COLLOID AND SURFACE CHEMICAL ASPECTS OF MESOPHASES (LIQUID CRYSTALS)

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Abstract—The characteristic behaviour of mesophases, especially anomalies observed in the surface tension and viscosity in some thermotropic mesophases, are discussed on the basis of thermodynamic and molecular kinetic theories.

Experimental data are presented for the surface and flow properties found in some lyotropic mesophases involved in the ternary systems: ammonium alkanoate + water + n-octanol; cetyltrimethylammonium bromide + water + n-hexanol.

Using these experimental data, the correlation between mesophases and colloidal systems is discussed with reference to the theories developed by Wo. Ostwald.

INTRODUCTION

The mesophases or mesomorphic phases are the intermediate states between the amorphous and crystalline states and are often called "liquid crystals". Since the discovery of this particular state of matter by Reinitzer[1] and Lehmann[2] at the end of the last century, it has become one of the keen interests not only of physicists and chemists but also of biologists. The progress of research into mesophases was rather sporadic during the first half of this century, but the present interest in this field is shown by the fact that the International Liquid Crystal Conference has already been held five times since 1965. The recent progress in liquid crystal research extends widely in both theoretical and applied fields.

Among materials exhibiting this particular intermediate state are soaps, synthetic surfactants, phospholipids and cholesteric compounds. These are important also from the viewpoint of colloid and surface science. At the beginning of the 1930's Ostwald[3] pointed out the close relationships between mesormorphic and colloidal systems in their structural features as well as in their physicochemical properties. It seems, however, worthwhile reconsidering the viewpoint of Ostwald in the light of recent experimental data.

Before entering into this problem the author would like to make some remarks on the surface tension and viscosity anomalies found in thermotropic mesophases, which may be compared with similar behaviour in lyotropic mesophases.

SURFACE TENSION ANOMALIES OF THERMOTROPIC MESOPHASES

The present author's own interest in liquid crystals derived from a study of the surface state equations for pure liquids and solutions,[4] in which it was noticed by Jaeger[5] that some liquid crystalline compounds like p-azoxyanisole, p-azoxyphenetole, etc., exhibit an anomalous behaviour in their surface tensions. The surface tension of these compounds first decreases with rise in temperature, then sharply increases near the transition temperature at which the anisotropic liquid crystalline phase changes into the isotropic liquid phase, and decreases again with further rise in temperature. Jaeger's findings were later confirmed by Ferguson and Kennedy.[6] More recently, the same anomalies have been observed with other types of liquid crystals, particularly

with cholesteryl myristate by Churchill and Bailey,[7] and with ammonium alkanoates by the present author and coworkers.[8]

On the other hand, however, Naggiar[9] and later Schwartz and Moseley[10] reported that they could not observe such a remarkable rise of surface tension at the transition point, although a slight hump appeared in the surface tension vs temperature curves obtained by Schwartz and Moseley. These authors considered that the distinct anomalies found by the former authors (Jaeger, Ferguson and Kennedy) might have been due to the non-equilibrium values of the surface tensions determined by them. The discrepancy between the experimental results of both sides seem to be due to the difference in the methods of measurement of the surface tension applied by these authors. Nevertheless, anomalies in the surface tension of liquid crystals which have been repeatedly observed by several investigators using different methods seem to require a reasoned explanation.

For the relationship between the surface tension of a liquid and its temperature, Eötvös[11] formulated the following equation:

$$\gamma(M/d)^{2/3} = \bar{K}(T_c - T) \tag{1}$$

where γ is the surface tension, M the molecular weight, d the density, T_c the critical temperature of the liquid and T the absolute temperature. $\bar{K}$ is Eötvös constant, approximately equal to 2 for so-called "normal" liquids. Thus from this equation the molar surface free energy decreases linearly with the temperature.

