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BINARY AND MULTICOMPONENT SOLUTIONS OF AMPHIPHILIC COMPOUNDS. SOLUBILIZATION AND THE FORMATION, STRUCTURE, AND THEORETICAL SIGNIFICANCE OF LIQUID CRYSTALLINE SOLUTIONS

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CONTENTS

I. INTRODUCTION

A. SCOPE

This article presents a selective and critical account of certain aspects of binary and multicomponent solutions of amphiphilic compounds. The general treatment is from the point of view of the *R* theory (131, 132) which is briefly recapitulated in the introductory section of the article. Modifications and extensions of the *R* theory as originally proposed, which are required by recent work, are at the same time discussed. This has required the presentation in the introductory section of conclusions, the experimental evidence for which is given in detail only later in the review. Emphasis is laid on the formation and structure of liquid crystalline solutions whose study, particularly by X-ray diffraction methods, has been one of the main sources of advance in the understanding of the constitution of amphiphile solutions over the last decade. Literature cited is mainly that published from 1954 onward. The earlier literature has already been well covered in books and review articles by several authors. Complete literature coverage is not attempted, but the citations given provide further references relevant to the particular aspects under consideration. A number of relevant recent symposia are covered by ref 13, 15, 16, 18, 23, 31, 40, 71, 81, 111. Books and review articles are provided by ref 37, 38, 63, 85, 87, 90, 131, 132.

B. DEFINITIONS

1. Amphiphilic Compounds

Amphiphilic compounds are characterized by possessing in the same molecule two groups which differ greatly in their solubility relationships. These are (i) a hydrophilic group which tends to be water soluble and hydrocarbon insoluble and (ii) a lipophilic group which tends to be hydrocarbon soluble and water insoluble. Typical hydrophilic groups are $-OH$, $-O(CH_2CH_2O)_nH$, $-CO_2Na$, $-SO_3K$, $-NMe_3Br$; typical lipophilic groups are $-C_nH_{2n+1}$, $-C_{17}H_{33}$, and $C_8H_{17}O_2C\underset{|}{C}H{-}CH_2CO_2C_8H_{17}$.

According to the relative magnitudes of the hydrophilic and lipophilic functions of the two groups, amphiphilic compounds may range from predominantly hydrophilic, water soluble and hydrocarbon insoluble (*e.g.*, $C_nH_{2n+1}CO_2K$, where $n = 1$ to 3), to predominantly lipophilic, hydrocarbon soluble and water insoluble (*e.g.*, $C_nH_{2n+1}OH$, where $n > 12$).

The most striking amphiphilic properties (micelle formation, formation of liquid crystalline solutions, solubilization, etc.) are shown most markedly by amphiphilic compounds, or mixtures of amphiphilic compounds, in which both the hydrophilic and lipophilic functions are strong and not too unequally matched (*e.g.*, $C_nH_{2n+1}CO_2Na$, where $n = 8$–20).

2. Solubilization

As a consequence of their dual character, such amphiphilic compounds or, more shortly, amphiphiles, possess certain striking solubility characteristics. Thus they tend to be miscible with both water and hydrocarbon. As a consequence of this, they show marked cosolvent effects. For example, a moderately concentrated aqueous soap solution is able to take into thermodynamically stable solution various organic compounds which in absence of soap show only a very small solubility in water. This phenomenon was termed "solubilization" by McBain (87) before its mechanism was understood. In a similar way a suitable amphiphile, for example, Aerosol OT (section II.A.2.a), dissolved in a hydrocarbon is able to solubilize water or an organic liquid (*e.g.*, ethylene glycol) which in the absence of the amphiphile is insoluble in the hydrocarbon.

In such systems, though it is common to speak of hydrocarbon solubilized *in* water by soap or of water solubilized *in* hydrocarbon by Aerosol OT, it is better to regard water and hydrocarbon as solubilized with amphiphile, the amphiphile acting as cosolvent.

3. Micelles

In an ideal solution of two or more nonpolar liquids, by definition all types of molecule statistically interact with each other equally and symmetrically, and under the influence of the thermal motion a random arrangement of the molecules arises. In a real solution derived from molecules of different types, and even in pure liquids containing polar molecules, a random arrangement no longer occurs.

Thus in water (57) itself, on account of the $^-O{-}H^+$ dipole, there is a tendency for intermolecular hydrogen bonding and for local groupings of molecules to arise in which each oxygen atom is surrounded tetrahedrally by four hydrogen atoms. This tendency, which probably plays a part in the stabilization of the majority of liquid crystalline phases considered below (*cf.* section III.B.3) becomes progressively less with increasing temperature as the disorganizing thermal motion of the molecules increases. As a further example of local ordering, the retention, when the higher alcohols are melted, of short-range ordering into lamellar regions simulating the crystal form, may be mentioned (121).

In solutions of amphiphiles in either aqueous or hydrocarbon solvents, there is a tendency for groupings of molecules to arise in which like is associated with like (*cf.* sections III.B.2 and IV.A.1). Thus in aqueous solutions of paraffin-chain salts, the nonpolar paraffin chains tend to associate together in fluid arrangement, leaving the polar groups in association with the polar water molecules. These local groupings will fluctuate under the influence of the thermal motion and will be in equilibrium with neighboring molecules. The essentially transitory groupings of amphiphile molecules arising in this way are termed micelles.

A simple form of micelle early recognized by Hartley (37) consists of a spherical aggregate of amphiphile molecules with the polar groups on its surface and the hydrocarbon chains forming a fluid core. This type of micelle predominates in isotropic aqueous soap solutions at rather low concentrations. It is, however, a very mobile structure, and on dilution of the solution it dissociates extremely rapidly (37, 52, 54, 65, 89, 92, 96). At higher concentrations, as will be discussed in more detail later, it is progressively replaced by more extended micellar forms, the forms fluctuating locally with the thermal motion and the average form changing with temperature and concentration (17, 18, 95, 131, 132).

Micelles are therefore of a statistical character, and it is important to guard against a general picture of micelles as persistent entities having well-defined geometrical shapes (40, 66). In certain special circumstances, however (for example, in liquid crystalline phases, as discussed in detail below), micellar groupings show marked persistence and long-range intermicellar order, but even here any local change in conditions, *e.g.*, in temperature, concentration, or shearing, will immediately alter them. Thus although attempts to dry, centrifuge, filter, and stain micelles have been made, such efforts necessarily tend to alter the micelles under investigation and lead to results which must be interpreted with caution (40, 74, 125).

C. MICELLAR CONSTITUTION OF SOLUTIONS OF AMPHIPHILES

1. Nature of Types of Intermolecular Forces Involved

Before the statistical structure (micellar constitution) of solutions of amphiphiles is discussed, the nature of the two main types of intermolecular forces, *viz.*, electrostatic and electrokinetic, which are operative in the systems under discussion, will be recalled. These are as follows.

a. Electrostatic (Hydrophilic) Interactions

These arise from the charges on ions and from the uneven distribution of charge in certain electrically neutral molecules (dipoles). Interaction between ions and dipoles leads to attractive orientations. These, however, tend to be destroyed by the thermal motion of the molecules and will decrease with rising temperature. The physical character of water and its solvent properties are largely determined by the electrostatic forces due to the $^-O–H^+$ dipole. Electrostatic interactions thus contribute mainly to hydrophilic character and have therefore been denoted by A_H in the following discussion.

b. Electrokinetic (Lipophilic) Interactions

Molecules which are electrically nonpolar and thus show no electrostatic interaction still attract one another. The attractive forces here are again electrical and are due to the movements of the electrons within the molecules. In neighboring molecules these movements tend to become in phase with each other and thus produce attraction. This electrokinetic interaction is almost wholly responsible for the interaction between paraffin molecules and conditions their lipophilic character. In what follows, electrokinetic interactions will therefore be denoted by A_L.

In a binary solution the molecular interactions may therefore be denoted by

$A_{AA} = A_{H_{AA}} + A_{L_{AA}}$ tending to promote clustering of molecules of A and ultimately phase separation

$A_{BB} = A_{H_{BB}} + A_{L_{BB}}$ tending to promote clustering of molecules of B and ultimately phase separation

$A_{AB} = A_{H_{AB}} + A_{L_{AB}}$ tending to promote mixing of molecules of A and B

All these interactions will be dependent on temperature and concentration.

2. Factors Affecting Micellar Shape. The R Theory and Accompanying Phase Classification

A characteristic feature both of binary aqueous solutions of amphiphiles and of solutions containing additional solubilized components is the formation, over certain ranges of composition and temperature which are well defined for each individual system, of liquid crystalline solutions. Several types of liquid crystalline solution are now well authenticated and will be discussed in detail below.

The most widely occurring and first recognized type of liquid crystalline solution has a lamellar structure as indicated in the top center of Figure 1, "neat phase" (G). In this phase, which arises under conditions to be considered further below, there are alternate extended aqueous ($\overline{W}$) and organic ($\bar{O}$) lamellae, both liquid in character (II.A.1.c). Intervening lamellae of amphiphile molecules ($\overline{C}$), also liquid in character, provide the uniting bridge between the aqueous ($\overline{W}$) and organic ($\bar{O}$) regions of the liquid crystalline solution. The barred symbols, $\overline{W}$, $\bar{O}$, $\overline{C}$, etc., are used because in multicomponent systems each region, as will shortly be discussed, may contain a number of components, these being distributed between the regions according to their solvent characteristics.

The organic region, $\bar{O}$, in a simple binary aqueous solution of an amphiphile is supplied by the juxtaposi-

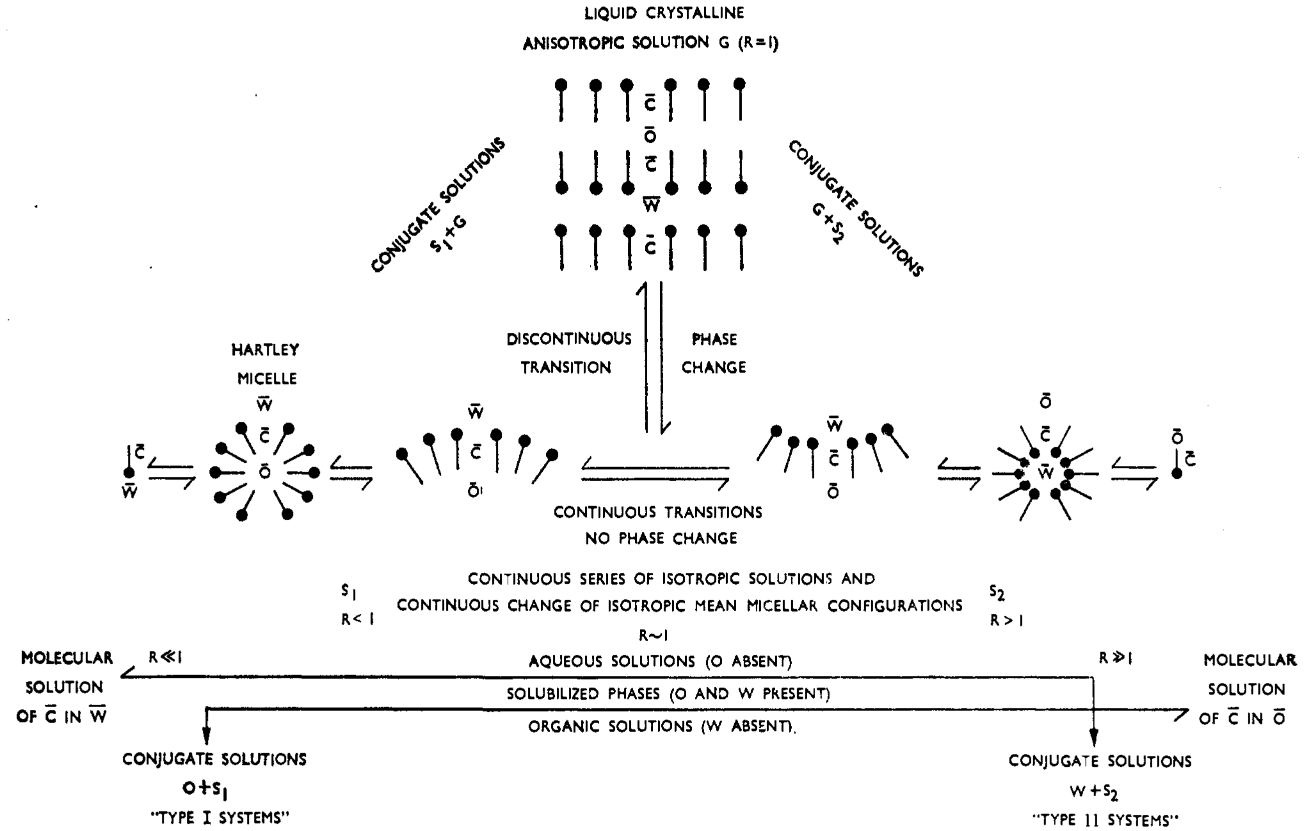

Figure 1.—Schematic illustrations of changes in the mean equilibrium form of the $\bar{C}$ region and of the resulting phase changes in aqueous and nonaqueous soap solutions and in solubilized phases which occur with variation in the value of R in systems in which the only liquid crystalline phase encountered is the lamellar phase, G.

tion of the hydrocarbon chains of the amphiphile layers themselves.

In a binary lamellar liquid crystalline phase, such as that formed from Aerosol MA (II.A.2.a) and water, additional hydrocarbon can be dissolved (solubilized) mainly (*cf.* section IV.A.1) within the hydrocarbon region, $\bar{O}$, of the solution. Inorganic salts or water-soluble organic materials (*e.g.*, methanol, sodium acetate, sugar, urea) can be dissolved mainly within the aqueous region, $\bar{\bar{W}}$, of the solution. Finally, water-insoluble amphiphilic molecules (*e.g.*, octan-1-ol) can be dissolved by incorporation mainly into the $\bar{C}$ region, their polar groups lying among the ionic groups and neighboring water molecules and their hydrocarbon groups lying among the hydrocarbon groups of the amphiphilic salt within the $\bar{O}$ region.

The extent of the solubilization of any of these components and likewise the amphiphile/water ratio, which are consistent with the stability of the lamellar phase, are limited, and changes in composition beyond these limits lead to breakdown of the lamellar liquid crystal with the production of new phases as discussed further below.

The essential feature of a lamellar liquid crystalline solution or G phase is a fluid planar amphiphilic monolayer, $\bar{C}$, which, within certain limits, is capable of dimensional changes with variation in temperature and concentration so that its effective thickness and the effective area per polar group are dependently adjustable (49, 74–77, 131). This planar $\bar{C}$ layer has a fluid aqueous environment, $\bar{W}$, on one side and on the other a fluid organic environment, $\bar{O}$, which is provided either by the juxtaposition of a second monolayer or by a combination of this process with the solubilization of nonpolar organic molecules.

The lamellar character of the liquid crystalline G phase indicates clearly that, within the range of stability of this phase, the flexible bridging amphiphilic monolayer, C, between the $\bar{O}$ and $\bar{W}$ regions shows no predominant tendency to become either concave or convex toward either the $\bar{O}$ or $\bar{W}$ environments. If we consider a ratio

$$R = \frac{\text{tendency of } \bar{C} \text{ to beome convex toward } \bar{O}}{\text{tendency of } \bar{C} \text{ to become convex toward } \bar{W}}$$

then it is evident that in the liquid crystalline lamellar G phase the ratio R must be uniformly one. (In other phases R may show small local fluctuations with the thermal motion or may be dependent on direction as discussed later.)

The tendency of the $\bar{C}$ region preferentially to spread out into the $\bar{O}$ region, *i.e.*, to become convex toward $\bar{O}$, will be assisted by $A_{\bar{C}\bar{O}}$ and resisted by $A_{\bar{O}\bar{O}}$. In this locally segregated system, A_{xy} will represent the interfacial interaction energy between x and y species per unit area of interface.

Similarly the tendency of the $\bar{C}$ region to become convex toward $\bar{W}$ will be assisted by $A_{\bar{C}\bar{W}}$ and resisted by $A_{\bar{W}\bar{W}}$. The way in which R will tend to vary in a particular system with changes in composition and temperature can therefore be considered on the basis of the relation

$$R = f\,\frac{A_{\bar{C}\bar{O}} - A_{\bar{O}\bar{O}}}{A_{\bar{C}\bar{W}} - A_{\bar{W}\bar{W}}}$$

or for a given $\bar{O}$ and $\bar{W}$

$$R = f\,\frac{A_{\bar{C}\bar{O}}}{A_{\bar{C}\bar{W}}} = f\,\frac{A_{\mathrm{H}\bar{C}\bar{O}} + A_{\mathrm{L}\bar{C}\bar{O}}}{A_{\mathrm{H}\bar{C}\bar{W}} + A_{\mathrm{L}\bar{C}\bar{W}}}$$

For example, if on a stable lamellar solution one imposed a gradual change (*e.g.*, dilution with water) which would tend relatively to increase $A_{\bar{C}\bar{W}}$, the stability of the lamellar phase could be maintained only by some internal rearrangement (increase in effective area per polar group accompanied by the dependent contraction in thickness of the $\bar{O}$ region) that restored the value of $R = 1$ (131d). If this degree of rearrangement were not energetically possible within the limits of the imposed change, then the lamellar phase G would break down giving a new phase (at first conjugate with remaining G) in which the $\bar{C}$ region was, on balance, convex toward $\bar{W}$.

Similarly, if on a stable lamellar phase one imposed a change which would tend relatively to decrease $A_{\bar{C}\bar{W}}$ (*e.g.*, removal of water or addition of an ionorganic salt to $\bar{W}$), the stability of the lamellar micelle could be maintained only by some internal rearrangement (decrease in area per polar group with dependent expansion in thickness of the $\bar{O}$ and $\bar{W}$ regions) that restored the value of $R = 1$. Beyond the limits where such rearrangements were energetically possible, the lamellar solution would break down giving a new micellar phase in which the $\bar{C}$ region was on balance concave toward $\bar{W}$. The possibility of the restoration of the value $R = 1$ by rearrangement (*e.g.*, increase in leaflet area, diminution in leaflet thickness) within the amphiphilic solution implies that $A_{\bar{C}\bar{O}}$ and $A_{\bar{C}\bar{W}}$ do not vary as precisely similar functions of area and thickness. From experimental evidence to be given later (II.A.1.d), it appears that $A_{\bar{C}\bar{O}}$ is comparatively little affected by the thickness of the $\bar{O}$ region. On the other hand, at least for an ionic amphiphile, $A_{\bar{C}\bar{W}}$ might be expected to be strongly dependent on the effective area per ionic group on the $\bar{W}$ face of the $\bar{C}$ region because of the increase in electrostatic repulsion between these groups with increasing proximity. The effect of any change in composition tending to increase $A_{\bar{C}\bar{W}}$ (*cf.* Table I, section I.C.2) could therefore, within limits, be offset by a lateral expansion and transverse contraction of the $\bar{C}$ region and, necessarily, of the accompanying $\bar{O}$ and $\bar{W}$ regions. If the stability of the lamellar micelle, as compared with that of other micellar forms, were favored on energetic grounds (93) additional to those involving the value of R, then the range of stability of the phase (consistent with the value $R = 1$) could thus be extended by dimensional changes of the type considered.

With the systems employed in the earlier experimental work (131) on the basis of which the R theory was developed, the breakdown of the G phase was always observed to occur with the formation of amorphous fluid phases (S_1 and S_2). Moreover, although at that time the existence of neat and middle liquid crystalline soap solutions (*cf.* below) as distinct phases was recognized, both were thought to be lamellar (107). The scheme suggested in Figure 1 was therefore proposed to interpret the phase changes observed with changes in composition with the particular systems investigated and with many others described in the literature.

More recently experimental and theoretical investigations, which are considered in detail later in this review, have made modifications of the above scheme necessary. In particular, it has been shown that, commencing with the lamellar G phase, changes in composition, which on the above view lead to a decrease or increase in R, do not always lead directly to the formation of amorphous fluid phases.

In many, though not all, binary aqueous amphiphile solutions, breakdown of the lamellar phase on dilution (decrease in R) leads first to the formation of a further liquid crystalline solution, whose structure has been shown by X-ray diffraction and other methods very probably to consist of amphiphile molecules micellized as cylindrical fibers of indefinite length (Figure 2, top left; "middle phase" (M_1)). These fibrous micelles contain a fluid hydrocarbon interior with the polar groups of the amphiphile molecules on its surface. Within local uniform domains the micelles themselves are parallel and disposed in a regular two-dimensional hexagonal array with intervening water. Over greater distances these domains may be contorted. The extent of uniformity will vary with local conditions, *e.g.*, shearing, presence of orienting surfaces, etc.

Certain instances of binary aqueous amphiphile solutions have also been found in which the lamellar liquid crystalline phase on increase in concentration (increase in R) breaks down to give a complementary inverse form of fibrous micelle in which the water and the polar groups together form the micellar core (Figure 2, top right; "inverse middle phase" (M_2)). These cores

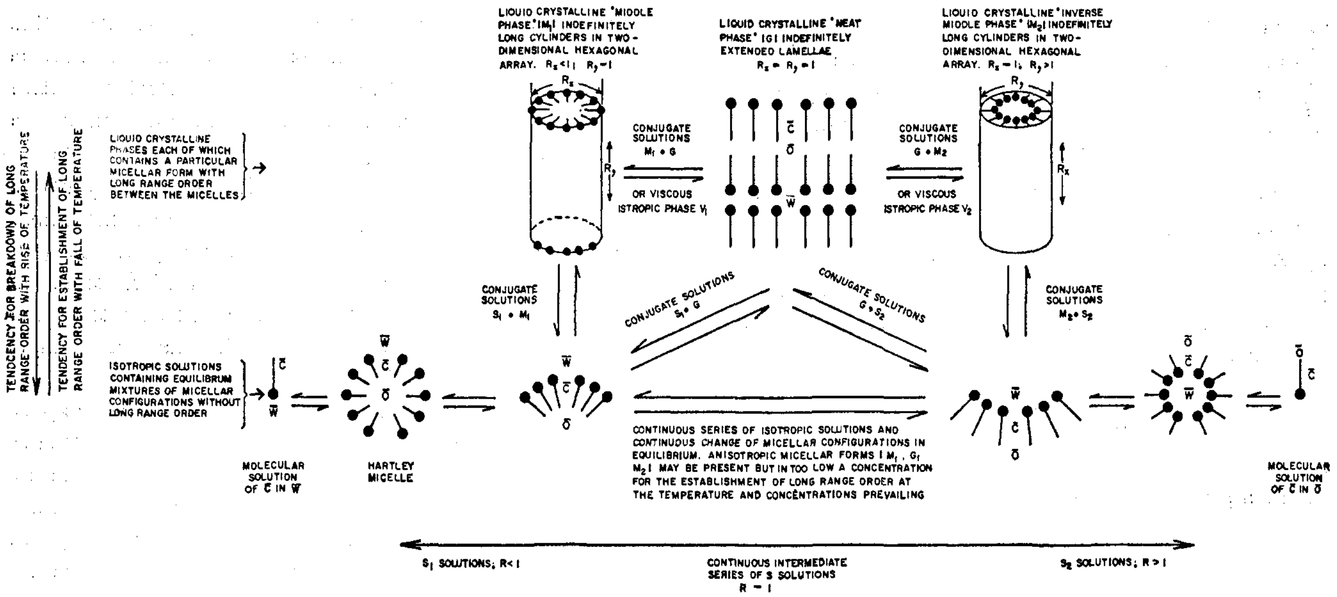

Figure 2.—Extension of scheme shown in Figure 1 to systems in which the liquid crystalline phases, M_1, V_1, G, V_2, and M_2, are encountered.

are again disposed in a two-dimensional hexagonal array. In this instance, the hydrocarbon chains of the amphiphile molecules form the intervening liquid between the fibrous cores.

