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The Structural Types of Aqueous Systems of Surface-Active Substances and their X-ray Diffraction Characteristics*

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In recent years many papers have dealt with X-ray diffraction by aqueous systems of detergents and colloidal electrolytes. The results have clearly indicated the existence of several different types of fine structure due to different colloidal particles, even in the phases belonging to a single surface-active substance. It is opportune to summarize this information to serve as a basis for further work. A classification of such structures is here suggested.

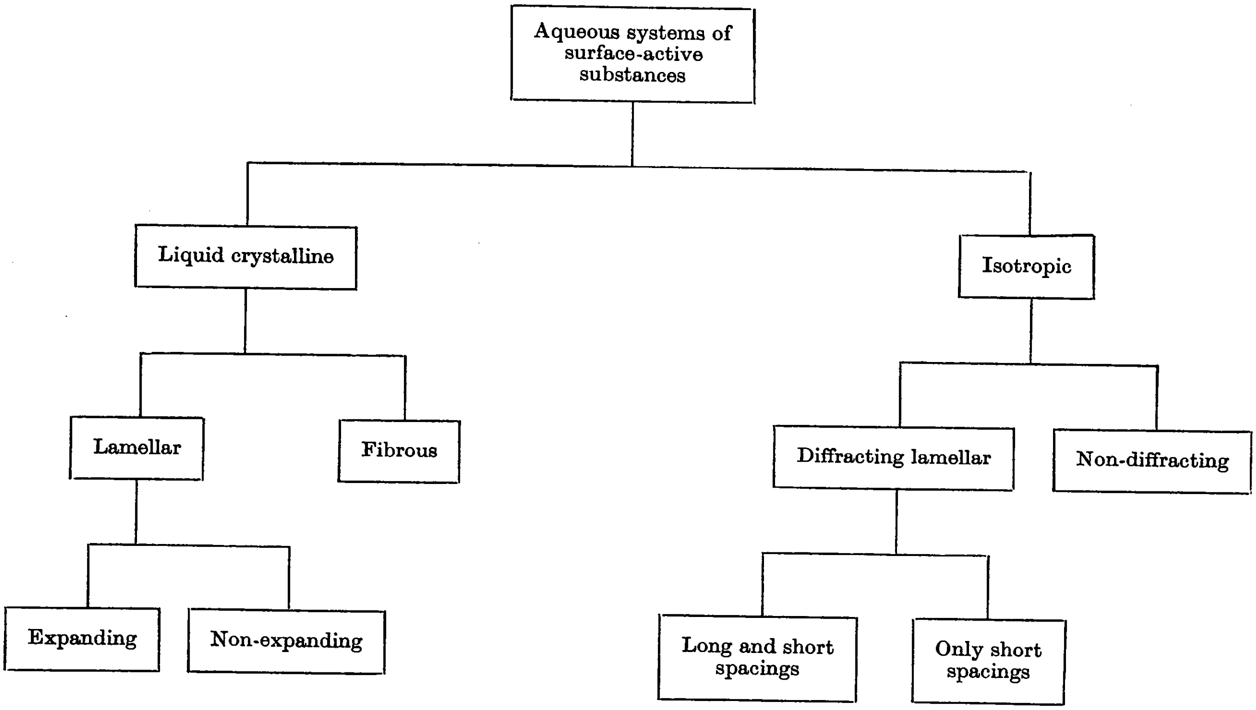

Fig. 1. Classification of structures

For this purpose anisotropic or liquid crystalline phases will be separated from isotropic solutions, as in the diagram, Fig. 1. The former, in turn, can be divided according to the type of particle indicated by the X-ray diffraction pattern, namely, lamellar and fibrous. The distinction between the X-ray patterns of the two types is to be found in the ratios of the numerical values of the several low-angle diffractions (long Bragg spacings) to each other, and in their relative intensities (see Table 1). The difference between the two types of structure lies in the nature and arrangement of the colloidal units which comprise them, i.e. lamellae and fibers.

1. The lamellar type of *primary* colloidal particle, as repeatedly described by McBain from 1923 onwards, consists of a double layer of close-packed molecules side by side, with their hydrophobic parts end to end, so that all the hydrophilic ends are exposed on the outer surface of the lamellae. The thickness of the McBain micelle is therefore twice the length of the surface-active molecules, times a factor sin β, where β is the angle of tilt (if any) of the molecules within the layer. The lateral dimensions of the layer may be large, but are not yet established. They may well depend, among other things, on the particular detergent concerned. The lamellae are probably neither square nor circular but will tend to have a much greater length than breadth. This will be referred to again. Mattoon, Stearns & Harkins (1947) note an indication of the thickness of the unit McBain micelle.

