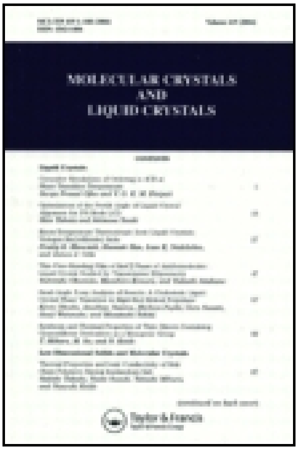

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A New Concept of the Nature of the "Viscous Isotropic" or "Cubic" Mesophases of Amphiphilic Systems; The Liquid Crystalline Character of Plastic Crystals; Constitutional Analogies Between Amphiphilic and Non-Amphiphilic Mesophases

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A New Concept of the Nature of the "Viscous Isotropic" or "Cubic" Mesophases of Amphiphilic Systems; The Liquid Crystalline Character of Plastic Crystals; Constitutional Analogies Between Amphiphilic and Non-Amphiphilic Mesophases

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Attention is drawn to the liquid crystalline character of the plastic crystals formed by "globular" molecules. The constitutional analogies of the nematic and smectic mesophases formed by non-amphiphilic "lath-like" molecules with the fibrous and lamellar mesophases formed by fibrous and lamellar micelles in amphiphilic systems are recalled and it is suggested that comparable constitutional analogies exist between the plastic crystal mesophases formed by non-amphiphilic globular molecules and the viscous isotropic cubic mesophases formed in micellar amphiphilic systems. It is suggested that the globular molecules with fairly free rotational motions and no long range orientational order which characterise the non-amphiphilic plastic crystal mesophase are replaced in the amphiphilic viscous isotropic cubic mesophases by globular micelles again with fairly free rotational motions and no long range orientational order. In both these classes of rotational mesophases the details of the cubic lattice adopted will be determined by the extent of the departure of the mean shape of the globular rotational units from strict sphericity with consequent variation in the degree of restriction of their rotational motions.

It is suggested that the cubic mesophase, "smectic D", formed by certain lath-like molecules, is again a rotational mesophase, the rotational units being globular multimolecular intermediate fragments formed in course of the transition from the indefinitely extended lamellae of the smectic C phase which are inclined to the direction of the statistically parallel molecular long axes (the molecular cross sections probably arranged with two-dimensional nematic order within the planes) to the indefinitely extended lamellae of the smectic A phase which lie normal to the direction of the molecular long axes (the molecular cross sections being in two-dimensional disorder within the planes). The interposition of the cubic smectic D phase between the smectic C and smectic A phases is thus visualised as mechanically resembling the interposition of the amphiphilic V_1 and V_2 phases between the G and the M_1 or M_2 phases respectively.

Finally, it is suggested that constitutional resemblances similar in type to those already noted may extend even more widely so as to include metastable systems, for example the aqueous two-dimensional hexagonal solution of tobacco mosaic virus, the aqueous cubic phase formed by tomato bushy stunt virus and even certain inorganic tactosols such as those formed by vanadium pentoxide in water or by barium carbonate in methanol.

INTRODUCTION

In aqueous amphiphilic systems, there occur, besides some less well authenticated mesophases, the following mesophases which have been definitively characterised $-S_{1C}$, M_1, V_1, G, V_2 and M_2[1,2,3,4] Although these mesophases do not usually all arise in a given system, those which do occur always follow one another in the sequence given, either from left to right or from right to left, on progressive changes in the composition or temperature.[1,2] Among these mesophases S_{1C}, V_1 and V_2 represent distinct "viscous isotropic" or "cubic" mesophases while M_1, G and M_2 represent the anisotropic mesophases, "middle", "soap boiler's neat" and "inverse middle" respectively.

The structures of the anisotropic mesophases are essentially well established[1,2,3,4]. The structures of the cubic mesophases S_{1C}, V_1 and V_2, however, must still be regarded as sub judice. Various structural models have been proposed for them from time to time – often only to be discarded later. It is not intended here to review these structural models but to suggest a new concept, namely that the structures of all the cubic amphiphilic mesophases may be interpreted on the basis of the R-theory[1,2] as micellar analogues of the so called "plastic crystals"[5] formed by many non-amphiphilic compounds, mostly organic, with "globular" molecules (cf below).

The non-amphiphilic "plastic crystals" have generally been categorised with conventional solid crystals and accordingly are usually considered in the literature of the solid state. From recent accounts[5,6,7,8] however, it seems clear that "plastic crystals" can more aptly be classified with *liquid* crystals than with conventional *solid* crystals, their properties being in many ways more closely analogous to those of nematic, cholesteric and smectic liquid crystals than to those of solid crystals. Indeed, in possessing relatively free thermal rotary motion (i.e. tumbling motion of their constituent molecules, which are therefore without any long-range orientational order) "plastic crystals" are even closer in character to conventional liquids, i.e. amorphous liquids, than are the nematic, cholesteric and smectic "liquid crystals" themselves in which molecular rotary motions are more severely restricted and in which some degree of inter-molecular long range orientational order is present.

The cubic amphiphilic mesophases, S_{1C}, V_1 and V_2, in contrast to the non-amphiphilic plastic crystals, have usually been classed as liquid crystals on account of their close sequential relationships to the anisotropic liquid crystalline mesophases M_1, G and M_2. Nonetheless, Luzzati and collaborators in their early accounts[9,10,11] of the cubic phase V_1 considered that it should be classified as truly crystalline.

In the following paragraphs special attention will first be drawn to the liquid crystalline character of non-amphiphilic plastic crystals. The structural analogies between the birefringent amphiphilic mesophases and the birefringent non-amphiphilic mesophases will next be noted. It will then be shown how the optically isotropic amphiphilic cubic mesophases can satisfactorily be viewed as plastic crystals in which the globular molecules of the non-amphiphilic series have been replaced by globular micellar units, the S_{1C}, V_1 and V_2 phases each corresponding to a particular type of unit. Finally, certain inadequacies of some of the more recently proposed structural models for the amphiphilic cubic phases will be noted.