The occurrence of the fibrous M_1 and M_2 phases is of great significance from the point of view of the *R* theory. In the *R* theory as originally proposed, the polar groups (then believed to be freely rotating) on the $\overline{W}$ side of the $\overline{C}$ layer and the hydrocarbon groups on its $\overline{O}$ side were considered to be in a mobile fluid state. The interactions about any polar group or hydrocarbon chain on either the $\overline{O}$ or $\overline{W}$ side of the $\overline{C}$ layer would therefore be distributed statistically in a radially uniform manner. This could lead only to forms of the $\overline{C}$ layer which were planar ($R = 1$) or tended toward uniform curvature toward $\overline{O}$ ($R > 1$; S_2 solution) or $\overline{W}$ ($R < 1$; S_1 solution) except in so far as the curvature might be modified locally by fluctuations in thermal motion. Stable extended cylindrical forms of micelle, such as have now been shown to form the constituent units of the M_1 and M_2 phases, were therefore then held to be unlikely.

In reaching this view, however, account was not taken of the possibility that the polar ends of the amphiphile molecules on the $\overline{C}$ face might exert non-radially symmetrical force fields which might cause these polar ends to take up an ordered pattern, their rotation being restricted.

In this case statistical radial symmetry would be lost and the spreading tendency about any point on the polar face of the $\overline{C}$ region need not be radially uniform but under certain conditions could vary with respect to the direction of mutual orientation of the polar ends. The term "polar end" rather than polar group is used here to take account of the fact that, on the $\overline{W}$ face of the $\overline{C}$ layer, not only the polar groups but a considerable area (increasing with dilution) of the neighboring methylene groups is in contact with the $\overline{W}$ region (*cf.* section II.A.1.f).

On this modified point of view, values of *R* in certain concentration ranges could be dependent on direction with respect to the mutually oriented polar groups. If $R_x = 1$ in one direction and $R_y < 1$ in a direction at right angles to it, the hydrophilic cylindrical M_1 micelles characterized in the middle M_1 phase would arise, the value $R_x = 1$ corresponding to the value of *R* along the cylinder (Figure 2). If $R_x > 1$ and $R_y = 1$, the lipophilic fibrous M_2 micelles characterized in the inverse middle phase would be produced.

Experimentally it is found that the M_1 and M_2 phases, like the G phase, remain stable at a given temperature over considerable ranges of composition. This implies, for reasons similar to those discussed above for the G phase, that the cylinder diameter and effective area per polar group (and probably also their relative mean interpolar separation distances in directions along and around the cylinders, respectively) must be interdependently variable and they will increase and decrease, respectively, with increase in concentration. These theoretical conclusions are well supported by the most recent X-ray evidence (28) although in earlier studies these effects were not detected for the M_1 phase (49, 74–77).

A modified and extended form of Figure 1 which includes also the M_1 and M_2 phases is shown in Figure 2. It will be noted in Figure 2 that additional phases are indicated as occurring in certain systems intermediate between the M_1 and G and the G and M_2 phases, re-

TABLE I

GENERAL METHODS FOR INFLUENCING PHASE EQUILIBRIA BY VARIATION OF R^a IN AMPHIPHILE SOLUTIONS CONTAINING AN ORGANIC LIQUID (O_1),^{b} AN AMPHIPHILIC SALT (C_1), AND WATER (W_1)

Method of classification	Details of method	Influence on R	Probable mechanism of influence on R	Effect on the phase ratio in an initially heterogeneous system containing any two in the following succession of phases^c (*cf.* Figure 2) O_1, S_1, M_1, V_1, G, V_2, M_2, S_2, W_1	Notes
Ia	Reduction in the relative proportion of W_1	R tends to be increased	$A_{\bar{C}\bar{W}}$ diminished by mass action	Increase in proportion of the right-hand phase present	Where a single-phase system is initially involved, the progressive application of a particular method will finally tend to the precipitation from this phase of the neighboring successional phase. With particular systems certain phases of the sequence do not appear, but the general order of succession with variation in R remains the same. Superimposed on the directional effects of methods Id and IIb is the general tendency of $\bar{W}$-soluble materials to inhibit the formation of liquid crystalline solutions (IV.B.8)
Ib	The addition to O_1 of an oil-soluble compound of more polar (hydrophilic) character than O_1. Alternatively, this may be regarded as the addition to C_1 of an amphiphilic compound more lipophilic than C_1	R tends to be increased	Reduction of $A_{H\bar{C}\bar{W}}$ by incorporation of amphiphilic additive in $\bar{C}$ layer and/or increase of $A_{H\bar{C}\bar{O}}$		
Ic	Increase in the relative lipophilic character of C_1, *e.g.*, by increase of molecular weight, substitution of an organic for an inorganic counterion, or by certain changes in constitution	R tends to be increased	$A_{L\bar{C}\bar{O}}$ increased and/or $A_{H\bar{C}\bar{W}}$ diminished		
Id	The addition to W_1 of an inorganic salt	R tends to be increased	$A_{H\bar{C}\bar{W}}$ diminished		
IIa	Reduction in the relative proportion of O_1	R tends to be decreased	$A_{\bar{C}\bar{O}}$ diminished by mass action	Increase in proportion of left-hand phase present	
IIb	The addition to W_1 of a water-soluble organic liquid of more lipophilic character	R tends to be decreased	$A_{L\bar{C}\bar{W}}$ increased		
IIc	Increase in the relative hydrophilic character of C_1, *i.e.*, method Ic in reverse	R tends to be decreased	$A_{H\bar{C}\bar{W}}$ increased and/or $A_{L\bar{C}\bar{O}}$ diminished		
IId	The addition to O_1 of a less hydrophilic oil-soluble component, *e.g.*, medicinal oil	R tends to be decreased	Reverse of mechanism of method Ib		

[a] $R = f(A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}}) = f[(A_{H\bar{C}\bar{O}} + A_{L\bar{C}\bar{O}})/(A_{H\bar{C}\bar{W}} + A_{L\bar{C}\bar{W}})]$. [b] If no organic liquid has been added O_1 must be taken to indicate the hydrocarbon region of the micellar system. [c] Here O_1 and W_1 indicate excess nonsolubilized organic or aqueous phase if present.

spectively. The detailed constitutions of these intermediate phases have not yet been fully established (II.A.1.e).

In the earlier work in which only the G liquid crystalline phase was recognized, a number of systematic methods were tabulated for varying R and for bringing about related phase changes. In amphiphile solutions in which the two principal values of R (R_x and R_y) are operative in determining micellar form, these methods would be expected to influence both R_x and R_y in a similar sense. The limited amount of experimental evidence as yet available supports this view, and an extension of the earlier scheme is given in Table I. At the moment, however, this extended scheme must be regarded as in some respects tentative and in certain details requiring further experimental corroboration (*cf.* section IV.B.7).

Table II shows the sequence of phase changes that are potentially realizable when a system, in which two principle R values, R_x and R_y, affect the mean form of the $\bar{C}$ layer, is subjected to a series of composition or temperature changes that tend to increase R.

It is unlikely that the mutual ordering of polar ends, which in the M_1 phase is thought to lead to the condition $R_x = 1$, $R_y < 1$, is lost in the G phase of higher concentration where, necessarily, $R_x = R_y = 1$. Although, as is evident from the experimentally established lamellar structure in this phase, both $R_x = A_{x\bar{C}\bar{O}}/A_{y\bar{C}\bar{W}}$ and $R_y = A_{y\bar{C}\bar{O}}/A_{y\bar{C}\bar{W}}$ are unity, this is not inconsistent with different values of $A_{x\bar{C}\bar{W}}$ and $A_{y\bar{C}\bar{W}}$ with compensating different values of $A_{x\bar{C}\bar{O}}$ and $A_{y\bar{C}\bar{O}}$.

Alternatively, even if, as might seem more likely from the apparent insensitivity of $A_{\bar{C}\bar{O}}$ to dimensional changes (II.A.1.d), $A_{x\bar{C}\bar{O}}$ and $A_{y\bar{C}\bar{O}}$ are equal, $A_{x\bar{C}\bar{W}}$ and $A_{y\bar{C}\bar{W}}$ could be maintained equal over the concentration range of the G phase by spontaneous adjustment of the relative mean interpolar separation distances in direc-

TABLE II

POTENTIAL PHASE CHANGES ACCOMPANYING A SERIES OF COMPOSITION CHANGES WHICH TEND TO INCREASE R IN A SYSTEM WHERE TWO PRINCIPAL R VALUES, R_x AND R_y, AFFECT THE MEAN FORM OF THE $\bar{C}$ LAYER

R_x	<1	1	1	>1	>>1
R_y	<<1	<1	1	1	>1

Phases present

$$S_1\ \underbrace{\underbrace{(S_1 + M_1)\ M_1\ (M_1 + G)^a}_{\text{may be replaced by } S_1 + G \text{ if } R_x = R_y}\ \ G\ \underbrace{(G + M_2)^a\ M_2\ (M_2 + S_2)}_{\text{may be replaced by } G + S_2 \text{ if } R_x = R_y}}_{\substack{\text{may be replaced by a continuous transition between } S_1 \text{ and } S_2 \\ \text{if the local concentration of } M_1\text{, G, or } M_2 \text{ micellar regions are} \\ \text{always insufficient to lead to the establishment of long-range} \\ \text{order at the temperature prevailing}}}\ S_2$$

[a] At higher temperatures the sequences $M_1 \rightarrow M_1 + S_1 \rightarrow S_1 \rightarrow S_1 + G \rightarrow G$ and $G + S_2 \rightarrow S_2 \rightarrow S_2 + M_2 \rightarrow M_2$ may appear (*cf.* Figures 2 and 3); further, in certain instances the place of the conjugate mixtures of (M_1 + G) and (G + M_2) may be taken by certain intermediate phases, in particular by the V_1 and V_2 phases, respectively (II.A.1.e). Additional mixtures of conjugate phases, *e.g.*, V_1 + G, G + V_2, etc., thus necessarily also arise.

tions corresponding to those along and around the M_1 micelles, respectively.

In general, as will be discussed in particular instances later, observed patterns of phase sequence are in line with the schemes indicated in Figure 2 and in Tables I and II. The complete potential phase sucession indicated in Table II has, however, probably not yet been realized in any single system. One or more individual phases in the sequence are usually absent (*cf.* section IV.B.7) but, when these absences are allowed for, the order of phase succession is always the same.

For example, with binary aqueous amphiphile solutions of gradually increasing concentration, Aerosol MA and Aerosol OT at room temperature show the phase sequence (conjugate mixtures being omitted)

$$S_1 \longrightarrow G \longrightarrow V_2 \longrightarrow M_2$$

Sodium undecane 3-sulfate shows the sequence

$$S_1 \longrightarrow M_1 \longrightarrow V_1 \longrightarrow G$$

Sodium laurate (section II.A.1, Figure 3) shows the sequence

$$S_1 \longrightarrow M_1 \longrightarrow G$$

at lower temperatures, while at higher temperatures the succession

$$S_1 \longrightarrow G \longrightarrow M_2$$

appears to occur (*cf.*, however, section II.A.1.g).

Circumstances in which these various types of behavior arise as well as the experimental evidence for the micellar structures in the individual phases will be considered in more detail in the later sections of this review.

II. Binary Aqueous Amphiphile Solutions

A. IONIC AMPHIPHILES

1. *Fatty Acid Soaps*

In recent years, studies on liquid crystalline systems, and preeminently the X-ray studies of Luzzati and associates at the Centre de Recherches sur les Macromolecules, Strasbourg, have provided much additional information on micellar constitution.

The advantage of liquid crystalline solutions for the X-ray study of micellar constitution is that each individual liquid crystalline phase (with the possible exception of the V_1 and V_2 phases and other "intermediate phases," section II.A.1.e) is made up of stable micelles of definite form arranged relatively to one another in a definite extended persistent geometrical pattern. In the amorphous (S_1, S_2) micellar solutions, on the other hand, an equilibrium of micellar forms occurs (*cf.* section II.A.1.f), and there is no extended or persistent long-range pattern. For these reasons the sharp X-ray diffraction bands obtained from liquid crystalline solutions are well defined and more easily interpreted theoretically than the diffuse bands obtained from the amorphous S_1 solutions toward which earlier X-ray work was largely directed (130, 131).

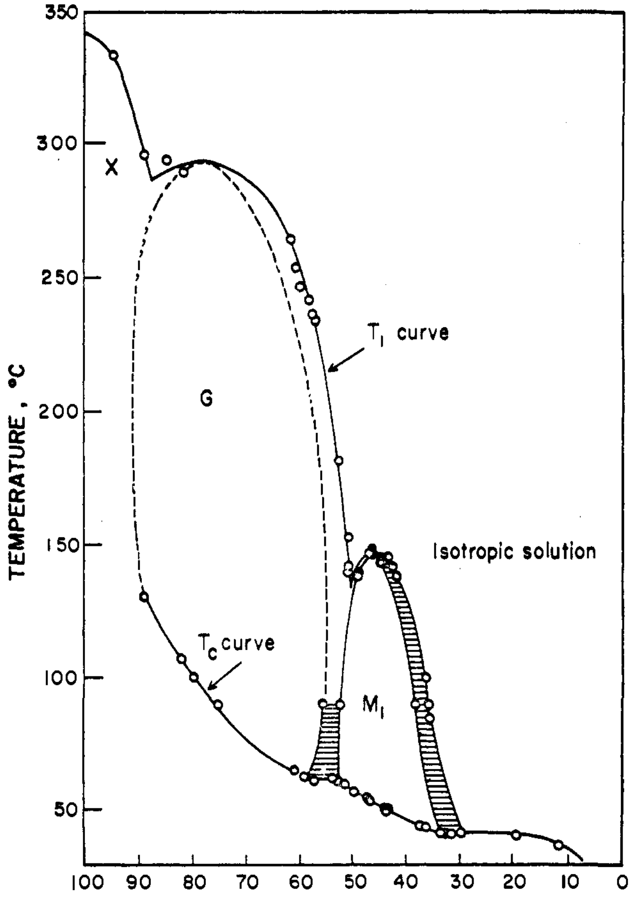

Figure 3.—Phase diagram for the sodium laurate–water system showing homogeneous fields of each of the different solution phases and isothermal tie lines connecting the phases in heterogeneous equilibria (86).

In the X-ray investigations of Luzzati and associates, particular attention has been directed to the fatty acid soaps of monovalent and divalent metallic cations. The soaps have been investigated over a wide temperature range, individually and in some cases in admixture, in absence of solvent, in binary aqueous systems, in binary systems with hydrocarbons, and in three-component systems with water and either water-soluble or water-insoluble organic liquids. The present subsection discusses binary aqueous systems containing the fatty acid soaps of the alkali metals.

Extensive phase studies of these systems were made earlier by McBain and his associates, and phase diagrams for many soaps were published (86). These diagrams are basically similar for different soaps, and the diagram for sodium laurate (Figure 3) may be used as an example.

a. The T_0 Line

The T_0 line may, with certain qualifications, be regarded as representing the curve which shows the depression of the melting point of the soap by water. For compositions at temperatures higher than those indicated by this line, the solid crystal lattice of the soap has been entirely broken down, and we are dealing with wholly liquid or liquid crystalline systems. Below the T_c line the soap retains, at least in part, its crystalline order. It may be noted that the scope of the present review is restricted almost wholly to systems, such as those above the T_c line, in which only fluid phases are present. The solubilization of solids (131c) will therefore not be discussed. Nonetheless, the very interesting thermodynamically stable "gel" phases which, in certain systems, fall immediately below the T_c line will be considered (II.A.1.i). In these phases the hydrocarbon groups of the amphiphile are apparently in a solid crystalline state, while the polar and aqueous regions are fluid.

b. The T_i Line

Between the T_c and T_i lines in Figure 3 lies the region in which mesomorphous or liquid crystalline amphiphile solutions are represented. On rise of temperature, a point is reached, corresponding to each composition, where the increased thermal agitation brings about breakdown of the extended long-range order existing in the liquid crystalline phase, and an isotropic micellar solution is produced. The T_i line thus indicates the variation in the temperature of breakdown of long-range liquid crystalline order with change in composition.

c. The Neat or Lamellar Phase (G)

i. X-Ray Diffraction Measurements.—All recent and earlier X-ray studies indicate that the hydrocarbon chains within the micelles of the neat phase, as well as within all other micellar solutions such as those represented in Figure 3 above the T_c line, possess a fluid arrangement resembling that found in liquid hydrocarbons of corresponding molecular weight. This arrangement gives rise to a weak and rather diffuse X-ray diffraction band at high angles corresponding to a Bragg spacing of about 4.5 A. In addition to this band, a diffuse band corresponding to a Bragg spacing of about 3.2 A and characteristic of liquid water is also common to all aqueous micellar solutions. With the neat phase sharp diffraction bands are found at low angles which relate to the interlamellar spacing. Several orders are observed giving rise to calculated Bragg spacings in the ratios 1:1/2:1/3:1/4. This is characteristic of a lamellar arrangement (*cf.* Figure 4).

For a binary aqueous alkali metal soap solution, the thickness of the bimolecular soap leaflets and the dependent mean effective area per polar group may be calculated directly from the X-ray long spacing, the composition of the system, and the partial specific volumes of its components (49, 74–77).

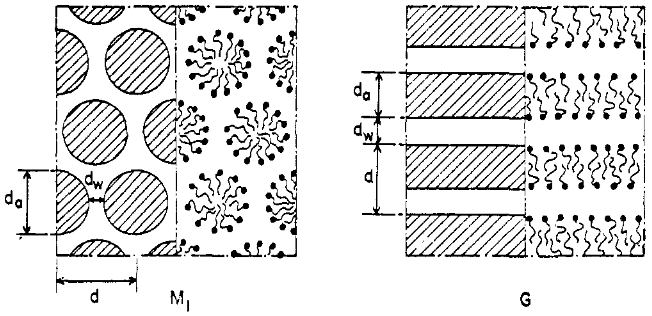

Figure 4.—The structure of the middle, M_1, and neat, G, phases in relation to the measured X-ray long spacings, *d* (77).

It is found that within the range of stability of the neat phase, the effective area per carboxylate group increases with increasing dilution. This increase with dilution is a general effect that is not confined to the neat phase (28, 105). It provides an experimental indication of the tendency of $A_{\overline{CW}}$ to increase with dilution with a consequent tendency to reduce R (Table I, method Ia). Within the range of stability of the lamellar phase, this tendency for $A_{\overline{CW}}$ to increase with dilution is offset by the lateral expansion of the $\overline{C}$ layer, the value of $R = 1$ being thus retained (I.C.2). An increase in area per polar group is also found for the alkali soaps with rising temperature. This is possibly related to increased ionization. As the water content of the neat phase is increased, there is a tendency for the thickness, *d*, of the bimolecular amphiphile leaflet to diminish owing to the increased lateral separation of the polar groups. At the same time the addition of water increases the thickness, d_w, of the water layer. The measured repeat distance, *d*, which is the sum of the thicknesses d_a and d_w (Figure 4), therefore varies in a rather complex manner with concentration.

ii. Optical Properties of the Neat Phase.—Although the hydrocarbon chains within the micelles of the neat phase possess an essentially fluid arrangement, this liquid character is restricted by the terminal attachment of the hydrocarbon chains to the polar groups in the hydrophilic faces of the bimolecular amphiphile leaflets. This restriction is probably the principal source[1] of the birefringence of the neat phase, and with *n*-alkyl amphiphiles it might be expected to lead to a predominant average orientation of C–C bonds normal to, rather than along, the leaflets. A uniformly oriented domain of neat phase therefore forms a uniaxial crystal with optic axis normal to the planes of the lamellae. If the C–C bonds also lie predominantly along the optic axis, the "intrinsic" or molecular birefringence will be positive (7, 39) (*cf.* Figure 5). There will also be a small negative form birefringence (94). This, however, with *n*-alkyl amphiphiles is outweighed by the intrinsic positive birefringence. (With branched-chain amphi-

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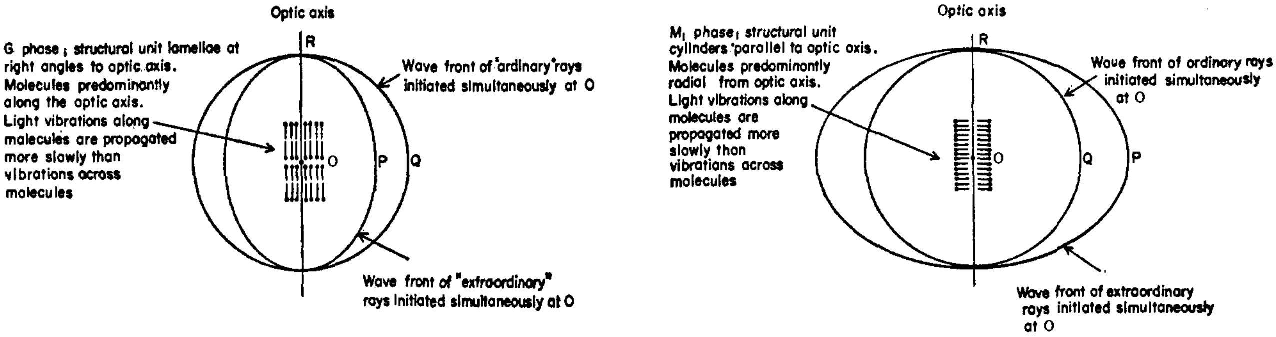
[1] Other possible sources of birefringence are the orientation of polar groups or of water molecules at the $\overline{C}$–$\overline{W}$ junction.



(a) G phase. Amphiphile molecules lie predominantly along the optic axis which therefore corresponds to the direction of minimum refractive index for the extraordinary ray. *Maximum birefringence* $= \mu_\epsilon - \mu_\omega = \frac{1}{OP} - \frac{1}{OQ}$, positive.

(b) M_1 phase. Amphiphile molecules lie predominantly across the optic axis which therefore corresponds to the direction of maximum refractive index for the extraordinary ray. Maximum birefringence $= \mu_\epsilon - \mu_\omega = \frac{1}{OP} - \frac{1}{OQ}$, negative.

Figure 5.—Diagram illustrating the origin of the positive and negative birefringence of the G and M_1 liquid crystalline phases, from *n*-alkyl amphiphiles. Sections parallel to optic axis in uniform domains of the uniaxial G and M_1 phase. Any extraordinary ray lying in the section vibrates at right angles to the ray and in the plane containing the ray and the optic axis (plane of the paper). The extraordinary ray OP in the G phase therefore vibrates along the amphiphile molecules, while the extraordinary ray OR vibrates across them. OP therefore corresponds to the slowest direction of propagation of extraordinary rays (direction of highest refractive index μ_ϵ) and OR to the fastest. Extraordinary rays traveling in intermediate directions travel with intermediate velocity. This gives rise to the elliptical cross section of the wave front for a series of extraordinary rays initiated simultaneously at O. Any ordinary ray in the section vibrates at right angles to the ray and in a plane at right angles to the plane of the paper, *i.e.*, at right angles to the plane of vibration of the corresponding extraordinary ray. All ordinary rays in the G phase thus vibrate across the amphiphile molecules at right angles to the plane of the paper and travel with the same velocity as the extraordinary ray OR which likewise vibrates across the amphiphile molecules but in the plane of the paper. The section of the wave front for a series of ordinary rays initiated simultaneously at O is therefore circular. If we consider the positions of the respective extraordinary and ordinary wave fronts at a time when a wave front simultaneously initiated at O *in vacuo* would have traveled unit distance, then the birefringence $= \mu_\epsilon - \mu_\omega = (1/OP) - (1/OQ)$. For the G phase, as outlined, this will be positive. When similar considerations are applied to the case of the M_1 phase, in which the amphiphile molecules are directed predominantly across, instead of predominantly along the optic axis, $OQ > OP$ and the birefringence, $\mu_\epsilon - \mu_\omega = (1/OP) - (1/OQ)$, will be negative.

philes in certain circumstances, the neat phase may show a negative optic sign (134).)

