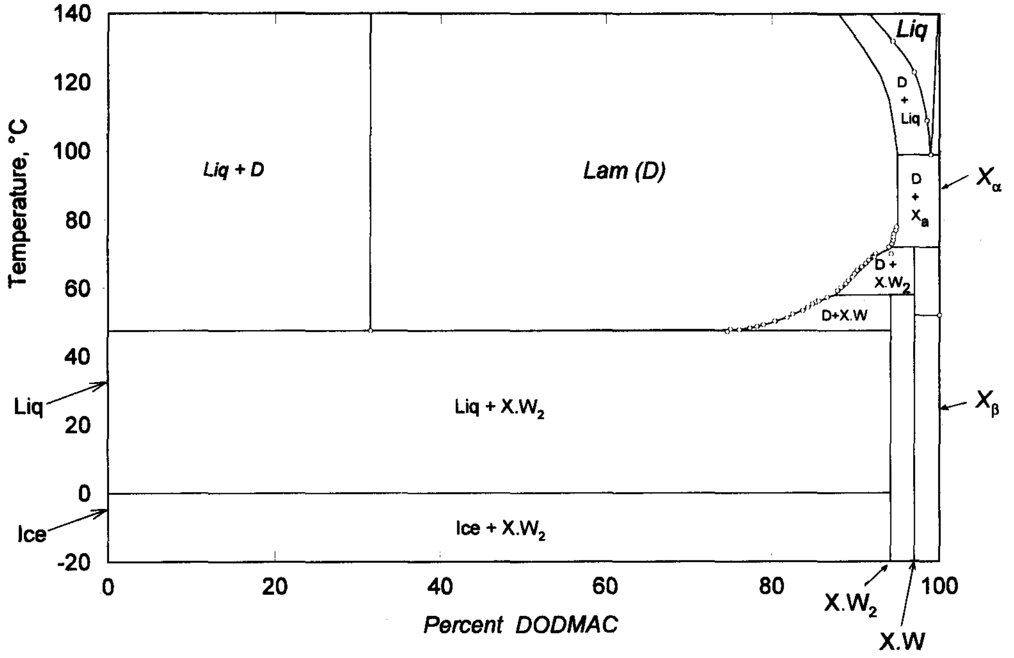


Figure 2. The dioctadecyldimethylammonium chloride-water phase diagram [7]. Reprinted with permission from The American Chemical Society, Laughlin, R. G.; Munyon, R. L.; Fu, Y.-C.; Fehl, A. J. *J. Phys. Chem.* **1990,** *94,* 2546-2552, Figure 5.

Consideration of the broad picture revealed that useful and predictive generalizations could be perceived which allow one to anticipate *a priori* which among the various reactions proceed directly and without mechanistic complexity, and which occur via reaction intermediates. This classification is most simply expressed using the classical phase science concepts of "congruent" and "incongruent" processes [19].

A "congruent" phase reaction is one in which the reactant and the product phases have the same composition (the phase analog of "isomerization"). Insofar as is presently known, *all congruent phase reactions occur simply (without the intervention of reaction intermediates) at a rate that is controlled by heat transfer processes [20].* In unary systems all phase reactions are necessarily congruent. In binary systems the most commonly encountered congruent process is the azeotropic transformation. The constant boiling azeotropic mixtures that may be encountered during distillation are familiar examples. Such azeotropes are invariably encountered in systems of two solvents which boil at roughly similar temperatures, when one or both are either strongly dipolar or hydrogen-bonding. Examples are acetonitrile plus water or the lower alcohols [21]. Azeotropic phase reactions also occur at the maximum temperature of existence of many liquid crystal regions [12,22]. At these points the liquid crystal is transformed isothermally (and reversibly) into a liquid phase by the addition of heat.