THE LIQUID CRYSTALLINE CHARACTER OF PLASTIC CRYSTALS

The mesomorphous character of the particular state of matter under consideration was first clearly recognised in 1935 by Timmermanns[12] and was later termed by him "plastic crystal". The general assimilation of his ideas has however been slow, possibly on account of his adoption of the term "plastic crystal" rather than "plastic liquid crystal". This engendered a divisive compartmentalisation between the knowledge concerning plastic crystals and that concerning the already extensively investigated nematic, cholesteric and smectic mesophases or liquid crystals. The essential similarity of the formation of the four types of mesophase on heating the solid crystal, or on cooling the amorphous liquid, will be clear from Figure 1 and Table 1.

The features of molecular structure which are conducive to the formation of the nematic, cholesteric and smectic mesophases have been discussed by Gray[13], by Usol'tseva and Chistyakov[14] and most recently by Sackmann and Demus.[15(b)] Briefly, the principal structural feature that favours the formation

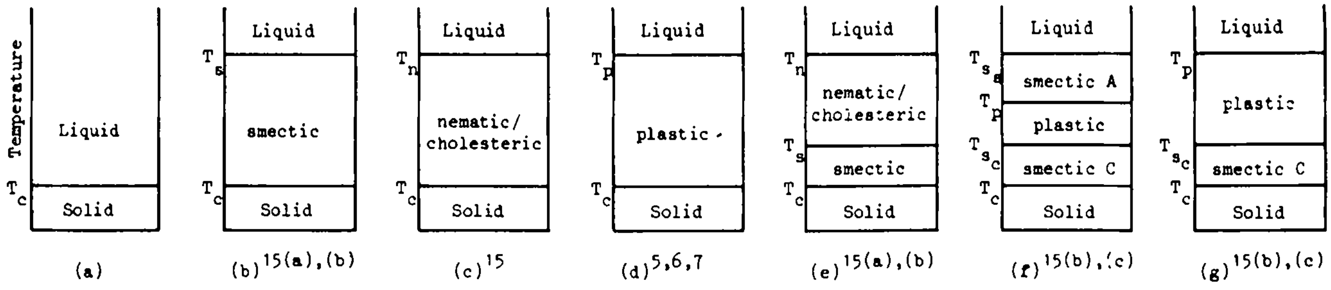

FIGURE 1 Schematic diagrams comparing the reversible behaviour on temperature change of compounds which form one or more mesophases (non-amphiphilic series)

Notes (a) Crystalline solid melts directly to amorphous liquid at T_C. No mesophase produced

(b) Crystalline solid gives smectic phase at T_C; smectic phase gives amorphous liquid at T_S.
The successive smectic phases, B, C and A of Sackmann and Demus[15(a), (b)] are here grouped together under "smectic"

(c), (d), (e) Similar notation. Nematic/cholesteric grouped together

(f), (g) Plastic phase here refers to the cubic "Smectic D" phase of Sackmann and Demus[15(b),(c)] which is here regarded as a plastic crystal

TABLE I

Some comparative thermochemical data for compounds which undergo transitions from the solid crystalline state to the liquid state either with or without an intermediate mesomorphous state

T_c (°C):	temperature of breakdown of the solid crystalline lattice
T_a (°C):	temperature of transition to the amorphous liquid. For compounds which do not form mesophases $T_a = T_c$
H_c	latent heat of transition at T_c
H_a	latent heat of transition at T_a. For compounds which do not form mesophases $H_a = H_c$

Note the similar character of the data whether they involve plastic, smectic or nematic mesophases.

Compound	Mesophase	T_c (°C)	H_c (15° cal/g)	T_a (°C)	Ha (15° cal/g)
n-hexane[a]	None	-95	36.0	$=T_c$	$=H_c$
2,2-dimethylbutane[a]	Plastic (two forms)	-146 (-132)	15.0 (0.8 heat of second transition)	-99	1.6
2,3-dimethylbutane[a]	Plastic	-137	18.0	-129	2.2
Cyclohexane[a]	Plastic	-87	19.0	6.5	7.5
Methylcyclohexane[a]	None	-126.5	16.3	$=T_c$	$=H_c$
1,2-dimethylcyclohexane (cis)[a]	Plastic	-100.7	16.7	-50	3.5
1,2-dimethylcyclohexane (trans)[a]	None	-88.2	22.4	$=T_c$	$=H_c$
Benzene[a]	None	-5.5	30.5	$=T_c$	$=H_c$
Carbon tetrachloride[a]	Plastic	-47.4	9.26	22.9	5.1
Carbon tetrabromide[a]	Plastic	46.9	4.3	91	2.8
Ethyl p-azoxybenzoate[b]	Smectic	114	13.8	122.6	3.5
p-azoxyanisole[c]	Nematic	118	27.0	135	0.53

[a] Timmermanns, J., *Physicochemical Constants of Pure Organic Compounds*, Elsevier, New York, 1950.

[b] Arnold, H., *Z. Phys. Chem.*, 226, 146 (1964).

[c] Arnold, H., and Roediger, P., *Z. Phys. Chem.*, 231, 407 (1966).

of all three of these mesophases is that their constituent molecules should be relatively elongated and fairly stiff and lath-like. The cholesteric phase arises as a modification of the nematic phase on introduction of any excess of either d- or l- optical activity into the system. If a nematic phase is formed by the dl-form of an optically resolvable compound then even partial resolution leads to the modification of the nematic phase to its cholesteric form. Many compounds containing lath-like molecules pass successively on progressive heating from the solid crystal through one or more of the above mesophases before finally giving the amorphous liquid (Figure 1).

The molecular feature most conducive to the formation of the plastic crystal mesophase was recognised by Timmermanns as "globular" character, i.e. roughly spherical shape, although the departures from strict sphericity may be considerable (cf Tables 1 and 2). Thus if tetramethylmethane is considered as spherical in type, hexamethylethane represents a prolate spheroid and cyclohexane an oblate spheroid. Pear-shaped molecules, e.g. 2,2 dimethylbutane, can also behave as

TABLE 2

Crystalline forms of some non-amphiphilic plastic crystals (7,16) and of some amphiphilic cubic mesophases.