The various "textures" (=appearances) of the neat phase when observed with the polarizing micoscope have been described by Rosevear (107). Certain of these textures arise from the tendency of the lamellae to arrange themselves parallel to surfaces, *e.g.*, those of bubbles or droplets. An arrangement of the lamellae parallel to slide and coverslip is often encountered, particularly with neat phases of high water content and not too thick consistency. This leads to the sample, which then forms a single uniformly oriented or "homeotropic" domain, being viewed along its optic axis. Under this condition, with parallel light, birefringence is not observed and the sample appears isotropic. With convergent light a uniaxial interference cross is observed (39c) which, at any rate in most instances, may be identified as positive. Neat phase locally oriented with lamellae parallel to the surface of a flattened air bubble between slide and coverslip is viewed at right angles to its optic axis which is normal to the bubble surface and, in this case, lies parallel to slide and coverslip. Again, when a suitable compensator is used, the optic axis may be identified as corresponding to the direction of the lowest refractive index for the extraordinary ray, in the case of optically positive neat phases.

d. Middle Phase (M_1)

i. X-Ray Diffraction Measurements.—The principal features of the X-ray diagrams from M_1 solutions are (1) an unorientated short spacing (4.5 A) corresponding to a fluid hydrocarbon micellar interior, (2) a series of Bragg spacings in the ratio $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$, characteristic of parallel fibers in two-dimensional hexagonal array. The distance between these fibrous micelles calculated from the X-ray measurements increases with increasing dilution.

Several models for these fibrous micelles have been suggested (11, 75, 82) (*cf.* section II.B.2.a), but the most satisfactory, and the only one consistent with the *R* theory, is that proposed by Luzzati, *et al.* (75). According to this model, the fibers consist of amphiphile molecules associated into cylindrical micelles, with hydrocarbon chains in fluid arrangement forming the interior and with the polar groups on the surface of the cylinders. With this model, from the spacing between the fibers as given by the X-ray long spacing (Figure 4), from the composition of the system, and from the partial specific volumes of its components, the diameters of the cylinders and the mean area available per carboxylate group on the surface of the cylinders can be calculated. For a given soap the mean available area per polar group, contrary to what

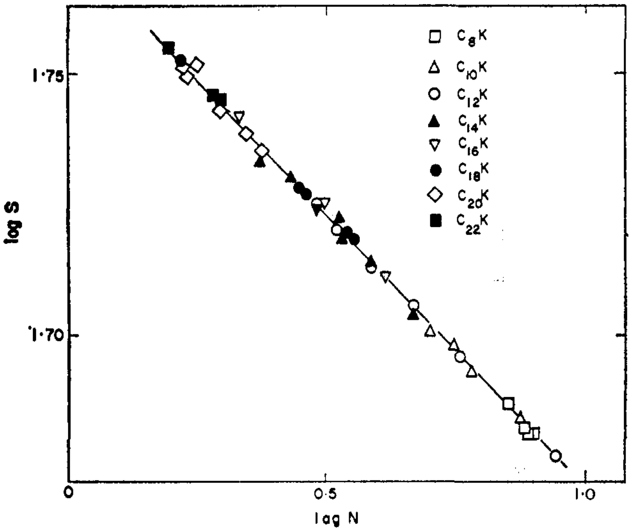


Figure 6.—Variation in the effective area S per polar group with change in concentration N (moles of soap/liter of water) for M_1 solutions of potassium soaps at 86° (28).

was first proposed (49, 75–77), increases with diminishing concentration over the range of stability of the middle phase (28). The diameter of the fibers is rather less than twice the fully extended length of the soap molecules and diminishes with dilution in consequence of the increased separation of the carboxylate groups. The available area per polar group in the micelles of middle phase is always markedly greater than the available area in the neat phase of the corresponding soap at higher concentration.

This has recently been clearly illustrated by Gallot and Skoulios (28) who have made an extensive comparison of the effective areas per polar group occupied on the faces of the cylindrical (M_1) and lamellar (G) micelles of the middle and neat phases, respectively, as functions of concentration, temperature, and the nature of the dissolved soap. For this comparison the concentration was expressed as N, the number of moles of soap per liter of water. A number of their results in graphical form are reproduced in Figures 6–10. It will be seen that with the normal-saturated soaps in both the neat G and middle M_1 phases, at constant temperature (86°) and for a given cation, the area S per polar group is dependent only on N. It is not perceptibly dependent on the chain length of the soap (Figures 6 and 7). For different alkali cations at a given temperature and concentration the area per polar group increases with atomic number (Figure 8).

For both the M_1 and G phases, the variation of S with N is given by relationships of the form

$$S = S_0 N^{-p}$$

or

$$\log S = \log S_0 - p \log N$$

where S_0 and p are constants for a particular soap at a given temperature.

The constants for the lamellar (G) and cylindrical (M_1) phases at 86° are given in Table III. The constant p is practically independent of temperature; the constant S_0 increases with temperature (Table IV and Figure 9).

Table III

Values of S_0 and p for M_1 and G Solutions of Fatty Acid Soaps at 86° (28)

	M_1 phase		G phase	
Cation	S_0, A^2	p	S_0, A^2	p
Na	57.6	0.095	63.1	0.24
K	58.9	0.105	58.9	0.20
Rb	61.7	0.11	56.3	0.19
Cs	63.1	0.115	55	0.18

Table IV

Effect of Temperature on Values of S_0 and p for Lamellar Solutions of Potassium Soaps (28)

Temp, °C	S_0, A^2	p
45	52.5	0.19
65	56.3	0.20
86	58.9	0.20
104	61.7	0.20

According to the point of view of the R theory, the area S per polar group for the G phase at a given concentration represents the area per polar group at which the mean interactions of the $\bar{C}$ region with the $\bar{O}$ and $\bar{W}$ regions are equal. The observation that, within the G phase, S for a given concentration N is, if not completely independent of, at least insensitive to hydrocarbon chain length (and consequently to the thickness of the lamellae) seems on this view to indicate that while, as would be expected, the interfacial spreading tendency of the polar groups on the $\bar{C}$ face may be adjusted by change in effective area, the interfacial spreading tendency on the $\bar{O}$ side of the $\bar{C}$ monolayers is insensitive to the thickness of the leaflets. This might be expected on account of the quasi-liquid arrangement of the hydrocarbon chains, particularly of their segments more remote from the polar faces of the leaflets. When, however, on account of increasing dilution with water and consequently increased spreading of the ionic group, the thickness of the $\bar{O}$ layer is reduced beyond a certain limit, rearrangement into the middle phase ($R_x = 1, R_y < 1$) occurs. The stability of the lamellar phase extends to lower concentrations with the longer chain salts than with the shorter ones. This is possibly because with the longer chains the quasi-liquid hydrocarbon region of the micelles is thicker and contains a larger proportion of hydrocarbon chain remote from the polar group and consequently of more random character. It is noteworthy from Figure 10 that, at a given value of N, the increase in area per polar group

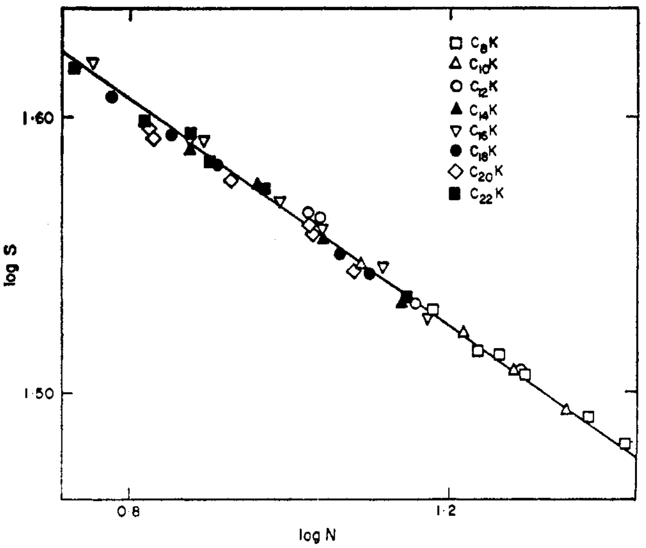


Figure 7.—Variation in the effective area S per polar group with change in concentration N (moles of soap/liter of water) for G solutions of potassium soaps at 86° (28).

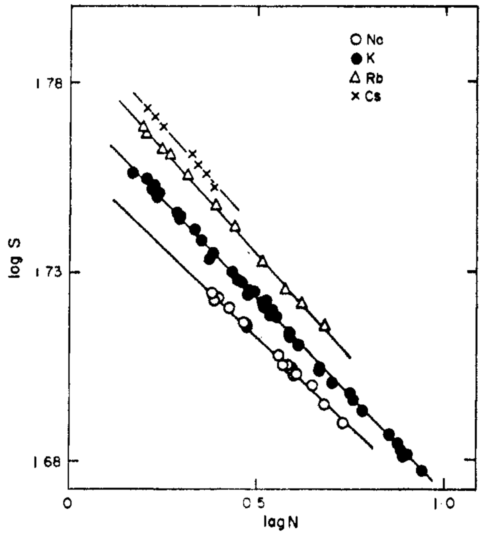


Figure 8.—Variation in the effective area S per polar group with change in concentration N (moles of soap/liter of water) for M_1 solutions of alkali metal soaps at 86° (28).

corresponding to the change in structure from G to M_1 is relatively large (*ca.* 20–25%).

Although in the last paragraphs only the interaction of water with the ionic groups has been mentioned, interaction between the water and the hydrocarbon region exposed between the polar groups will also occur. Although this will be similar for neighboring homologs in a series of saturated soaps at a given concentration, N, it would be expected to be increased by introduction into the hydrocarbon chain of a relatively polarizable double bond. Such an increased interaction may account for the experimental observation that at a given concentration the area per polar group for the oleates is greater than that for the saturated soaps (49, 93). This effect has been noted with both the G and M_1 phases.

A method of calculating the differences in the changes in free energies of a phase with composition according to whether it has a G or an M_1 structure has been proposed by Parsegian (93). The method involves calculating differences in the electrostatic free energies of charging and in the water–hydrocarbon interfacial free energies for the two liquid crystalline structures. The transition between the two forms and the changes in dimensions within a phase with changes in composition are reasonably interpreted.

ii. Optical Properties of the M_1 Phase.—This phase, like the neat phase, is semitransparent and birefringent. The characteristic textures shown by the middle phase when examined with the polarizing microscope have been described by Rosevear (107).

The model of the M_1 phase as parallel fibrous cylindrical micelles in two-dimensional hexagonal array represents the phase as uniaxial, the optic axis lying along the cylinders. Although the hydrocarbon interiors of the cylindrical micelles possess a fluid arrangement, on account of the terminal attachment of the hydrocarbon chains to the polar groups in the micellar surface, for a *n*-alkyl amphiphile the number of –C–C– links directed along the cylinders, and consequently along the optic axis, might be expected to be statistically less than the number of those directed across them.

On the cylindrical model, therefore, the intrinsic birefringence of the middle phase should be negative (39) (*cf.* Figure 5). In addition the model indicates a small additional positive form birefringence (94).

Although the usual sign of the birefringence of the neat phase has long been established as positive (II.A.1.c), the optic sign of middle phase seems to have been determined only recently (133). This is because, while the basal sections of the neat phase, which are used for the determination of its optic sign, are readily obtained on account of the tendency of the lamellae to orientate spontaneously parallel to slide and coverslip, basal sections of the middle phase with cylinders accurately normal to slide and coverslip, as might be expected, arise much less readily.

It has recently been observed, however (133), that approximately basal textures in the M_1 phase in the sodium caprylate–water system are rather readily formed when an isotropic 20% aqueous solution, introduced between slide and coverslip, is allowed to undergo peripheral evaporation for several days at room temperature. Rosevear's "fan-like" textures (107) are also produced. By careful selection of the most accurately basal of the approximately basal sections, it is possible to observe conoscopically a uniaxial interference cross which, using a compensator, may be characterized as negative (39).

Although middle phases rarely yield accurately

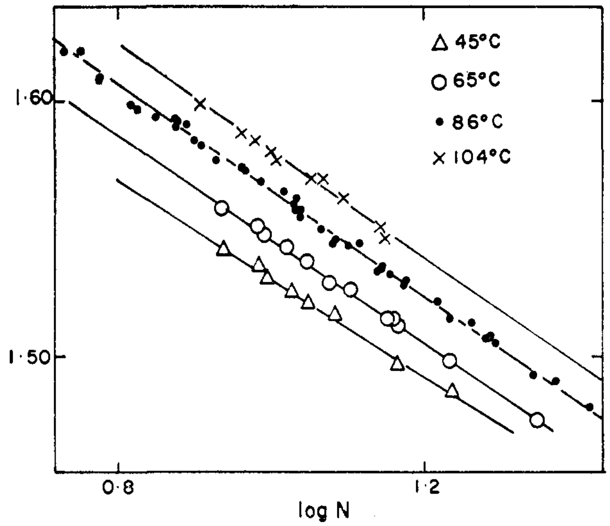


Figure 9.—Variation in the effective area *S* per polar group with change in concentration *N* (moles of soap/liter of water) for G solutions of potassium soaps at 45, 65, 86, and 104° (28).

basal sections, they readily give rise to extended textures which, when observed conoscopically, give characteristic optic normal interference figures (39, 133). These textures, which frequently appear when the peripheral evaporation technique just mentioned is used, are characterized, when viewed with parallel light, by a number of fine parallel striations and may be regarded as examples of Rosevear's (107) fan-like textures, the fans here being of infinite radius. The apparent optic axis, as determined by the movement of the isogyres on rotation of the sample when observed conoscopically, is normal to the striations and corresponds to the direction of maximum refractive index for the extraordinary ray. The optic sign is therefore negative. Textures with these parallel striations, and showing optic normal interference figures, are readily obtained from sodium caprylate, "Triton X100,"[2] N,N,N-trimethylaminododecanoimide, laurylpyridinium chloride, etc.

Textures giving optic normal interference figures are also obtained by uniformly shearing samples of a M_1 phase between slide and coverslip. The optic axis, which as before corresponds to the direction of maximum refractive index for extraordinary rays, lies along the direction of shear. Further, striations, less well marked than those formed by the evaporation technique, develop at right angle to the direction of shear. These striations in both types of sample must indicate that the sections are predominantly, rather than uniformly and entirely, in the optic normal orientation. The nature of these striations is not as yet determined (*cf.* section II.A.2.a). Nevertheless, the observations seem further to indicate the negative optical character of the M_1 phases examined. This supports the cylindrical model for this phase and contraindicates the suggested alternative string-of-spheres model to be discussed later (II.B.2.a).

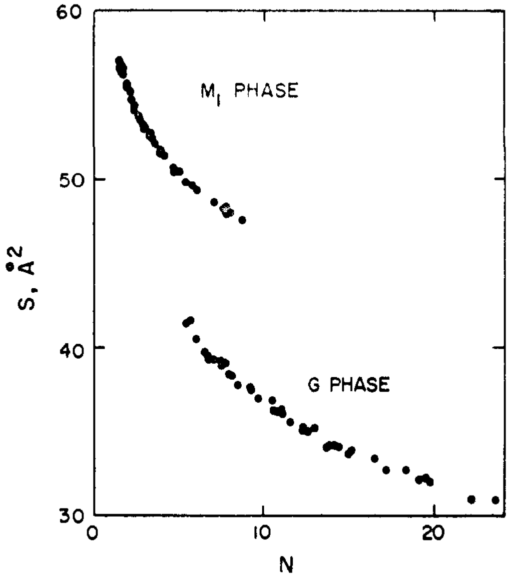


Figure 10.—Variation in the effective area *S* per polar group with change in concentration *N* (moles of soap/liter of water) in M_1 and G solutions of potassium soaps at 86° (28).

e. Phases Intermediate between the Neat (G) and Middle (M_1) Phases

Although in Figure 3 at compositions between those of the G and M_1 phases only conjugate mixtures of the G and M_1 phases are indicated, Luzzati and collaborators have found that in certain other systems matters are more complicated. On the basis of X-ray evidence, they originally suggested (77) a succession of phases intermediate in composition between the middle and neat phases and having the constitutions shown in Figure 11. In any particular amphiphile–water system, not all the phases necessarily arise, but those which are found are believed always to follow one another with increasing concentration in the order given.

Of these phases the cubic phase V_1 is very definitely characterized by its X-ray diffraction diagram, by its isotropic character, and by its very high viscosity. It is formed at 100° with potassium laurate, myristate, and palmitate, but not with the corresponding sodium salts. It is also formed at room temperatures, *e.g.*, with sodium 2-ethylhexyl sulfate, sodium undecane 3-sulfate, N,N,N-trimethylaminododecanoimide, etc. The constitution of this phase will be discussed in more detail later (II.B.2.a), but it may be remarked here that, in place of the structure originally suggested and indicated in Figure 11, an inverse, or "cubic II," structure for this phase has recently been preferred by Luzzati and Reiss-Husson (78).

The remaining phases seem less well characterized.

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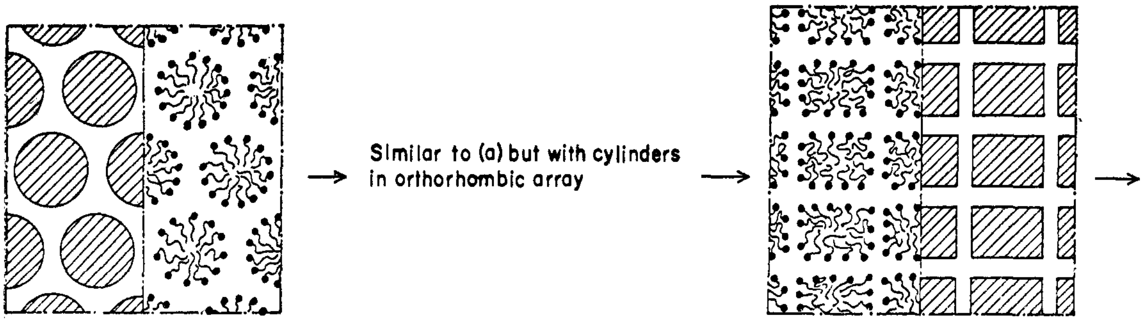
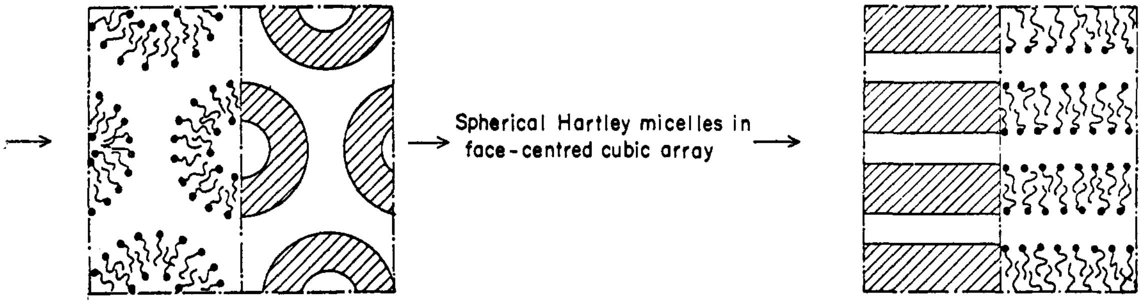
[2] Triton X100 = a C_8 alkylphenol condensed with about ten ethylene oxide units.



(a) Middle phase (M_I) Indefinitely long cylinders in hexagonal array

(b) Deformed middle Indefinitely long cylinders in orthorhombic array

(c) Rectangular phase. Parallelepipeds of rectangular cross-section and indefinite length



(d) Hexgonal complex phase Indefinitely long hollow cylinders of amphiphile, water filling the internal cavity and exterior volume

(e) Cubic or viscous isotropic phase (V_I)

(f) Neat phase (G)

Figure 11.—Structures suggested by Luzzati for succession of phases between middle (M) and neat (G) phases formed on progressive increase of concentration (77).

The original description (77) remarks: "The experimental study of the intermediate region is often difficult because the region of existence (in concentration) of each phase is narrow and the equilibrium slow to establish. It is therefore rare to succeed in preparing samples containing one individual phase; usually we have obtained two coexistent phases (it has not been infrequent to find three phases in single samples, probably on account of inhomogenity)."

With the exception of the well-defined cubic or viscous isotropic phase, the intermediate phases show textures under the polarizing microscope which are very different from those of the neat phase but which resemble the nongeometric textures of middle phase and which are indistinguishable one from the other.

In contrast to the logically regular succession of micellar structures shown by the main phases as represented diagrammatically in Figure 2, in the succession of structures (Figure 11) suggested by Luzzati for the intermediate phases (whether either the cubic I or cubic II structure be adopted for the cubic phase), no clear underlying structural trend is evident and certain features appear anomalous, *e.g.*, the parallelepiped fibers with liquid interior suggested for the rectangular phase. Anomalous aspects of the cubic I and cubic II structures are noted in section II.B.2.a. Such features suggest that Luzzati's intermediate structures should be accepted with reserve. It must be remembered that conjugate mixtures of the anisotropic neat and middle phases would be expected readily to form complex series of emulsions, neat-in-middle, middle-in-neat, or even multiple. The properties of such emulsions of liquid crystalline phases have apparently been little studied (*cf.* section II.A.1.h), but the dispersed phase would not be expected to take up the form of spherical droplets, as in emulsions of amorphous liquids. The possible constitution of the cubic phase as a thermodynamically stable isotropic interdispersion of micro units of the M_1 and G phases in free rotary Brownian movement is considered in section II.B.2.a. The possibility of the interpretation of the remaining anisotropic intermediate phases in terms of the succession in properties of an intermediate series of anisotropic middle–neat microinterdispersions, possibly thermodynamically stable, deserves careful examination.

f. Amorphous Micellar Phase (S_1–S_2) without Long-Range Order

The long-range order existing between the micellar units in aqueous liquid crystalline solutions of the alkali metal soaps may be broken down either by rise of temperature or by dilution. In either case one passes from points below to points above the T_i line. In the transition region liquid crystalline and micellar solutions coexist as conjugate phases in equilibrium, the liquid crystalline phase being richer in amphiphile.

Reiss-Husson and Luzzati (104–106) have recently made absolute measurements of the small angle X-ray scattering of a number of amphiphile solutions corresponding in composition to solutions represented within and to the right of the M_1 phase in diagrams such as Figure 3.

In the zone of conjugate phases they found that the X-ray diffraction record showed simultaneously the broad band scattered by the micellar solution, with its one or two maxima depending on the amphiphile, and the sharp diffraction lines of the middle phase. In most cases examined, the maximum or maxima coincide in position with the first and second lines. According to Reiss-Husson and Luzzati, this suggests that "rod-shaped micelles exist in both phases. These rods, which display crystalline order in the two-dimensional lattice of the middle phase, show only loose correlation in the micellar solution." Nevertheless, where the maxima for the two phases coincide, it would seem that the precise two-dimensional hexagonal correlation found in the M_1 phase is that "correlation" showing maximum probability in the S_1 phase. This might be expected where the conjugate phases are close in composition, *e.g.*, close to the apex of the M_1 region in Figure 3. However, in a case where the S_1 phase was considerably more dilute than the conjugate M_1 phase, the inter-rod distance (water spacing) at the preferred correlation in the S_1 phase might be expected to be greater than that in the M_1 phase so that the maximum of its diffraction band should occur at a lower angle. This has been observed by Luzzati in the single instance of cetyltrimethylammonium chloride solutions. Neither in this case nor in those where the bands coincide have the compositions of the separate conjugate phases been given. Only over-all compositions are quoted. On this account the conclusion of Reiss-Husson and Luzzati that for cetyltrimethylammonium chloride "the micellar solution seems not to contain rods" does not appear necessarily to be valid.

For those lower concentrations at which intermicellar correlation becomes unimportant, Reiss-Husson and Luzzati have developed a method for establishing whether the micelles present are mainly monodisperse and also for distinguishing between lamellar, cylindrical, and spherical forms. A summary of their conclusions is given in Table V.

TABLE V

APPROXIMATE CONCENTRATION RANGES[a] FOR THE DIFFERENT TYPES OF MICELLES (105)

Amphiphile	Temp, °C	Spherical micelles	Sphere-rod transition	Rod-like micelles	Middle phase
Cetyltrimethylammonium chloride	27	0.05	0.40		0.40
Sodium oleate	27			0.04	0.20
Sodium lauryl sulfate	27	0.07	0.25		0.40
	70	0.05	0.15		0.40
Sodium laurate	70	0.05	0.10		0.36
Sodium myristate	70	0.06	0.10		0.28
Sodium palmitate	80	0.05	0.18		0.23
Sodium stearate	90	0.05	0.16		0.22
Cetyltrimethylammonium bromide	70	0.05	0.25		0.32
	50	0.05	0.17		0.26
	27		0.05	0.10	0.25

[a] Grams of amphiphile/gram of solution.

