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Conditions Governing the Formation of Lyotropic Liquid Crystals by Molecular Association

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The lyotropic liquid crystals which are considered here are obtained with substances or mixtures of substances having amphiphilic molecules, the solvent being water. In order to understand the behaviour of these mixtures of amphiphilic substances it may be helpful to recall the behaviour of similar systems with only one amphiphilic substance, such as soaps or phospholipids. In fact lyotropic systems are also thermotropic and it is the cooperative action of the temperature and of the solvent which enables them to pass successively from the solid crystalline state to the liquid crystalline state and to the isotropic liquid or dissolved state.

A Cooperative Phenomenon of Melting and Solution

In the case of thermotropic systems the transition from the solid crystal to the liquid crystal corresponds to a certain decrease of cohesion due to the increase of the kinetic energy of the molecules. This decrease of cohesion is manifested by a sudden increase of the specific volume. Another sudden increase of the volume takes place at a higher temperature, when the ordinary melting occurs, and the substance passes from the liquid crystal to the isotropic liquid state. With substances which exist in more than one crystal liquid state, several similar discontinuities of the specific volume evidently occur. We are not referring here to the second order transformations which appear in liquid crystals and to which correspond sudden changes in the expansion coefficient dV/dT.[1]

With lyotropic liquid crystals the cohesion is diminished both by thermal agitation and by the dissolution in the solvent (here water) of a certain region of the molecule of the amphiphilic substance. Temperature acts more specifically on the melting of the hydrocarbon region (or chains), while water acts on the hydrosoluble part of the amphiphilic molecules.

It is convenient, as was done by Hartley, to consider the crystalline structure of amphiphilic substances as the superposition of two lattices: a paraffinic lattice, constituted by the whole of the paraffinic ends of the molecules packed together, and a polar or ionic lattice, constituted by the whole of the polar or ionic ends of the molecules. To summarize it could then be said that the increase of temperature melts the paraffinic lattice while the water dissolves the polar or ionic lattice.

In fact the two effects cooperate. Thus, with anhydrous K-stearate,[2] the lamellar paracrystalline phase (smectic, called neat soap, appears only at 260° and the ordinary liquid phase at 340°; but, in presence of *c.* 40% of water, the paracrystalline lamellar phase appears already at 60°. On the other hand, whatever the quantity of the water present (even if it is above 95%), water cannot penetrate into the ionic lattice of the soap crystal: i.e. it cannot dissociate the hydrosoluble groups so long as the temperature is below 50°. If the temperature is higher than this particular point, there is *simultaneously* dissociation of the ionic lattice by penetration of the water and melting of the paraffinic lattice.

The particular temperature (Krafft Point) at which, in presence of a large quantity of water, there is dissociation of the ionic lattice and melting of the hydrocarbon chains depends on both the length of the hydrocarbon chains and the nature of the hydrophilic group and of the counter-ion.[3]

For a given hydrophilic group and a given counter-ion, the Krafft point varies with the chain length in a way similar to the variation of the melting points of the long chain fatty acids, alcohols, esters or hydrocarbons. Furthermore, with aqueous mixtures of two soaps having different chain length, the Krafft point is lower than that of either of the two pure soaps. More precisely, with varying proportions of the two mixed soaps, the Krafft point passes through a minimum corresponding to a eutectic.[4] This is similar to the variation of the melting points of mixtures of two fatty acids with different chain lengths. All these facts confirm that a melting of the paraffinic lattice takes place in this phenomenon.

On the other hand the fact that the Krafft points of the potassium soaps are lower to those of sodium soaps (e.g. Na-stearate 75°, K-stearate 49°, Na-laurate 36°, K-laurate 9°) shows that at the same time a dissolution of the ionic lattice takes place. Indeed, in general, the solubilities of the sodium salts of the carboxylic acids are weaker than the solubilities of their potassium soaps.