Material	Cubic plastic crystal; classification of cubic lattice	Solid crystals at lower temperatures; crystal type
CCl_4	fcc	
CBr_4	Pa3	Monoclinic
CMe_3 Cl	fcc	
CMe_3 Br	fcc	
$C(NO_2)_4$	$I\bar{4}3m$	
$CCl_3.CCl_3$	Im3m	Triclinic
$CBr_3.CBr_3$	fcc	
$C(CH_3)_3.C(CH_3)_3$	fcc	
Cyclobutane	fcc	
Cyclopentane	(hexagonal)	
Cyclohexane	fcc	
Cyclohexanone	fcc	
Cyclohexyl chloride	fcc	
dl Camphor	fcc	Rhombic
S_{1c} sodium caprylate/xylene/water[35]	Pm3n	
S_{1c} dodecyltrimethyl ammonium chloride/water[25]	Pm3n	
S_{1c} decaethyleneglycol mono-lauryl ether/water[38]	Pm3n	
V_1 dimethyldodecylamine oxide/water[31]	fcc	
V_1, V_2 various, anhydrous[33, 34] or with water	fcc I_a3d	
V_2? phosphatidylethanolamine/water[36]	Pn3n	

globular. Many, though not all compounds with such globular molecules undergo sharp transitions on heating, first (usually with a change in crystalline form (Table 2)) from the optically anisotropic solid crystal to the cubic optically isotropic plastic crystal mesophase, and secondly to the amorphous liquid. Compounds whose molecules are neither pronouncedly lath-like nor globular, i.e. the majority of compounds, on progressive heating usually pass directly from the solid crystal to the amorphous liquid.

It should be noted here that in certain relatively rare instances (15) an optically isotropic plastic crystalline mesophase arises as a further mesophase towards the high-temperature end of the series of optically anisotropic mesophases formed by lath-like molecules (Figure 1, f and g). The mode of formation of such optically isotropic mesophases will be considered later (p. 14) in relation to the mode of formation of the amphiphilic cubic mesophases V_1 and V_2.

CHARACTERISTICS OF NON-AMPHIPHILIC PLASTIC CRYSTAL BEHAVIOUR

In order that a clear analogy can later be drawn between the behaviour of non-amphiphilic plastic crystals and that of the amphiphilic cubic mesophases, some of the more relevant characteristics of the non-amphiphilic plastic crystals will now be considered.

Examples of a few of the very numerous compounds which form plastic crystals are listed in Table 2 which further records certain crystallographic characteristics of the various phases involved as well as some comparative information relative to certain amphiphilic cubic mesophases.

It has been established that whereas in conventional solid crystals the molecules are virtually fixed, in the plastic crystal mesophases they undergo relatively free thermal rotary tumbling motions[6,7,8] at the lattice points as well as appreciable positional fluctuations.

This relatively free molecular mobility is reflected in many of the physical properties of the plastic crystal mesophase, e.g. its optical isotropy, high plasticity, low entropy of transition to the amorphous liquid, high dielectric constants[6,7,8] and somewhat blurred X-ray diffraction patterns.[16]

Further, plastic mesophases, unlike solid crystals or smectic, nematic or cholesteric mesophases in which thermal rotary motions of the molecules are severely restricted, often give high resolution NMR spectra[6,7,8] similar to those of the amorphous liquids to which they give rise on heating. In some instances involving near-spherical rotors with which the transition from solid crystal to plastic mesophase is second order, there may be a progressive line-narrowing with rise of temperature leading to a high resolution spectrum as the transition to the amorphous liquid is approached.

Plastic crystals are optically isotropic and "clear almost glass-like, tacky and easily deformed"[6] – a description which also applies accurately to the viscous isotropic amphiphilic mesophases S_{1C}, V_1 and V_2. The plastic crystal mesophases thus show much "thicker" consistencies than do the nematic and cholesteric mesophases but are approached in consistency by the "thickest" smectic phases, e.g. by smectic B[15ab]. Plastic crystal mesophases possess cubic lattices (occasionally hexagonal) of a number of types (Table 2) as determined by the degree of restriction of the thermal rotary motions occasioned by departure of the molecular shape from strictly spherical.[6,7] The more strictly spherical rotors give face-centred cubic lattices.

A feature of the non-amphiphilic cubic crystal mesophases, of importance in considering the structures of the amphiphilic cubic mesophases, is that they frequently show complete miscibility, even when formed from dissimilar compounds, over the range of temperatures consistent with their joint stability. Indeed this temperature range may be more extended in the case of certain mixtures (e.g. krypton/methane; cyclohexane/2,2-dimethylbutane) than in the case of the individual components. This has been attributed to "co-operative rotation" of the two molecular species.[7] Owing to the details of their respective geometries the molecules can execute rotatory motions with less mutual hindrance when side by side in admixture than when side by side individually. Alternatively, the dissimilar molecules may fit together to form a two-component globular unit which undergoes rotary motions as a whole. This miscibility of plastic crystalline mesophases formed by constitutionally dissimilar compounds over the common thermal range of stability further emphasises their fused character. Similar miscibility is shown by corresponding[15b] smectic mesophases, by nematic phases, and of course, by amorphous liquids. Nematic phases are also completely miscible with their modification – the cholesteric phases – the mixture itself being cholesteric.[15b] Such miscibility is not shown by conventional solid crystalline phases of constitutionally dissimilar compounds.

CONSTITUTIONAL ANALOGIES BETWEEN AMPHIPHILIC AND NON-AMPHIPHILIC MESOPHASES. THE PLASTIC CRYSTALLINE CHARACTER OF THE AMPHIPHILIC CUBIC MESOPHASES

When comparing non-amphiphilic with amphiphilic mesophases attention may be drawn to the analogies between the geometrical arrangements of the molecules in the former and of the micelles[†] in the latter – these micelles being taken

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[†] In this account the term "micelle" is used irrespective of micellar size and thus includes Ekwall's "aggregates".[4]

to include the micellised amphiphilic molecules with the associated "bound water" and "attached" counter ions[18, 19]. There is presumably nothing analogous in the non-amphiphilic series to the intermicellar liquid ("free water" + non-micellised amphiphile + "free" counter ions) of the amphiphilic series.[1,2] However, even in amphiphilic mesophases, intermicellar liquid is not always present. Thus, even in the pure state at room temperature, sodium sulpho-di(2ethyl-hexyl) succinic ester, undecane-3 sodium sulphate and calcium ω-phenylundecanoate, respectively yield M_2, G and V_2 mesophases. Many other examples of anhydrous amphiphilic mesophases of these types are known, some occurring at room temperatures and others, derived from compounds which give solid crystals at room temperatures, only at higher temperatures above the melting point of the crystals (alkali and alkaline earth n-alkanoates etc.[3]).

