Supermolecular liquid-crystalline structures in solutions of amphiphilic molecules

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This paper reviews the physical properties of liquid-crystalline phases arising in solutions containing molecules of amphiphilic substances. The basic characteristics of micelle formation in dilute solutions, models of sphere—disk or sphere—cylinder structural transformations, as well as phase transitions related to the appearance of lyotropic mesophases in the system, including nematic, lamellar, hexagonal, and others, are examined. The results of experimental and theoretical investigation of "solvation" forces acting between micelles in the solvent, as well as recently studied models of swelling of lamellar phases are presented. The phenomena occurring near the inversion point of microemulsions in amphiphile—oil—water systems are examined briefly. The role of liquid-crystalline ordering in some biological systems is discussed.

CONTENTS

1. INTRODUCTION

Lyotropic liquid crystals (LLC) or, in other words, lyotropic mesophases, arise in solutions containing asymmetrical molecules of amphiphilic (AP) substances,[1] which, due to their structural characteristics, have a tendency to combine into aggregates called micelles, containing several tens and more molecules. As the concentration of the substance increases, the number of micelles in the solution increases and thermodynamically stable mesophases, namely, nematic, hexagonal, lamellar (smectic), cubic, and possibly others, can form.

In spite of the fact that the existence of a liquid-crystalline phase in an aqueous solution of ammonium oleate was established by O. Leman about 100 years ago, significant progress in the study of LLC has been achieved only in the last twenty years. During this period, phase diagrams of solutions of different amphiphiles were studied and the basic physical properties of lyotropic mesophases were established.[1-3] Interest in these investigations was due primarily to their close relation to the general biological problem of the self-assembly of supermolecular structures of living cells: cell membranes, chloroplasts, myelin sheath of neurons, gray matter of the brain, and other structures are in an essentially liquid-crystalline state[4] and, in addition, they include a considerable amount of AP substances—lipids and phospholipids. In addition, the totality of interactions determining the collective behavior of AP molecules in solutions plays an important role in the formation of the structure of high-molecular compounds making up living organisms: proteins, nucleic acids, polysaccharides, etc.

A number of physical phenomena occurring in lyotropic systems, such as structural transformations of micelles, alternation of mesophases, and others, turn out to be related to the change in the number of water molecules bound to the polar heads of the amphiphile. In ad-

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[1] Another name—surface-active substance—reflects the tendency of amphiphiles to concentrate on the surface of an interface between phases.

dition, the more concentrated systems correspond to a smaller amount of water per polar head. This characteristic is observed in the analysis of experimental data obtained while studying both LLC[1-3] themselves and dilute micellar solutions[5] in systems of AP molecules. We note that analogous phenomena usually do not arise in thermotropic liquid crystals and, correspondingly, are not discussed in reviews concerned with thermotropic mesomorphism.[6-8]
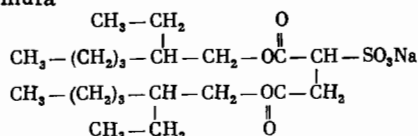
This review is not concerned with an exposition of all original papers concerned with the problem under study, whose number is increasing rapidly. A more complete list of references on the problems considered here can be found in Refs. 1-5.

## 2. STRUCTURE OF BASIC LYOTROPIC MESOPHASES

a) Lyotropic mesogens: amphiphilic substances and block copolymers

The specific physicochemical properties of LLC are due to the asymmetric structure of the constituent AP molecules: these are usually quite long (20–30 Å) molecules, which have distinct hydrophilic, i.e., having a strong affinity to water, and oleophilic, i.e., having a strong affinity to oil, parts. We shall present several examples.