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Table 1. *Ratios of low-angle spacings and their relative intensities*

Class	Types of structure	Ratios of principal long spacings to one another, with relative intensities (*a*)	Variation of repeating distance with concentration C, the volume fraction of surface-active substance
Anisotropic	Expanding lamellar (*e*)	$1(s) : \frac{1}{2}(m) : \frac{1}{3}(w \text{ or } vw)$	C^{-1}
	Non-expanding lamellar (*d*)	$1(s) : \frac{1}{2}(m) : \frac{1}{3}(w \text{ or } vw)$	C^{0}
	Fibrous (*b*, *d*)	$1(s) : \sqrt{3}(m) : \sqrt{4}(m \text{ or } w) : \sqrt{7}(w \text{ or } vw)$	$C^{-\frac{1}{2}}$
Isotropic	Diffracting lamellar (*e*, *f*, *g*)	$1(s \text{ or } m) : \frac{1}{2}(w \text{ or } vw)$	Antibatic to C, but to no set power
	Only short spacings (*e*)	—	—
	Non-diffracting micelles (*c*)	—	—

(*a*) s = strong; m = medium; w = weak; vw = very weak.
(*b*) These spacings correspond to a hexagonal pattern with indices $10\bar{1}0$, $11\bar{2}0$, $20\bar{2}0$, $21\bar{3}0$, $30\bar{3}0$.
(*c*) Spheres and cylinders could give no sharp spacing from within the micelle (other than from neighboring molecules) but only continuous halos.
(*d*) Marsden & McBain (1948*c*).
(*e*) McBain & Hoffman (1948).
(*f*) Hess, Gundermann, Kiessig, Philippoff & Stauff (1937–42).
(*g*) Harkins, Mattoon & Corrin (1946*a*, *b*); Harkins (1948).

Hess, Gundermann, Kiessig, Philippoff & Stauff, and others, found that the McBain micelles can arrange themselves in parallel, at definite distances from each other, and Brady has very recently shown that these distances may be predicted from the properties of the diffuse ionic layer. The observed X-ray pattern of this secondary aggregate or 'Gross-micelle' or Hess micelle consists of strong low-angle diffractions corresponding to the first, second and third orders of the repeating structures of the successive lamellae. The high-angle diffraction consists of one or sometimes two halos indicative of the imperfect lateral arrangement of the close-packed molecules in the lamellae, corresponding to a liquid or liquid crystalline structure, or possibly sometimes due in part to the very small dimensions of the structure.

We now find that there are two repeating lamellar types: the German expanding type (which we find extends also to certain anisotropic phases), and a new non-expanding type. As water is added to the expanding lamellar type, the long spacing increases with increase in dilution of the surface-active component. It is believed that the water goes into layers of uniform thickness between the McBain micelles. The repeating structure thus consists of a bimolecular layer of surface-active agent *plus* a layer of water; the resulting long spacing can be relatively large compared with ordinary molecular dimensions (some up to 200 A. have been found (Marsden & McBain, 1948*a*)). Some anisotropic phases of this subtype have been found to expand to a limit, after which all of the water added goes into another phase rather than into the aqueous layer (e.g. α-*n*-decyl glyceryl ether), while others have been found to expand until the long spacing could no longer be observed (e.g. diethylene glycol monolaurate, glyceryl monolaurate). It has been previously shown by the authors (Marsden & McBain, 1948*a*) that for the ideal case of the expanding lamellar type in anisotropic liquid phases* the observed long spacing varies as the reciprocal of the volume fraction of the surface-active substance as if *all* of the water goes into the layers. If this relation does not hold for other systems, then it can be said that water is either (1) penetrating between the sides of the surface-active molecules *within* the layer while this layer is still maintained intact although expanded laterally, or (2) going into another phase in the system, or (3) liberating some of the McBain micelles from each other, or (4) breaking up the micelles into fragments (see below).

For the non-expanding repeating lamellar type, as its name implies, the long spacing does not change with the addition of water to the system. It still has the bimolecular layer of surface-active molecules as the fundamental McBain unit, but water added to these systems goes either into a second phase or penetrates between the surface-active molecules *within* the layer of surface-active molecules. The 'superneat phase' of the system dodecyl sulfonic acid–water is an example of this subtype (Marsden & McBain, 1948*b*). A variation is that in which the water layer reaches a certain thickness and then remains constant as more water is added, the water going into a second phase (e.g. α-*n*-decyl glyceryl ether (Marsden & McBain, 1948*a*) in a different concentration range from that referred to above).