In the amphiphilic series the mesophases M_1 and M_2 may be regarded as analogous to the non-amphiphilic nematic mesophases in that the statistically parallel arrangement of lath-like molecules found in the latter is replaced by a parallel arrangement of indefinitely long fibrous micelles in the former. This increase in length of the parallel units, as might be expected, results in the M_1 and M_2 mesophases showing much higher viscosities than those of the nematic mesophases and also in a long-range two-dimensional hexagonal arrangement of the micellar units.

The lamellar mesophases of the amphiphilic series (neat phase G) are constitutionally closely analogous to the smectic A mesophases of the non-amphiphilic series. The parallel sheets of molecules in the smectic phases of the non-amphiphilic series are replaced in the amphiphilic series by parallel indefinitely extended lamellar micelles. Both the consistencies and the optical properties in the two series show close similarities.

It will now be proposed that a third constitutional analogy, similar in type to the two just considered, exists between the "viscous isotropic" cubic mesophases of the amphiphilic series and the "plastic crystalline" cubic mesophases of the non-amphiphilic series. This analogy involves similarities not only in the geometric arrangement of the units but also in their thermal rotary motions at the lattice points. The thermal rotary motions of the uni-molecular (or in some instances multi-molecular) units at the lattice points in the cubic plastic crystal mesophases of the non-amphiphilic series have their counterpart in the thermal rotary motion of the micellar units in the cubic mesophases of the amphiphilic series.

Analogies in macroscopic properties

As already mentioned, the amphiphilic S_{1C}, V_1 and V_2 mesophases, like the non-amphiphilic plastic crystalline mesophases, are commonly clear, almost glass-like, tacky and easily deformed.[6] Further in suitable circumstances they may be obtained as single crystals, often with well developed crystal faces.[20,21]

Analogies in crystal structure

Like the cubic plastic crystalline mesophases of the non-amphiphilic series the amphiphilic cubic mesophases have been shown by X-ray diffraction measurements to form a number of different cubic lattices (Table 2). In the non-amphiphilic series, as already noted, these different lattices are ascribed to different degrees of restriction in the thermal rotatory motions of the units at the lattice points,[7] owing to the units not being strictly spherically symmetrical. In the amphiphilic series a similar mechanism may well be operative since the mean shape of the micellar units, as discussed below, would be expected in many cases to depart from strict sphericity.

Analogies in NMR behavior

Like many plastic crystal mesophases of the non-amphiphilic series[6,7] the cubic amphiphilic mesophases give high resolution NMR spectra (for both the amphiphile and water present) closely similar to those given by the amorphous liquid phases produced either on heating the mesophases or on small changes in composition.[18,19,22,23] This is believed to indicate relatively free (cf references 6 and 7) thermal rotary motions of the micellar units at the lattice points analogous to the thermal rotary motions of the molecular units in the non-amphiphilic plastic crystals.

In support of this view, with the M and G phases in which, as is clear from their accepted structures, rotary motions of the micelles must clearly be greatly restricted, high resolution spectra are not given by the micellised amphiphile molecules. However, a high resolution spectrum is given by the free intermicellar water present[18,19,22,23] although not by the water "bound" at the micellar surface.[18,19] Whether or not a high resolution spectrum is given by the intermicellar amphiphile in those M_1 and G phases where its concentration might be expected to be considerable[1] has not yet been recorded in the literature. A further point of great significance is that although, as just noted, a G phase alone does not give a high resolution spectrum for the amphiphile, in certain cases where a G phase can exist in equilibrium with a conjugate highly dilute amorphous aqueous solution, ultra-sonic agitation converts the mixture into a very fine dispersion which shows a high resolution spectrum. This is because the very small individual dispersed particles of G phase (diameter ~230 Å) can undergo thermal Brownian rotary motions.[24]

THE NATURE OF THE MICELLAR UNITS IN THE AMPHIPHILIC CUBIC MESOPHASES

In considering the feasibility of plastic crystalline types of structure for the S_{1C},

V_1 and V_2 mesophases it is necessary to enquire whether globular micelles of a character and of a sufficient concentration† to give such structures would be expected at those points in the progression of amphiphilic phases where the respective cubic mesophases are found. The general features of this progression of phases and of the underlying micellar mechanics as interpreted according to the R-theory have recently been discussed[1,2] and are diagrammatically represented in Figure 4. According to this view the micelles adopt a preferred mean form (or equilibrium of forms) dependent on R as determined by composition and temperature. The preferred mean micellar shape at a given composition and temperature is thus inherent and although, since the micelles are liquid in character, it may be modified by external constraints (packing), it is not in the first place determined by them. Only in special cases (S_1 solutions at concentrations not too greatly above the critical concentration for the formation of micelles) will this preferred mean shape be strictly spherical. In most cases it will be either more or less prolate or more or less oblate, the extremes of prolateness and oblateness being found in the M and G phases respectively.

The S_{1c} phase

From the position of the S_{1c} phase in the progression of amphiphilic phases the micellar unit in the S_{1c} phase may reasonably be expected to be essentially of the spherical S_1 (Hartley) type found in amorphous solutions (S_1) at lower concentrations. It is proposed that if the chemical nature of the system is such that these micelles can persist up to a sufficiently high concentration without first changing to other micellar forms,[2] then at a suitable temperature the S_1 micelles adopt positions at the points of a cubic lattice (cf below) while retaining thermal rotary motions similar to those in the amorphous liquid phase. The stability of this lattice is dependent on the intermicellar forces (i.e. on the balance between the repulsive and attractives forces between the S_1 micelles) and on the degree of thermal motion within the system as a whole.