However, $\bar{K}$ is in general not constant but varies according to the nature of liquids and also changes with temperature over a wide range. In the present author's study on the surface state equations for pure liquids the following general equation was derived:

$$\gamma(M/d)^{2/3} = kN^{2/3}(T_c - T) + \phi(r) \tag{2}$$

where k is the Boltzmann constant, N the Avogadro's number and the additional term $\phi(r)$ is a function of the molecular interaction potential energy or of the Clausius second virial coefficient. From this equation the Eötvös constant may be expressed as:

$$\bar{K} = kN^{2/3}\left\{1 + \frac{\phi(r)}{kN^{2/3}(T_c - T)}\right\} \tag{3}$$

showing that $\bar{K}$ is a function of the molecular interaction energy at the liquid surface as well as of the temperature.

For the anisotropic melts of liquid crystals, it was found that $\bar{K}$-values are exceptionally large, for example, about 5 for p-azoxyanisole and about 8 for p-azoxyphenetole. These anomalous values of $\bar{K}$ for liquid crystals can be attributed to the large contribution of the function $\phi(r)$, i.e. the strong interaction energy between anisometric molecules which possess large dipole moments. For liquid crystalline anisotropic melts the following equation can be assumed:

$$\gamma(M/d)^{2/3} = kN^{2/3}(T^* - T) + \phi(r) \qquad (4)$$

in which T^* is the transition temperature of the anisotropic–isotropic phase change. From this equation, at the transition temperature:

$$\gamma(M/d)^{2/3} = \phi(r) \qquad (5)$$

indicating that the molecular surface energy is equal to the molecular interaction energy at the transition temperature.

Now, the molecular interaction energy depends on the structure and the mutual orientation of molecules at the surface; if it is assumed that, at the transition temperature, a certain rearrangement of molecules would take place at the surface so as to increase the interaction energy, the experimental findings of a sudden increase at this temperature of the molar surface free energy, and accordingly, of a decrease of the molar surface entropy, which is evaluated as several ergs per degree, could be explained. Such was the author's *per tempa* hypothesis for the surface tension anomalies so far experimentally observed.

However, in the determination of the surface tension of liquid crystals there are technical difficulties on the one hand, and theoretical difficulties on the other. Therefore, the problem here discussed requires further investigation.

VISCOSITY ANOMALIES IN THERMOTROPIC MESOPHASES

Another anomalous behaviour of mesophases reveals itself in their flow properties such as viscosity. Ostwald[12] called attention to the fact that some liquid crystals, esters of cholesteryl carbonic acids, show sharp maxima in their viscosity vs temperature curves near the transition temperature of the anisotropic to isotropic phase change and from this experimental evidence, he suggested that there are analogies between mesomorphic systems and colloidal segregating systems like albumin and starch sols. He also pointed out that the viscosity of some liquid crystals, such as cholesterol esters or p-azoxybenzoate, is distinctly dependent on the shear stress. Thus the flow of these substances is non-Newtonian, but plastic accompanied by a certain yield stress value, and in this respect, Ostwald suggested there is a resemblance between liquid crystals and colloidal systems like gelatin and rubber sols. These suggestions were criticised by Lawrence[13] who thought that further work on the viscosity behaviour of liquid crystals should be done to support the concept of the existence of molecular aggregates, or swarms, of colloidal dimensions, in liquid crystals.

The anomalous flow properties of mesophases have been studied more precisely in recent years by several investigators[14] with various types of mesophases, not only cholesteric and nematic but also smectic.[15] One of the results obtained with smectic mesophases is illustrated by