There is good agreement between the dimensions of the spherical micelles calculated from the X-ray results and those obtained by other methods. The persistence of rod-shaped micelles of sodium oleate at low concentrations (Table V), which is confirmed by the anisotropic electrical conductivity of sodium oleate solutions developed on streaming (33, 34, 40), is of particular interest. On the *R* theory the hydrophilic interaction of the double bond of the $C_{17}H_{33}$ chain with water could well promote a non-radially symmetrical distribution of $A_{\bar{C}W}$, thus favoring a cylindrical as compared with a spherical form of micelle.

The X-ray measurements discussed show that the form of the micelles, as suggested in the *R* theory, is a function of the temperature, concentration, and nature of the amphiphile. In the group of systems studied (*i.e.*, systems resembling those to the right of the M_1 phase in Figure 3), the equilibrium of micellar forms present tends to vary from the monodisperse spherical form at high dilution, approaching the cylindrical form as compositions approaching the M_1 phase are reached. This change in form may, on the extended *R* theory, be associated with an increase in the degree of statistically non-radially symmetrical character in the $A_{\bar{C}W}$ interaction of the polar groups as these are brought closer together with increasing concentration, gradually approaching the conditions prevailing in the M_1 phase. The virtual absence of lamellar micelles, remarked by Reiss-Husson and Luzzati in the particular micellar solutions studied, is not unexpected since in all these instances compositions giving rise to the M_1 phase are approached with increasing concentration. Lamellar regions would, however, be expected to occur in the micellar solutions represented on the right of the G phase in Figure 3 or in the micellar solutions of Aerosol MA which yield a liquid crystalline G phase and no M_1 phase on increase of concentration at room temperature (49, 74). Further, in the micellar solutions indicated by the downward projecting tongue between the G and M_1 phases in Figure 3, one might expect to find an equilibrium of micellar regions, fluctuating with the thermal motion of the molecules, intermediate between fibrous and lamellar. It seems possible that it is by the reduction in mobility of such a fluctuating system at lower temperatures that the cubic or viscous isotropic V_1 phase arises (*cf.* section II.B.2.a).

The effective area per polar group on the surface of the micelles formed at high dilution is, in general, very much greater (up to three times) than the area per polar group (23 A^2) occupied in the crystal (72). The polar groups themselves are therefore widely separated, and it might be expected that the polar ends would undergo rotary Brownian motion in the surface of the micelle. This would lead to a statistically symmetrical radial distribution of $A_{\bar{C}\bar{W}}$ about each molecule and hence to the formation of spherical micelles. Increasing concentration and consequently diminished separation of polar groups on the micellar surface, or increasing size of polar groups, would, other things being equal, be expected to favor polar group interaction with resulting non-radially symmetrical distribution of $A_{\bar{C}\bar{W}}$ and production of the cylindrical M_1 form of micelle and ultimately the separation of the M_1 phase. On the other hand, with a compact polar group, a bulky hydrocarbon group would hinder close approach of the polar groups and thus tend to maintain $A_{\bar{C}\bar{W}}$ radially symmetrical. This should oppose the formation of the M_1 phase. Examples of such effects observed in practice with certain amphiphiles are mentioned later (II.A.2.a and II.B.1.a).

Much recent work has been carried out on aqueous micellar solutions at lower concentrations (*cf. e.g.*, 1, 8–10, 12, 17, 18, 41, 48, 84, 91, 95, 122–124). This work largely confirms the classical theory of Hartley and emphasizes the great facility of formation and breakdown of micelles.

The flexibility of the extended cylindrical form of micelle in isotropic solutions of higher concentration has been indicated by viscosity measurements (124).

g. Inverse Middle Phase (M_2)

The structure of the inverse middle phase, M_2, is discussed below (II.A.2.a) in connection with the sodium sulfodialkyl succinates which readily yield this phase at high concentration at room temperatures. However, solutions of the longer chain fatty acid soaps themselves crystallize at room temperature (16), and highly concentrated solution phases are formed only under conditions of high temperature and pressure where manipulation is difficult. Possibly for this reason, the inverse middle phase has not been explicitly characterized in binary water fatty acid soap systems. Nevertheless, on general grounds it seems reasonable to expect that the region marked X in Figure 3 (corresponding regions also occur in the phase diagrams of other soaps (86)) should represent the inverse middle phase M_2. This conclusion, however, is not in accord with X-ray studies by Skoulios and Luzzati (110) according to whom sodium laurate, for example, after undergoing various transitions, melts to give the lamellar G phase at 255° and isotropic liquid at 336°. It is, however, difficult to reconcile this behavior with Figure 3, and the matter would repay further investigation, *e.g.*, with the polarizing microscope. Gallot and Skoulios (29–31) have also reported the formation of the liquid crystalline G phase from cesium and potassium soaps at high temperatures. This result also should be confirmed by observations with the polarizing microscope.

h. Emulsions Containing Liquid Crystalline Phases

It was suggested above that the "intermediate phases," lying in composition between M_1 and G and between G and M_2, may possibly be constituted as thermodynamically stable interdispersions of micro units of the G phase with micro units of the M_1 or M_2 phases, respectively.

Whether or not this be the case, coarser thermodynamically unstable two-phase dispersions containing $M_1 + G$, $G + M_2$, or M_1, G, or M_2 phases with isotropic phases (S_1, S_2) are frequently encountered. Although on agitation mixtures of amorphous liquids tend to give spherical droplets, for example, mineral oil in water or water in oil, mixtures containing anisotropic liquid crystalline solution phases, on account of the anisotropic surface tensions of these liquids, tend to give nonspherical droplets. These nonspherical droplets readily coalesce on encounter and further, on account of the ready transfer of molecules between the two phases in these systems, larger droplets of the disperse phase can grow at the expense of smaller ones by solution and redeposition processes. These dispersions, which have as yet received little systematic study, are of considerable theoretical interest. This is the more so since the long-range molecular orientation within the birefringent droplets may readily be studied with the polarizing microscope (39a).

A characteristic form of droplet which is often encountered is the "batonnet." Batonnets, which typically take the form of figures of revolution (Figure 12), arise in certain circumstances on precipitation of the M_1, G, or M_2 phases from conjugate isotropic S phases (107). The writer has found that with both M_1 and M_2 batonnets the optical properties as examined with crossed polars (39) indicate that the micellar fibers of the M phases lie symmetrically around and not along the batonnets.

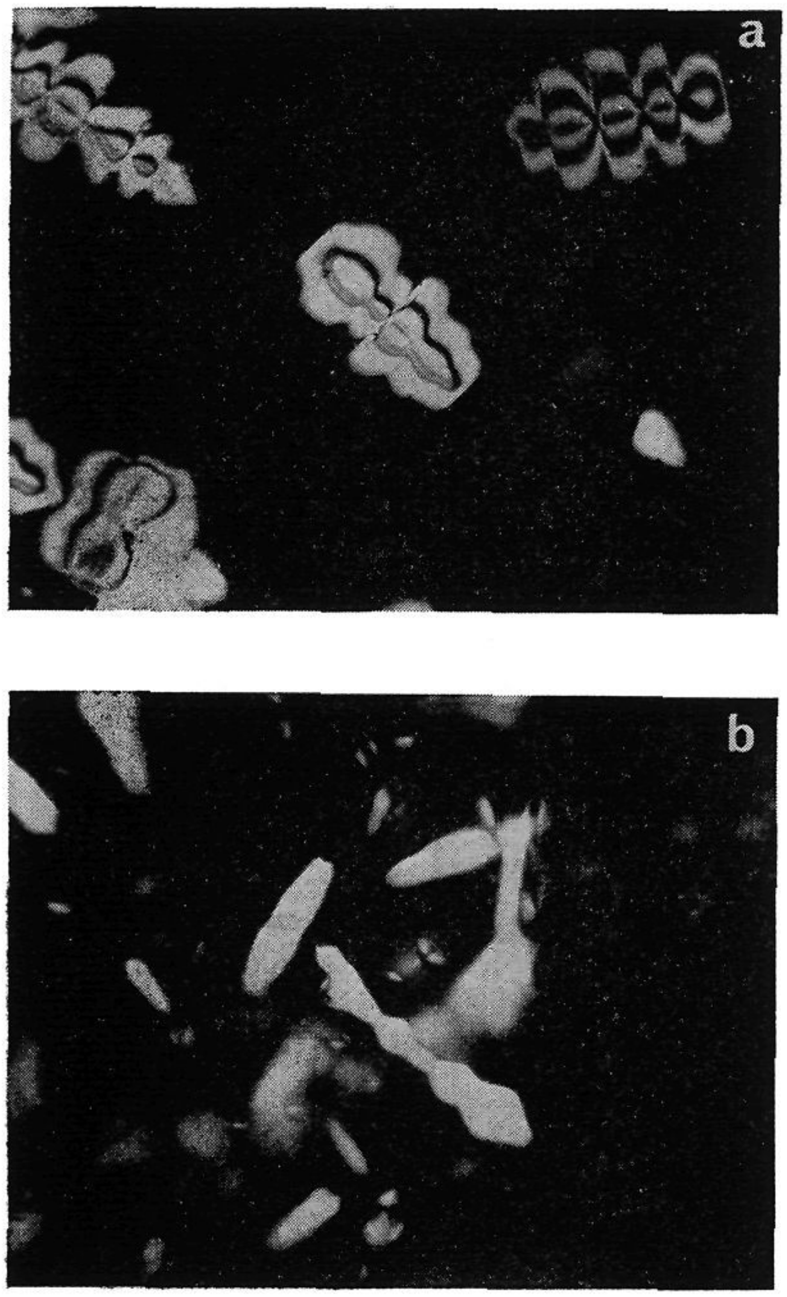


Figure 12.—Batonnets of the M_1 phase precipitated after peripheral evaporation (section IV.B.7) of a 30% isotropic aqueous solution of sodium caprylate for several days at 20° (×65, crossed polars). The interior markings derive from interference colors. (b) Batonnets of the G phase precipitated at the S–G phase boundary in the N,N,N-trimethylaminododecanoimide–water system (section II.B.2): sample prepared by peripheral hydration of supercooled liquid imide at 20% relative humidity at 20°; the batonnets successively redissolve and reprecipitate when illumination of slide is cyclicly increased and diminished (×150, crossed polars).

For batonnets of the G phase, the optical properties indicate a structure similar to that of the batonnets of the smectic phase of compounds such as ethyl *p*-axozybenzoate, which have been described in detail by Friedel (27) in his classical articles on liquid crystals. In these batonnets the micellar lamellae lie at right angles to the geometric axis so that the optic and geometric axes of the batonnets coincide.

i. The "Gel" Phase and the "Coagel"

i. Occurrence.—As noted earlier the present article is largely restricted to systems in which all the components present are in the liquid state. The very interesting border-line state shown by amphiphile solutions existing in the "gel" condition, recently studied by means of X-ray diffraction and polarization microscopy (126–128), will, however, be considered.

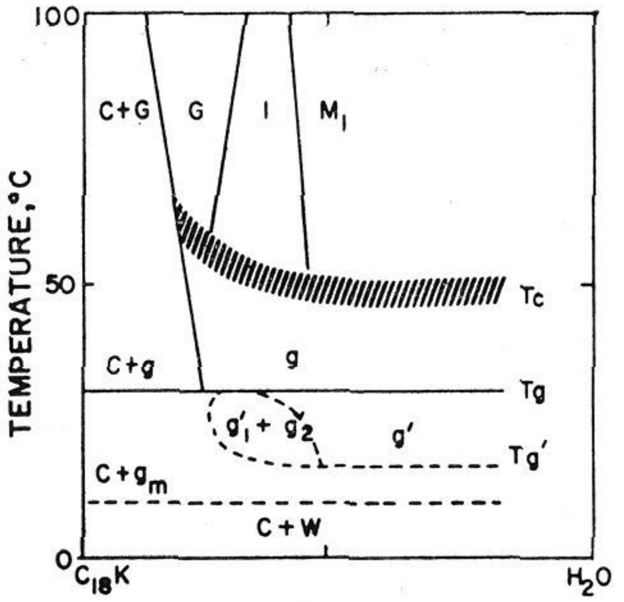


Figure 13.—Phase diagram for the system potassium stearate–water: M_1, middle phase; G, neat phase; I, intermediate phases; C, crystalline soap; W, dilute aqueous solution; g, thermodynamically stable "gel"; g′, "gel" in zone of metastability; $g'_1 + g'_2$, zone of separation of conjugate metastable gels; C + g_m, soap crystals + unstable "gel" (126).

The region of the occurrence of "gel" and "coagel" is that represented in Figure 3 (or similar diagrams) below the T_c line. It has been the subject of many earlier studies by Vincent and Skoulios (126–128).

A mixture of a soap and water, when strongly heated and then cooled to a temperature below that indicated by the T_c line, can show, according to circumstances, two different appearances. In one case it appears as a translucent jelly, in the other as an opaque mass. For example, a mixture of potassium stearate and water cooled from 100° to room temperature appears (if it contains less than 70% potassium stearate) as a homogeneous and clear jelly; if it contains more than 70% soap, it yields an opaque product which is microscopically heterogeneous. According to current terminology, in the first case we are dealing with the "gel" and in the second with the "coagel."

The X-ray diffraction diagram of the "coagel" contains lines characteristic of solid soap (72), which are independent of the water content of the system; the "coagel" is thus characterized as a dispersion of hydrated solid soap.

The diffraction diagram of the "gel" is, however, quite different both from that of the "coagel" and from those of the liquid crystalline phases above the T_c line. With the "gel," the spacings indicated by the central lines are, in contrast to the comparable spacings for the "coagel," dependent on water content. At high angles the "gel" gives a characteristic narrow band in contrast to the broad high angle band of low intensity, indicative of the disordered configuration of the hydrocarbon chains, which is found for all phases indicated above the T_c line.

An approximate phase diagram for the potassium stearate–water system given by Vincent and Skoulios is reproduced in Figure 13. Above the T_g line, the "gel" is thermodynamically stable. Below the T_g line it passes eventually to "coagel" but is able to remain supercooled for long periods above the curve T_g'. Between T_g and T_g', over a limited range of concentration two conjugate "gels," g_1 and g_2, exist apparently in equilibrium with each other although supercooled.

The formation of "gel" phases in soap–water systems is dependent on the nature of both the cation and the fatty acid. Lithium and sodium soaps do not yield "gels" and pass directly from the liquid crystalline phases to the "coagels."

With potassium the C_{14}, C_{16}, C_{18}, and C_{22} soaps all form similar "gels," the T_c line being displaced to lower temperatures the lower the molecular weight of the fatty acid. With equimolar mixtures of pairs of these potassium soaps differing in chain length by C_2 or C_4, X-ray diffraction diagrams indicate the formation of a mixed "gel" phase containing both soaps; with a difference in chain length of C_6, however, two conjugate "gels" are formed simultaneously. How the soaps individually are distributed between the separate "gel" phases has not been determined.

Rubidium and cesium soaps form thermodynamically stable "gel" phases with water over a wide range of composition and temperature. The approximate phase diagram for rubidium stearate is shown in Figure 14.

As an extension of the studies on alkali metal soaps, Vincent and Skoulios also examined the system cetyltrimethylammonium bromide–water. The phase diagram for this cationic soaps is analogous to that for rubidium stearate; the "gel" exists, in the thermodynamically stable form only for water contents greater than about 20% and for temperatures between −5 and +20°. At lower temperature ice crystallizes from residual "gel." Within the range of thermodynamically stable "gel," two conjugate "gel" phases are found at 15° at water contents (expressed as $(1 - c)/c$) between 0.96 and 0.30. These are analogous to the conjugate "gels" formed in the potassium stearate system in the supercooled "gel" region.

ii. Structure of "Gel" Phase.—The model proposed by Vincent and Skoulios for the "gel" phase in all the above instances is illustrated by Figure 15.

The thickness of the amphiphile layer, d_a, is of the order of the length of a fully extended soap molecule. The hydrocarbon chains are perpendicular to the plane of the lamellae and arranged in either the hexagonal (g_H) or the rectangular (g_R) form found with paraffins. With the "gel" of potassium stearate, only the hexagonal form appears; both are found with rubidium stearate. The change of one form into the other with change in composition appears to be a continuous process.

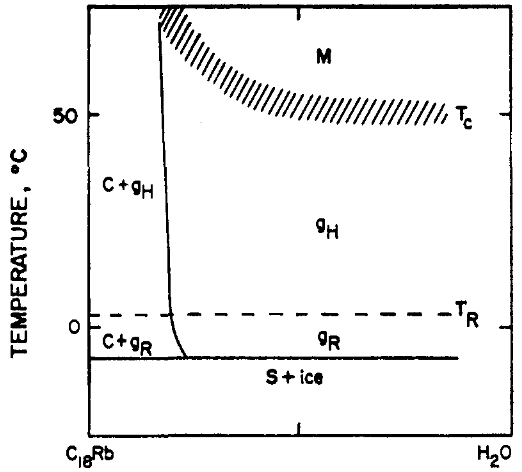


Figure 14.—Phase diagram for the system rubidium stearate–water: M, liquid crystalline phases; g_R and g_H, gel (indices R and H refer to a lateral arrangement of soap molecules according to a rectangular or hexagonal lattice); C, crystalline soap; S, soap ("gel" or crystals). The hachured zone corresponds to conjugate gel and liquid crystalline phases (127).

The area per polar group (derived from the X-ray long spacing), within the accuracy of experiment, is independent of concentration and of the order of 39.8 A.^{2} The cross-sectional area per paraffin chain, ϵ (derived from the line at high angles), is 19.9 A^2. Since, on the model shown in Figure 15, the polar groups are situated alternately on one side or the other of the palisade of hydrocarbon chains, ϵ should be equal to half the area per polar group. This is found to be so (Table VI).

Table VI

Dimensions of the "Gel" Phase of Several Soaps (127)[a]

Soap	Temp, °C	d_a, A	S_a	S, A^2	2ϵ, A^2	d_w, A
$C_{14}K$	0	20.0	1.11	39.7	39.0	12.0
$C_{16}K$	25	22.7	1.09	39.6	39.4	10.7
$C_{18}K$	25	25.2	1.09	38.8	38.8	10.8
$C_{18}K$	45	25.2	1.06	39.8	39.8	9.3
$C_{22}K$	25	30.3	1.06	39.9	39.6	10.8
$C_{16}Rb$	25	23.6	1.21	39.6	39.6	7.4
$C_{18}Rb$	25	26.2	1.17	39.9	39.2	8.0
$C_{18}Cs$	25	26.8	1.33	38.9	39.2	6.8
$C_{16}H_{33}N(CH_3)_3Br$	15	27.6	1.13	38.8	39.2	10.4

[a] The lengths of alkali metal soap molecules are approximately 18.5, 21.0, 23.5, and 28.5 A for the C_{14}, C_{16}, C_{18}, and C_{22} soaps, respectively. d_a = thickness of the amphiphile layer, S_a = specific gravity of amphiphiles, S and 2ϵ = effective area for polar group calculated from the low- and high-angle lines, respectively, and d_w = minimum thickness of water layer.

For potassium stearate at 45°, when the water content is below $(1 - c)/c = 0.34$, the system consists of crystalline soap and "gel" in equilibrium. The thickness, d_w, of the water layer between the leaflets is 9.3 A, corresponding to about six water molecules per molecule of soap. For water contents $0.34 < (1 - c)/c < 3.00$, only gel is present. The thickness of the water layer increases continuously from 9.3 to about 80 A, while the area for polar group is reported to remain sensibly constant at 39.8 A^2. It would seem, however, on thermodynamic grounds that this constancy cannot be absolute (28). For higher water contents, the

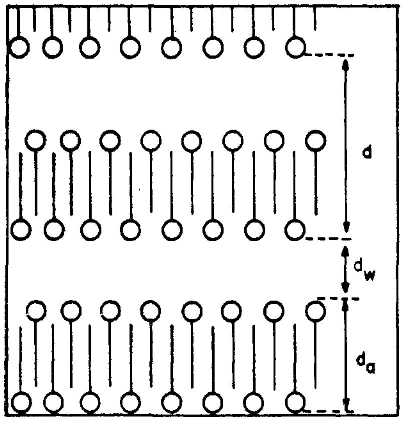


Figure 15.—Schematic representation of the structure of the gel phase (126).

system ceases to be transparent and homogeneous. The measured long spacing, $d = (d_w + d_a)$, no longer varies linearly with $(1 - c)/c$ but tends to a maximum value. These observations show that below a certain concentration the system ceases to form a single phase.

At 25°, for water contents in the range $0.44 < (1 - c)/c < 0.92$, the potassium stearate–water system is no longer composed of a single "gel" phase as at 45°, but contains two conjugate "gel" phases in which the thicknesses of the water layers between the leaflets are approximately equal to 12 and to 25 A, respectively. The thicknesses of the soap leaflets for both "gels" are, as previously, sensibly equal to that of a fully extended soap molecule. Such a separation of two "gels" also occurs with the cetyltrimethylammonium bromide system, in this case not in a region of supercooling as with the potassium stearate system, but in a region where the "gel" phase is the thermodynamically stable condition. It is clear on thermodynamic grounds that the amphiphile lamellae in these conjugate "gels" of greatly different water content cannot be entirely similar. Possibly the phenomenon is connected with the presence of a third substance as impurity.

With these "gel" systems, in which the hydrocarbon region of the amphiphile leaflets is apparently crystalline, the point of view of the *R* theory which relates only to systems entirely in the liquid state cannot be applied. The following interpretation of the formation of the "gel" phase has been proposed by Vincent and Skoulios.

The minimum thicknesses of the water layers separating the leaflets of soap are identical for soaps of the same cation but fall on passing from soaps of potassium to those of rubidium and cesium (Table VI). This agrees with the known decrease in hydration of alkali cations with increase in atomic number. This phenomenon coupled with the lowering of the T_0 line with increasing atomic number clearly shows the importance of the ionization of the soaps to the stability of both the liquid crystalline and "gel" phases. It seems then that the formation of the "gel" constitutes a compromise answer to the conflict between the tendency of the polar groups to ionize and spread apart from one another and the tendency of the hydrocarbon chains to crystallize and draw together. To illustrate this, the case of potassium stearate may be considered. At low temperatures the two tendencies are of similar intensity, the polar groups are ionized and the chains crystallized, and the system adopts the "gel" structure. On this basis it is easy to understand why the soaps of sodium and lithium are incapable of yielding a "gel" phase; their tendency to ionize is insufficient to give rise to a separation of polar groups compatible with the formation of the "gel" structure (*cf.* sections III.B.1 and IV.B.9).

The formation of a ternary gel phase with modified structure, from water, potassium stearate, and octadecanol, which has been reported by Vincent and Skoulios (128), represents a rather novel type of solid solubilization and will therefore be considered later (IV.B.9).

It may be noted here that the term gel is used with several detailed meanings in the literature on amphiphile solutions. It would seem preferable to keep the term "gel" (with quotation marks) only for phases arising and constituted as discussed in the present section. The occasional use of the term gel also to denote the liquid crystalline phases (M_1, G, etc.) (26) could lead to misunderstanding and seems best avoided.

A further use of the word gel is to describe the viscoelastic soap solutions produced by adding electrolytes, with or without long chain alcohols, to aqueous solutions of potassium or ammonium oleates, or of certain other amphiphiles (97, 98, 100, 101). The structure of these viscoelastic solutions is uncertain, but it now seems likely that the participation of the elongated M_1 type of micellar structure, rather than of the lamellar G structure (131), is involved.