A fascinating system in which both upper and lower azeotropic points exist is the dodecylammonium chloride-water system. This phenomenon was discovered in 1951 [23] and later verified by Fontell [24]. In this diagram the hexagonal liquid crystal region exists as an island that is surrounded by the micellar liquid phase. Along isopleths which pass through the lower azeotropic point, *the liquid is transformed by the addition of heat into the liquid crystal* (liquid + heat ⇄ liquid crystal). At the upper azeotropic point the far more common reverse process (liquid crystal + heat ⇄ liquid) occurs. For the present purpose, the important point is that these azeotropic phase reactions apparently do **not** occur by a complex mechanistic path. They occur at a rate that is governed by heat transfer [20], and they occur simply (without the intervention of intermediates). It is well to keep in mind that, if investigated using fast reaction kinetic methods, all these reactions are extremely slow relative to the elementary processes that are involved (hydrogen bond or ion pair formation, molecular rotation, etc.).

Two phase reactions in the DODMAC system have been found to display complex and interesting reaction mechanisms; these are the peritectic reactions that occur when the crystal hydrates are heated [16]. In fact, the presently available information suggests that *the peritectic phase reaction described by the stoichiometric reaction equation (above) never actually occurs.* Instead, the initial reaction at peritectics is fast, simple, congruent "melting" to form a liquid crystal phase having the same composition as the crystal hydrate. This phase is metastable in that it is more concentrated than the equilibrium liquid crystal which exists at this temperature. The fast melting process is followed by much slower nucleation and growth of the equilibrium crystal phase from this metastable state - which eventually drives the composition of the liquid crystal to its equilibrium value. These steps are described by the following equations:

$$\begin{array}{llll} X{\cdot}W_n^{cryst} + q & \rightarrow & D{\cdot}W_n^{meta} & (fast) \\ D{\cdot}W_n^{meta} & \rightarrow & X{\cdot}W_{(n-1)}^{equil} + D^{equil} & (slow) \end{array}$$

A particularly interesting thermodynamic aspect of these phase reactions is the fact that the first reaction is kinetically favored in spite of the excessively large cost in enthalpy that is incurred. Far more heat must be added to force this reaction to occur than would be required if the equilibrium process had occurred - yet congruent melting is kinetically favored. The excess heat added is recovered during formation of the equilibrium crystal from the metastable liquid crystal. It is likely that this reaction is kinetically favored because of its large, positive entropy. Phase reactions characterized by a large positive entropy change, such as the transformation of crystals to any fluid state, are often kinetically favored in spite of the extremely large cost in added heat energy that is incurred.

When n = 1 in the above equation the equilibrium reaction product is the dry crystal X, and when n = 2 it is the monohydrate X·W. The indirect path of these reactions was accidentally discovered in the monohydrate crystal, after which further investigation disclosed that the same path occurs in the dihydrate crystal.

For reasons that are not entirely clear, the monohydrate crystal is strongly favored kinetically whenever crystals are formed from this liquid crystal phase. The monohydrate is also the crystal which is normally isolated by conventional recrystallization after exposure to atmospheric moisture. It decomposes rapidly above its peritectic temperature - but much more slowly (at a rate governed by diffusion of water through the solid state) below this temperature. The dry crystal must be kept at a water activity of <0.2, as it reacts with water vapor within tens of seconds at higher water activities to form X·W. In striking contrast, the monohydrate requires about one year to form the dihydrate $X\cdot W_2$ by reaction with liquid water, and about four years by reaction with water vapor. If the monohydrate is stressed by being heated for a few minutes to just above its peritectic and then exposed to water vapor at lower temperatures, a new crystal dihydrate forms which is metastable [7].