the following figures. Figure 1 shows the shear rate vs shear stress relation for ammonium myristate at different temperatures. It can be seen that flow of the anisotropic melt is non-Newtonian but plastic accompanied by approximately yield stress values, while the flow of the isotropic melt is Newtonian. Figure 2 shows the viscosity vs temperature relation for the same compound at different shear rates. The viscosity of the anisotropic melt first decreases with the rise of temperature, at a certain temperature near the transition point it increases to a maximum, and then falls rapidly with subsequent rise in temperature. This figure is remarkable, in that the maximum point in the viscosity falls with the increase of the shear rate.
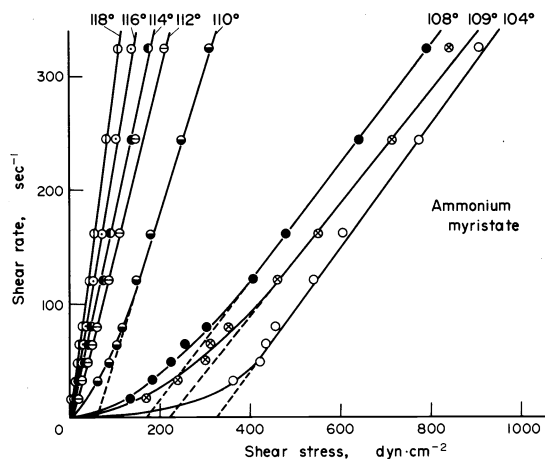

Fig. 1. Shear rate vs shear stress relation for ammonium myristate at different temperatures.
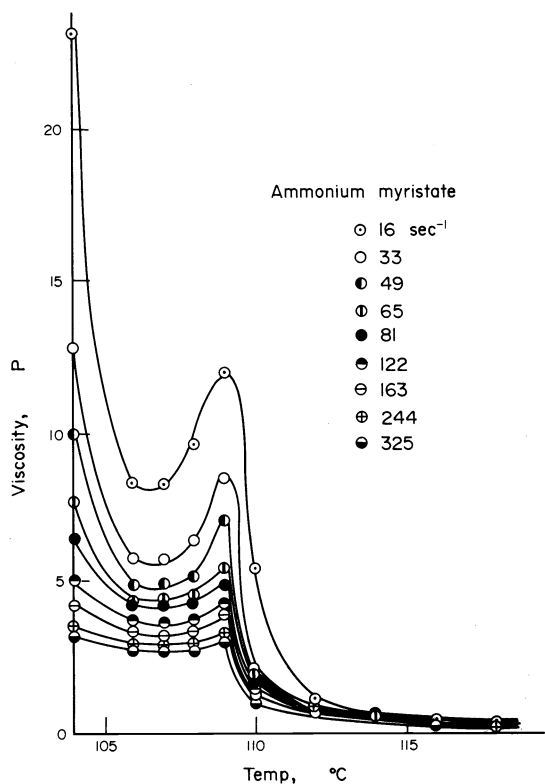

Fig. 2. Viscosity vs temperature relation for ammonium myristate at different shear rates.

Some investigators like Lawrence considered that the sharp rise in viscosity near the transition temperature might have been due to the effect of turbulence in the nematic or cholesteric melt at this temperature.[16] However, from the experimental results obtained here with the smectic mesophases whose viscosities are fairly high, it seems unnecessary to assume turbulence, expecially at lower shear rates at which the maximum appears. The present author would like to assume that the rise of viscosity near the transition temperature is probably due to the mutual interaction, even entanglement, of molecules caused by their rotational thermal motions along their axis perpendicular to the longer axis of the anisometric molecules. Such rotations would be excited at this temperature. If temperature rises further, the greater thermal motions will free the molecules from their mutual interactions and accordingly reduce the internal resistance and viscosity. Furthermore, the fact that the viscosity of the anisotropic melt is highly dependent on the shear rate or shear stress, can be explained by a mechanism such as the following. The long shaped molecules will be reoriented, probably in nematic state, parallel to the direction of the shear stress and if the shear stress is great enough, the flow rate will increase linearly, so that the apparent viscosity will become constant.