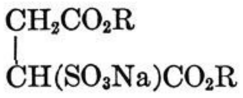
2. Other Ionic Amphiphiles

References to binary aqueous solutions of straight-chain ionic amphiphiles containing the polar groups $-SO_4Na$, $-NMe_3Cl$, and $-NMe_3Br$ have already been made above when the fatty acid soaps were discussed. Such amphiphiles behave in general similarly to the alkali carboxylates and will not be discussed in further detail.

The study of certain branched-chain soaps at room temperature reveals a number of typical features of amphiphile behavior which are less readily observed with the straight-chain soaps, except perhaps at high temperatures, because of the much greater tendency of the straight-chain compounds to crystallize (16). The tendency to crystallize is usually much less for branched-chain soaps, so that liquid crystalline solutions of very high soap content can be observed even at room temperature.

a. Sodium Sulfosuccinic Diesters (Aerosols)

These amphiphiles have the constitution



$$\begin{array}{l}CH_2CO_2R\\ |\\ CH(SO_3Na)CO_2R\end{array}$$

where R is an alkyl group, usually branched. The branched-chain salts have a low tendency to crystallize and are soluble in water at room temperature (giving isotropic or liquid crystalline phases, according to concentration) and in organic liquids. Two of the best studied are Aerosol MA ($R = -CH_2CH(CH_3)CH(CH_3)_2$ and Aerosol OT ($R = -CH_2CH(C_2H_5)CH_2CH_2CH_2CH_3$).

Aerosol MA has been studied by X-ray diffraction by Husson, Mustacchi, and Luzzati (49, 74) and found to give a neat phase, G, over a wide range of concentration. The G phase on dilution gives the isotropic micellar phase, S_1, directly without the appearance of an intermediate middle, M_1, phase. The absence of the M_1 phase may be interpreted on the *R* theory as connected with the greater cross-sectional area of the branched hydrocarbon group in Aerosol MA as compared with that of a straight hydrocarbon chain. This will tend to give rise to a greater separation of polar groups on the hydrophilic face of the $\overline{C}$ layer and therefore to decrease the tendency toward radial dissymmetry in the interaction between the polar groups which is believed to promote the stabilization of the cylindrical M_1 micelles with the straight-chain soaps. The M_1 phase is also absent with Aerosol OT.

i. Inverse Middle (M_2) and Inverse Viscous Isotropic (V_2) Phases.—On slow peripheral evaporation between slide and coverslip of the aqueous G phase from either Aerosol MA or Aerosol OT, the following phase sequence may be observed with the polarizing microscope (Figure 16)

$$G \longrightarrow V_2 \longrightarrow M_2$$

the liquid crystalline "inverse middle" phase persisting even with the anhydrous salt (3). The thermodynamically necessary intermediate two-phase regions ($G + V_2$) and ($V_2 + M_2$) are often not clearly observable with this technique.

The inverse middle phase is believed to have the M_2 structure given in Figure 2. The polar cores and water form cylindrical parallel fibers which are arranged in two-dimensional hexagonal array with the hydrocarbon groups of the amphiphile, in a disordered state, lying between them. This inverse middle structure, M_2, was first proposed by Luzzati and Husson for a phase of low water content obtained with a phospholipid isolated from brain (74, 79). The phase behavior of this system is illustrated by Figure 17. Here compositions intermediate between the inverse middle (M_2) and neat (G) phases yield these two phases conjugately. In the Aerosol OT and Aerosol MA systems, however, an intermediate highly viscous isotropic phase is found (3). This phase (V_2) presumably has a constitution which is the inverse of that of the viscous isotropic (V_1) or cubic phase found intermediate between the M_1 and G phases in certain systems (*cf.* also ref 81). This constitution will be considered further later (II.B.2.a).

Figure 16.—G–V_2–M_2 phase sequence produced on peripheral evaporation of G phase in Aerosol OT–water system (×100; crossed polaroids).

ii. Optical Properties of Inverse Middle Phase.—The considerations advanced (II.A.1.d) concerning the optical properties of the middle phase (M_1) may be extended (with the obvious necessary modifications) to the inverse middle phase (M_2).

This is confirmed by observations with the polarizing microscope. The textures observed with the inverse middle phase of Aerosol OT and, still more clearly, of Aerosol MA, prepared by the peripheral evaporation method are exactly analogous to those obtained with M_1 phases. Basal sections are rare, but approximately basal sections have been obtained by the writer on peripheral evaporation between slide and coverslip of a concentrated solution of Aerosol MA in toluene. Sections giving optic normal interference diagrams are readily formed, as with the M_1 phase, by the peripheral evaporation of aqueous solutions (S_1, G, or V_2 phases)

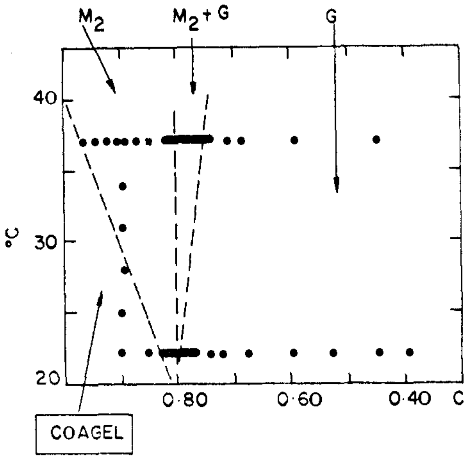


Figure 17.—Phase diagram of phospholipid-water system and position of the experimental points (74).

or by shearing a sample of the M_2 phase between slide and coverslip. As with the M_1 phase, the interference figures may be characterized as negative. Striations similar to those found with the M_1 phase also occur at right angles to the optic axis (*cf.* section II.A.1.d). The negative birefringence of the M_2 phase contraindicates an inverse string-of-spheres structures for this phase (*cf.* section II.B.2.a).

iii. Electron Micrographs of Inverse Middle Phase.—The observation that Aerosol OT and several of its homologs in the pure state exist as the liquid crystalline inverse middle phase has been used by Balmbra, Clunie, and Goodman to obtain very striking electron micrographs of this phase (3). Although the detailed interpretation of the micrographs is not yet possible, stepped growth patterns are discernible. The step heights correspond to the spacings determined by low-angle X-ray diffraction measurements and are approximately equal to twice the length of the soap molecules. Bands of feather-like structures appear which are possibly related to the striations observed with the polarizing microscope as mentioned above. The electron micrographs, like the optical observations, do not suggest the uninterrupted rectilinear extension of the fibrous micelles in hexagonal arrangement over microscopically long distances. For further consideration of these electron micrographs, reference should be made to the original paper in which good reproductions are given.

b. Sodium 2-Ethylhexyl Sulfate

Sodium 2-ethylhexyl sulfate has been found by Balmbra, Clunie, and Goodman (3) to exist in the anhydrous condition as the neat phase. The present writer has also observed this with sodium undecane 3-sulfate, used in earlier work (131). When water is added, both sulfates undergo the phase changes

$$G \longrightarrow V_1 \longrightarrow M_1 \longrightarrow S_1$$

The reverse changes are readily observed by the peripheral evaporation method. Electron photomicrographs of the anhydrous neat phase of sodium 2-ethylhexyl sulfate have been obtained (3). Good reproductions are published in the original paper. The photomicrographs, which are markedly different from those of the M_2 phase, again show stepped growth patterns.

B. NONIONIC AMPHIPHILES

1. *Poly(ethylene glycol) Derivatives*

a. Effect of Size of Polar Group on the Formation of M_1 and G Phases

X-Ray diffraction measurements and observations with the polarizing microscope have been made by Husson, Mustacchi, and Luzzati (49, 74) and also by Francois, Gilg, Spegt, and Skoulios (26) on the Arkopals, technical compounds that are condensation products of *p*-nonylphenol with poly(ethylene glycols), $C_9H_{19}C_6H_4O(CH_2CH_2O)_nH$. In these compounds, the polyethanoxy chain constitutes the hydrophilic group.

By observation with the polarizing microscope, the following liquid crystalline phases were identified (49).

$$\left.\begin{array}{l} n = 6 \\ n = 8 \end{array}\right\} \text{G phase only}$$

$$n = 9 \;\Big\}\; \text{M}_1 \text{ and G phases separated by an isotropic nonliquid crystalline region at intermediate concentrations}$$

$$\left.\begin{array}{l} n = 10 \\ n = 11 \\ n = 13 \\ n = 15 \end{array}\right\} \text{M}_1 \text{ phase only}$$

The micellar dimensions within these phases vary less with concentration than they do for the ionic amphiphiles. Within the aqueous G phases formed in the Arkopal–water systems, the increase in effective area per polar group that occurs on dilution is small.

In correlation with the behavior of Aerosol MA and Aerosol OT where the bulky lipophilic group apparently inhibits the formation of the M_1 phase (II.A.2.a), the bulky polar group in those Arkopals for which $n >$ 9 conversely promotes the formation of the M_1 phase and inhibits the formation of the G phase.

2. *N,N,N-Trimethylaminododecanoimide* *($C_{11}H_{23}CON^-N^+Me_3$)*

The N,N,N-trimethylaminododecanoimide–water system has been studied by the X-ray diffraction method by Clunie, Corkhill, and Goodman (11). This system has the advantage, from the manipulative point of view, that it yields each of the three liquid crystalline phases, M_1, V_1, and G according to concentration, at room temperature. Its phase diagram is given in Figure 18. The zones corresponding to the necessary mixtures of conjugate phases are very narrow and are not indicated.

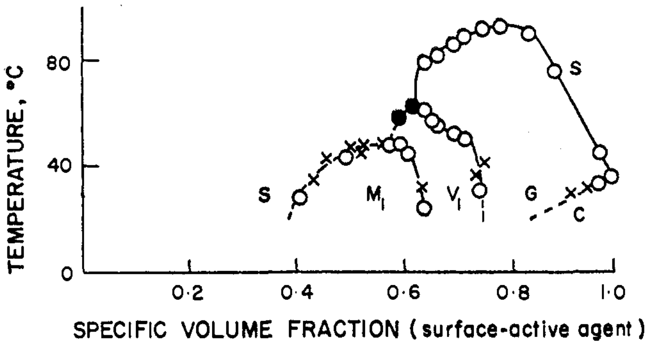


Figure 18.—Phase diagram for the N,N,N-trimethylaminododecanoimide–water system. Phase boundaries were determined from optical O, density ×, and X-ray diffraction ● measurements. S, isotropic solution; M_1, middle phase; V_1, viscous isotropic phase; G, neat phase; C, crystals (11).

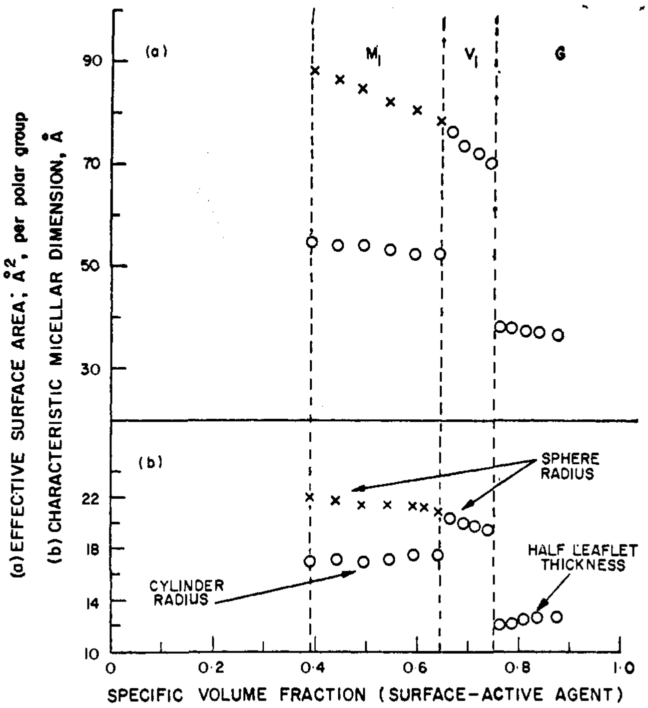


Figure 19.—Calculated dimensions of micellar units in the N,N,N-trimethylaminododecanoimide–water system in the M_1, V_1, and G phases. The dimensions indicated by O were calculated on the bases of the cylindrical, "Cubic I", and lamellar models for the M_1, V_1, and G phases, respectively. The dimensions for the M_1 phase indicated by × were calculated on the "string of spheres" model (11).

a. Proposed Alternative Structures for the M_1 and V_1 Phases

Methods similar to those developed by Luzzati were used to interpret X-ray diffraction diagrams which characterized the middle M_1, viscous isotropic V_1, and neat G phases as hexagonal, face-centered cubic, and lamellar, respectively. With Luzzati's models for these phases the micellar dimensions indicated in Figure 19 were calculated. It will be noted that on these models the effective area per polar group, which might be expected to increase progressively with dilution, is considerably greater in the V_1 phase than in either the M_1 or G phases, between which the V_1 phase is intermediate in composition. A similar anomalous result had been recorded earlier by Husson, Mustacchi, and Luzzati for water–potassium soap systems (49), although at that time they did not appreciate its significance. To account for the anomaly, Clunie, Corkhill, and Goodman proposed a revised structure for the middle phase in which the micellar fibers arranged in two-dimensional hexagonal array were supposed to consist, not of cylinders, but of "pre-existing spherical units linearly aggregated like a rigid string of beads," the units being Hartley micelles. The surface areas per polar group calculated on this model, as shown in Figure 19, are greater than those calculated for the cubic V_1 phase, and to this extent the anomaly referred to above is resolved. However, other anomalies remain; for instance, it is difficult to understand why hydrophilic spherical micelles, whether ionic or nonionic, should aggregate in this way into strings which, as indicated by their hexagonal arrangement, must themselves be mutually repulsive.

Further, spherical micelles should be intrinsically isotropic, and, although their aggregation into strings arranged in two-dimensional hexagonal array might lead to weak positive form birefringence (94), it could not result in the marked negative birefringence observed experimentally with middle phases (II.A.1.d). Further objections to the string-of-spheres structures have been raised by Luzzati and Reiss-Husson (78) who prefer to retain their original cylindrical model for the M_1 phase while revising their "Cubic I" model for the V_1 phase.

In place of their Cubic I model containing spherical hydrophilic Hartley or S_1 micelles (77) dispersed in water at the points of a face-centered cubic lattice, they propose an inverse "Cubic II model" in which the water and polar groups provide the spherical diffracting centers and the hydrocarbon chains fill the gap between the spheres. On this model, with some amphiphiles, though not with all, acceptable relationships between area and concentration were obtained.

Certain objections to the Cubic II model may, however, be pointed out. Luzzati and Reiss-Husson suggest that "the very high viscosity of the cubic phase can be explained by the presence, in Cubic II, of a paraffin matrix; this matrix is likely to determine the rheological properties of the whole structure." It must be remembered, however, that the micellized hydrocarbon chains in aqueous amphiphile solutions take up a disordered liquid-like conformation. On this basis, a matrix of C_{12}–C_{16} hydrocarbon chains would be expected to be mobile rather than viscous, and the high viscosity of the V_1 phase would remain unexplained.

A further objection to the Cubic II model is that it would represent the V_1 phase on Figure 2 as a hydrocarbon-continuous phase, intermediate between G and M_1. This seems quite out of place. Such a hydrocarbon-continuous structure, if it occurred, might with greater liklihood apply to the inverse viscous isotropic phase, V_2, found intermediate between the G and M_2 phases in the Aerosol MA–water or Aerosol OT–water systems discussed above (II.A.2.a). Also if the V_1 phase possessed the hydrocarbon-continuous Cubic II structure, it might be expected to show a considerably lower electrical conductivity than either of the neighboring G or M_1 phases. This is not found experimentally (133).

The writer has suggested (133) that the V_1 and V_2 phases represent thermodynamically stable interdispersions of micro units of the M_1 + G and G + M_2 structures, respectively, the dispersed units being arranged according to a face-centered cubic lattice.

Although a detailed molecular picture of such a microinterdispersion cannot at present be suggested, the idea of a phase constituted as a thermodynamically stable dispersion of two parts is well established. Thus, isotropic solutions of amphiphiles at concentrations slightly above the critical concentration for formation of micelles (cmc) are generally believed to consist of thermodynamically stable microemulsions of Hartley micelles in intermicellar solution at a concentration close to the cmc, a ready interchange of amphiphile molecules between the two parts taking place (I.B.3). In a similar manner it seems possible that the V_1 phase consists of a molecularly mobile microinterdispersion of units partaking respectively of the structural characteristics of the M_1 and G phases (*cf.* section II.A.1.f), the units, though disposed according to a face-centered cubic lattice, being capable of rotary Brownian motion in a manner somewhat analogous to the free rotation above 125° of the ammonium and nitrate ions in the ammonium nitrate crystal (39) or of the molecules in various "plastic crystals" such as camphor (113–115). This would confer isotropic character on the V_1 dispersion and would account for the absence of diffraction lines associated with M_1 and G phases from its X-ray diffraction diagram.

The V_2 phase might similarly be derived from the G and M_2 structures. Such mobile microstructures would accord with the observation, first made with the water–dimethyldodecylamine oxide [$CH_3(CH_2)_{10}CH_2NO(CH_3)_2$] system by Lawson and Flautt (70) and confirmed also by the present writer with the water–N,N,N-trimethylaminododecanoimide system (133), that while the V_1 phase gives a sharp nmr spectrum characteristic of the amphiphile molecules, the M_1 and G phases, with their extended and stably oriented micellar structures, do not. Similarly, while the V_2 phase in the Aerosol OT–water system gives a sharp nmr spectrum characteristic of the Aerosol OT molecules, the neighboring M_2 and G phases do not (133). Although the mean molecular mobility in the V_1 and V_2 phases must therefore be considerably greater than in neighboring birefringent M_1, M_2, and G phases, the latter phases themselves, as indicated by comparative measurements of nmr line widths, possess greater mobility than the solid (35, 36, 69, 70). These and other results show that the use of nmr measurements for differentiation between liquid crystalline phases and for investigating the mobility and environment of molecules or groups within micelles is potentially of great value (*cf.* section IV.A.2.b).

b. Supercooling of the G Phase at the G → V_I Phase Transition

An interesting observation with the N,N,N-trimethylaminododecanoimide–water system is that in the phase transition G → V_1, which as indicated in Figure 18 occurs with appropriate compositions on fall of temperature, the G phase can show marked supercooling (133). Thus, in conformity with Figure 18, a 65 wt % solution of the imide in water occurs at room temperature as the translucent birefringent highly viscous M_1 phase. When gradually heated it passes successively into the glass-clear, even more viscous, isotropic V_1 phase, then into the much thinner translucent birefringent G phase and finally into the mobile isotropic S phase. These phases changes are reversed with fall of temperature, when the transitions S → G and V_1 → M_1 occur at the same temperature, or more accurately over the same narrow range of temperature, as before. The G phase, however, shows marked supercooling of up to 9° at the end of which it rapidly transforms into the glass-clear V_1 phase, the phase change spreading rapidly outward from some center of initiation. The possibility of such metastability in the course of the transformation between liquid crystalline states is of much interest and is difficult to interpret. In this connection the recent report of the existence of certain isotropic liquids, including water, in different modifications which may show metastability may be mentioned (15).

3. *Dimethylalkylphosphine Oxides*

a. Micellar Properties, Cloud Points, and Critical Opalescence in Isotropic Solutions

Phase studies have recently been published (42) for the water–dimethylalkylphosphine oxide [$C_nH_{2n+1}P(CH_3)_2O$] systems in which n = 8, 10, and 12. S, M_1, and G phases are encountered. At a given temperature the M_1 and G phases appear respectively at decreasing concentration with increasing value of n. At higher temperatures in the C_{10} and C_{12} systems the isotropic solutions show the phenomenon of the "cloud point" above which they separate into two conjugate isotropic phases. This phenomenon, which is also characteristic of polyethylene glycol derivatives (II.B.1), is discussed in detail with numerous references to other systems. The critical opalescence in the region of the lower consolute point and the micellar properties of the isotropic solutions were examined by light-scattering measurements. For details the original paper should be consulted. In the region showing critical opalescence the rate of change of osmotic pressure with concentration approaches zero. This permits the relatively large thermal fluctuations in composition which are associated with the critical opalescence (131a). Light scattering which arises from this critical opalescence effect must be distinguished from the light scattering which arises from scattering from micelles at concentrations and temperatures remote from the critical consolute point.

III. Binary Solutions of Amphiphiles in Organic Solvents

As regards their solubility in organic solvents, ionic amphiphiles may be divided broadly into two main classes: (1) crystalline compounds of high melting point and (2) compounds which do not crystallize readily or are of low melting point (*cf.* section II.A.2). As examples of the former, the fatty acid soaps or the *n*-alkane -1 or -2 alkali metal sulfates or sulfonates may be mentioned. These compounds show low solubilities at room temperature. The noncrystalline or low melting point ionic amphiphiles on the other hand show ready solubility in a wide range of organic solvents, forming solutions of much technical importance in many fields, *e.g.*, dry cleaning, paints, cutting oils, corrosion inhibition, etc.

As examples of these noncrystalline ionic amphiphiles, the branched-chain sodium dialkylsulfosuccinic esters (Aerosols), the branched-chain sodium alkylnaphthalene sulfonates, and various cyclic and/or branched-chain salts (sulfonates and naphthenates), obtained as by-products of the petroleum industry, may be mentioned. A review of the properties of organic solutions of heavy metal soaps has been given by Pilpel (99).

A. SOAPS OF HIGH CRYSTALLINITY

At room temperature the crystalline alkali metal and alkaline earth fatty acid soaps show little solubility in hydrocarbons. When heated, the soaps alone undergo a process of complex stepwise melting in which first the hydrocarbon chains and then the polar groups undergo progressive disordering. These changes have been studied (110, 116, 117, 119) by X-ray diffraction methods for soaps of the alkali and alkaline earth metals, but will not be considered here. Over the intermediate ranges, hydrocarbons can be dissolved in limited amounts in the disordered hydrocarbon regions of the soap while the polar groups of the soap largely retain their crystalline order (109, 118). These solutions form a hydrocarbon counterpart to the aqueous "gel" phases discussed (II.A.1.i) in which the ionic groups can be regarded as in solution, while the hydrocarbon chains remain in the crystalline state.

B. SOLUTIONS OF IONIC AMPHIPHILES OF LOW CRYSTALLIZING TENDENCY

1. General Characteristics

The study of solutions of ionic amphiphiles of low crystallizing tendency, the so-called "oil-soluble soaps," in a variety of organic solvents has been extended in recent years by a number of investigators (*e.g.*, 25, 62, 99, 102, 103) and particularly by Singleterry and associates. An account of the constitution and properties of certain of these solutions, including their solubilizing effects, has been given by Bascom, Kaufman, and Singleterry (4). More recently an extensive experimental investigation of solutions of alkali dinonylnaphthalene sulfonates in different organic solvents has been described by Little and Singleterry (71) and accompanied by a theoretical discussion of the factors involved in the formation of these solutions.

Various classes of salts may be distinguished. The divalent heavy metal soaps behave largely as covalent compounds and form solutions in which they are only slightly associated. The alkali and alkaline earth metal soaps show ionic behavior and their mode of association depends on the nature of the soap, on the solvent, and on the presence of impurities, *e.g.*, water or acidic contaminants.

Many of the oil-soluble soaps in hydrocarbon solvents form micelles containing less than 50 molecules of soap. The soap molecules are believed to be arranged with the ionic portion forming a highly polar central core in which the condition of the ions approximates to that in a fused salt (4). This core is surrounded and shielded by the hydrocarbon portions of the molecules. The solubility of such micelles in a hydrocarbon solvent would be expected to follow the general rules applicable to a liquid hydrocarbon having unsaturation, aromaticity, and chain branching similar to that of the hydrocarbon tails that make up the exterior of the micelle.

Association micelles of this type are formed by the sodium sulfosuccinic dialkyl esters, by sodium dinonylnaphthalene sulfonate, and by many petroleum sulfonates.