The range of existence of the S_{1c} phase in the binary dodecyltrimethylammonium chloride/water system[25] is illustrated by the phase diagram in Figure 2. It should be noted that with increasing concentration there is a tendency for the micellar form to become fibrous, a change which ultimately results in the transition to the M_1 mesophases in Figure 2. It is therefore not unlikely that the mean micellar form in the S_{1c} phase (particularly towards its upper

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† i.e. sufficiently close approach to each other.

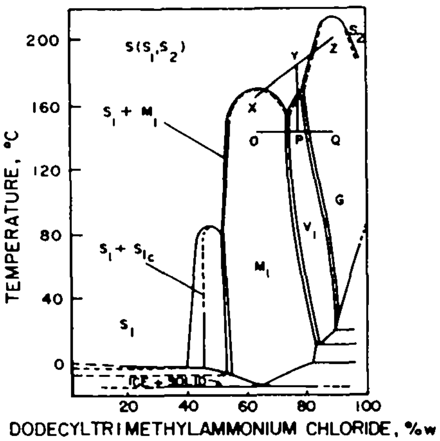

FIGURE 2 Phase diagram for the dodecyltrimethylammonium chloride/water system[25]

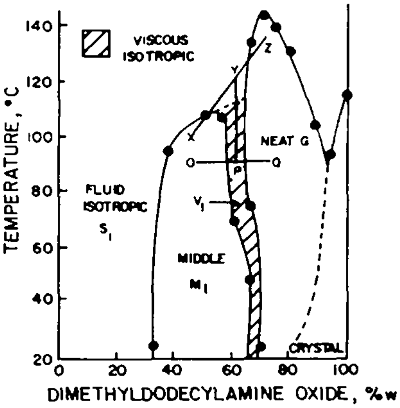

FIGURE 3 Aqueous system of dimethyldodecylamine oxide[22,23,31]

limit of concentration) should deviate from strictly spherical towards prolate. Such a deviation would regulate the detailed pattern of the rotary motions and hence[7] the details of the cubic lattice adopted (cf references 25, 35, 38).

The V_1 and V_2 phases

The V_1 mesophase, as can be seen from Figures 2, 3 and 4, has a range of stability intermediate between those of the lamellar mesophase G and the fibrous hexagonal mesophase M_1. The V_2 mesophase occupies a complementary position between the lamellar mesophase G and the inverse fibrous hexagonal mesophase M_2 (Figures 4 and 5). It is believed[1,2,26,27,28] that in amorphous solution phases S, close in composition and temperature to the S/M_1 phase boundary, mobile groups of micelles are locally present similar in character and local arrangement to the indefinitely extended fibrous micelles in the neighbouring M_1 phase but of finite lengths and without the uniform and relatively immobile long-range order characteristic of the M_1 mesophase itself. In a similar manner[1,2,29] in S phases at compositions and temperature close to the S/G phase boundary, mobile groups of micelles are locally present similar in character and arrangement to the indefinitely extended lamellae in the G mesophase but of finite extension and without the relatively immobile long-range order characteristic of the G mesophase itself. The mobile character of the micelles in the amorphous liquid phase S, in contrast to the relatively immobile long-range order of the micelles in the M_1 and G phases, is reflected in the fact that high resolution NMR spectra for the amphiphilic molecules are given by the S phase but not by the M or G phases.

In passing, with increasing concentration, from the M_1 mesophase to the G mesophase in Figures 2 and 3 along the lines marked OPQ, one encounters the phase sequence

$$M_1 \longrightarrow (M_1+V_1) \longrightarrow V_1 \longrightarrow (V_1+G) \longrightarrow G$$

However when operating at higher temperature along paths such as those marked XYZ one encounters the phase sequence

$$M_1 \longrightarrow (M_1+S_1) \longrightarrow S_1 \longrightarrow (S_1+G) \longrightarrow G$$

In passing continuously in the S phase (here S_1) from the boundary with the M_1 phase to the boundary with the G phase, an S phase initially containing disordered groups of fibrous micelles of the M_1 type changes continuously to an S phase containing disordered groups of lamellar micelles of the G type. The detailed mechanism of this continuous process, which is represented diagrammatically in Figure 4, has been discussed elsewhere.[1,2] It is not thought that at any precise temperature and composition only one definite micellar form will be present but rather that there will be a mobile thermal equilibrium of fluctuating micellar forms, the average form progressively varying with the conditions along XYZ in the way broadly indicated in Figure 4. In this manner, at a point Y approximately mid-way between X and Z, the mean micellar form may become "globular" in the sense used above in considering globular molecules. It is suggested that on fall of temperature along a line such as YP these globular micelles, while still retaining their thermal rotary motions, take up positions at the points of a cubic lattice and thus give rise to the first order phase change $S_1 \longrightarrow V_1$. The details of the cubic lattice adopted will be determined by the details of the