A particularly interesting reaction mechanism occurs at the peritectic discontinuity of the crystal monohydrate in the dioctadecylammonium cumenesulfonate (DOACS)-water system. The equilibrium diagram of this system is shown in Figure 3. The equilibrium phase behavior of this system is unusual - especially when compared with that of DODMAC-water (Figure 2). In both systems a crystal monohydrate exists, but in the DODMAC system the peritectic temperature of this monohydrate (72 °C) lies above that of the Krafft eutectic (47.5 °C). (The Krafft eutectic is that which exists at the lower limit of the liquid crystal region.) In the DOACS system this peritectic (64 °C) lies below that of the Krafft eutectic (70 °C). The equilibrium phase reaction at the DOACS monohydrate peritectic is

$$X\cdot W \; + \; q \; \rightarrow \; Liq \; + \; X$$

as the liquid crystal phase is not an equilibrium state at this temperature. Nevertheless, the mechanism by means of which this crystal hydrate decomposes is precisely the same as that found in the DODMAC monohydrate. The fast initial reaction is congruent melting to form a metastable lamellar liquid crystal of the same composition, which in a slower step forms (by nucleation and crystal growth) the equilibrium crystal.

This situation leads to unique swelling behavior during DIT (Diffusive Interfacial Transport) phase studies [25]. In using this phase studies method the sample is fused, allowed to wick into a rectangular cross-section silica capillary, and an interface between water and the compound is created. The temperature is quickly adjusted to the desired value, and the swelling of the compound observed. After a period of time discrete phase bands are typically formed and their compositions determined *in situ* using either refractive index data [25], or more preferably near-infrared microspectroscopy [26]. During DIT studies of DODMAC, the crystals swelled in a normal fashion to generate clean lamellar liquid crystal/crystal interfaces at temperatures above the Krafft boundary [27].

In the DOACS system, islands of lamellar liquid crystal (which are readily identified by their characteristic microscopic texture [28]) appeared quickly throughout the crystal phase band when the temperature exceeded the monohydrate peritectic temperature. These liquid crystal regions appeared at distances from the original interface far beyond the range allowed by the diffusive transport of water. Further, the formation of liquid crystals was not accompanied by movement of the crystal/liquid interface; that is, no swelling of the crystal phase band occurred. (Normally, the intrusion of water into a crystal phase causes the interface to move in the direction of the water band.)

These observations are consistent with the premise that a liquid crystal is formed by rapid congruent melting of the monohydrate crystal. This liquid crystal is supersaturated with water, because the equilibrium state at this temperature consist of the aqueous liquid plus the dry crystal. Further, the liquid crystal is formed below the Krafft eutectic temperature (below which equilibrium liquid crystals do not exist). Above the Krafft eutectic temperature, normal swelling is observed.