SOME CHARACTERISTIC BEHAVIOUR OF LYOTROPIC MESOPHASES

So far, in this present review of the anomalous behaviour of the thermotropic mesophases, temperature has been the main factor controlling the characteristic intermediate state of the matter. There is another type of mesophase where the solvent acts as a substance to form the intermediate state between crystal and liquid. This type of mesophase is called a lyotropic mesophase. Substances forming lyotropic mesophases are generally of amphipathic or amphiphilic nature whose molecules have hydrophilic groups on one part and oilphilic groups on the other in their single molecules. Soaps, synthetic surfactants, phospholipids and some kinds of synthetic dyes are examples of such compounds. From the viewpoint of a comparative study of mesophases and colloids, the lyotropic mesophases should be considered before the thermotropic ones, because colloidal systems are frequently also solvated systems.

Binary systems of soap(surfactant) + water and ternary systems of soap(surfactant) + water + organic solvent have been extensively studied by many investigators in connection with the formation of lyotropic mesophases in such systems.[17] In the author's laboratory, studies have been carried out on the ternary systems; ammonium alkanoate + water + n-octanol, cetyltrimethylammonium bromide + water + n-hexanol, with special reference to their flow and surface properties. Regarding the former system, the phase equilibria and the rheological properties of the different phase regions have already been reported in comparison with the viscosity behaviour of the thermotropic mesophases formed by the same substance, ammonium laurate.[18] Regarding the latter system, cetyltrimethylammonium bromide + water + hexanol, studies on its phase equilibria and some physicochemical properties have been carried out by Lawrence,[19] and Ekwall and his collaborators.[20] In the present author's laboratory a study on the same system has been recently carried out with a special reference to the phase diagram and flow and surface properties of the various regions in

the phase diagram, the result of which will be presented here.

Figure 3 illustrates the phase diagram for this system at a temperature of 25°C. In this diagram the notation is: L₁, aqueous micellar solution; L₂, inverse micellar solution or microemulsion; 2L, two liquid phases or emulsion; LC, liquid crystalline phase; L + LC, liquid crystal in equilibrium with solution; LC + S, liquid crystal in equilibrium with crystal; and a, b, c, etc., local positions of the samples prepared for examination. With these samples of
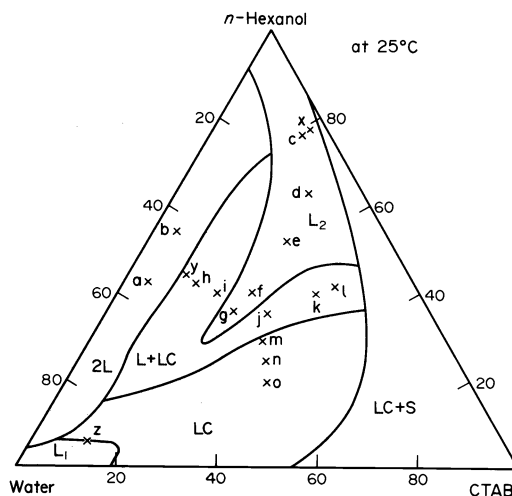

Fig. 3. Phase diagram of system: cetyltrimethylammonium bromide + water + n-hexanol at 25°C.

various phase regions having various chemical compositions, the flow properties were measured by a Couette type autoviscometer working in the ranges of shear rate: 10–700 sec⁻¹ and shear stress: 50–10,000 dyn cm⁻¹. With other corresponding samples the surface or interface tensions were measured by the Wilhelmy-type hanging plate method. All measurements were carried out at 25°C. The formation of the liquid crystal was detected by observing the samples at the crossed polaroids and their structure was examined by observing their polarization microscopic pictures and low-angle X-ray diffraction patterns. The results are summarised in Table 1.

The region L₁ is not broad in this system owing to the small solubility of the surfactant in water, its critical micelle concentration being determined as 7.10^{-4} mol · l⁻¹ at 25°C. The region L₂ is visually homogeneous but ultramicroscopically heterogeneous and may properly be called "microemulsion". The flow type of the samples of this region is nearly Newtonian as shown in Fig. 4. However their viscosities increase with the content of the soluilized water. The surface tension of the samples of this region was measured to be about 24.5 dyn · cm⁻¹ independent of their chemical compositions, and this value is almost identical with the surface tension of hexanol. This suggests that no adsorption takes place at the surface of such microemulsions.

