

# Inorganic Reactions in Organized Media



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## PREFACE

The symposium, "Inorganic Reactions in Organized Media," and this volume grew out of the editor's belief that, while organic chemists have paid due attention to reactions in organized media, (that is, micelles, microemulsions, and vesicles), inorganic chemists as a group have virtually ignored the potential utility of these systems. Indeed, if one surveys the literature, he/she will be struck by the innumerable uses that have been found by the organic and physical chemists for organized media, yet how paltry are the references to reactions that involve inorganic species. As a consequence, it was deemed desirable to bring together not only inorganic chemists who are working in structured solutions, but also those individuals in other disciplines who have acknowledged expertise in the area. In this way, new insight may be developed into ways in which organized media can beneficially be used in the study of inorganic reactions and mechanisms.

A variety of interactions are examined in this volume. The first paper provides a general background on structures obtained from surfactant association and references some of the important literature in the area. The next five chapters focus on photochemical processes in organized assemblies. Chapter 2 focuses on cage and magnetic isotope effects of micellization. Chapter 3 discusses light-induced electron-transport processes in micellar systems and Chapter 4 addresses photoprocesses in synthetic vesicles. Chapter 5, 6, and 7 describe exciting new developments in the study of photoinduced reactions at the surface of colloidal oxides. Of particular importance are studies involving the photochemical splitting of water and hydrogen sulfide discussed in Chapter 7. Chapter 8 describes work wherein micelle-like structures, which modify electrochemical reactivity, are formed on platinum electrodes when surfactant is introduced into particular systems.

Chapters 9 through 12 focus on the use of microemulsions to modify reaction rate and pathway. Included are studies of porphyrin metalation, transmetalation, the Wacker process, and the hydrolysis of chlorophyll.

The last two chapters deal with chemical reactions in solids and solid surfaces, bridging the final gap between reactions in organized liquids and reactions in crystalline solids.

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September 1, 1981

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# Surfactant Association Structures

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The phase regions for micellar solutions and lyotropic liquid crystals form a complicated pattern in water/amphiphile/hydrocarbon systems. The present treatment emphasizes the fact that they may be considered as parts of a continuous solubility region similar to the one for water/short chain amphiphilic systems such as water/ethanol/ethyl acetate.

Hence the different phases may be visualized as a series of association structures with increasing complexity from the monomeric to the liquid crystalline state. The transfer from the monomeric state to the inverse micellar structure is discussed for two special cases and it is shown that packing constraints may prevent the formation of inverse micelles. Instead a liquid crystalline phase may form.

The surfactant association structures have a long history of research ranging from the McBain introduction of the aqueous micellar concept<sup>(1)</sup> over the interpretation of micellization as a critical phenomenon<sup>(2,3)</sup> to the analysis of the structure of lyotropic liquid crystals<sup>(4)</sup> and the comprehensive picture of the phase relations in water/surfactant/amphiphile systems.<sup>(5)</sup> These studies have emphasized the relation between the association structures in isotropic liquid solutions and the liquid crystalline phases. Parallel extensive investigations in crystalline/liquid crystalline lipid structures<sup>(6,7)</sup> have provided important insight in the mechanisms of the associations.

The thermodynamics of these systems have been extensively discussed in recent years including the micellization,<sup>(8,9)</sup> the liquid crystals<sup>(10)</sup> and inverse micellization.<sup>(11,12)</sup> In addition the more general problem of the stability of microemulsions has been extensively covered.<sup>(13-16)</sup>

This article will, in addition to a short description of the essential features of surfactant systems in general, concentrate on the energy conditions in premicellar aggregates, the transition premicellar aggregates/inverse micellar structures and the direct transition premicellar aggregates/lyotropic liquid crystals.

### Surfactant Systems - A Word of Caution

The inverse micellar solubility areas in systems of water, surfactants and a third amphiphilic substance frequently are of a shape according to Fig. 1. <sup>(17)</sup> Such shapes are also found in W/O microemulsions <sup>(18,19)</sup> when water solubility is plotted against cosurfactant/surfactant fraction.

It is tempting to evaluate this solubility curve as showing a maximum of water solubility at the apex point.

It is essential to realize that any thermodynamic evaluation of this solubility "maximum" with standard reference conditions in the form of the three pure components in liquid form is a futile exercise. The complete phase diagram, Fig. 2, shows the "maximum" of the solubility area to mark only a change in the structure of the phase in equilibrium with the solubility region. The maximum of the solubility is a reflection of the fact that the water as equilibrium body is replaced by a lamellar liquid crystalline phase. Since this phase transition obviously is more related to packing constraints <sup>(8)</sup> than enthalpy of formation <sup>(20)</sup> a view of the different phases as one continuous region such as in the short chain compounds water/ethanol/ethyl acetate, Fig. 3, is realistic. The three phases in the complete diagram, Fig. 2, may be perceived as a continuous solubility area with different packing conditions in different parts (Fig. 4).