Therefore, the sudden decrease of cohesion between the amphiphilic molecules, when they pass from the crystalline state to solution in water, takes place at a lower temperature as the length of the chain decreases and the solubility of the ionic end increases. But, to obtain the lyotropic paracrystalline phases, a certain degree of cohesion is necessary. With chains shorter than eight carbon atoms no paracrystalline phase is obtained, because the cohesion between the chains is too weak. Conversely, even with a longer chain, the presence of several hydrophilic groups in the molecule also prevents the formation of paracrystalline phases. Such is the case, for example, with the bile salts, such as sodium cholate, which dissolve in water in the micellar form without going through a paracrystalline phase. Thus a certain balance between the cohesion of the paraffinic lattice and the solubility of the polar or ionic lattice is necessary in order to obtain lyotropic liquid crystals at a given temperature.

The term liquid crystal itself implies that, although the molecules are partly organized as in a crystal, they are nevertheless in a liquid state. In their investigation by X-ray diffraction of phospholipids swollen by water, Palmer and Schmitt,[5] already in 1941, had ascertained that the lines corresponding to the short spacing were in fact blended into a diffuse band, and they concluded that "the hydrocarbon phase may be considered as essentially liquid". MacBain and de Bretteville,[6] examining anhydrous Na-stearate at temperatures at which the thermotropic paracrystalline phases and the ordinary liquid phase appear, had found that not only the side spacing gave a diffuse band but that the large spacing was shortened as though the hydrocarbon chains had collapsed. Chapman[7] also has shown by infrared spectroscopy that, even at relatively low temperatures, the atoms in the chain have a certain movement which increases with the increasing temperature.

In order to derive from the measurements of Stauff[8] the thickness of the water layer in the paracrystalline phases of soaps swollen by water (lyotropic phase) Dervichian[9] had to use, for the thickness of the lipidic layer, the value which corresponds to the large spacing of the anhydrous soap at temperatures at which the chains are melted (thermotropic phase). Indeed the more recent results of Luzzati *et al.*[10] have shown that the thickness of the lipidic layer in the neat phase of soaps swollen by water is very approximately the same as the thickness of the double layer of molecules in the same phase (thermotropic) of anhydrous soaps.

As has been remarked above, the lyotropic paracrystalline phases are produced by the cooperative action of the dissolution or hydration of the polar ends and the melting of the paraffinic parts of the molecules. If therefore this melting does not occur at the temperature of the experiment, the paracrystalline phase is not formed in the presence of water. On the contrary too great a thermal agitation of the paraffinic part and/or too great a solubility of the hydrophilic end may lead to dispersion into an isotropic phase, which may be a mere solution of the substance in water.

This cooperative action, in which both the cohesion between the paraffinic parts of the molecules and the solubility of the polar ends in water have to be considered, may be related to the concept of lipophilic–hydrophilic balance, which is familiar to those who are concerned with surface active substances.

Lipophilic–Hydrophilic Balance and Hindered Solubility

To illustrate the application of this concept to the present case, we can consider the behaviour of three types of substances: (a) a triglyceride, (b) a lecithin and (c) a soap or lysolecithin. In triolein, the hydrocarbon part is important since it is formed of three chains, while the hydrophilic end of the molecule, constituted by the three ester functions, is poorly, if at all, soluble in water. Consequently triolein, as well as being insoluble, does not swell in water.

On the contrary, in the soap molecule the paraffinic part is formed of only one hydrocarbon chain and the hydrophilic end is an ionized soluble group. Lysolecithin (which is derived from lecithin by loss of one of the two hydrocarbon chains) is in a similar situation, since it has only one hydrocarbon chain and, besides the free OH group of glycerol, contains a phosphorylated amino-alcohol group strongly ionized. Lysolecithin, like soap, can therefore, not only swell in water, but dissolve completely in the micellar form when the amount of water is large. Thus these substances give paracrystalline phases, up to a certain concentration of water, and then an isotropic phase (solution) when the quantity of water is increased.

Lecithin stands between these two extreme cases: it has two hydrocarbon chains which counterbalance the solubility in water of the ionized phosphorylated cholin. Lecithin swells in water to give a lamellar paracrystalline phase, but it does not dissolve: whatever the quantity of the water added, the paracrystalline phase, swollen to its maximum, remains in equilibrium with the excess of water.[11]

The appropriate degree of lipophilic–hydrophilic balance may be obtained by mixing different amphiphilic substances each of which is more or less hydrophilic or lipophilic. According to the nature and the proportion of the mixed amphiphilic substances, one can thus obtain either paracrystalline phases swollen by water or complete dispersion by dissolution. Stress is laid in the present article more particularly upon these mixtures.