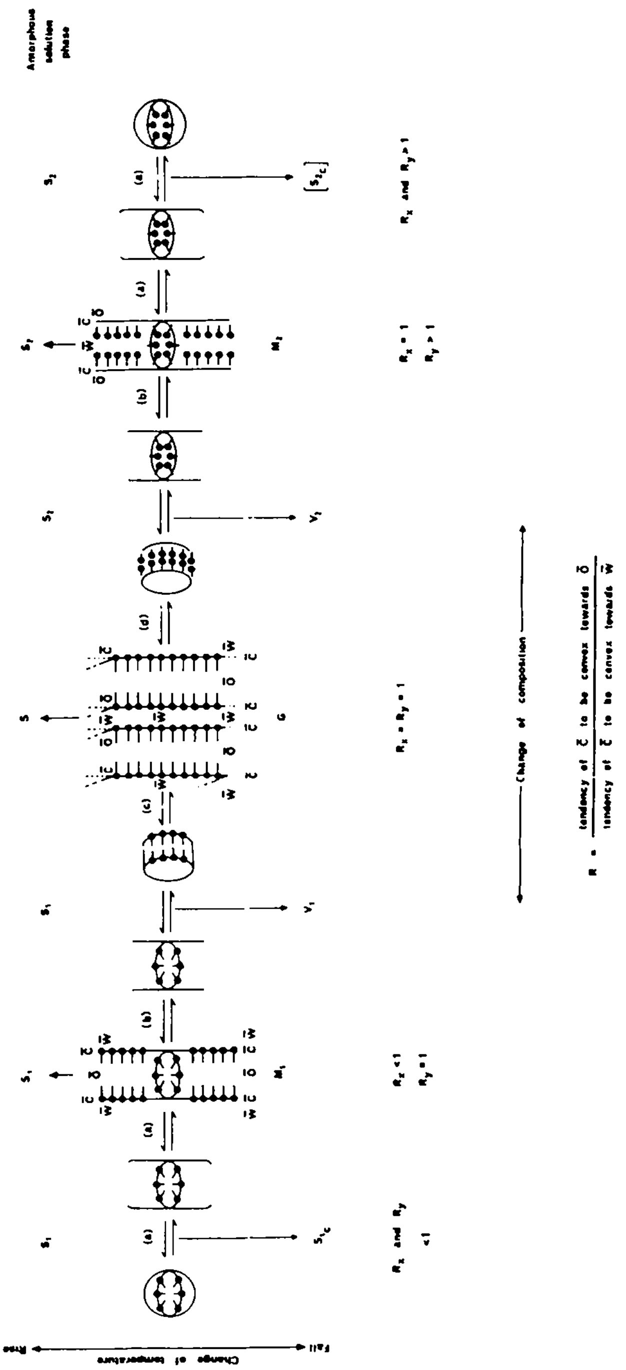

FIGURE 4 (See caption next page)

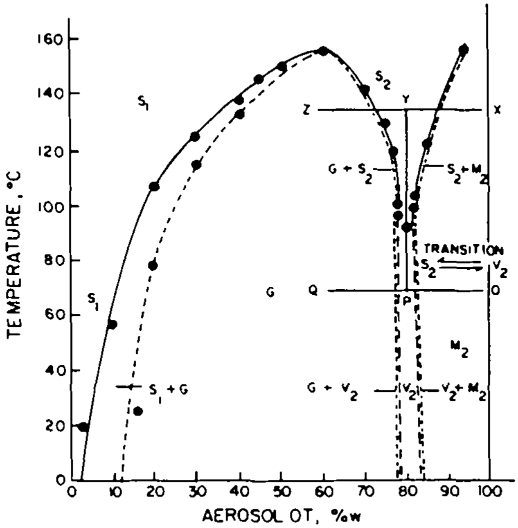

FIGURE 5 Phase diagram for the Aerosol OT*/water system[2]. *Sodium sulpho-di (2-ethyl-hexyl) sucinic ester

rotary motions which, in turn, will be determined by the extent to which the mean micellar form departs from strict sphericity. With strict sphericity the lattice would be face-centred cubic (cf Table 2).

Complementary considerations apply to the formation of the V_2 phase. This is indicated in Figure 4 (right-hand side) and by the lines OPQ and XYZ in Figure 5 which correspond to the similarly denoted lines in Figures 2 and 3.

FIGURE 4 The nature of the succession of amphiphilic mesophases of the fused type in relation to the underlying micellar equilibria (1,2).

S_1 and S_2	positional and rotational disorder
S_{1_c} and $[S_{2_c}]$†	rotational disorder but units in three dimensional cubic lattice
M_1 and M_2	indefinitely extended parallel cylindrical micelles in two-dimensional hexagonal lattice
G	indefinitely extended parallel lamellar micelles in lamellar lattice
V_1 and V_2	rotational disorder but units in three-dimensional cubic lattice
$\bar{W}$	aqueous zone
$\bar{C}$	amphiphilic zone
$\bar{O}$	hydrocarbon zone

(a) breakdown of long rods owing to tendency to develop convexities longitudinally

(b) breakdown of indefinite extension of long rods owing to tendency to develop planar regions circumferentially

(c) breakdown of indefinite lamellae owing to tendency to develop convexities towards $\bar{W}$

(d) breakdown of lamellae owing to development of convexities towards $\bar{O}$

† Note: S_{2C} yet to be definitely identified

This concept of the "plastic crystalline" character of the V_1 and V_2 mesophases is supported by the fact that the S and V phases of related composition show closely similar high resolution NMR spectra,[18,19,22,23] spin lattice and spin-spin relaxation times.[30] In the model proposed it is not suggested that all the globular units in a given V phase are instantaneously of precisely similar size and composition. Thermal fluctuations in both are to be expected as in the amorphous liquid phases. In this connection, it should be remembered that miscibility involving mixtures of "globular" molecules is found in the non-amphiphilic plastic crystalline phase.[7] These considerations may be relevant to the insensitivity of X-ray long spacing to composition (Figure 6) noted in the case of the V_1 phase of the dimethyldodecylamine oxide/water system.[31]

In the proposed thermo-kinetic model of the micellar structure of the V_1 and V_2 phases all the amphiphile molecules are considered to play statistically equivalent roles. This feature, which is a priori to be expected, is also evident in the usually accepted structural models for crystalline solid amphiphiles, the M_1, G and M_2 mesophases, and in the model suggested above for the S_{1C} mesophase.

Mode of formation of high-temperature cubic mesophases by certain lath-like molecules. Possible analogy with the mode of formation of the amphiphilic V_1 and V_2 cubic phases.

At this point in the discussion of the mode of formation of the amphiphilic V_1 and V_2 mesophases, it is opportune to revert to the question mentioned earlier

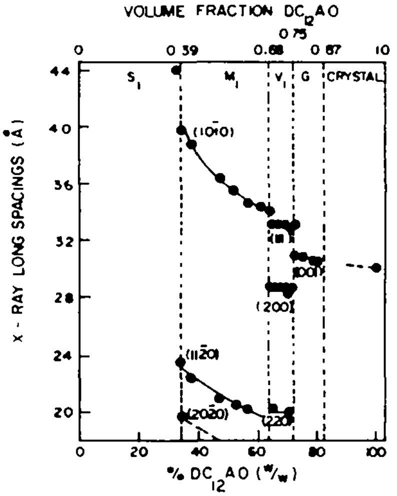

FIGURE 6 The X-ray long spacing as a function of the concentration in the dimethyldodeclamine oxide/water system[31]

of the mode of formation of high-temperature cubic mesophases by certain lath-like molecules e.g. 4'-n-hexadecyloxy-3'-nitrobiphenyl-4-carboxylic acid.[15b,c; 17a, b]