In the presence of small amounts of water, carboxylic acids, or phenols, the alkali and alkaline earth arylstearates (derived from the Friedel–Crafts reaction between oleic acid and aromatic hydrocarbons) also form micelles (45–47), in the same size range. When, however, the arylstearates are carefully freed from contaminants, they show a much more complex behavior and give rise to viscous solutions whose viscosity is most readily explained by the assumption that

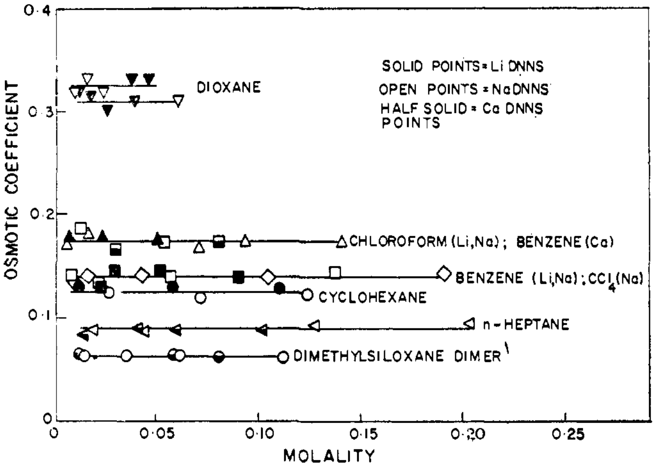


Figure 20. Osomotic coefficient against concentration for sulfonates in low polarity solvents (35°) (71).

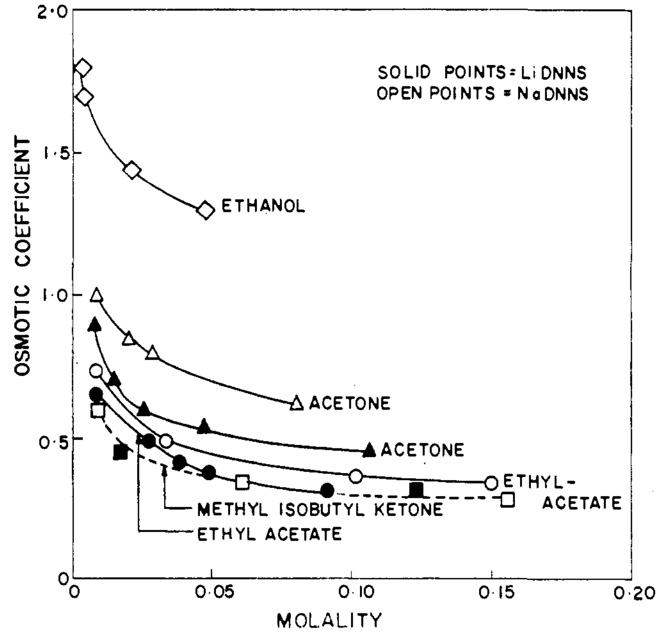
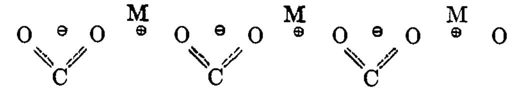


Figure 21.—Concentration dependence of osmotic coefficients of sulfonate in polar solvents (35°) (71).

the pure anhydrous soap is associated in extended linear aggregates through interaction between the polar heads. A possible structure is represented by



in which each resonant carboxyl group is coordinated by two equivalent oxygen atoms to two different metal ions. The tendency to such ion association is accentuated by the low dielectric constant of the medium and is sensitive to the size of the alkali cations, being particularly marked with the relatively small lithium ion. The chains may be broken down by the addition of compounds (alcohols, acids) which themselves may preferentially coordinate with the metal ions. Bifunctional additives produce very complicated variations in viscosity which, however, will not be further considered here.

The size and shape of micelles of the sodium and potassium soaps of *p*-tripentylmethylbenzenesulfonic acid in *n*-heptane have been investigated by light scattering and sedimentation methods by Reerink (102, 103). The micelle size depends strongly on soap concentration, temperature, and the nature of the cation and is very sensitive to the presence of impurities. With the potassium soap fibrous micelles up to 1400 A in length are believed to be formed. With the sodium salt the micelles are much smaller.

Micelle formation by sodium dinonylnaphthalene sulfonate has been studied by Little and Singleterry (71) with a variety of organic solvents. This soap forms relatively small isometric micelles (S_2 type, Figure 2).

Different solvents may be divided into four rather arbitrary classes according to their behavior with this sulfonate.

Class I.—Sulfonate is miscible with the solvent in all proportions; micellar size is constant in a given solvent. This type of behavior is found principally in hydrocarbon solvents and is illustrated by Figure 20. The micellar weight is higher the less polar the solvent. The electrical conductivity of the solution is very low.

Class II.—Sulfonate is miscible with the solvent in all proportions, but the extent of association and/or ionic dissociation is concentration dependent. This type of behavior is found in organic solvents which are themselves amphiphilic in character. Dissociation is greatest and association least in those of most hydrophilic character. These features of behavior are illustrated by the appropriate examples from Figure 21 and Table VII. In water (included for comparison in Table VII), the dinonylnaphthalene sulfonate micelles will be of the S_1 type (Figure 2), and the degree of association is much higher than in the amphiphilic solvents.

TABLE VII

EQUIVALENT CONDUCTANCE OF ALKALI METAL DINONYLNAPHTHALENE SULFONATE SOLUTIONS AT 35° (71)

Solvent	Solvent type	Dielectric constant (25°)	Soap	Soap concn, *M*	Equiv conductance
Cyclohexane	I	2.01	Li	0.01	<0.005
Dioxane	I	2.21	Li	0.01	<0.005
Carbon tetrachloride	I	2.24	Li	0.01	<0.005
Benzene	I	2.27	Li	0.01	<0.005
Ethyl acetate	II	6.02	Na	0.018	0.036
1,1,5-Trihydroperfluoroamyl alcohol	III	16.93^a	Li	0.002	0.18
1,1,5-Trihydroperfluoroamyl alcohol	III	16.93^a	Cs	0.002	0.97
Acetone	II	20.7	Li	0.002	12.2
Ethanol	II	24.3	Li	0.002	23.5
Ethanol	II	24.3	Cs	0.002	27.7
Nitroethane	III	28.6	Li	0.002	0.13
Nitroethane	III	28.6	Cs	0.002	36.4
Nitromethane	III	36.6	Cs	0.002	63.2
Water	III	78.54	Li	0.002	72.2

[a] At 20°.

Class III.—Miscibility is limited and dependent on temperature. Solvents included in this class are the higher members of the polymethylsiloxanes, fluorinated esters, nitroparaffins, and alkyl cyanides. For details of the behavior in individual cases, the original paper (71) should be consulted. It appears that in these systems the alkali metal sulfonates behave essentially as liquids, and the miscibility behavior is of the type shown by pairs of liquids having a critical solution temperature above which they are miscible in all proportions. This behavior is illustrated by Figure 22. In general, the miscibility of the dinonylnaphthalene sulfonates with organic solvents roughly parallels the miscibility of dinonylnaphthalene with these solvents.

The comparative conductances of solutions of the cesium and lithium sulfonates shown in Table VII are interesting. In the solvent series ethanol, nitroethane, nitromethane, the limiting conductance of the cesium salt increases with dielectric constant. On the other hand, the conductance of the lithium salt is much less in nitroethane than in ethanol. While the cesium salt readily dissociates in nitroethane, the lithium salt does not. Measurements indicate that the lithium salt is moderately associated in both nitroethane and nitropropane with an aggregating number of 5 in both solvents. The difference in conductance reflects the difference in cation radii; the small radius of the lithium ion favors ion pairing with the sulfonate anion. Related effects of the cation radius have already been noted in connection with the linear aggregation of arylstearate molecules and in connection with the formation of "gel" and "coagel" (II.A.1.i).

Class IV.—The sulfonate may show no detectable solubility. Solvents in this class include fluorocarbons and higher molecular weight silicones which are immiscible with dinonylnaphthalene.

2. Relation of Micelle Size to Solubility Parameter

Little and Singleterry have pointed out a relationship between the size of the micelles formed in the class I and certain of the class II solvents mentioned above and the "solubility parameter" (43) of the solvent. This parameter is equal to $\sqrt{-E/V_e}$, where $-E$ is the energy of vaporization to zero pressure and V_e is the liquid molar volume. It measures the square root of the "internal pressure" or "cohesive energy density" of the liquid. They suggest that the changes in micelle size result from a tendency for the effective solubility parameter of the solvent-accessible portions of the micelle to match those of the intermicellar solvent.

Examination of molecular models suggests that the maximum size of a spherical aggregate of dinonylnaphthalene sulfonate molecules will contain 15–20 of these. The micellar core will then be completely shielded from the solvent, and the solubility parameter of the micellar surface will possess its minimum value which will be about equal to that of dinonylnaphthalene (7.5). With solvents of solubility parameters of this order the sulfonates are miscible in all proportions. With solvents of considerably lower solubility parameter, the sulfonates show limited solubility of the liquid-liquid type, the micellar size being at its maximum value. As the solubility parameter of the solvent is increased, the micelles tend to assume a smaller size. This size reduction gives a looser packing of the dinonylnaphthalene tails and thus exposes the more interactive and polar parts in such a way as to minimize the difference between the solubility parameter of the solvent and the effective solubility parameter of the micelle. With further increase in the solubility parameter of the solvent, the tendency to match solubility parameters leads to breakdown of the micelles and to the formation of solutions showing little or no association, or even, in solvents of high dielectric constant, substantial ionic dissociation. With solvents of high solubility parameter, the mismatch between the solubility parameters of the solvent and the dinonylnaphthalene radicals of the sulfonate may lead either to limited miscibility (*e.g.*, nitroethane, $\delta = 12.6$; acetonitrile, $\delta = 11.9$) or to the formation of S_1 micellar solution (*e.g.*, water, $\delta = 23.8$) in which the dinonylnaphthalene chains are segregated from the water within a Hartley-type micelle.

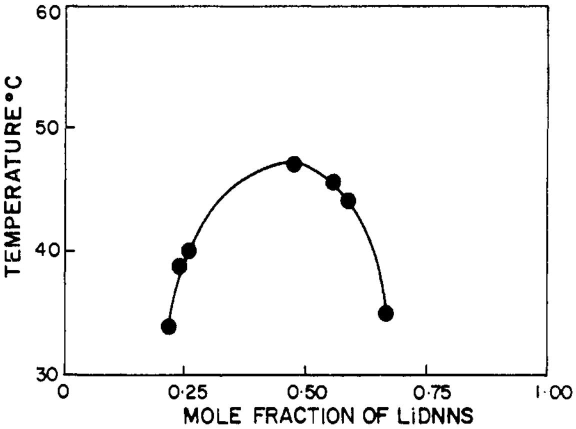


Figure 22.—Mutual solubility of lithium dinonylnaphthalene sulfonate and dimethylsiloxane heptamer (71).

A relationship between micellar size and cohesive energy density similar to that found for the dinonylnaphthalene sulfonates was also noted by Debye and Coll (14) for solutions of the monoglycerides in chloroform, carbon tetrachloride, benzene, and cyclohexane. Clustering, as indicated by vapor pressure measurements, increases with decreasing cohesive energy density of the solvent.

3. Formation of Liquid Crystalline Solutions

In contrast to the ready formation of aqueous liquid crystalline solutions of amphiphiles, anhydrous liquid crystalline solutions in organic solvents are rarely encountered. Those amphiphiles which themselves occur in the liquid crystalline state (*e.g.*, Aerosol OT or Aerosol MA) can take up small amounts of organic solvent before passing into thick highly concentrated isotropic solutions. Ternary liquid crystalline solutions of organic liquid, amphiphile, and water are, however, readily formed as discussed later in this article.

These facts suggest that hydrogen bonding within the $\overline{W}$ region plays an important part in the structure of most amphiphilic liquid crystalline phases. As an exception to the rule, monoethanolamine oleate in the presence of oleic acid readily gives a G phase in hydrocarbon (131). This is possibly because, with this soap, an intercation hydrogen-bonded structure is possible even in the absence of water. Rather surprisingly, solutions of amphiphiles in ethylene glycol, which might be expected to replace water in a similar way, do not readily form liquid crystalline phases (131).

It has been mentioned above that the electrical conductivity of S_2-type micellar solutions in hydrocarbon is very low. This would be expected, since, although the quasi-molten (4) ionic polar micellar cores would show a considerable internal ionic conductance, they will be insulated from one another by intervening hydrocarbon which, on account of its low dielectric constant, will contain few free conducting ions. If, however, extended micelles of the M_2 form could be produced at low concentrations, in a manner analogous to that in which M_1 micelles arise in dilute aqueous solutions in potassium oleate (II.A.1.f), extended intramicellar conducting paths would arise within the solution. In the case of the aqueous potassium oleate solutions, the effect seems to be related to the introduction of the polarizable, relatively hydrophilic, double bond into the hydrocarbon chain. How a similar effect might be produced in hydrocarbon solution is not clear. Presumably, some special characteristics of the polar ends of the amphiphiles forming the micelles would be necessary. It is interesting to speculate whether the exceptionally high electrical conductivities conferred on hydrocarbons by small amounts of certain mixtures of amphiphilic salts, *e.g.*, mixtures of the virtually covalent aluminum or chromium dialkylsalicylates with the ionized metal dialkylsulfosuccinic esters (64), may arise from some such effect.

4. Solubility of Mixtures of Soaps

Although crystalline soaps show a low solubility in organic solvents in comparison with noncrystalline soaps, mixtures of certain crystalline lithium salts of aliphatic and alicyclic acids (9–16 carbon atoms) at 27° show a much enhanced solubility (58–60). The pure crystalline salts whether straight-chain, branched-chain, or alicyclic have low solubilities, the straight-chain salts being least soluble. However, with a mixture of nine salts the solubility was increased to 400 times that of the sum of their separate solubilities. The salts of isomeric mixed acids from commercial products have solubilities as great as 1000 times that of the individual salts of which they were composed. Effects of this type, which are also found with aqueous systems, arise in the following way (4, 16). For a hypothetical initially randomly dispersed mixture of, say, potassium palmitate and water at a given temperature, the final equilibrium state will depend on whether the most stable condition consists of crystalline soap or of micellized soap, each in equilibrium with the aqueous intervening liquid. In the first case a two-phase system (crystals + saturated solution) results, and in the second a single-phase micellar solution (micelles + intermicellar solution). Any factors which impede the formation of a crystalline soap phase, *e.g.*, chain branching or the presence of a mixture of soaps which tend to prevent each others crystallization, will therefore favor the competitive tendency to form a micellar solution.

5. Hygroscopicity of Solutions of Amphiphiles in Organic Solvents

It should perhaps be noted that the strictly anhydrous solutions in organic solvents, to which most of the foregoing discussion refers, can only be maintained in a dry atmosphere. When exposed to atmospheric humidity such solutions will take up, or solubilize, moisture until in equilibrium with their surroundings (2, 27, 44, 61, 83, 108, 129) at the particular water vapor pressure and temperature prevailing. With a solution in a hydrophilic solvent, *e.g.*, ethanol, the uptake of water will be partly due to the hygroscopicity of the solvent itself. With solutions in a hydrocarbon, the water will be taken up by the micelles and will modify their properties considerably. When the properties of any technical solution of an amphiphilic salt in hydrocarbon are considered, the possibility that the solution contains significant amounts of solubilized water must always be borne in mind.

IV. MULTICOMPONENT SOLUTIONS OF AMPHIPHILES. SOLUBILIZATION

A. DISTRIBUTION OF THE COMPONENTS BETWEEN THE $\overline{O}$, $\overline{W}$, AND $\overline{C}$ REGIONS OF A MICELLAR SOLUTION

1. General Considerations

Within the $\overline{O}$, $\overline{W}$, and $\overline{C}$ regions of a micellar solution, whatever its phase, it is possible to "solubilize," *i.e.*, to dissolve, additional molecules of suitable type up to some limit of concentration at which a phase change is initiated.

The activity of any component in a given phase at equilibrium will necessarily be uniform throughout and will therefore be the same in the $\overline{\mathrm{O}}$, $\overline{\mathrm{W}}$, and $\overline{\mathrm{C}}$ regions within that phase and, in more detail, at different points within a particular region, *e.g.*, in the $\overline{\mathrm{C}}$ or $\overline{\mathrm{W}}$ regions at points relatively close to or far from the polar groups. It will also be the same throughout any conjugate phase in equilibrium with the first phase.

In a given phase, therefore, a particular solute, or solubilizate, will be distributed between the $\overline{\mathrm{O}}$, $\overline{\mathrm{W}}$, and $\overline{\mathrm{C}}$ regions so that its concentration is highest in that locality where its activity coefficient is least, *i.e.*, in that locality which it most resembles in solvent type or solubility parameter. Hence, if to an aqueous solution of an ionic amphiphile, *e.g.*, sodium laurate (G, $\mathrm{M_1}$, or $\mathrm{S_1}$ phase), a third substance X is added in an amount insufficient to cause separation of a new phase, the distribution of X within the phase would be expected to depend on the chemical nature of X in the following way.

(a) If X is an amphiphilic salt, *e.g.*, sodium or potassium caprate or myristate, X will be almost wholly incorporated into the $\overline{\mathrm{C}}$ region, polar groups beside polar groups and hydrocarbon tails beside hydrocarbon tails. A small proportion of X will be molecularly dispersed in the $\overline{\mathrm{W}}$ region and a small proportion in the $\overline{\mathrm{O}}$ region.

(b) If X is an amphiphilic salt of lower molecular weight and high water solubility, the same type of distribution will be found as in (a), but the proportion of X in the $\overline{\mathrm{W}}$ region will be greater. If X = HCOONA or $\mathrm{CH_3COONa}$, X will be largely confined to the $\overline{\mathrm{W}}$ region.

(c) If X is an inorganic salt or highly hydrophilic organic solute, *e.g.*, sodium formate or cane sugar, X will be very largely confined to the $\overline{\mathrm{W}}$ region.

(d) If X is an amphiphilic organic solute, *e.g.*, 1-butanol, tending to be soluble both in water and organic solvents, X will be distributed between the $\overline{\mathrm{O}}$, $\overline{\mathrm{C}}$, and $\overline{\mathrm{W}}$ regions of the solution according to its relative hydrophilic, amphiphilic, or lipophilic character. If, for example, X were methanol, it would be largely confined to the $\overline{\mathrm{W}}$ region; if it were dodecanol-1 it would be expected to be mainly concentrated in the $\overline{\mathrm{C}}$ region, while a relatively nonpolar compound such as ethyl laurate would be located mainly in the $\overline{\mathrm{O}}$ region.

(e) If X is a nonpolarizable hydrocarbon it will tend be to confined to the $\overline{\mathrm{O}}$ region. It will not, however, be sandwiched between the ends of the hydrocarbon tails as is sometimes envisaged (IV.B.2). The hydrocarbon tails of the amphiphile, apart from their attachment to the polar face of the $\overline{\mathrm{C}}$ region, have a fluid arrangement. Moreover, the effective area per polar group in the $\overline{\mathrm{C}}$ face is usually considerably greater than the cross-sectional area of a hydrocarbon chain. The interpenetration of the hydrocarbon chains of the amphiphile and the dissolved hydrocarbon can therefore occur without necessarily affecting the effective area per polar group.

The hydrocarbon solute will be distributed among the hydrocarbon chains of the amphiphile in such a way that its activity is uniform throughout the region. Polarizable hydrocarbons, such as benzene, will show a considerable electrostatic interaction ($A_{\mathrm{H}\overline{\mathrm{C}}\overline{\mathrm{O}}}$) with the polar groups and will therefore show a lower activity coefficient when close to the polar groups than would molecules of a less polarizable hydrocarbon such as *n*-hexane. The distributions of polarizable and nonpolarizable hydrocarbons would therefore be expected to be different, as is confirmed by several lines of evidence (*cf.* sections IV.A.2.b and IV.B.2). With benzene there will be an appreciable content of hydrocarbon even in the $\overline{\mathrm{W}}$ regions of the solution (51).

The incorporation of a particular added solute in a given phase will tend to bring about changes in R (or in both R_x and R_y). Changes in molecular spacing may, within limits, compensate this tendency (I.C.2) so that a given micellar form (*e.g.*, the lamellar form) may be retained over a certain range of additive concentration. Beyond these limits phase changes occur which, for ionic amphiphile solutions, have been found (*cf.* section IV.B.7) to be in line with Table I. Probable mechanisms for the effects of different changes in composition are suggested in Table I.

With nonionic amphiphiles derived from polyethylene glycols ($\mathrm{R(OCH_2CH_2)_{\mathit{n}}OH}$) the distribution of solutes, and in particular of amphiphilic solutes such as alkanols, between the $\overline{\mathrm{O}}$, $\overline{\mathrm{W}}$, and $\overline{\mathrm{C}}$ regions would be expected to differ considerably from that arising with ionic amphiphiles. For example, within a solution of potassium dodecanoate, water, and ethanol, the ethanol would be expected to be mainly concentrated in the $\overline{\mathrm{W}}$ region (32). On the other hand, within a solution of $\mathrm{C_{12}H_{25}(OCH_2CH_2)_6OH}$, water, and ethanol, the ethanol would be expected to be located to a considerable extent in the polyethanoxy zone of the $\overline{\mathrm{C}}$ region, which actually occupies a greater volume than the hydrocarbon zone. At the same time hydrogen bonding of the ethanol hydroxyls with the ether oxygen atoms of the polyethanoxy chains would be competitive with bonding of these oxygen atoms with water hydroxyls. In the potassium laurate–water–ethanol system, therefore, the ethanol might be expected to tend to diminish R or, if R is maintained constant by a compensating change in molecular spacing, to increase the effective area per ionic group, through increase in $A_{\mathrm{L}\overline{\mathrm{C}}\overline{\mathrm{W}}}$ (Table I). On the other hand, in the dodecylhexaethylene glycol ether–water–ethanol system, the ethanol might possibly be expected to increase R by its incorporation into the polyethanoxy zone of the $\overline{\mathrm{C}}$ region and by reduction of $A_{\mathrm{H}\overline{\mathrm{C}}\overline{\mathrm{W}}}$ as suggested above. Experimental effects in this sense were noted earlier (131b) though they were not then accounted for. Related effects have been indicated recently in X-ray diffraction studies (section IV. B.5).

2. Experimental Study

a. Measurements of Colligative Properties

Information on the location within an amphiphile solution of particular solutes may be obtained from measurements of colligative properties. Thus Bascom and Singleterry (5) have shown that when acetic acid is dissolved in benzene its vapor pressure is reduced considerably less than when it is dissolved at a corresponding concentration in a solution of sodium dinonylnaphthalene sulfonate in benzene. This is on account of its preferential inclusion in the amphiphilic S_2 micelles ($\overline{C}$ region) within the solution. The term solubilization has therefore been extended by these authors to include all cases in which "the partition of solute between solvent and micelle is such as to produce a substantially higher mole fraction of solute in the micellar microphase than in the solvent."

In this sense acetic acid, methanol, propylamine, acetone, ethyl acetate, and ether have all been reported (55,56) to show solubilization in micelles in hydrocarbon solvents; dinonylnaphthalene, on the other hand, is not appreciably solubilized in solutions of sodium dinonylnaphthalene sulfonate in cyclohexane (71).

This extended definition of solubilization is itself, however, somewhat restrictive. Thus, in a ternary solution of water, benzene, and Aerosol MA, it is equally legitimate to consider additions of sugar or inorganic salt as solubilized in the $\overline{\overline{W}}$ region, additions of dodecanol-1 as mainly solubilized in the $\overline{C}$ region, or additions of *n*-hexane as solubilized mainly in the $\overline{O}$ region. In this example, additions of inorganic salt or of sugar would be found appreciably to depress the temperature for the crystallization of ice but not of benzene, indicating their inclusion in the $\overline{\overline{W}}$ region rather than in the $\overline{O}$ region. Addition of hexane would appreciably depress the crystallizing temperature of the benzene but not that of the ice, indicating the preferential inclusion of the hexane in the $\overline{O}$ region. If Aerosol MA were added to a solution of 1-butanol in either water or benzene, it is likely that the crystallizing temperature (or partial vapor pressures) of the water and the benzene would be raised. Butanol dispersed in either the $\overline{\overline{W}}$ or $\overline{O}$ regions would be withdrawn into the associated amphiphilic $\overline{C}$ region of the ternary solution. The partial vapor pressure of the butanol itself would be diminished. A number of examples of this type of behavior have been discussed by the writer (131c).

b. Measurements of Nuclear Magnetic Resonance Spectra

The study of their nuclear magnetic resonance (nmr) spectra has recently provided a very effective additional method for investigating the constitution of micellar melts and micellar solutions.