The flow type of the region 2L(emulsion) is slightly plastic as shown in Fig. 5. The apparent viscosities of the emulsions increase with the content of the surfactant. The interfacial tension between the two liquid phases decreases rapidly with the increase of the surfactant content and becomes negligibly small when the emulsion becomes very stable. Figure 6 illustrates such an emulsion.

Table 1. Flow properties of samples from various regions of the phase diagram of ternary
system: cetyltrimethylammonium bromide + water + n-hexanol

| Sample	Composition CTAB/hexanol (%)	Phase-type	Flow-type	Viscosity (P) /Shear rate (sec⁻¹)
a	5/43	2L (emulsion)	slightly plastic	0.6–1.0/600
b	5/55			
c	19/76	L₂ (microemulsion)	Newtonian	0.4–1.0/600
d	27/63			
e	28/52			
f	27/40			
g	25/37			
h	15/42	upper L	Newtonian	
i	20/40	L+LC		
j	33/34	lower LC	plastic	1.0–13/600
k	37/38			
l	40/40			
m	35/30	LC (lamellar)	plastic	3–10/600
n	38/24			
x	20/78	L₂/LC + S	plastic and thixotropic	0.4/600
y	10/45	2L/L + LC	plastic and viscoelastic	25/600
z	10.7/2.2	LC (hexagonal)	plastic and thixotropic	1.5/600
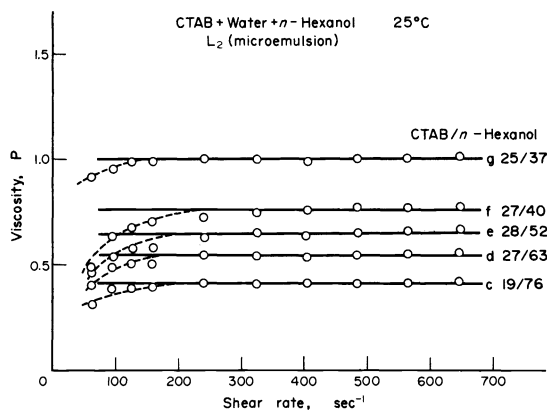
Fig. 4. Viscosity vs shear rate relation for L₂(microemulsion) region.
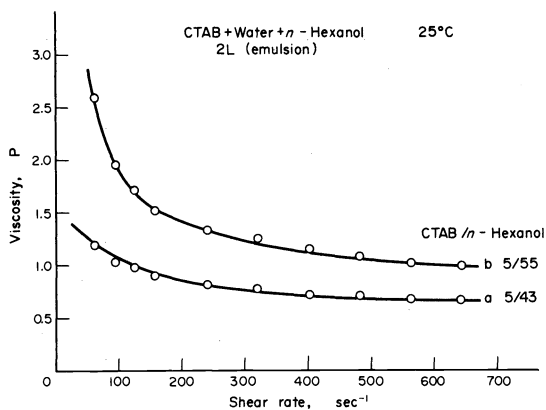
Fig. 5. Viscosity vs shear rate relation for 2L(emulsion) region.

In the region of L + LC there appears to be a distinct surface line between the upper clear solution and the lower liquid crystalline phase at equilibrium, but its interfacial tension is difficult to determine, because the interface line is too labile. The flow type of the LC-phases separated from the upper solutions are remarkably plastic with significant values of yield stress and apparent viscosity, while the flow of the upper solutions are almost Newtonian, as seen in Fig. 7.

The flow type of the LC-phase region which is apparently homogeneous, is also plastic with large values of yield stresses and apparent viscosities, whether its structure is lamellar or hexagonal. Figures 8 and 9 show the flow curves of the samples of this region, m, n (lamellar) and z (hexagonal), respectively. Figures 10 and 11 illustrate the corresponding microscopic pictures. It is difficult to obtain reproducible results when determining the surface tension of the LC-phase against ordinary air. The limiting surface line changes gradually with the time of observation, so that it is difficult to get a real equilibrium value of its surface tension. This is a problem to be examined in future.