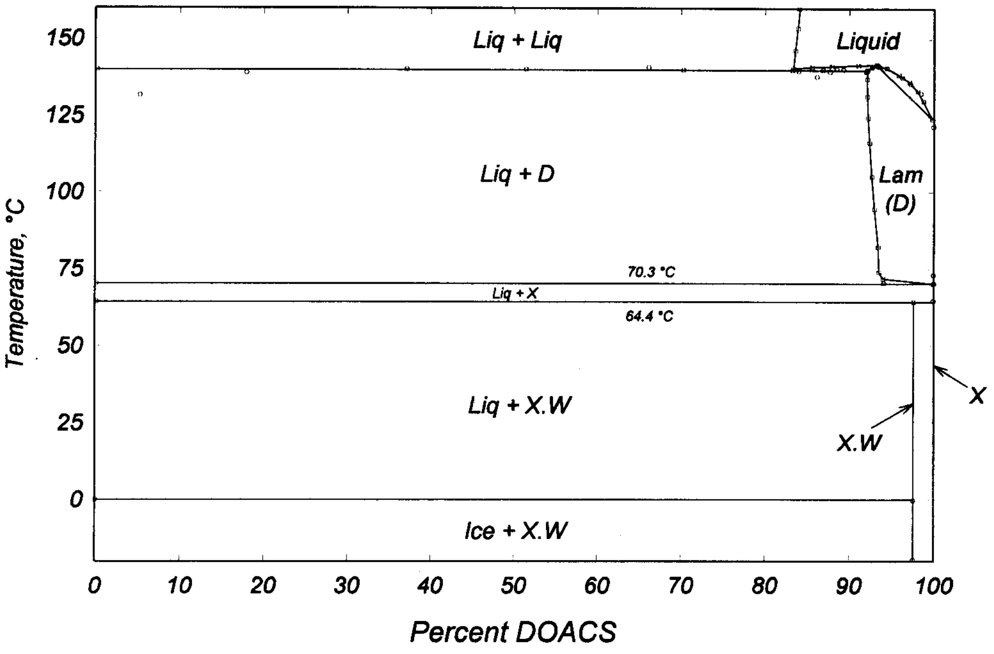


Figure 3. The dioctadecylammonium cumenesulfonate-water phase diagram [28]. Note the tiny area occupied by the lamellar liquid crystal phase, the unusual existence of thermotropic liquid crystals along the 100% border, and the fact that the monohydrate peritectic temperature (64.4 °C) lies below the Krafft eutectic temperature (70.2 °C).

4. NONSURFACTANT SYSTEMS.

Little information on the mechanism of phase reactions exists in the phase literature of nonsurfactant systems, but it seems likely that similar rules prevail with one important exception: the congruent melting of nonsurfactant crystal hydrates likely produces initially a metastable *liquid* phase, rather than a metastable liquid crystal phase. This is suggested, for example, by the physical behavior of sodium sulfate decahydrate [29]. The phase diagram of this system (Figure 4) shows that this phase compound disproportionates at a classical peritectic discontinuity to the dry crystal plus the saturated solution (ca. 33%). This system is somewhat unusual in that no equilibrium crystal hydrates of intermediate composition exist, but a metastable heptahydrate does exist which is far more soluble and has a lower peritectic decomposition temperature than does the decahydrate.

It is easily possible to measure in a conventional manner the "freezing point" of this decahydrate. This signifies that equilibrium of state is rapidly attained on cooling. One may add to this phase compound another

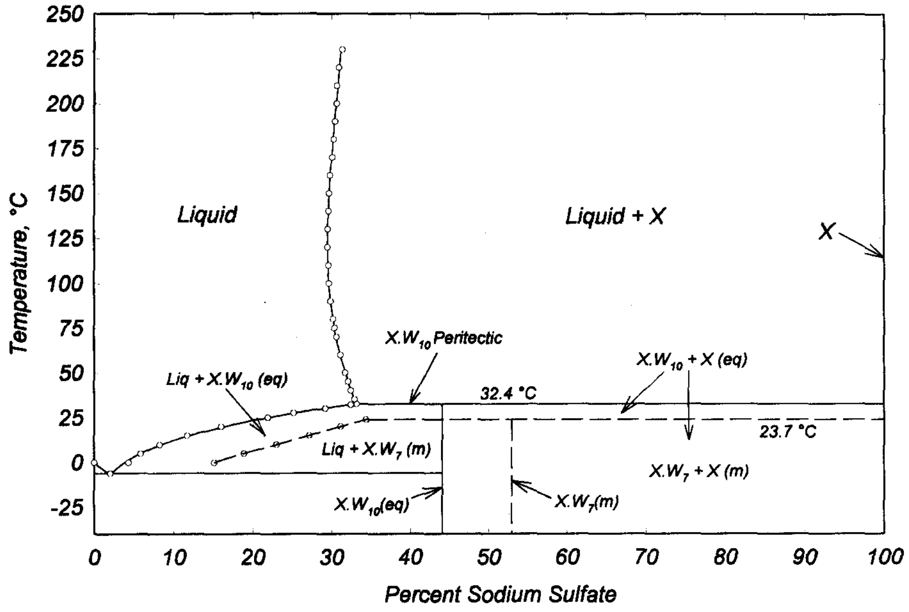
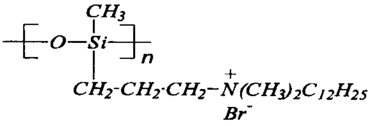