With this compound on rise of temperature the optically anisotropic smectic C mesophase transforms first to the cubic plastic crystal mesophase "smectic D". On further progressive rise of temperature this cubic mesophase transforms first to the optically anisotropic smectic A mesophase and thence to the amorphous liquid (Figure 1,f). In the Smectic A phase the lath-like molecules with their long axes statistically parallel are grouped in a succession of parallel indefinitely extended planes lying normal to the molecular long axes. The lath cross-sections are statistically disordered within these planes as in a two-dimensional amorphous liquid.[17c,d] In the smectic C phase the lath-like molecules with their long axes statistically parallel are once again grouped in a succession of parallel indefinitely extended planes but these planes are inclined to the molecular long axes. This inclination is possibly connected with a higher degree of order of the lath cross sections within the planes, for example with order as in a two-dimensional nematic liquid.[17c,d] To use an anthropomorphic simile the molecules within a plane in the smectic A phase may be likened to a crowd of people standing on a horizontal plane and facing in all directions at random. The molecules within a plane of the smectic C phase, on the other hand, may be likened to a crowd of people standing on a planar slope with everyone more or less looking outwards from that slope. The degree of order in the indefinitely extended planes of the lower-temperature Smectic C phase is thus greater and qualitatively different from that in the indefinitely extended planes of the higher temperature smectic A phase. At temperatures intermediate between those corresponding to the stable indefinitely extended smectic C and smectic A arrangements respectively it seems likely that more mobile and less extended transitional groupings of parallel molecules should arise and it is now suggested that such smaller intermediate groupings of molecules constitute the globular units which, without long range orientational order, build the intermediate cubic mesophase (Figure 1,f). In the case represented in Figure 1,g the cubic phase formed on rise of temperature from the smectic C phase, passes on further rise of temperature directly to the amorphous liquid (4'n-octadecyloxy-3'-nitrobiphenyl-4-carboxylic acid (15(b),(c), cf however 17(a),(b))). The difference in behaviour illustrated in Figures 1,f and 1,g is not necessarily indicative of a difference in constitution of the cubic phases represented in the two cases. More probably it indicates that, although the smectic A phase tends to arise in both instances the temperature in the second system is too high for its actual realization. This may be related to the nature of the individual compounds involved or to slight differences in their degree of purity.

It will be seen that the mechanism just suggested for the mode of formation of the non-amphiphilic cubic "smectic D" mesophase is, in essence, analogous to that proposed earlier above for the amphiphilic cubic mesophases V_1 and V_2 which lie intermediate between the optically anisotropic G and M_1 or M_2 mesophases respectively.

SOME UNSATISFACTORY ASPECTS OF ALTERNATIVE STRUCTURES FOR THE AMPHIPHILIC CUBIC MESOPHASES

Structure involving networks of rod-like units

The feature of statistical molecular equivalence mentioned earlier is not evident in the network models suggested by Luzzati and collaborators for the V_1 and V_2 mesophases,[32,33,34] in their sphere-in-a-cage model for the S_{1C} phase[35] or in their tetrahedral model.[36] In these models the role of molecules at the ends of the jointed rods is not apparently equivalent to the role of molecules midway along the rods and, in the cage structure, neither role is apparently equivalent to the role of the molecules in the encaged spherical micelle. This inequivalence may perhaps warrant reserve in accepting these models. Some additional apparently unsatisfactory features of the rod models may be noted as follows:

a) According to Luzzati,[37] and as emphasised in the R-theory (1, 2) the aqueous, hydrocarbon and amphiphilic structural zones of "fused" amphiphilic phases are all liquid in character and devoid of internal rigidity. It is therefore very difficult to see what equilibrium of forces could maintain the rigid networks proposed for the V_1, V_2 and S_{1C} mesophases.

b) If the micellar structures of the V_1 and V_2 phases involve indefinitely extended networks with both positional and orientational long-range order the NMR properties of these mesophases might be expected to resemble those of the G and M phases with their indefinitely extended parallel lamellar or fibrous micelles respectively. As already noted the NMR properties of the V_1 and V_2 phases are similar both to those of the S_{1C} phase and to those of the amorphous liquid phase S, but differ markedly from those of the G and M mesophases.

c) The details of the dimensions of the various structures proposed by Luzzati and co-workers have apparently all been calculated on the approximation that all the organic molecules and all the water molecules are respectively collected in separate amphiphilic and aqueous zones of the system. This approximation is made in order that the relative volumes of these zones, Va and Vw, may be estimated and used in calculating the micellar dimensions. Although with certain compositions this approximation will be justifiable, with others this will not be so.[1,2] Thus in the sodium caprylate/xylene/water system for which the sphere-in-a-cage structure of the S_{1C} phase was proposed[35] the sodium caprylate content of the aqueous zone may well be of the order of 20%w.[1] Using this value the order of Va/Vw becomes 0.36/0.64, whereas with the usual approximation employed in developing the sphere-in-a-cage model, Va/Vw is of the order of 0.46/0.54.

Structures involving spherical units

A structure involving essentially spherical micellar units (S_1 or Hartley micelles) in an aqueous matrix has been proposed above for the S_{1C} phase. Similar structures (but usually neglecting the aspect of thermal rotary motions) have often been put forward for the V_1 phase; indeed such a structure was initially suggested by Luzzati and collaborators in their earlier publications in which the formation of this phase was first reported. However, they later recognised[37] serious difficulties in this interpretation and proposed as an alternative a structure involving reversed spherical micelles in a hydrocarbon matrix. In neither case, however, is the character of the hypothetical micellar building unit compatible with the position of the V_1 phase in the general sequence of amphiphilic phases.[18]