Detergents—salts of fatty acids—contain a flexible paraffin chain C_nH_{2n+1} ("fatty tail") connected to a polar group ("head") (Fig. 1a). The number of atoms in the paraffin chain $n \sim 6-20$ and, in addition, there can be several chains. The head consists of a group of atoms connected by polar bonds—COOK, $-NH_3Cl$, $-OSO_3$ Na, etc., which can dissociate completely or partially in a polar solvent. Molecules of this type include, in particular, the following: sodium dodecyl sulfate $C_{12}H_{25}-OSO_3$ Na (SDS), which is widely used in experimental investigations of LLC; common soap which is a mixture of sodium salts of stearic and palmitic acids; and, aerosol OT (AOT), which has the following structural formula

$$CH_3-CH_2 \qquad\qquad O$$
$$CH_3-(CH_2)_3-CH-CH_2-OC-CH-SO_3Na$$
$$CH_3-(CH_2)_3-CH-CH_2-OC-CH_2$$
$$CH_3-CH_2 \qquad\qquad O$$

In biology, the lipids and phospholipids, which are biological detergents and also have amphiphilic properties, play an important role. The former includes, for example, cholesterol and the latter includes lecithins

$$O$$
$$CH_2-O-C-R_m$$
$$R_n-C-O-CH \quad O^-\qquad\qquad CH_3$$
$$CH_2-P-O-CH_2-(CH_2)_2-N^+-CH_3,$$
$$O\qquad\qquad\qquad CH_3$$
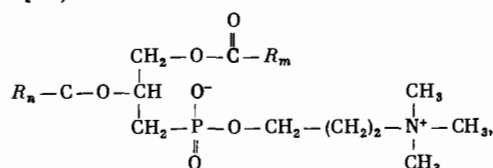
where R_n and R_m are paraffin chains.

Molecules of alcohols have an amphiphilic nature but they do not form lyotropic mesophases by themselves, although they can greatly alter the composition of an existing LLC. These compounds belong to the group of so-called "cosurfactants."

FIG. 1. Schematic illustration of lyotropic (a) and thermotropic (b) mesogens.

For comparison, Fig. 1b illustrates schematically the structure of a molecule of a thermotropic mesogen, whose characteristic features are the presence of a rigid section (shaded rectangle in Fig. 1b), which is responsible for the elastic behavior of the liquid crystal, and comparatively flexible "tails."

In contrast to thermotropic mesogens, molecules of AP substances forming LLC, as a rule, do not contain rigid structural parts. The appearance of elastic properties in solutions of amphiphiles is related to the specific capability of the latter to combine into micelles—aggregates, which, for a fixed composition, temperature, and pressure of the solution, have a definite shape and size corresponding to the minimum of the thermodynamic potential of the system. In addition, it is precisely the high conformational flexibility of hydrocarbon tails, which permits the latter to pack easily into micelles with different geometrical shapes (spheres, cylinders, layers), that is the necessary condition for the observed variety of lyotropic mesophases in systems of AP molecules.[9,10]

Some of the types of aggregates forming in solvents with different polarity are illustrated in Fig. 2. In all cases, the heads of the AP molecules are surrounded by the polar solvent (usually water), while the tails are located in the fatty (hydrophobic) environment. The "golden" rule of chemistry is thereby satisfied: "like dissolves in like."

By examining the change in the free energy of the solution due to the addition of a single AP molecule to the solvent, we can estimate independently the contributions from the lipophilic and hydrophilic parts: $\Delta F = \Delta F_{LP} + \Delta F_{HP}$. Such a separation makes sense for sufficiently long molecules and, on the whole, corresponds

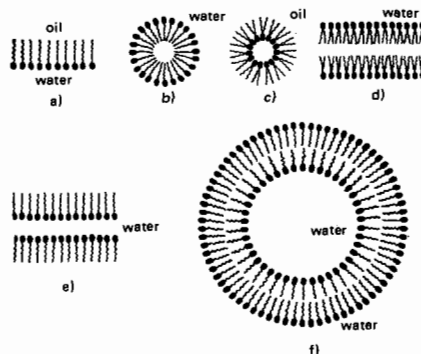FIG. 2. a) Gibbsian monolayer on the interface between fatty and polar media; b) spherical micelle formed by amphiphilic molecules in a polar solvent; c) inverted spherical micelle in a fatty medium; d) lamella (bilayer) in a polar medium (cell membranes have a similar structure); e) inverted lamella (soap film); f) bubble-vesicle formed by amphiphilic molecules in a polar medium.