It is recognized that the non-expanding lamellar subtype is somewhat similar to the 'smectic' type of Friedel (1922); however, the water is a necessary constituent of the phases of which this type consists.

2. A very different type of structure is that in which the fundamental units are long fibers or rods or laths arranged hexagonally with respect to one another and with water in between. This structure is that found for certain aqueous systems of tobacco mosaic virus by Bernal and Fankuchen. The low angle diffractions for this type are Bragg spacings which are in the ratio of $1 : \sqrt{3} : \sqrt{4} : \sqrt{7}$, and correspond to the hexagonal indices $10\bar{1}0$, $11\bar{2}0$, $20\bar{2}0$, $21\bar{3}0$. The intensity of the second line is greater than that of the third. Again the high-angle diffraction consists of one and sometimes two halos which are indicative of an imperfect

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* This type had sometimes been termed the 'hydrous smectic liquid crystal', but it is believed that the terminology used here is more advantageous.

but parallel arrangement of molecules within the fiber.

Only one example of this fibrous type has been reported (Marsden & McBain, 1948*c*), that being the 'middle soap' phase of the dodecyl sulfonic acid–water system. This is of an 'expanding fibrous type', i.e. the distance between the fibers increases as water is added to the phase. Although no 'non-expanding fibrous type' phases are now known, it is possible, in analogy with the non-expanding lamellar type, that they may exist.

The dimensions of the fibrous micelles are unknown. It has been suggested that they are highly elongated ellipsoids of circular or elliptical cross-section, with the molecules lying approximately in the plane of the cross-section. Like the concept of strictly spherical micelles, this runs into considerable geometrical difficulty owing to the volume of the hydrophobic portions being so much greater than could correspond to a surface comprised of polar heads, and owing to the difficulty of close packing in any such arrangement with only partially flexible molecules whose length is only a few times their breadth and thickness. Instead, there must be a tendency for the molecules to lie parallel rather than radially.

It may be suggested that there is a close relation between the lamellar and fibrous micelles, and that the latter may be merely very narrow or lath-like lamellar micelles. This suggestion is supported by the well-established fact that crystalline soap curd fibers have this habit of growth. There the molecules lie in the *ac* plane side by side and end to end; and the cross-section, as has been shown by electron microscopy (Ross, 1942), is of the order of multiples of the double molecule length. In the *b* direction, at right angles to the *ac* plane, the length of the crystal fiber may amount to centimeters instead of being of molecular or ultramicroscopic dimensions. Were a McBain micelle to become so elongated in proportion to its width, the same electrical and other forces that hold broad lamellae parallel to each other would operate to arrange these micelles in a hexagonal pattern sideways with the long axes normal to the hexagonal plane.

The presence of a small number of these narrow lamellar or fibrous micelles in the midst of a large number of lamellar micelles would account for the relatively faint 'ghost' lines to be seen in some of the photographs of anisotropic potassium laurate solutions (McBain & Hoffman, 1948) which occupy the intermediate positions that could have been attributed to the $11\bar{2}0$ and $21\bar{3}0$ spacings.

Although fibers are the commonest form of crystallized soap, extremely thin lamellae are often observed many millimeters in length and breadth, but of ultramicroscopic thickness. Thus there are well-established crystalline analogs of the lamellar and fibrous micelles.

3. Turning to the isotropic systems or solutions, these are likewise divided into three types according to the kind of micelles they contain, as indicated by their X-ray diffraction patterns as well as other physical-chemical data. Those containing Hess lamellar micelles may give both long and short spacings (in addition to that corresponding to the thickness of the McBain micelles), the long spacing expanding with dilution, or they may give only short spacings (McBain & Hoffman, 1948). Other isotropic solutions which are undoubtedly fully colloidal, and, further, all sufficiently dilute solutions, give no X-ray diffraction pattern (McBain & Hoffman, 1948).

In solutions above the so-called critical concentration for the initial formation of micelles, there must be various small micelles of many types ranging upwards from ion pairs and triplets (and possibly even the McBain ionic micelle) to larger fragments of the McBain micelles. Sketches of such small micelles have been drawn by various investigators (McBain, 1948, Chap. 7; Stauff, 1941), and we believe that each of these possibilities will be represented in proportion to the degree to which it lowers the free energy of the system by taking hydrophobic portions of the molecules out of contact with the water and forming as many hydrogen bonds as possible. Their relative numbers will depend upon concentration, temperature, molecular weight, and other details of molecular composition and structure, as well as the respective requirements of the law of mass action.

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