From the rheological point of view there are still more interesting findings; for example; the sample x whose position is near the dividing line of L₂ and LS + S clearly behaves thixotropically as shown in Fig. 12; the sample y, which is located near the dividing line of 2L and L + LS, exhibits high viscoelasticity, whose viscosity is as great as 25P under the shear rate of 600 sec⁻¹. This sample demonstrates the Weissenberg effect.[21] Figure 13 illustrates its flow curve.

RELATIONSHIPS BETWEEN MESOPHASES AND COLLOIDAL SYSTEMS

The rheological properties observed in the above ternary system involving the lyotropic mesophase are often demonstrated also in some colloidal systems. The
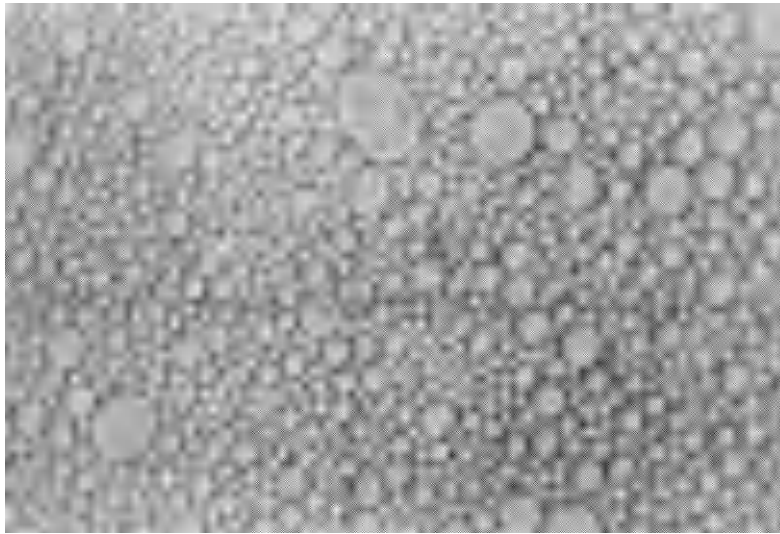
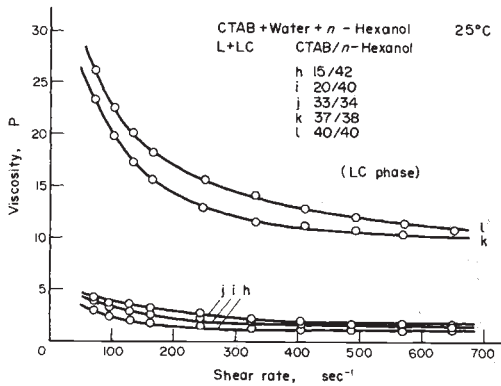Fig. 6. Microscopic photograph of emulsion.

Fig. 7. Viscosity vs shear rate relation for L + LC region: L(upper phase), LC(lower phase).
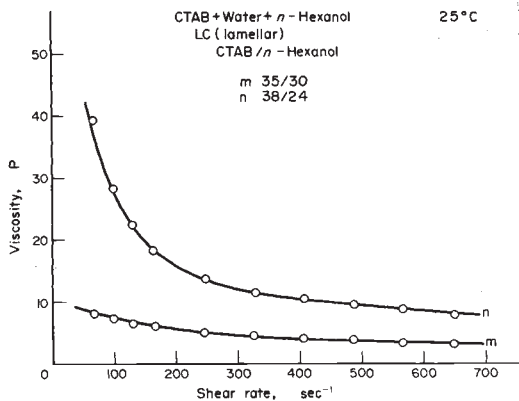

Fig. 8. Viscosity vs shear rate relation for LC(lamellar) region.