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to the actual experimental situation, in particular, for substances similar to AOT or SDS. Due to its large dipole moment or charge (if the head is ionized), the polar group of the amphiphile attracts molecules of the solvent, forming together with them several hydrogen bonds and, in the process, the free energy of the system decreases in polar media: $\Delta F_{HP} < 0$. On the other hand, the change in free energy contributed by the fatty tail in a polar solvent (so-called hydrophobic interaction energy) turns out to be positive due to the large decrease in the entropy of the liquid near the dissolved molecules. In fatty media, the energy of solvation of the molecule is low and the decrease in the entropy of the solvent makes dissolution disadvantageous. The ratio between the absolute values of ΔF_{HP} and ΔF_{LP} characterizes the so-called hydrophilic-lipophilic balance of the amphiphile (Sec. 6c).

Thus, when a molecule of the amphiphile is located on the boundary of the fatty and polar media, as illustrated in Fig. 2, its energy is lower than in the polar medium by the magnitude of the energy of the hydrophobic interaction and is less than in the fatty medium by the magnitude of the energy of solvation of the polar head.

Liquid crystalline phases can also arise in solutions containing some polymers. The simplest examples of this kind are, apparently, solutions of polypeptides,[11] for example, poly-γ-benzyl-L-glutamate (PBG), which can exist in some solvents in the form of α helices, stabilized by hydrogen bonds. Under certain conditions, these helices may be viewed as being rigid.

A more complicated mesomorphic behavior is observed in solutions of so-called block copolymers. This term refers to chain-like molecules constructed from various types of monomers A, B, C, and so on, which are joined into chains in the form of large blocks, for example,

$$\ldots \underbrace{A \ldots A}_{n_A} \underbrace{B \ldots B}_{n_B} \underbrace{C \ldots C}_{n_C} \ldots$$
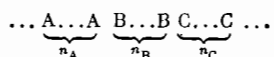
Polymers constructed from different monomers $(A)_{n_A}$, $(B)_{n_B}$, and so on, in most cases, do not intermix,[12] inasmuch as the gain in entropy obtained with the mutual penetration of two macromolecules is insufficient to compensate for the loss in the interaction energy of the monomers arising in this case. In the case of block copolymers, complete separation of segments of the chain is prevented by covalent bonds between the monomer blocks, on the strength of which the solution does not separate into macroscopic phases. However, the tendency for spatial separation of different sections of the polymer molecule, as in the case of AP substances, leads to the appearance of microheterogeneity in the solution.

In this paper, LLC in solutions of polymers are not examined in detail. A review of their properties can be found in Refs. 11 and 13.

b) Review of the properties of lyotropic liquid crystals

The structural unit of LLC are micelles, which are aggregates of AP molecules whose shape and size are determined by the physical properties of the corresponding lyotropic mesophases.

Most experimental data obtained in investigations of LLC (x-ray diffraction, NMR and EPR spectroscopy, optical and magnetic measurements, viscoelastic properties, and others[1-3]) of different composition, as well as dilute micellar solutions (data from NMR, elastic and quasi-elastic light scattering, low-angle neutron scattering, fluorescence, and viscosity[5]) can be matched assuming that the following basic types of micelles appear in the solutions: spherical (normal and inverted), cylindrical (normal and inverted), and disk-shaped (see Fig. 2). The shape, dimensions, and concentration of micelles can vary depending on the composition and temperature of the solution; in this case, the physicochemical properties of the system also change considerably. The following macroscopic phases, which are intermediate between the pure solvent and the pure AP substance, are distinguished experimentally.

1) Isotropic micellar solutions. When the concentration of AP substance exceeds some critical value c^*, called the critical concentration for micelle formation (CMC), at sufficiently high temperatures $T > T_{Kr}$ (T_{Kr} is the so-called Krafft temperature[5]), micelles, which are thermodynamically stable aggregates usually containing several tens of AP molecules each, are formed in the solution. For a small excess of the solution concentration above c^*, the shape and the aggregation number of the micelles remain practically unchanged and their concentration increases approximately proportionately to $c - c^*$. A dilute micellar solution with $c \gtrsim c^*$ is not, strictly speaking, a separate phase, differing from the true molecular solution existing with $c < c^*$, and it is not separated from the latter by some special line on the phase diagram. However, micelle formation is accompanied by a considerably change in the structure of the short-range order of the solution: a predominant mutual orientation of AP molecules, analogous to their orientation in LC phases, appears within a single aggregate (see Fig. 2). From a general point of view, micelle formation in solution represents a pretransitional phenomenon, analogous, for example, to the appearance of cybotactic clusters in nematics near the point at which the smectic modification of a thermotropic LC appears.[14,15] As more AP molecules are added, two different cases are encountered:

A) At some concentration $c = c^{**}$ (so-called second critical concentration for micelle formation), the structure of the micelles can change, for example, a sphere-disk or sphere-cylinder transition can occur. The change in the structure of the aggregates can also be caused by a change in temperature or (and) composition of the solution.

B) The solution can separate into two phases containing a different amount of AP substance[16] and, in this case, there exists a critical stratification point near which critical scattering of light by the solution is observed.[17] The phase containing a large amount of amphiphile, depending on the shape and concentration of the micelles, can be both isotropic and anisotropic (liquid-crystalline). The shape and size of the aggre-

gates usually change with the formation of the LC phase. For example, the isotropic-solution–hexagonal-phase phase transition occurs due to the increase in the length of cylindrical micelles (Figs. 3 and 4).[2]

2) Hexagonal phases are formed by cylindrical micelles (CM) of indefinite length, packed into a two-dimensional lattice with hexagonal symmetry (Fig. 5). The structure of the micelles can be normal or inverted depending on the type of AP substance and on the solvent. Thus SDS molecules in a polar solvent usually form normal micelles (Fig. 4), while aerosol OT molecules, which contain two fatty tails, form inverted aggregates (see Fig. 3). The diameter of normal CM is approximately 10–30% shorter than the length of the completely extended molecule of the amphiphile, and the distance between the cylinders varies in the range 8–50 Å depending on the water content. For inverted micelles, the diameter of the water cylinder is 10–20 Å and the distance between them is about one-and-a-half times the length of the fatty tails of the AP molecules.[1-3]

3) Lamellar (smectic) phases are formed by disk-shaped micelles (DM) with an indefinite diameter (lamellae). The thickness of the lamellae is approximately 10–30% smaller than twice the length of the amphiphile (Fig. 6), and the size of the water gap varies from several angstroms to several tens of angstroms, depending on the water content in the system. If a given substance forms hexagonal phases with both the normal and inverted micelles, then the position of the lamellar phase on the phase diagram, as a rule, corresponds to AP concentrations that are intermediate between the hexagonal phases. However, exceptions to this rule are possible (Fig. 7). As the temperature increases, the lamellar phase goes over into an isotropic micellar solution, as illustrated in Figs. 3, 4, and 7, and sometimes into another liquid-crystalline phase (see Fig. 7a).

Depending on the temperature and composition of the solution, the AP molecules in the lamellae can be in the "melted" or "crystalline" states (see Fig. 6). Models of structures in which molecules with both liquid and solid hydrophobic tails are present in a single lamella have also been proposed.[1,22,23] However, it is noted in Ref. 3 that the x-ray diffraction data, on the basis of which this conclusion was reached, can also be brought into agreement with the assumption of the existence of a mixture of two phases in the system, as illustrated in Figs. 6a and b, whose separation is impeded by the high viscosity of the solution.
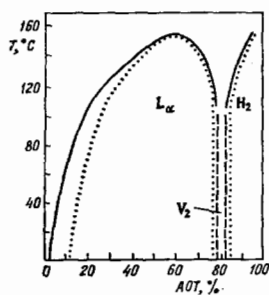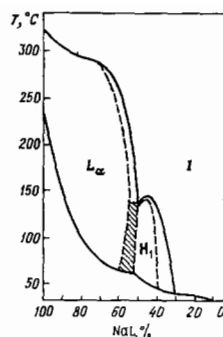

FIG. 4. Phase diagram of sodium laurate and water.