Figure 4. The sodium sulfate-water diagram [29], showing the decahydrate ($X.W_{10}$) peritectic which figures in the determination of the molecular weight of polyanions. Note also the metastable heptahydrate ($X.W_7$) which is more soluble and has a lower peritectic temperature than the equilibrium decahydrate.

material, and redetermine the "freezing point". "Freezing point depression" is typically observed when water-soluble sodium salts are present, and (in the days before negative ion mass spectrometry) the magnitude of the "freezing point depression" could be analyzed (using a Clausius-Clapeyron thermodynamic model) to estimate the molecular weight of the anion of the added sodium salt [30]. The sodium ion of the added salt has no effect on the freezing point depression - but if a potassium salt were added the potassium ion as well would influence the freezing point. Extensive explorations of not only this phase transformation, but of other classes of simple and complex phase transformations, have been performed in attempts to develop useful methods for determining the molecular weights of anions [31]. This method was used successfully to investigate the chemical stability of sodium tripolyphosphate [30], and also to determine the degree of polymerization of polysiloxane polycations having the structure



$$\left[-O-\overset{CH_3}{\underset{CH_2\text{-}CH_2\text{-}CH_2-\overset{+}{N}(CH_3)_2C_{12}H_{25}\;Br^-}{Si}}-\right]_n$$

For these investigations the hexahydrate of calcium bromide was used, so as to eliminate the influence of bromide ion on the results. The data obtained suggested that the average degree of polymerization (n in the above formula) was about fifteen [32].

These experiments suggest that both the forward and reverse peritectic phase reactions of sodium sulfate decahydrate behave in a manner resembling melting points, which in turn implies that the mechanism of this peritectic reaction is similar to that found at surfactant crystal hydrate peritectics. Formation of the crystal hydrate of sodium sulfate from the dry crystal and the saturated solution is unusually fast, as might have been expected from the high concentration of sodium sulfate in the liquid phase. If this analysis is valid, then it may be inferred that the above suggested reaction mechanism for the peritectic reaction may be widely applicable. Further work will be required to establish with certainty whether or not this is true.

5. EUTECTICS.

It may be expected that eutectic phase reactions in the cooling direction proceed via mechanisms analogous to those documented (above) at peritectic discontinuities. The conditions are the same in both instances: the phase reaction which occurs involves disproportionation in composition, and the entropy change during supercooling is very small while the entropy of crystal formation is highly unfavorable.

6. KINETICALLY- VS. THERMODYNAMICALLY-FAVORED PHASE REACTIONS.

It was noted above that all congruent phase reactions occur simply in a mechanistic sense. However, it is also important (as suggested by a referee) to recognize that congruent phase reactions (while simple mechanistically) do *not* always produce the thermodynamically-favored phase reaction product; kinetically-favored states may result instead. An excellent illustration of this principle is found in the physical science of the triglycerides [33].

The equilibrium crystal phase of a pure symmetrical saturated triglyceride (such as tristearin) is typically the β polymorphic phase, which is rapidly converted at its melting point by isothermal addition of heat to the equilibrium liquid phase. Provided nucleation crystals exist, the β crystal is rapidly reformed from the liquid by cooling. However, if the liquid (free of crystals) is cooled sufficiently rapidly severe supercooling occurs, and the initially-formed crystal is the α polymorph. This structurally disordered and metastable crystal is transformed on warming (well below the melting point of the β crystal) into a third (β') crystal, which on further warming is transformed (also below the melting point of the β crystal) into the β crystal. Cooling the β crystal, once formed, does *not* regenerate either the α or the β' crystal phases. The phase structures of all these polymorphs and the enthalpic differences between them have been determined.

Such phenomena are widely encountered in triglycerides and related long-chain molecules. They play an especially important role in the engineering of fats and oils technologies, and strongly influence the quality of foods such as chocolate.

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