Fig. 9. Viscosity vs shear rate relation for LC(hexagonal) region.

anomalous behaviour which is characterized by the dependence of viscosity on the shear stress or shear rate is shown in a colloidal solution such as an aged vanadium pentoxide sol or gelatin sol. The plastic flow which is characterized by the existence of Bingham yield stress in the shear rate vs shear stress relation, is exhibited by a colloidal suspension such as a bentonite suspension. The thixotropic behaviour was originally found in colloidal solutions such as concentrated iron oxide or other metal oxide sols, and the viscoelasticity or Weissenberg effect is demonstrated by colloidal systems such as rubber or polystyrene in organic solvents.[22]

A common factor in the wide variety of colloidal systems showing the above mentioned anomalous flow properties is the anisodimensionality or anisometry of the shape of their colloidal particles, i.e. they have either rod, fibril or plate-like forms. Considering that the lyotropic mesophases are also formed by anisometric, amphiphilic molecules, it would be reasonable to suppose that there may be some analogous mechanism in colloidal and mesomorphic systems which exhibit similar flow properties.

The colloidal systems characterized by such anomalous flow properties as mentioned above are systems in which anisodimensional colloidal particles are dispersed irregularly in any solvent media, although there may be greater or smaller interaction among them. However, when they are put under shear stress, the anisodimensional particles will be oriented parallel to each other in the direction of the shear stress and the viscosity of the system will be smaller. On the other hand, in the mesomorphic systems,
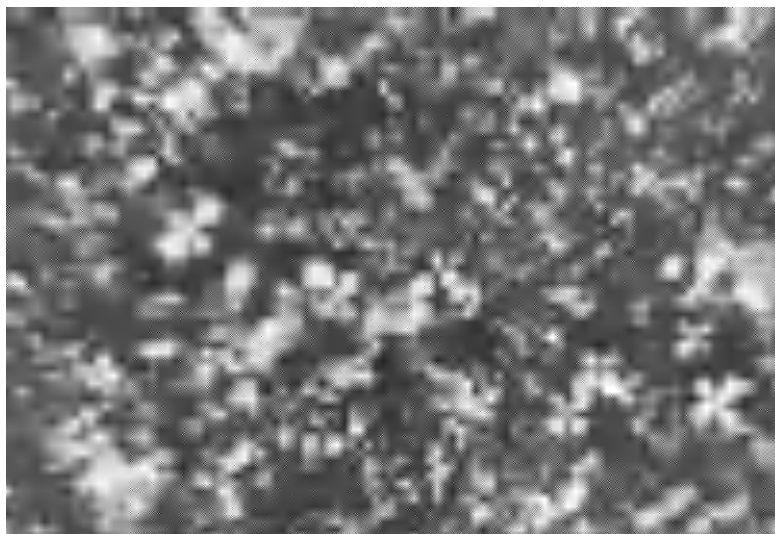
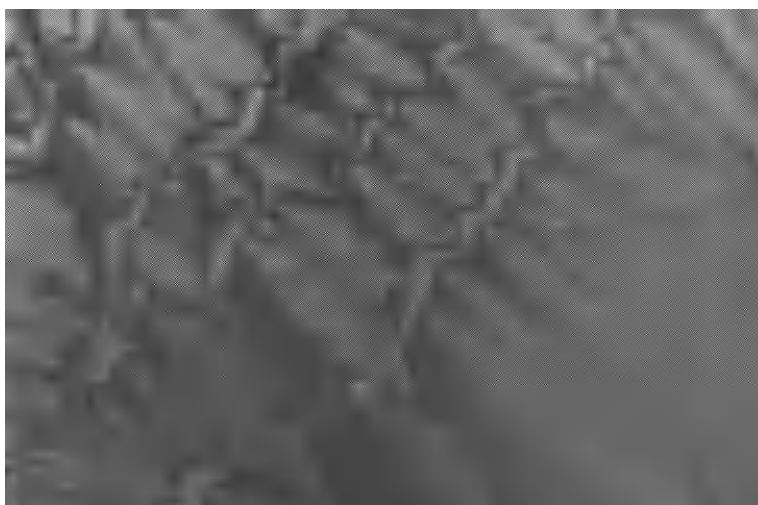Fig. 10. Polarization microscopic photograph of lamellar phase.