Lamellar phases arising on solidification of paraffin chains accompanying a decrease in temperature have been given the name "gels." The thickness of the lamellae in these phases can equal one[24] or two[25] lengths of a completely extended AP molecule. The molecules are packed into a two-dimensional hexagonal lattice, and the area per molecule in the bilayer is close to the minimum possible value, 20 Å^2. The long axes of the molecules can be tilted relative to the normal to the AP layer.[25] The water gap is 10–20 Å wide, but it can increase to ~200 Å with the addition of a small amount of ionic amphiphile (such as soap).[26,27]

Thus, according to the classification adopted for thermotropic LC, gels correspond to B_A and B_C smectic phases.[6]

4) Cubic phases can arise in the case of solution concentrations between the hexagonal phase and the isotropic micellar solution (Fig. 8) or between the lamellar and hexagonal phases (see Figs. 3, 4, 7a, and 8). These phases are essentially not liquid-crystalline, but belong to the class of so-called plastic crystals, since they exhibit a three-dimensional periodicity. Due to the high viscosity ($\eta \sim 10^2$ poise) and the isotropy of the optical and magnetic properties, the cubic phases are also called viscous isotropic phases. Their structure has not been uniquely established. For phases situated between the hexagonal phase and the micellar solution, it has been proposed that the most likely structure is one in which spherical micelles are packed into a cubic lattice (Fig. 9a), while for a phase in a range of concentrations intermediate between the lamellar and hexagonal modifications, it is possible to have a structure formed by a system of comparatively short rod-shaped micelles connected into two interpenetrating networks[29] (Fig. 9b). For this range of concentrations, another structure has also been proposed in the form of a con-

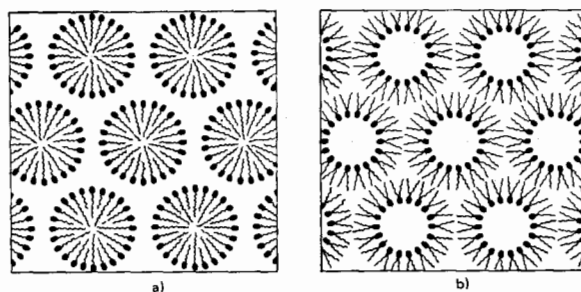FIG. 3. Phase diagram of the binary solution AOT/ H$_2$O. [18]

FIG. 5. Schematic diagram of the packing of normal (a) and inverted (b) micelles in the hexagonal phase.

[2] The notation is explained in Table I.

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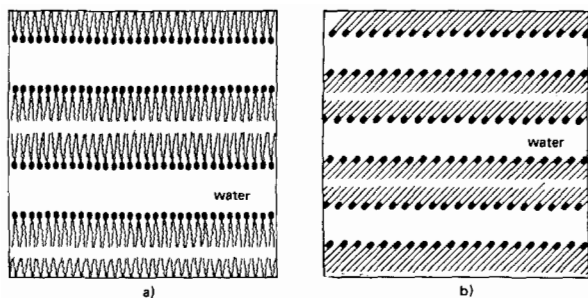
FIG. 6. Structure of L_α (a) and $L_{\beta'}$ (b) lamellar phases.

FIG. 8. Phase diagram of a solution of dodecylammonium chloride in water.[28]

tinuous periodic surface, separating the entire space into two interpenetrating regions: polar and fatty.[30]

The mesophases examined, i.e., hexagonal, lamellar, and cubic, belong to "classical" LLC, often arising in binary systems. However, as a rule, a specific AP substance forms only some mesophases of those enumerated above. In multicomponent systems, containing, in addition to the amphiphile, cosurfactants and inorganic salts as well, all the indicated phases can be observed. A large number of phase diagrams of solutions of AP substances, including multicomponent systems, has been compiled by Ekwall.[1]

5) So far, it has been possible to obtain nematic and cholesteric mesophases only in some multicomponent systems, containing, in addition to the AP (sodium decyl sulfate NaC_{10},[31] potassium laurate KL,[32] and others) and water, a certain cosurfactant and (or) some amount of inorganic salt as well; in addition, these phases are stable over a quite narrow range of temperatures and concentrations of components.[33,34] The existence of three types of nematics has now been established experimentally: uniaxial, consisting of disk-shaped micelles N_D[31,32] and cylindrical micelles N_C,[34-36] and biaxial.[37] There are no experimental data on the shape of the micelles in the latter case.