From their X-ray work on the dimethyldodecylamine oxide/water system, Lawson, Mabis and Flautt[31] favoured a structure for the V_1 phase "made up of distorted spherical units packed in a face-centred-cubic lattice", water forming the matrix. As a result of NMR studies, Lawson and Flautt concluded that there was isotropic rotational motion of the structural units.[23] However, Lawson, Mabis and Flautt recognised the difficulty of accounting for the existence of such spherical units in a phase succeeding the M_1 phase with increasing concentration. In discussing the sequence they write "... at the upper limit of existence of the middle phase. By some mechanism, the energetics of which are not clear, the units of the middle phase break up and rearrange to form the three dimensional face-centred-cubic structure of the viscous isotropic phase ...". Complementarily, of course, one might write that with decreasing concentration "at the lower concentration limit of the G phase the lamellar units break up and rearrange to form the three dimensional cubic phase V_1". In discussing the changing shapes adopted by the micellar units in the successive phases, Lawson, Mabis and Flautt[31] consider the influence of the *inter*micellar packing. However, in the view expressed in the R-theory, the main feature which determines the changes in micellar shape is not the *inter*micellar packing, but rather *intra*micellar changes in curvature of the amphiphilic layer which result from changes in R consequent upon changes in composition and/or temperature.[1,2] In other words the micelles possess a preferred shape of their own rather than a shape determined by the effects of packing. This view has been discussed elsewhere[1,2] and provides a qualitative understanding, embodied in Figure 4, of the breakdown of the units of either the M_1 or the G phase at intermediate compositions to give globular units which can constitute the V_1 phase as already considered above.

A correlative account of a number of amphiphilic cubic mesophases has been given by Fontell,† Mandell and Ekwall.[38] The structural models they suggested were all based on essentially spherical units, and emphasis was given to packing considerations and to the possible effects of "bound water". Thus the high viscosities were throughout attributed to mechanical close packing. If the measured lattice spacing was incompatible with close packing of the unsolvated micelles, then a large rigid hydration layer was postulated in explanation: it must be remembered, however, that the NMR investigations both of Lawson and Flautt and of the writer collectively indicate that, except at the highest concentrations,[18] much of the water in all the amphiphilic mesophases (M_1, V_1, G, V_2 and M_2) retains a high mobility. If the measured lattice spacing was too small to accommodate spherical micelles, the micelles were supposed to be deformed towards dodecahedra. These would hardly be expected to show the thermal rotary motion suggested by NMR studies. If the measured lattice spacing was too great to be accounted for by simple micelles then "complex" micelles were assumed (Figure 7). Such micelles, however, are clearly not acceptable according to the R-theory and do not represent the roles of all the molecules of a given species as statistically equivalent.

The view that the high viscosities of the cubic phases are due to close packing of micelles conflicts with the generally held belief that these micelles are liquid and highly deformable and that the interfacial tension – micelles/intermicellar liquid – is zero. It is therefore not clear that their close packing would lead to high viscosities. Indeed, it has been found that, in contrast to emulsions, amorphous micellar solutions of O/W (S_1) or W/O (S_2) character do not show very high viscosities even at very high (9:1) volume ratios of the "disperse" moiety.[39] Further, if micellar close packing is supposed to account for the high viscosities of the cubic mesophases it is not evident why at the transition to the amorphous micellar solution phase S, the viscosity should suddenly drop. A further objection to the spherical-close-packing models of the cubic mesophases is that on this basis all the phases might be expected to possess face-centred cubic lattices. In fact, although a face-centred cubic lattice may occasionally be found[31] body-centred and primitive lattices are more frequent (Table 2).

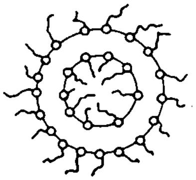

FIGURE 7 Postulated cross-section of "complex" type of micelle (either spherical or cylindrical) Complementary forms can be envisaged[38]

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† More recently (private communication), Fontell has favoured Luzzati type structures

With the plastic crystalline models now proposed for the amphiphilic cubic phases all the above difficulties are avoided. The maintenance of the thermally rotating units at the lattice points is believed to result not from mechanical close packing but from the balanced effects of attractive (Van der Waals) and repulsive forces (Van der Waals forces and forces opposing the interpenetration of electrical double layers). It is the stability of the lattice which confers the high viscosity on the cubic mesophases. At higher temperatures this lattice is broken on account of the greater thermal motion and "melting" results, with a consequent sharp fall in viscosity. The mean shapes of the thermally rotating micellar units are not believed necessarily to be strictly spherical but to involve an intermicellar equilibrium and to be variable (both with concentration and temperature) towards both oblate and prolate forms. A cubic mesophase can arise if a suitable combination of mean micellar shapes and micellar concentrations (mean intermicellar approach distance) exists under conditions where the thermal motion (temperature) is not too great to prevent the thermally rotating units from falling into a cubic lattice. The details of this lattice will be determined by the mean shape (or possibly range of shapes) of the units and by the consequent details of their rotary motions. Also the mean "micellar weight" and consequently the cubic lattice constant can increase through increase of either mean oblateness or prolateness. These possibilities avoid the difficulty involved in the acceptance of "complex" spherical micelles and also account for the fact that the amphiphilic cubic mesophases only rarely show simple face-centred lattices. Further, it is to be anticipated that in a given amphiphile/water system (or in a system containing additional components) change in form of the intermediate micelles with change in composition or temperature might, even within a given phase (S_{1C}, V_1 or V_2), lead to more than one type of cubic lattice (cubic polymorphism) or even, by analogy with the hexagonal plastic crystals formed by cyclopentane (Table 2), to a hexagonal form of close to zero birefringence.

CONCLUDING REMARKS

In the above account it has been suggested that constitutional analogies exist between the thermodynamically stable cubic mesophases formed by globular molecules, by globular transitional groupings of molecules derived from certain non-amphiphilic mesogens, and by globular micelles in amphiphilic systems.

Further, constitutional analogies have been noted between the thermodynamically stable amphiphilic M_1 and M_2 phases and the non-amphiphilic nematic/cholesteric phases and between the amphiphilic G phase and the non-amphiphilic smectic phase (in this case smectic A).[15a,b] Constitutional analogies of these types may extend even more widely so as to include metastable systems, for example, the aqueous two-dimensional hexagonal solution of tobacco-mosaic virus,[40] the aqueous cubic phase formed by tomato-bushy stunt virus[41] and even certain inorganic tactosols, such as those formed by vanadium pentoxide in water[42] and by barium carbonate in methanol.[43]

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