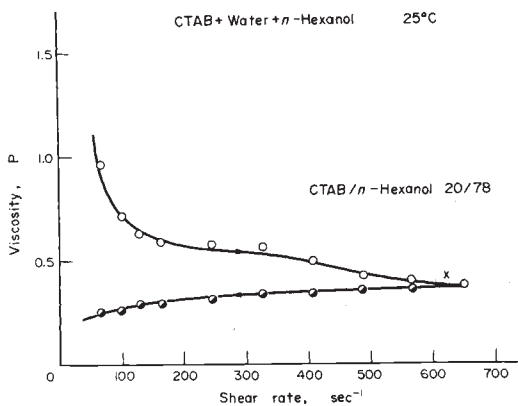Fig. 11. Polarization microscopic photograph of hexagonal phase.

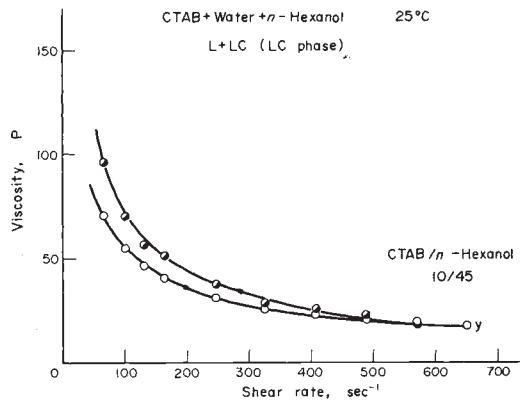Fig. 12. Viscosity vs shear rate relation for thixiotropic region(x).   Fig. 13. Viscosity vs shear rate relation for viscoelastic region(y).

anisometric molecules are oriented in regular patterns involving the solvent. But, when they are put under shear stress, their structures will be deformed or partially disrupted into smaller molecular aggregates or swarms which will be reoriented in the direction of the shear stress as in the case of the colloidal particles. Therefore, the high viscosity of the system will also fall. By such a mechanism the similarities in flow properties of both systems can be understood.

Ostwald considered the mesomorphic system to be a type of disperse system in its wider sense. According to him, the mesomorphic system is a "well-ordered disperse system". It is to be noticed here that in the recent Faraday Discussions of The Chemical Society on Gels and Gelling Processes, Flory[23] counted "well-ordered lamellar structure, including gel mesophase" as one of the four types in his structural classification of gels. Gel is a colloidal disperse system having a certain value of the modulus of elasticity. Lyotropic mesophases are generally characterized by plasticity, but their deformation at lower stresses is held to be recoverable, and hence they are also more or less elastic.

So far as the lyotropic mesophases are concerned, it seems reasonable to assume the intimate relationships between mesophases and colloidal systems as Ostwald pointed out. It is however questionable if such analogies are also applicable to the thermotropic mesophases, because there seems to remain still a doubt about the existence of the molecular aggregrates or swarms of colloidal dimensions in those systems. There is moreover a question to be asked. In the process of establishing the phase diagrams for two or three component systems involving mesophases, it is considered that the liquid crystalline phase represents a homogeneous single phase in the meaning of the Gibbs' phase rule. The liquid crystalline phase is considered, on the other hand, to be heterogeneous disperse system. Are these two considerations not contradictory? Is it really meaningless to ask whether mesomorphic or colloidal systems are homogeneous or heterogeneous? The same question arises for microemulsions or micellar solutions, which are considered, on the one hand, single homogeneous phases but, on the other, they are considered disperse systems. Shinoda and Frigerg[24] have treated the problem of microemulsions from both points of view.

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