This means that the phase changes observed have comparatively less importance for the thermodynamics of the system. On the other hand, the changes and modifications of the association structures within the isotropic liquid hydrocarbon or alcohol phase pose a series of interesting problems. Some of these have recently been treated in review articles by Fendler <sup>(21)</sup> who focussed on surfactant inter-association emphasizing consecutive equilibria and their thermodynamics. The following description will focus on the intermolecular interaction between different kinds of molecules and the importance of these interactions for the "inverse" association structures.

It should be emphasized that these structural changes within a one-phase region may change the kinetics of a chemical reaction in a pronounced manner. As an example may be mentioned the catalytic effect of inverse micelles on ester hydrolysis. Fig. 5 is from the first publication <sup>(22)</sup> on this subject. It clearly shows the lack of catalytic effect by the premicellar aggregates and the sudden increase of hydrolysis rate in the concentration range where the inverse micelles begin being formed.

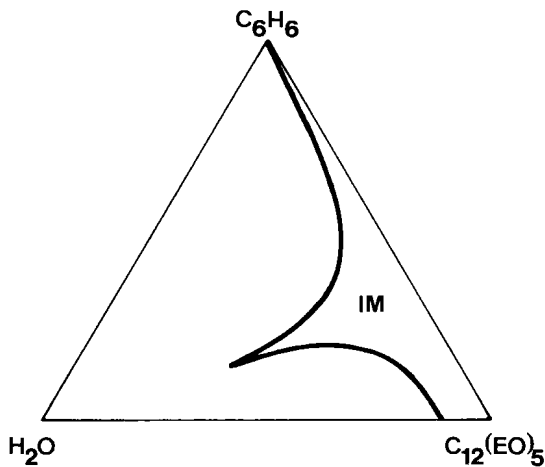


Figure 1. The solubility area of water in a hydrocarbon ( $C_6H_6$ ) penta(ethylene glycol) dodecyl ether ( $C_{12}[EO]_5$ ) solution at  $30^\circ C$ . Key: IM, inverse micellar solution.

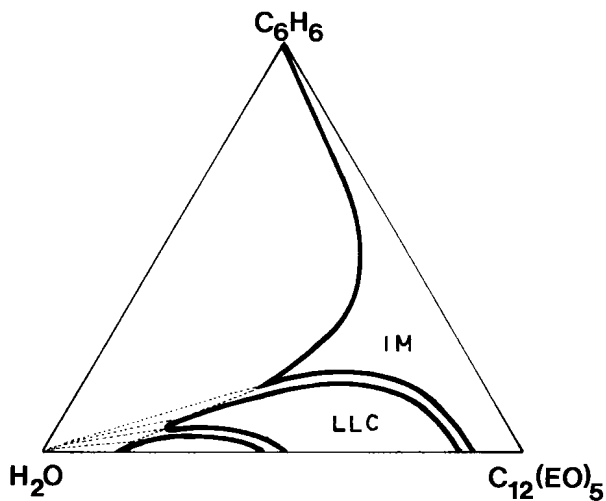


Figure 2. The phase diagram water/benzene/penta(ethylene glycol) dodecyl ether at  $30^\circ C$ . Key: IM, inverse micellar solution; LLC, lamellar liquid crystal; and unmarked, aqueous micellar solution.

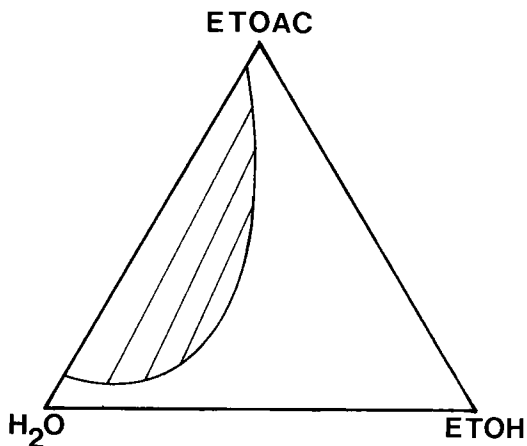


Figure 3. The phase diagram water/ethanol (ETOH)/ethyl acetate (ETOAC).