One of the basic properties of nematics is their ability to align in a magnetic field. The time of the corresponding transient process in a field of the order of 10^4 G varies in the range from $1-10^4$ s depending on the water content of the specimen. The size of the micelles can be determined from an analysis of x-ray diffraction and NMR data. For the system sodium decyl sulfate (decanol) Na_2SO_4, the CM are 600–800 Å long and have a diameter of about 40 Å, while the diameter of the DM constitutes 500–1000 Å. The distance between the cylin-
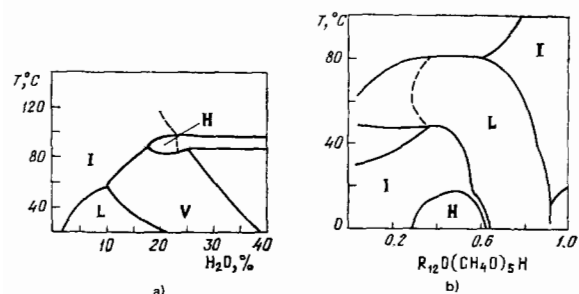
ders varies in the range 100–200 Å and the distance between disks varies in the range 100–500 Å.[38]

Nematics of the type N_C have negative dielectric and positive diamagnetic anisotropy: $\varepsilon_a < 0$ and $\chi_a > 0$. On the other hand, for N_D, $\varepsilon_a > 0$ and $\chi_a < 0$.[35] In absolute magnitude, ε_a and χ_a are much smaller than in the case of thermotropic LC. Thus the magnitude of the anisotropy of the index of refraction of a lyotropic nematic (LN) is of the order of $n_a \sim 10^{-3}$, while for thermotropic systems, characteristically, $n_a \sim 10^{-1}$.[33] Frank's moduli for LN are, apparently, also smaller than for thermotropic LC.

The cholesteric modifications of LLC can be obtained either by adding chiral molecules to a nematic[39] or in a nonracemic mixture of levo- and dextrorotary AP substances.[40] Chiral phases in solutions of DM and CM and phase transformations of the type $N_C^* \rightleftharpoons N_D^*$ have been investigated.[34,36,40,41]

6) Different investigators have indicated the possibility of the appearance of more complicated mesophases, not mentioned in Secs. 1–5, in some comparatively rare cases. These include, in particular, complicated cubic phases consisting of bilayer bubbles (vesicles) of the type illustrated in Fig. 2f, complicated hexagonal phases consisting of bilayer CM, tetragonal phases containing CM with a rectangular or elliptical cross section, and others.[1] However, as noted in Ref. 3, the experimental data (primarily x-ray diffraction data), on the basis of which the structures mentioned have been proposed, in a number of cases, have not been confirmed by more careful investigations and, in other cases, admit an ambiguous interpretation. For this reason, further experimental investigations are re-

FIG. 7. Phase diagrams of monoolein/water (Ref. 20) (a) and $CH_3—(CH_2)_{11}(C_2H_2O)_5H/H_2O$ (Ref. 21 (b) systems.
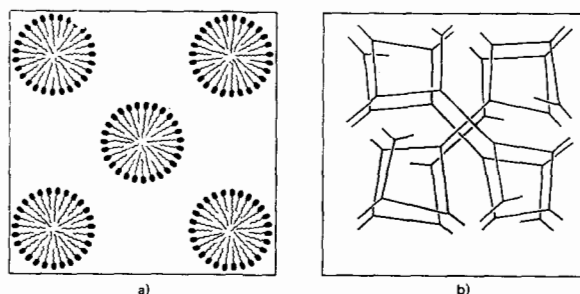

FIG. 9. Schematic diagram of the packing of spherical micelles in the phase of the cubic I_1 type (a) and a model of the structure of the V_1 phase (b).

quired in order to confirm the thermodynamic stability of complex mesophases.