Thus by measuring the relative widths of bands corresponding to particular groups of hydrogen atoms (CH_3-, -CH_2-, -OH, -$N(CH_3)_3$, etc.), information concerning the relative thermal mobility of the groups within the solution may be obtained. This may be supplemented by measurements of spin lattice relaxation times. Comparison of the chemical shifts of a particular grouping in the micellar solution with the chemical shift corresponding to that grouping when in solution in a standard solvent (*e.g.*, cyclohexane or water) gives information concerning the environment of the grouping within the micellar solution.

i. Measurements of Line Widths.—In general the width of a nmr line is inversely proportional to the amount of thermal motion of the particular grouping producing the line. Thus the groups in an organic solid usually give a line width between 10 and 20 gauss while a group in a liquid such as water gives a line width of only a few milligauss Groupings in liquid crystalline phases or in "plastic solid" phases (113–115) give lines of intermediate widths, and, from the changes in the relative line widths that accompany phase transitions, information concerning the relative thermal mobility of particular groupings within successive phases may be obtained.

Investigations by Grant and Dunnell (35, 36) and by Lawson and Flautt (69) on variation in the line widths corresponding to the hydrocarbon chains of a number of individual soaps with changes in temperature have shown that at each phase transition there is a change in line width. The line width usually diminishes with rise of temperature indicating increased thermal molecular mobility in the successive phases. The transition temperatures indicated by the nmr methods correspond to those determined by other means.

Preceding these investigations on one-component amphiphile systems, McDonald (88) had noted that, while both two- and three-component isotropic aqueous micellar solutions of amphiphiles give sharp nmr spectra comparable with those obtained from organic liquids and nonmicellar solutions, when these isotropic solutions undergo a transition, arising from change in temperature or composition, into liquid crystalline systems "there is a reduction in intensity of the water proton signal while that from the hydrocarbon chain protons is completely suppressed." More recent work by Lawson and Flautt (70), by Zlochower and Schulman (135), and by the writer (133) has confirmed this result for the birefringent M_1, G, and M_2 liquid crystalline phases. This evidence, as McDonald pointed out, "suggests that there is a greater degree of order in the hydrocarbon portion of the liquid crystal layer in these systems than has heretofore been suspected." This ordering may well be related to such mutual orientation of the polar groups in the M_1, G, and M_2 phases as suggested in section I.C.2. It should, however, be pointed out that the differences between the nmr band widths of different phases seem to be of degree rather than of kind. Thus in the binary fatty acid soap–water systems studied by Lawson and Flautt (70), the line widths decreased discontinuously between the succession of anisotropic phases with both increase of temperature and of water content. Variations with composition in the narrow band widths in the high-resolution spectra of mobile isotropic phases containing solubilized materials have recently been noted by Eriksson and Gillberg (23). These variations, which are accompanied by viscosity changes, may possibly be related to displacements of the intermicellar equilibrium of the type indicated at the bottom of Figure 2 where, although liquid crystalline phases do not appear, more extended and persistent micellar aggregates would be expected toward the middle of the diagram ($R \sim 1$) than at either side ($R \ll 1$ or $R \gg 1$). For further discussion the original paper should be consulted.

In contrast to the birefringent M_1, G, and M_2 liquid crystalline phases, the isotropic cubic liquid crystalline phases V_1 and V_2 yield sharp nmr spectra. The significance of this has been considered in section II.B.2.a.

ii. Measurement of Spin-Lattice Relaxation Times.—Measurements of the spin-lattice relaxation times of both the water protons and the hydrocarbon chain protons in aqueous solutions of sodium alkyl sulfates have been made by Clifford and Pethica (8, 10). When micelles are formed, the relaxation rate of the CH_2 protons is greatly increased as their environment changes from water (H_2O or D_2O) to hydrocarbon. The relaxation rates of the CH_2 groups in micelles increase with both chain length and concentration. The hydrocarbon chains of the sodium alkyl sulfates dissolved in water at concentrations below the cmc increase the relaxation rate of adjacent water molecules. When micelles are formed, there is a resultant reduction in the effect of the solute on the water protons. The experimental results collectively are consonant with the well-recognized fact (*cf.* section II.A.1.f) that part of the alkyl chains in the micelles are exposed to water and further indicate that molecular motion in the micellar interior is more restricted than in a comparable liquid hydrocarbon.

iii. Measurements of Changes in Chemical Shift.—The positions of the nmr spectral peaks corresponding to particular groups of protons within an organic molecule depend both on the nature and position of the group within the molecule itself and on the local environment of the molecule. Sharp spectra arise only when the thermal mobility of the molecules is relatively high, *e.g.*, in isotropic melts and solutions (53). In solution the position of a particular peak shifts with the nature of the external environment of the molecules giving rise to the peak. From the observation of shifts, inferences may therefore be made concerning the molecular environment.

A striking example of this type of investigation is provided by the study of the behavior of the nmr peaks corresponding to the phenyl protons of a series of ω-phenylalkyltrimethylammonium bromides when these form micelles in isotropic solutions in water or in deuterium oxide (92). With the individual bromides the peak of the phenyl protons shows no shift with increasing concentration until the cmc is reached, whereafter it shifts to higher fields. This is interpreted as owing to a change in environment of the phenyl group from water (below the cmc) to hydrocarbon (when included in micelles). At concentrations where the proportions of micellized and nonmicellized bromide are both significant, a single intermediate peak position is observed. This indicates rapid exchange of the phenylalkyltrimethylammonium bromide molecules between the micelles and the intermicellar solution.

Further very interesting results were obtained with solutions of mixtures of ω-phenylpentyl- and ω-phenyloctyltrimethylammonium bromides in different proportions (52). At concentrations below the cmc of the mixtures, only one phenyl peak is observed. At concentrations above the cmc the phenyl proton signal shifts to higher fields and splits into two peaks, the peak at higher fields being due to the bromide of longer alkyl chain length. The significance of these results with regard to the formation of mixed micelles is considered in the original paper. Within the mixed micelles, which it is concluded are formed, the ω-phenyl groups of the pentyl and octyl compounds must apparently respectively occupy statistically dissimilar positions (nearer or further from the polar groups) in order to account for the peak splitting which is observed.

Line-shift experiments concerning solubilization in isotropic micellar solutions of cetyltrimethylammonium bromide (0.1729 *M*) or of cetylpyridinium chloride (0.1723 *M*) have been made by Eriksson and Gillberg (22, 23). The results obtained indicate that, at low and intermediate solubilizate concentrations, benzene, bromobenzene, N,N-dimethylaniline, and nitrobenzene are predominantly solubilized at the polar micelle–water junction. Isopropylbenzene and cyclohexane are predominantly solubilized in the hydrocarbon region of the micelles. Where a distribution of the solubilizate between hydrocarbon and polar regions occurs, a single nmr peak of intermediate position is observed. This indicates that ready exchange of solubilizate between different micellar regions takes place. This result may be contrasted with the behavior of phenyl groups when chemically attached to the amphiphile (anchored to the polar groups) as discussed in the preceding paragraphs. In both types of system a study

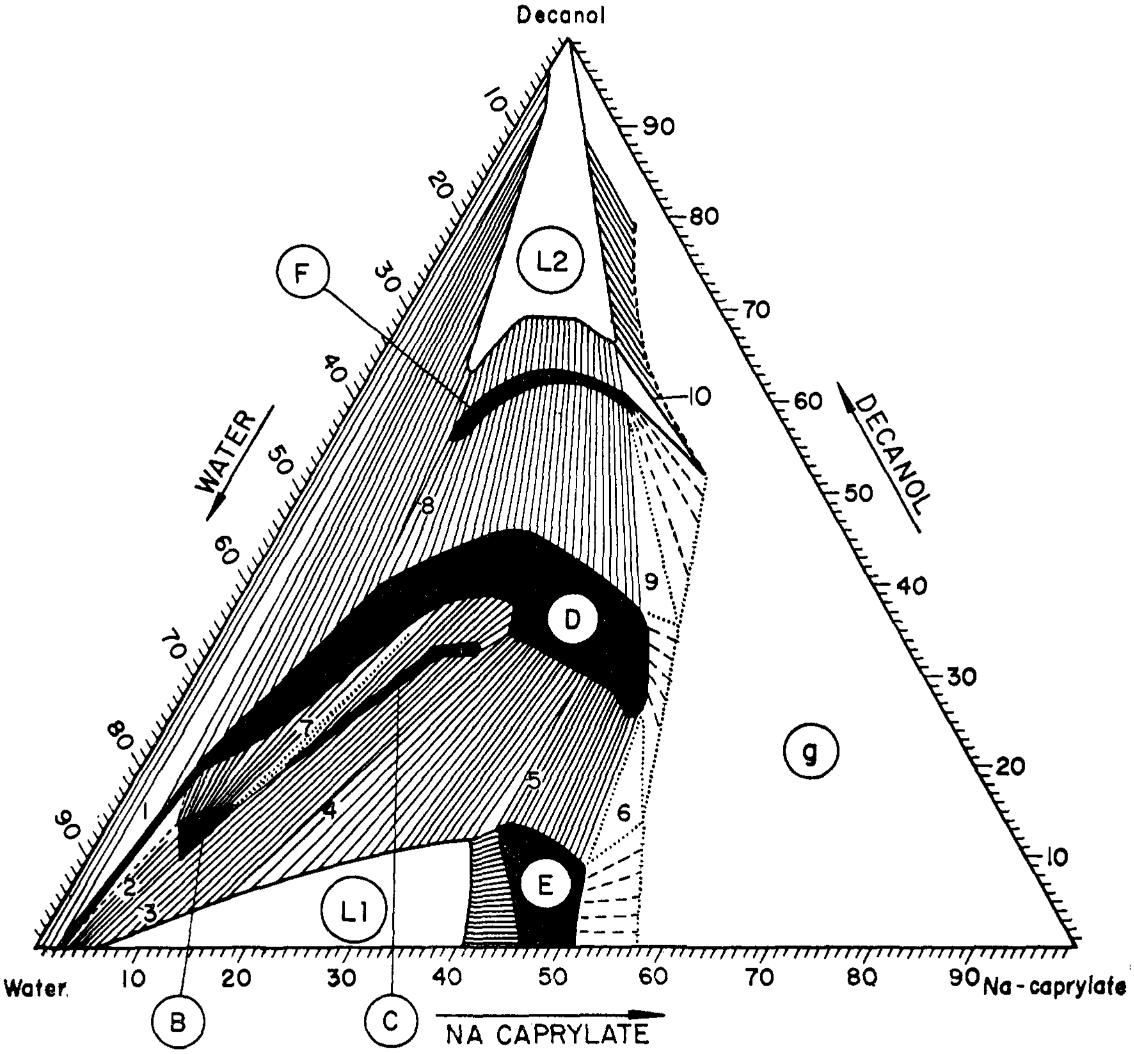


Figure 23.—Phase diagram for the three-component system sodium caprylate–decanol–water at 20°. The concentrations are % by weight (81). L1, homogeneous isotropic solutions in water; L2, homogeneous isotropic solutions in decanol; B, C, D, E, F, homogeneous mesomorphous phases; g, solid crystalline sodium caprylate and hydrated sodium caprylate with fiber structure; 1–10, three-phase triangles.

of the behavior at higher concentrations, where liquid crystalline solutions would be expected, would be of much interest.

B. SELECTED MULTICOMPONENT SYSTEMS

Work on a wide range of multicomponent systems has recently been published (*e.g.*, 6, 67, 68). The earlier work has already been reviewed by several writers (I.A). In the present section certain recent studies are selected for comment.

1. *The Sodium Caprylate–Water–Decan-1-ol System*

This system has been extensively studied by Ekwall and collaborators (19, 20, 24, 80, 81), and their most recent phase diagram is reproduced in Figure 23. X-Ray diffraction measurements were made on the individual phases (24, 81). Related systems with other alcohols and with caprylic acid were also studied, although in less detail, and found to show essentially similar features. Figure 23 should be compared with earlier diagrams for systems containing soaps and alkanols, mostly of lower molecular weight, investigated by Lumb (73).

The most theoretically significant features of the new work are (1) the clear structural identification of phase E as the middle phase, M_1, having the fibrous hexagonal structure; (2) the identification and characterization of phase F as the inverse middle phase, M_2, having the inverse fibrous hexagonal structure; (3) the relationship on the phase diagram of these phases to the lamellar phase, G, in region D and to the mobile isotropic micellar phases in regions L1 (S_1) and L2 (S_2). The experimental phase changes indicated in Figure 23 are in good accord with Table I and Figure 2.

Some further tentative comments on Figure 23 may be offered. (i) It seems possible that region B may represent an extension of region D (G phase) rather than a new phase. In experiments by the writer, it

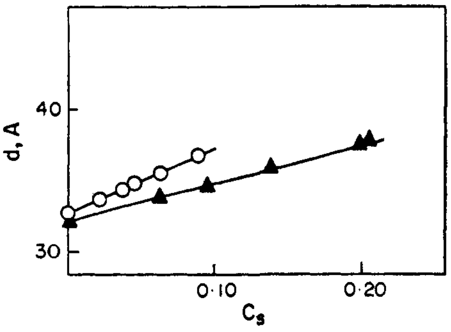


Figure 24.—Expansion in X-ray long spacing, *d*, on solubilization at 82° of *n*-octadecane (○) and ethylbenzene (▲) in aqueous solutions (G phase) of sodium myristate (75 and 65 wt %, respectively). C_s hydrocarbon solubilized (wt/total wt) (109).

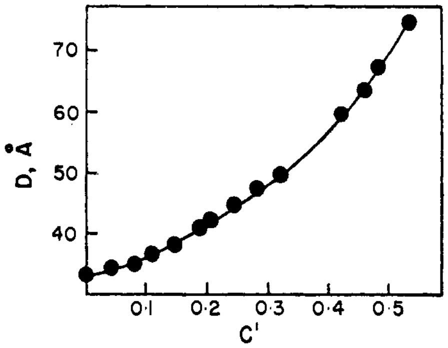


Figure 25.—Variation in the diameter *D* of the cylinders in the middle phase M_1 of the sodium myristate–water system on solubilization of ethylbenzene (C' = ethylbenzene–ethylbenzene + soap) (109).

was found that a composition in the region B was clear and birefringent and readily showed the electrooptical turbidity effect previously noted with many dilute G phases (131). (ii) It does not seem certain that the "Weisse Phase C," which it is suggested by Ekwall is a second lamellar phase, is indeed a single phase. It seems to the present writer to be more probable that C represents a viscous dispersion of the neat phase D (G) in the isotropic phase S_1. This would accord with the opacity of C, which contrasts with the translucency of the remaining liquid crystalline phases. It would also accord with the complete ring of the X-ray diffraction diagram of C, indicating lack of any preferred orientation (24, 81) of the lamellar domains. This is in contrast to the type of diffraction diagram showing persistent orientation obtained from individual G, M_1, and M_2 phases. If the "C" phase, as suggested above, actually consists of a fine dispersion of G in S_1, the particles of G phase (unless highly anisometric) might be expected not to show persistent orientation on account of the averaging effect of Brownian movements over the period of exposure of the film.

2. *X-Ray Diffraction Studies of the Liquid Crystalline Phases in Amphiphile–Water–Hydrocarbon Systems*

Spegt, Skoulios, and Luzzati (120) have carried out an X-ray diffraction study of the liquid crystalline phases occurring at 82° in the ternary systems sodium myristate–water–ethylbenzene and, in less detail, sodium myristate–water–*n*-octadecane.

Their main conclusions were that the hydrocarbons may be included in both the hexagonal, M_1, and lamellar, G, phases without, up to a certain limit of concentration at which a phase change is initiated, changing their essential structures. With octadecane dissolved in the lamellar phase, the thickness of the bimolecular leaflet for a given water/soap ratio increases (within the limits of accuracy of the experiment) linearly with the hydrocarbon content, while the effective area per polar group remains constant. On the other hand, when ethylbenzene is dissolved in the lamellar phase the effective area per $-CO_2Na$ group increases with ethylbenzene content. The thickness of the bimolecular leaflet consequently increases less rapidly with hydrocarbon content with ethylbenzene than with octadecane. This is illustrated by Figure 24.

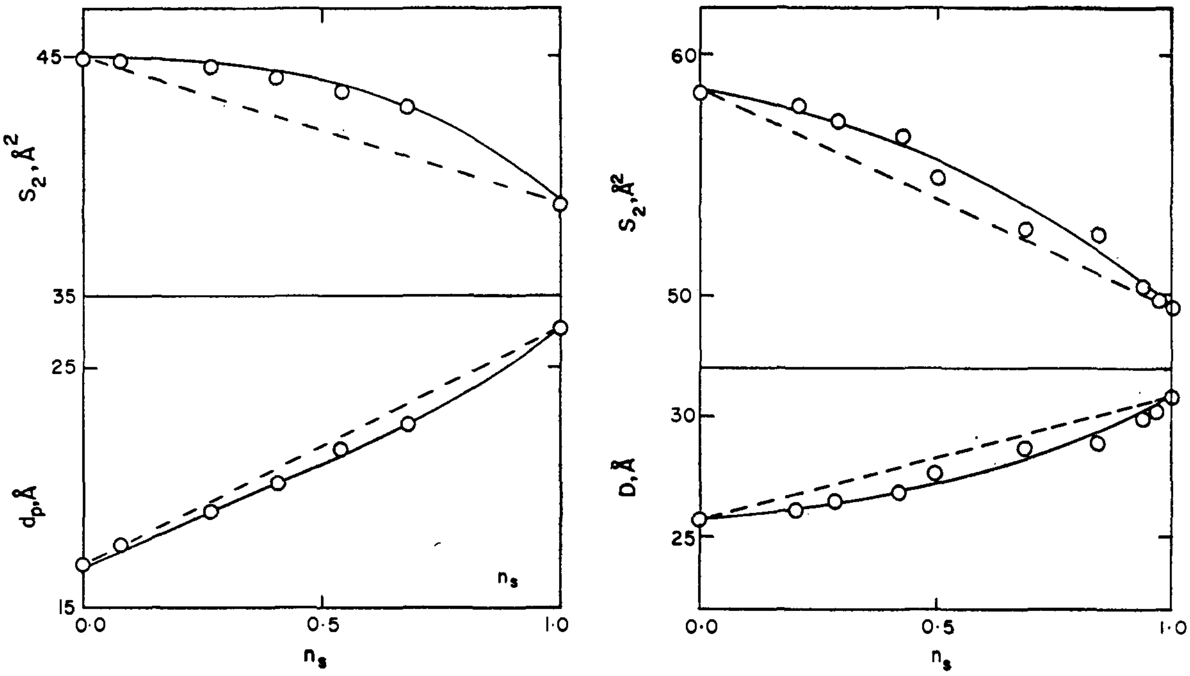
The increase in area per polar group with increase in ethylbenzene content is probably due to the localization of a proportion of the polarizable ethylbenzene molecules between the polar groups (*cf.* section IV.A.1) whose separation is thereby increased. This effect is not appreciable with the less polarizable *n*-octadecane molecules which will be more confined to the hydrocarbon region of the micelles where, like chemically bonded additional methylene groups, they exert little effect on the area occupied by the polar groups on the hydrophilic surface of the micelle.

The effect of ethylbenzene solubilized in the hexagonal phase of the sodium myristate–water system is mainly to increase the diameter of the cylindrical micelles (Figure 25). In this phase, within the limit of experimental accuracy, the effective area per polar group remained constant (52 A^2) with change in hydrocarbon and water content. Some variation might, however, have been expected (II.A.1.d and i).

An extension of the above X-ray diffraction study to the solubilization of hydrocarbons, long-chain alcohols, and acids in aqueous M_1 and G solutions of nonionic amphiphiles (Arkopal type), as well as of ionic soaps, has recently been published (26). In addition the behavior of mixtures of nonionic amphiphile + soap in both M_1 and G phase solutions was studied.

Arkopal 060 ($C_9H_{19}C_6H_4(OCH_2CH_2)_nOH$, $n = 6$) was used for the preparation of the lamellar G solutions, and Arkopal 130 ($n = 14$) for the preparation of the fibrous hexagonal M_1 solutions.

The dimensional changes on solubilization of hydrocarbon, indicated by the X-ray diffraction measurements, accord with the following conclusions. When dissolved in either a nonionic aqueous G phase (70 wt % Arkopal 060) or in a nonionic aqueous M_1 phase (50 wt % Arkopal 130), both *n*-decane and ethylbenzene



(a) Arkopal 060 + water + potassium oleate

(b) Arkopal 130 + water + potassium laurate

Figure 26.—Micellar dimensions (a) in mixtures of Arkopal 060 and potassium oleate (75 wt % total concentration, G phase) and (b) in mixtures of Arkopal 130 and potassium laurate (50 wt % total concentration, M_1 phase) at 24° (26); S_2 = effective mean area per polar group ($-O(C_2H_4O)_2H$ + $-CO_2K$); d_p = thickness of paraffin layer of lamellae in G phase; D = diameter of hydrocarbon core of cylinders in M_1 phase.

were principally located in the $\bar{O}$ region of the solution, increasing the bimolecular leaflet thickness or the fiber diameter, respectively. In contrast to their differing behavior in the ionic aqueous sodium myristate system considered above, both hydrocarbons here behaved similarly. While little change in the effective area per polar group[3] was found with variation in hydrocarbon (or water) content in the lamellar phase from Arkopal 060, a moderate increase in area with increase in hydrocarbon (or water) content was found with the M_1 phase from Arkopal 130. The implications of these observations are not clear. The authors consider that in the lamellar solutions the constancy of the effective surface area of the polar groups (in this phase, equal to the mean cross-sectional area per amphiphile molecule) during the addition of hydrocarbon "proves that the added hydrocarbon is localized, at least in its major part, in the center of the leaflets without penetrating significantly among the hydrophobic chains of the Arkopal." This seems to the writer to be thermodynamically unlikely (IV.A.1). Further the mean area per amphiphile molecule (*ca.* 46 A²) in these solutions is considerably greater than the cross-sectional area of a fully extended hydrocarbon or polyethanoxy chain (about 20 A²) so that in the absence of dissolved hydrocarbon the fluid hydrocarbon chains of the amphiphile molecules must statistically be considerably crumpled. Solubilization of hydrocarbon could occur with the extension of the hydrocarbon chains of the amphiphile accompanied by their mixing with the added hydrocarbon molecules. These processes need not involve any considerable change in the effective area per amphiphile molecule. It may be remarked also that in the Arkopal 060 lamellar phase the effective area per amphiphile molecule is likewise little dependent on water content (26, Appendix) although from activity measurements penetration of water among the $-(CH_2CH_2O)_nH$ chains, rather than its sandwiching between them, is virtually certain (21).

3. *X-Ray Diffraction Studies of the Liquid Crystalline Phases in Aqueous Solutions of Mixtures of Amphiphiles*

It has long been known that solutions of mixtures of long-chain soaps show single X-ray diffraction maxima intermediate between those corresponding to the individual soaps. This indicates the cooperation of the two amphiphiles in micelles formation (*cf. e.g.*, 130).

Recently (26) a study has been described of the joint formation by Arkopal 130 and potassium laurate (at 50 wt %, over-all concentration) and by Arkopal 060 and potassium oleate (at 75 wt % over-all concentration) of aqueous M_1 and G solutions, respectively. Results are illustrated by Figure 26. These results indicate that in these systems the two types of molecule are able to participate jointly in micelle formation in both the fibrous (M_1) and lamellar (G) structures.

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(3) As calculated at the $-C_6H_4-\cdots-O(CH_2CH_2O)_nH$ linkage.