For instance, lysolecithin and cholesterol in equimolecular proportions swell to give a lamellar paracrystalline phase as does lecithin alone. The insoluble cholesterol molecule hinders the solubility of the lysolecithin, or the soluble lysolecithin enhances the solubility of the cholesterol. This is similar to the "acid-soap", i.e. 1:1 molecular ratio of a potassium or sodium soap to its free fatty acid. The acid soap swells in water to give a lyotropic liquid crystal.[12] The fatty acid alone is of course insoluble, whereas the soap is soluble. This same result can be obtained by associating cholesterol with: sodium and potassium soaps, alkyl sulfates, alkyl phosphates, long-chain amines, alkyl choline chlorides.

Further, one can substitute for cholesterol another insoluble amphiphile, such as a cholesterol ester or a long-chain alcohol, and obtain a paracrystalline phase with certain soluble compounds, as was pointed out by Dervichian and Magnant[13] in a study of a large series of mixtures of amphiphilic substances.

The Required Fluid State of the Mixed Layers

It should be emphasized that, in the case of mixtures of amphiphilic substances also, it is necessary that the whole of the paraffinic parts of the associated molecules are melted. In fact the molecular association can be considered as being due to a mutual solution of the paraffinic parts of the different species of molecules oriented by water.

These conditions were established by the individual study of each of the two layers which form the structure of the lyotropic paracrystalline phases. Indeed each of these layers is very nearly in the same condition as a monolayer spread on water. The parallel study on monolayers was carried out using all the pairs of substances which gave the different paracrystalline swollen phases.[14] Those mixtures giving lyotropic paracrystalline phases in the bulk always gave fluid monolayers. For example, cholesterol, which gives a fluid film, and sodium stearyl phosphate, which gives a solid film, when mixed together form a mixed liquid film. An equimolar ratio of cholesterol and sodium stearyl phosphate gives a liquid crystal appearing as myelin forms. Further, cetyl alcohol, which gives a fluid film, and digitonin, which gives a fluid film, when mixed together give a liquid film, and in the bulk give either myelin figures or batonets, depending upon the proportion of cetyl alcohol to digitonin. On the other hand, cholesterol, which gives a liquid film, when mixed with digitonin, which gives a liquid film, together form a solid film. In this case, no lyotropic paracrystalline phase is observed in the bulk.

The Formation of Different Lyotropic Paracrystalline Phases

The alteration of the lipophilic–hydrophilic balance can also lead to different types of lyotropic liquid crystals. This may be done by altering the proportions of the two components. For instance, cholesterol and sodium lauryl sulfate in a 1:1 mixture gave myelin figures, whereas, on increasing the sodium lauryl sulfate to 1:2 or 1:3, batonets of Friedel are formed. This may perhaps be better illustrated by considering the ternary phase diagram, lecithin, sodium cholate and water, which is given in the work done in this at department by Small and Bourgès.[15] It can be seen by looking the diagram that at least three paracrystalline phases exist, depending upon the relative proportion of the three components. For instance, if we follow a line at 45% water and note what happens to the phases, as more and more of the soluble amphiphile sodium cholate is added, we note that one passes from the lamellar paracrystalline phase to a hexagonal paracrystalline phase and finally out of the paracrystalline region into a micellar solution. If we follow a line at constant water at 32%, one passes from the lamellar phase into a cubic phase. Finally, if we follow a line of constant water at 20%, there is no change of phase, the lattice is simply saturated until sodium cholate precipitates yielding two phases: the lamellar phase saturated with sodium cholate and the sodium cholate crystals.

In summary, in order to form a lyotropic paracrystalline phase by association, the paraffinic lattice must be liquid. Further, the type of paracrystalline phase formed depends not only on the amount of solvent, i.e. water, but ultimately on the balance of the free energy of molecular cohesion between the lipophilic elements and the free energy of the affinity of the head groups for water and for each other.

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