c) Notation

Different systems of symbols are used in the literature to denote lyotropic mesophases.[1,3,42,43] In this paper, we shall follow the notation used by a French group[42]; some additions are introduced in Ref. 3. In this notation, the lamellar phases are denoted by the symbol L (lamellar, neat) with the lower subscript α if the hydrocarbon chains within the micelles are liquid (L_α), ρ is the chains are solid but normal to the plane of the lamellae (L_ρ), β^1 if rigid molecules are tilted with respect to the surface of the bilayer, and γ if part of the molecules are in the liquid state and the remaining molecules are in the solid state ($L_\gamma \equiv L_{\alpha\beta}$). The hexagonal phases are denoted by H_1 and H_2 (hexagonal, middle), where the subscript 1 indicates that the micelles forming the LLC are normal and the subscript 2 indicates that the micelles are inverted. The cubic phases are labeled by the symbols I_1 and I_2 (isotropic) for spherical micelles and V_1 and V_2 (viscous) for cylindrical micelles. We shall denote the nematic phases by N_C and N_D for CM and DM, respectively, and by N_{bx} for the biaxial phase. In what follows, just as in Ref. 6, an asterisk is used to denote mesophases that do not coincide with their mirror image (chiral LLC), for example, N_C^*, N_D^*, and so on. Finally, we shall denote micellar solutions by I_S, I_D, or I_C depending on the form of the micelles arising: spherical, disk-shaped, and cylindrical, respectively. All notation is collected in Table I, where, for convenience, the notation used in Refs. 1, 42, and 43 is also presented.

3. ISOTROPIC MICELLAR SOLUTIONS

a) Thermodynamics of micelle formation

Micelles arise in solutions of AP molecules when the concentration of the latter exceeds a certain critical value c^* (CMC). Experimentally, a break is observed at $c = c^*$ in the concentration dependence of the coefficients of surface tension, osmotic pressure, viscosity, electrical conductivity, light scattering, and others.[5] The change in some of the physical properties of the

solution, related to the onset of the formation of micelles, is shown schematically in Fig. 10. The quantity c^* greatly depends on the temperature of the solution and the presence of salts, alcohols, etc. For each type of molecule, there exists a critical temperature, below which micelles do not form: the Krafft temperature.[5] The CMC decreases with increasing length of the fatty tail in a homologous series of substances and, in addition, for a small number of carbon atoms in the chain, $n \sim 10-15$, this dependence is linear, while for large values of n and in the presence of several hydrocarbon chains, there can be a deviation from the linear law.[44] For molecules of the type SDS with $n \sim 10$, the CMC is usually several hundredths of a mole per liter at room temperature.

We shall examine a solution containing a collection of aggregates with a different number of molecules N (aggregation number), which can dissociate according to the chemical reaction

$$A_N \rightleftarrows A_{N-1} + A_1. \tag{1}$$

Assuming that the solutions of the monomers A_1 as well as of the micelles A_N are weak, we shall write the condition of thermodynamic equilibrium of the system under study in the form[45]

$$\mu_1^{(0)} + T \ln c_1 = \mu_N^{(0)} + TN^{-1} \ln c_N, \tag{2}$$

from where we find the equilibrium concentration of micelles with aggregation number N:

$$c_N = c_1^N \exp\left(N \frac{\mu_1^{(0)} - \mu_N^{(0)}}{T}\right). \tag{3}$$

The total concentration of AP molecules is given by the expression

$$c_t = c_1 + \sum_{N=2}^{\infty} Nc_1^N \exp\left(N \frac{\mu_1^{(0)} - \mu_N^{(0)}}{T}\right). \tag{4}$$

In (2)-(4), $\mu_N^{(0)}$ indicates the standard chemical potential of the amphiphilic molecules forming the micelle. The dependence of $\mu_N^{(0)}$ on the aggregation number must be found from an analysis of the microscopic structure of the micelle (see Sec. 3c). Two types of dependences of $\mu_N^{(0)}$ on N are, in principle, possible, leading to different behavior of solutions with increasing c_t.[46] In the first case, $\mu_N^{(0)}$ decreases monotonically with increasing aggregation number and reaches a finite limit as $N \to \infty$, i.e.,

$$\mu_N^{(0)} \approx \mu_\infty^{(0)} + \alpha TN^{-p}, \quad \alpha, \ p > 0. \tag{5}$$

TABLE I. Notation for lyotropic mesophases.