In both types of structure the curve for the mean effective area per polar group lies slightly above the straight line joining the areas for solutions of the two compounds individually. This effect probably arises from the decreased binding of counterions on the surface of the micelle as the anionic charge density per unit area is reduced by substitution of ionic by nonionic polar groups (12, 50). A mixture of two homologous ionic amphiphiles or of two homologous nonionic amphiphiles might be expected to give more closely straight-line graphs. In this type of system, therefore, we have the cooperation of amphiphile molecules together in the $\bar{C}$ region in contrast to the largely different functions of amphiphile and hydrocarbon in the systems considered in the preceding section. As for the manner in which joint micelle formation of the type indicated by the X-ray diffraction measurements discussed above will tend to affect $R = f(A_{\bar{C}\bar{O}}/A_{\bar{C}\bar{W}})$, and thus to influence micellar shape, this will depend on its effects on both $A_{\bar{C}\bar{W}}$ and $A_{\bar{C}\bar{O}}$. One might expect $A_{\bar{C}\bar{W}}$ to approximate to the mean interaction of the two types of polar groups separately with the $\bar{W}$ region plus an additional interaction due to the increased ionic dissociation of the carboxylate groups on account of their reduced concentration per unit area of micellar surface. From the evidence in section II.A.1.d.i, $A_{\bar{C}\bar{O}}$ seems to be rather insensitive to the thickness and molecular distribution within the $\bar{O}$ region when this remains of purely paraffinic character. In the example under consideration, because of the partly aromatic character of the Arkopal side chain, this condition will not strictly apply.

4. X-Ray Diffraction Studies of Amphiphile–Water–Fatty Acid or Fatty Alcohol Systems

The X-ray diffraction study of the solubilization of longer chain, water-insoluble alcohols or fatty acids in aqueous M_1 or G solutions of either nonionic (Arkopal 060 or 130) or ionic (potassium laurate) amphiphiles indicates that these compounds, instead of being mainly localized either in the hydrocarbon or amphiphilic retions of the solution, as in the two previous examples, respectively, are distributed between both the $\bar{O}$ and $\bar{C}$ regions along the lines to be expected from the introductory paragraphs of the present section. For particulars the original paper (26) should be consulted. One detail which is emphasized is that, whereas with the Arkopals the changes in the structural parameters (area per polyethanoxy group, cylinder diameter, or leaflet thickness) seem to depend only on the volume of fatty alcohol or fatty acid solubilized, with the soaps the parameters depend in addition on the molecular weight or chemical character (acid or alcohol) of the solubilizate. It is suggested in the original paper that this difference is connected with the influence of the polarity of the environment on the distribution of electric charge in the ionic amphiphile solutions. While this certainly will play a part, it must be emphasized that the localization of a solubilized alcohol or acid in the micellar region derived from a soap or from an Arkopal might be expected to differ considerably (IV.A.1). Thus, in the Arkopal micelles there is a $(-CH_2CH_2O)_n-H$ region which in size is equal to or larger than the hydrocarbon region. This polyethanoxy region will exert a considerably greater solvent affinity toward polar solutes of the fatty alcohol or fatty acid type (whether in the water-soluble or hydrocarbon-soluble range of molecular weight) than will be exerted by the compact ionized "inorganic" polar group of the soaps. Thus the relative distribution of fatty alcohol and fatty acid additives might vary less with their molecular weight within micelles of polyethylene oxide derivatives than within micelles of ionic amphiphiles. In this connection the study of solubilization with compounds having compact nonionized polar groups, *e.g.*, N,N,N-trimethylaminododecanoimide, would be of interest. The manner in which solubilization of the character indicated by the X-ray diffraction measurements discussed in this section will tend to affect the ratio R, and consequently micellar shape, will be more complex than in the case of the simple cooperative micelle formation discussed above. In the present instance, $A_{\bar{C}\bar{W}}$ will be affected along the lines mentioned before but, also, since the hydrophilic interactions of the $-CH_2OH$ and $-CO_2H$ groups with the $\bar{W}$ region will be much less than that of ionized carboxylate groups, dilution of carboxylate groups in the polar face of the micelle with CH_2OH or CO_2H groups will decrease $A_{\bar{C}\bar{W}}$. The introduction of fatty alcohol or fatty acid into the $\bar{O}$ region might be expected to have little effect on $A_{L\bar{C}\bar{O}}$. $A_{H\bar{C}\bar{O}}$, however, and consequently $A_{\bar{C}\bar{O}}$ over-all should be increased. Solubilization of the character discussed in this section would therefore be expected to tend to increase R (*cf.* Table I, method Ib).

5. X-Ray Diffraction Studies of Aqueous Amphiphile Solutions Containing Water-Soluble Organic Materials

Gilg, Francois, and Skoulios (32) have carried out an investigation of the effects of partially replacing the water in aqueous liquid crystalline solutions of various ionic and nonionic amphiphiles with water-miscible organic solvents. This was found to be possible within the range where the percentage of organic solvent did not exceed 40–50 wt %. At higher concentrations phase changes occur.

We will consider first the effects observed with ionic amphiphiles. Figure 27 illustrates the influence of replacing the water by an equal weight of a mixture of water with certain water-soluble organic solvents on the effective area per $-CO_2K$ group on the surface of the M_1 micelles formed by a 45 wt % aqueous solution of potassium laurate at 25°.

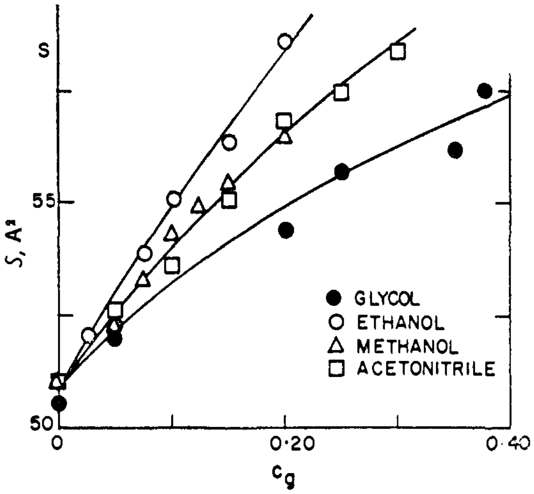

Figure 27.—Variation in the effective area, S, per $-CO_2K$ group as a function of the content of the aqueous fraction in water-soluble additives (45 wt % solutions of potassium laurate at 25° in (water + water-soluble additive), M_1 phase (32). The abcissa is for weight of additive/weight of additive + weight of water.

In these soap systems, on the basis of partition experiments, the organic additive is believed to be very largely confined to the $\overline{W}$ region. It will be seen that in all cases the area per $-CO_2K$ group increases with the proportion of organic solvent; *i.e.*, the organic solvent favors the separation of the carboxylate groups on the face of the micelle. This effect is in line with the experimentally observed effect of such compounds on phase changes noted in Table I. In Table I the effect of the organic solvent in tending to decrease R was attributed to its increasing $A_{\overline{C}\overline{W}}$ by increasing $A_{L_{\overline{C}\overline{W}}}$, *i.e.*, the lipophilic interaction, through dispersion forces, between the $\overline{W}$ and $\overline{C}$ regions. Gilg, Francois, and Skoulios have suggested, on the other hand, that the increased separation of the $-CO_2K$ groups arises from the influence of the changed composition of the $\overline{W}$ region on its electrical interactions with the ionized polar groups. In support of this view they point out that in the systems under consideration the variation in area per polar group parallels very closely the variation in dielectric constant of the $\overline{W}$ region (Figure 28). They further point out that, in a variety of systems, both hexagonal (M_1) and lamellar (G), the variation of S/S_0 (S and S_0 being respectively the mean effective areas per ionized group in presence and absence of water-soluble-type compounds) with the dielectric constant of the W region is approximately the same, independently of the chemical nature of the ionic amphiphile and the structural type (M_1 or G) of the system (Figure 29). When these results are considered, it must be remembered that the parallel variation of dielectric constant and of area per polar group may be related as parallel effects of change in composition rather than as direct cause and effect, the one of the other. It is difficult to see how a reduction in the dielectric constant of the $\overline{W}$ region should, *per se*, tend to increase the lateral separation of the polar groups. The opposite might seem more likely.

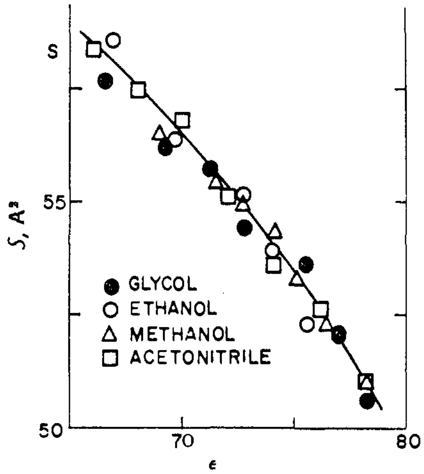

Figure 28.—Variation in the effective area, S, per $-CO_2K$ group as a function of the dielectric constant of the aqueous fraction (45 wt % solutions of potassium laurate at 25°) in (water + water-soluble additive); M_1 phase (32).

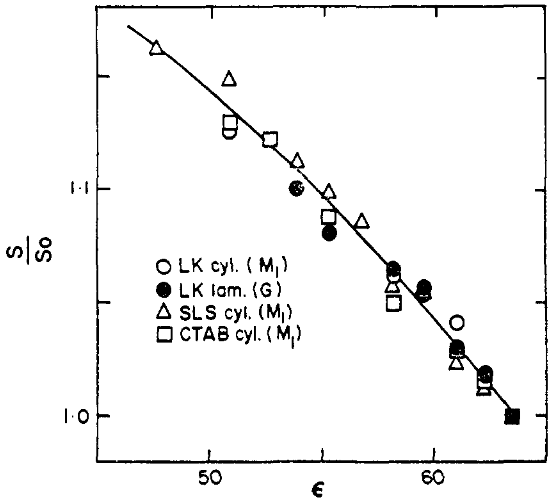

Figure 29.—Variation in the relative effective surface areas S/S_0 per $-CO_2K$ group as a function of the dielectric constant, ε, of the aqueous fraction. S = area in mixed solvent; S_0 = area in the same phase at the same concentration but with water alone as solvent (32).

With the nonionic amphiphiles Arkopal 060 and Arkopal 130, in contrast to the behavior observed with the ionic amphiphiles, the area per polar group (in this case defined as the effective cross-sectional area per amphiphile molecule at the $-C_6H_4-\cdots-O(CH_2CH_2O)_nH$ link) was found to be independent of the composition of the water/organic solvent ratio with both the lamellar and hexagonal phases. It was suggested by Gilg, Francois, and Skoulios that this difference in behavior arises from the absence of ionization in the Arkopal systems. It may be remarked, however, that in these systems, in contrast to the systems containing the ionic amphiphiles, the effect of the change in solvent on $A_{\mathrm{L}\overline{\mathrm{CW}}}$, if this is considered to operate at the $-C_6H_4-\cdots-O(CH_2CH_2O)_nH$ link, would be minimized by the screening afforded by the chemically attached polyethylene glycol chain. Further, the distribution of the organic additive between the amphiphilic and aqueous regions of solution is uncertain, since no partition experiments relevant to this case were carried out. The interpretation of the observations in terms of intermolecular forces is therefore not unequivocal.

It may be recalled here that the phase behavior which indicates a reduction of R on the introduction of water-soluble organic liquids into solubilized systems containing ionic amphiphiles (Table I, method IIb) is not found on their introduction into systems containing nonionic amphiphiles (IV.A.1). Thus, the difference in behavior between the two classes of amphiphiles noted in the X-ray diffraction study is in accord with their difference in affecting phase behavior as interpreted from the point of view of the R theory.

The possibility that organic solutes, themselves amphiphilic though with hydrophilic bias, may affect both the polar ($A_{\mathrm{H}\overline{\mathrm{CW}}}$) and nonpolar ($A_{\mathrm{L}\overline{\mathrm{CW}}}$) interactions between the $\bar{\mathrm{W}}$ and $\bar{\mathrm{C}}$ regions gives rise to difficulty in interpreting the significance, in terms of intermolecular forces, of the X-ray diffraction results with liquid crystalline amphiphile solutions containing such solutes. It would appear that comparable experiments with water-soluble inorganic solutes might be more readily interpreted. In this case, polar effects would be expected greatly to predominate, and one might expect a decrease in area per polar group with increasing salt content in line with Table I, method Id. Such experiments, however, have not yet been described.

6. Ternary and Quaternary Aqueous Systems Containing Bile Salt, Lecithin, and Cholesterol

In a recent study of these systems (111, 112), G, V_1, M_1, and S_1 phases were encountered. The close resemblance of the phenomena observed with these systems, containing rather complicated polycyclic molecules to those considered earlier is remarkable.

7. Methods for Effecting Particular Phase Changes in Solubilized Systems

As discussed (I.C.2), Table I represents a tentative extension of an earlier scheme of methods for effecting particular phase changes in solubilized systems. The earlier scheme, which referred particularly to systems containing ionic amphiphiles and to systems in which the only liquid crystalline phase encountered was the G phase, was supported experimentally by the observation of many phase changes. The later scheme again refers primarily to systems containing ionic amphiphiles but tentatively includes the liquid crystalline phases M_1, V_1, V_2, and M_2 in addition to the G phase and the isotropic micellar phases S_1 and S_2. As already mentioned, the additional phases appear only in certain circumstances.

Just why particular conditions should favor or inhibit the formation of a particular phase is by no means always evident. Possible reasons why Arkopal 060 and Aerosol MA should favor the production of the G phase while Arkopal 130 favors the M_1 phase have been suggested (sections II.A.1.f, II.A.2.a, and II.B.1.a). It is not clear, however, why at 100°, in ranges of composition intermediate between the M_1 and G phases, the potassium soaps of lauric, myristic, and palmitic acids should give rise to the cubic phase, V_1, while the corresponding sodium soaps do not. In an analogous manner, while in the composition range between G and M_2 at room temperature, Luzzati and Husson's (74) phosphatide gives conjugate mixtures of G, and M_2 Aerosol OT and Aerosol MA yield the inverse viscous isotropic phase V_2 (3). Table I gives no indication of which particular liquid crystalline phases will appear in a particular system (which will clearly depend on temperature) but merely indicates the order, with changes in composition of the system, of the appearance of those phases which are actually formed.

Experimental evidence regarding transitions involving the M_1, V_1, V_2, and M_2 phases is scantier than that involving only the S_1, G, and S_2 phases recorded earlier (131). Investigations on the M_1, V_1, V_2, or M_2 phases in systems containing added inorganic salts have not yet been reported so that the application of method Id to these phases as suggested in Table I remains to be investigated experimentally.

A simple qualitative technique for observing successive phase changes with solutions of amphiphiles is to subject a disk of a particular phase, held between cover-slip and slide, to peripheral conditions which, by a diffusion process, bring about the succession of phase changes under consideration. The progress of these changes as diffusion proceeds may then be observed with the polarizing microscope. Some examples of phase changes which have been studied in this way are recorded in Table VIII. Their relation to the scheme of Table I is noted.

The methods enumerated in Table I do not apply in all cases to solutions of nonionic amphiphiles. In addition while in a given system containing alkali metal soaps a rise of temperature usually leads to phase changes which may be interpreted on the bases of a diminished R (increased $A_{\mathrm{H}\overline{\mathrm{CW}}}$ probably due to increased ionic dissociation), with nonionic amphiphiles changes in the opposite sense are observed (decrease in $A_{\mathrm{H}\overline{\mathrm{CW}}}$ probably due to increased dissociation of hydrogen bonds). In agreement with this observation it has been found from X-ray diffraction measurements with M_1 and G phases that, with the soaps, rise of temperature

TABLE VIII

PHASE CHANGES PRODUCED BY CERTAIN PERIPHERAL TREATMENTS OF DISKS OF PARTICULAR SOLUBILIZED PHASES

	Nature of original disk	Treatment at periphery	Phase succession observed	Method (Table I) involved in phase changes
A	Aqueous solution of cetyltrimethylammonium bromide M_1 phase (77)	Loss of water by evaporation at 70°	Middle (M_1) → "Cubic" (V_1) → neat (G)	Method Ia
B	Crystals of N,N,N-trimethylaminododecanoimide (11)	Surrounded by water[b]	Crystals → micellar isotropic S_2 → neat (G) → viscous isotropic (V_1) → middle (M_1) → micellar isotropic (S_1)	Method Ia in reverse
C[a]	Aqueous M_1 phase from N,N,N-trimethylaminododecanoimide	Surrounded by decan-1-ol	Middle (M_1) → viscous isotropic (V_1) → neat (G) → inverse middle (M_2)	Method Ib
D[a]	Anhydrous Aerosol OT, inverse middle phase (M_2)	Surrounded by water[b]	Inverse middle (M_2) → viscous isotropic (V_2) → neat (G) → micellar isotropic (S_1)	Method Ia in reverse
E[a]	Aqueous G phase from Aerosol OT	Surrounded by decan-1-ol	Neat (G) → viscous isotropic (V_2) → inverse middle (M_2) → inverse micellar isotropic S_2	Method Ib
F[a]	Anhydrous sodium undecane 3-sulfate, neat phase (G)	Surrounded by water[b]	Neat (G) → viscous isotropic V_1 → middle M_1 → micellar isotropic S_1	Method Ia in reverse

[a] Previously unpublished observations by the writer. [b] Or exposed to moist air (relative humidity >98%).

leads to an increase in the lateral spacing between the ionic groups (28). Corresponding X-ray diffraction experiments with nonionic amphiphiles do not seem to have been reported.

8. Conditions Conducive or Antagonistic to the Formation of Liquid Crystalline Solutions of Amphiphiles

In section II.A.1 it was noted that the formation of M_1, G, and M_2 liquid crystalline phases depends on the long-range ordering of M_1, G, and M_2 micellar forms. The organization of the intermediate phases V_1 and V_2 is less clear.

Concerning conditions which favor the establishment of the long-range order which gives rise to the M_2 phase, little can be said at present, and further work on this aspect is required. This phase appears in systems of relatively low water content and high amphiphile content. The M_2 phase found with Aerosol MA or Aerosol OT at low water content and in the anhydrous condition is readily broken down on addition of hydrocarbon or other organic solvents giving isotropic solutions.

With regard to the range of composition over which the M_1 and G phases can exist in binary aqueous solutions of ionic amphiphiles or in such aqueous solutions containing solubilized organic liquids, the following general effects, which are modified by or modify the specific effects recorded in Table I, are noteworthy (73, 81, 131).

The formation of liquid crystalline solutions is promoted by factors which might be expected to favor hydrogen bonding both within the $\overline{W}$ region itself and between the $\overline{W}$ region and the $\overline{C}$ layer. Such factors are (i) low temperature; (ii) high concentration of amphiphiles; (iii) relatively close packing of polar groups, *e.g.*, $-SO_4Na$ and $-OH$ on the polar face of the $\overline{C}$ layer [Such close packing will be favored by the presence of *n*-alkane salts, 1-alkanols, and *n*-carboxylic acids. With these salts close packing of the polar groups will be facilitated in comparison with the packing with branched-chain salts (*e.g.*, Aerosol MA) or alcohols (*e.g.*, methylcyclohexanol).]; (iv) the absence from the $\overline{W}$ region of dissolved molecules or ions which could interrupt hydrogen bonding between the $\overline{W}$ and $\overline{C}$ regions and/or within the $\overline{W}$ region itself. Such molecules or ions may be provided by (a) the lower alcohols, either completely water soluble (methanol, ethanol, propanol) or partially miscible with water (*e.g.*, branched cyclic or straight-chain alcohols below about C_7); (b) other covalent water-soluble organic compounds, *e.g.*, ethylene glycol; (c) inorganic salts, *e.g.*, sodium nitrate, sodium chloride; (d) organic salts molecularly soluble in water, *e.g.*, potassium acetate; (e) the nonmicellized portion of shorter chain amphiphilic salts (*e.g.*, potassium hexoate, cyclohexylammonium chloride (68), etc.).

These considerations are of practical as well as theoretical interest. In the formulation of solutions containing amphiphiles and added solubilized materials for use as concentrates for cutting oils, plant protection products, etc., it is desirable to prevent the formation of viscous liquid crystalline solutions both in the product itself and during dilution when the product is added to water for the preparation of its emulsion at working concentration.

9. Solubilization in the "Gel" Phase

In the systems previously considered in this section, all the components have been present in the liquid state. In the "gel" phase, on the other hand, the hydrocarbon chains are apparently crystallized while the ionic groups (or at least the counterions) and aqueous region are liquid.

In such a structure, solubilization of water-soluble

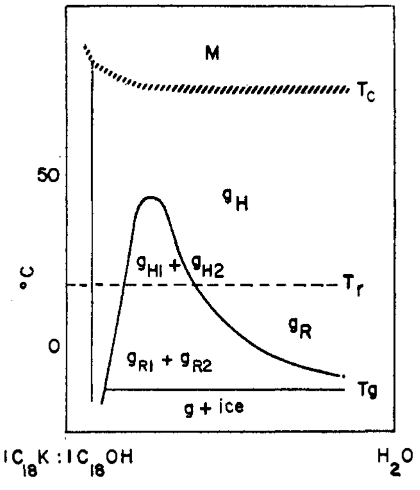

Figure 30.—Phase diagram for the system containing an equimolecular mixture of potassium stearate and octadecanol with water; g, "gel" (the indices 1 and 2 correspond to two conjugate "gels" in equilibrium and the indices H and R to lateral arrangements of molecules according to an hexagonal or rectangular lattice, respectively). The hachures correspond to the zone of conjugate mixtures of "gel" with liquid crystalline phases, M (128).

materials within the liquid $\overline{W}$ region might be expected as with the wholly liquid phases but, to maintain the identity of the "gel" phase, solubilization of organic compounds containing hydrocarbon chains would necessarily involve cocrystallization of the hydrocarbon chains of the dissolved material with the hydrocarbon chains of the amphiphile. The steric requirements necessary for this to occur would be expected to be quite specific. This specificity has already been encountered in considering the formation of the "gel" phase from mixtures of the potassium soaps of homologous fatty acids (II.A.1.i).

A further interesting example of cocrystallization within a "gel" phase is provided by the behavior of the binary system derived from water and an equimolecular mixture of potassium stearate and *n*-octadecanol (128). When crystalline potassium stearate and crystalline octadecanol are mixed in equimolecular proportions at room temperature, the mixture remains heterogenous and the soap and alcohol do not cocrystallize. The same behavior is observed even if the mixture is first heated above the melting point of the alcohol. If, however, as little as 8 wt % of water is added to the system, "gel" is obtained as a homogeneous phase. At lower water contents the "gel" is in equilibrium with solid soap. At higher water contents the "gel" exists over a wide range of temperature and concentration. The phase diagram is given in Figure 30.

The structure of the "gel" phase as deduced from X-ray diffraction experiments is shown in Figure 31. For a detailed discussion the original paper should be consulted. The mixed "gel" differs from the "gels" of potassium stearate alone, in containing a bimolecular amphiphile leaflet in place of a monomolecular one (II.A.1.i). The reason for this seems to be that the formation of a bimolecular leaflet from soap alone would involve too close an approach of the ionized carboxylate groups. With the equimolecular mixture the bimolecular leaflet is permitted on account of the separation of the polar groups by the hydroxyl groups. In both the soap and soap–alcohol "gels," the available area per carboxylate group is approximately 39.6 A² and is virtually independent of water content (*cf.* section II.A.1.i). The hydrocarbon chains are normal to the leaflets and incorporation of water occurs between the leaflets. The thickness of the combined layer therefore increases rectilinearly with water content.

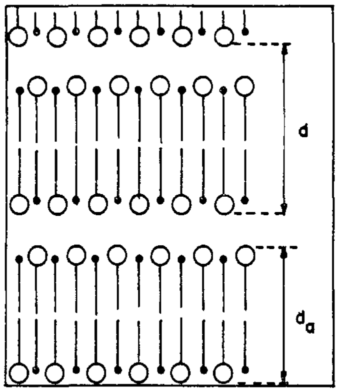

Figure 31.—Schematic representation of the structure of the "gel" phase from an equimolecular mixture of octadecanol and potassium stearate (128).

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