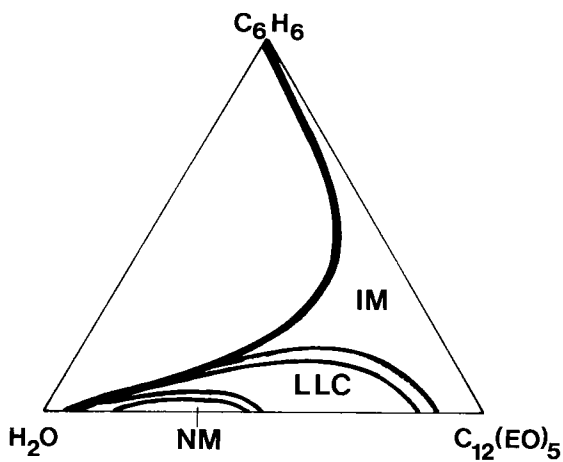


Figure 4. The similarity of Figure 3 to Figure 4 is seen if the maximum solubility of water is emphasized.

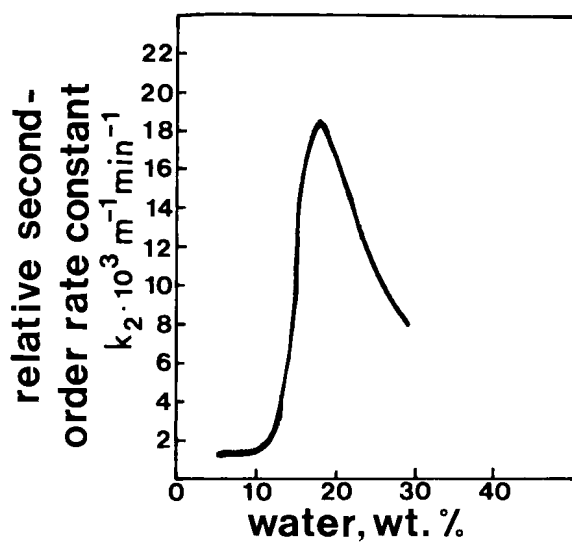


Figure 5. The premicellar aggregates (< 12% water) do not catalyze the hydrolysis of an ester (22).

Two solutions to illustrate these structural changes within one phase were chosen with emphasis both on their practical importance and on the pronounced difference in behavior brought about by a small difference in composition. The two liquids chosen are both soap/water solutions in a) an alcohol and b) a carboxylic acid. The alcohol solutions form the basis for the W/O micro-emulsions<sup>(18)</sup> and the carboxylic acid solutions show a pronounced difference in properties which merit an evaluation of the intermolecular forces between the solvent and the solute. The primary difference is in the minimum concentration of water that is required to form the solution.

#### Minimum Water Content

The two inverse micellar solutions will first briefly be described followed by an evaluation of the available experimental and theoretical information.

The Sodium Carboxylate/Carboxylic Acid System. This system has been investigated using IR and NMR<sup>(23)</sup> showing the extremely strong hydrogen bonds present. It appeared evident early that the strong hydrogen bonds between ionized and nonionized carboxylic groups were responsible for the stability of the 4 acid:2 soap complex<sup>(24)</sup> but no information could be obtained on the energy for formation of the complex nor could the stability be based on a thermodynamic calculation.

An answer has been given after calculations of the binding energies using the CNDO/2 semi-empirical approach<sup>(25)</sup> to quantum mechanical calculations. The results<sup>(26)</sup> illustrated the importance both of the hydrogen bond and the carbonyl/sodium ion ligand bond of the proposed structure. The values for the hydrogen bond strength (19.5 Kcal/mole, 82 kJ/mole) compared well with the generally accepted values for other ion/molecule systems.<sup>(28)</sup> In addition to the hydrogen bond the 4:2 molecular compound is stabilized by the acid carbonyl/sodium ligand bond, 36.1 kcal/mole (151 kJ/mole).

The calculations<sup>(27)</sup> involving a thermodynamic cycle from the solid crystalline soap and the liquid acid as reference states showed the 4:2 complex to be stable even in the gaseous state. The transition from gaseous to liquid state should give further stabilization to the structure. The excellent stability of the compound was illustrated by the fact that dilutions to a composition of the 7% sodium octanoate/octanoic acid, 93% by weight CCL<sub>4</sub>, gave no change of the structure.

These conditions are conspicuously in contrast with those in the carboxylate/alcohol system.

The Carboxylate/Alcohol System. A comparison between different alcohol solubility areas with different surfactants and water<sup>(5)</sup> reveals the fact that a minimum water/surfactant ratio

is necessary in order to ensure solubility of the surfactant in the alcohol. This is in contrast to the behavior of a liquid carboxylic acid that will dissolve a soap with no water present<sup>(29)</sup> (Fig. 6).

The difference is pronounced. In an alcohol solution a minimum of approximately six water molecules are required per soap to bring it into solution. A liquid carboxylic acid will dissolve the soap without water to a soap/acid molecular ratio of 1/2. It appears reasonable to evaluate these differences from terms of intermolecular forces. These forces, the strong hydrogen bonds and ligand bonds to the metal ion will be treated in the following section.

Experimental Information. The review by Ekwall<sup>(5)</sup> offers a whole series of phase diagrams which all show similar behavior. In order to dissolve an anionic surfactant with a sodium counter ion in an alcohol a minimum water/surfactant molar ratio of about six is needed to achieve solubility. The corresponding ratio for the potassium ion is three.

At the same time investigations using light scattering, electron microscopy, positron annihilation, dielectricity and transport properties<sup>(19,30-34)</sup> indicated the surfactant molecules not to be involved in associations to colloidal size aggregates at these low water contents. The low light scattering intensity rather points to the surfactant molecules not to be inter-associated (Fig. 7).

An approximate thermodynamic evaluation<sup>(27)</sup> based on liquid water and crystalline sodium octanoate as reference states has recently evaluated the energy conditions in the premicellar aggregate. The calculations essentially were concerned with the free energy of a gaseous soap/water complex. No attempt was made to evaluate the chemical potential changes in any of the components when dissolved in the pentanol.

Accepting the facts that the calculations may be considered a zero order approach, the results are illustrative of the reason for the stability of these small aggregates. The calculations included heat of evaporation of the surfactant, heat of evaporation of water and the free energy association in the gaseous phase. The enthalpy of the latter was calculated using the CDNO/2 approach<sup>(25)</sup> modified for larger aggregates.<sup>(35)</sup>

CDNO/2 has a proven record for accuracy in describing the energy of interaction for water clusters around metal ions in aqueous solutions.<sup>(36,37)</sup> The entropic contribution due to the different spatial arrangements of the particles was calculated using the liquid volume according to Ruckenstein<sup>(13)</sup> and Reiss.<sup>(38)</sup>

The following model was employed. The water molecules were consecutively entered into a regular octahedron around the sodium ion with the two first water molecules hydrogen bonded to the carboxylate group. Water molecules in excess of the six first



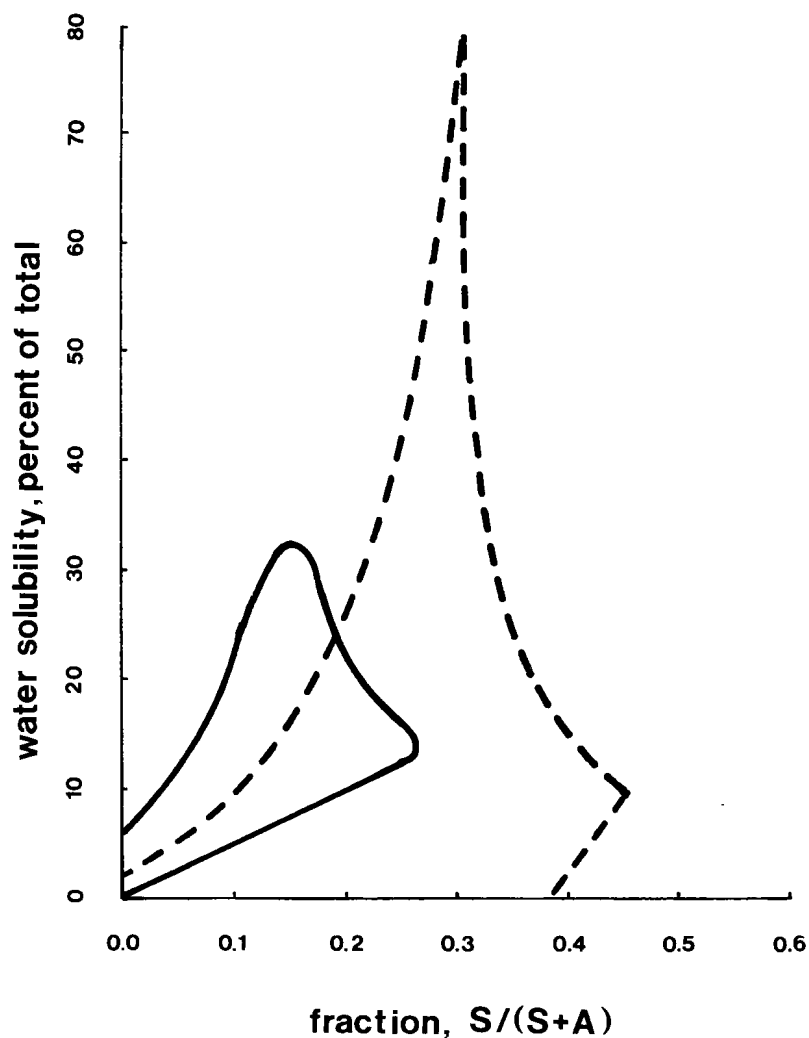


Figure 6. The solubility of water (weight percent of total) in sodium octanoate (S)/octanoic acid (A) (---) and sodium octanoate (S)/octanol (A) (—) mixtures (weight fraction).