| Phases	Ekwall[1]	Luzzati[42]	Winsor[43]	This paper
Isotropic micellar solutions				I_S, I_D, I_C
Nematics				N_C, N_D, N_{bx}
Cholesterics				N_C^*, N_D^* etc.
Lamellar phases:				
Liquid layers	B, D	L_α	G	L_α
Solid layers	D_s	L_β, $L_{\beta'}$		L_β, $L_{\beta'}$
Intermediate case		$L_{\alpha\beta}$, L_γ, P_γ		$L_{\alpha\beta}$, L_γ
Hexagonal phases:				
Normal micelles	E	H_I	M_1	H_1
Inverted micelles	F	H_{II}	M_2	H_2
Bilayer micelles	H_c	H_c	H_c	H_c
Cubic phases:				
Spherical micelles	I_1, I_1', I_2	Q_I, Q_{II}	S_{1c}	I_1
Cylindrical micelles	I_1', I_2', I_2^*	Q_I, Q_{II}	V_1, V_2	V_1, V_2
"Tetragonal phases":				
Normal micelles	C			C
Inverted micelles	K			K
"Rectangular phase"	R			R
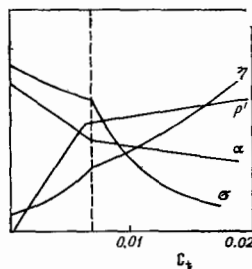
FIG. 10. Variation of the osmotic pressure of the solution (p'), coefficients of viscosity (η), electrical conductivity (σ) and surface tension (α) near the critical micelle concentration for SDS ($c^* \approx 8 \cdot 10^{-3}$ M).

For $p > 1$, the series (4) converges for all values $C_1 < C_0$ and the average aggregation number $\overline{N}$ is a smooth function of c_t, increasing indefinitely when the concentration of AP molecules of the system reaches the value c_0. For $p < 1$, the series (4) diverges, beginning with some critical value of the concentration at which aggregates with $N = \infty$ begin to form spontaneously in the solution. The behavior of the system for the intermediate case $p = 1$ depends strongly on the value of α: for small α, only small micelles arise, while for large α, aggregates with $\overline{N} \sim 2\sqrt{c_t e^\alpha}$ arise.[46]

The second of the possibilities mentioned above is realized if $\mu_N^{(0)}$ reaches a minimum for some finite value $N = M$. In this case, the average aggregation number of micelles arising in the solution is $\overline{N} \approx M$. As a rule, the number M is large and, depending on the composition of the solution, can reach values $M \sim 10^2 - 10^5$.[5] We find the critical concentration for micelle formation, defined as the concentration of the amphiphile for which $C_1 \approx C_m$, from (3):

$$\ln c^* \approx \frac{M}{M-1} \frac{\mu_M^{(0)} - \mu_1^{(0)}}{T} - \frac{\ln M}{M-1} \approx \frac{\mu_M^{(0)} - \mu_1^{(0)}}{T}. \tag{6}$$

The quantity c^* defined in this manner is, in some sense, an arbitrary characteristic of the solution, inasmuch as its thermodynamic functions vary smoothly as a function of c_t near c^*. The micellar solution is not separated by a special line on the phase diagram from the true molecular solution of AP molecules and, for this reason, is not a special phase with respect to it. Nevertheless, it is possible to establish a definite analogy between CMC and the point of the true phase transition.[47] It turns out that the width of the region in which the change in the analytical dependence of the thermodynamic functions of the solution, for example, the osmotic pressure, is of the order of $\Delta c_t \approx c^* M^{-1}$ and decreases to zero is $M \to \infty$. Thus, as the aggregation number increases to infinity, the CMC becomes a singular point of the thermodynamic functions of the solution, just as the critical point in a second-order phase transition.[47]

We shall examine, following Ref. 47, the simplest model of a micellar solution, in which only aggregates of one type containing M AP molecules are present. In this case, instead of (3, 4) we have

$$c_M = c_1^M \exp\left(M \frac{\mu_1^{(0)} - \mu_M^{(0)}}{T}\right), \tag{7}$$

$$c_t = c_1 + M c_1^M \exp\left(M \frac{\mu_1^{(0)} - \mu_M^{(0)}}{T}\right). \tag{8}$$

Let us calculate the osmotic pressure of the solution

$$p_{osm} = T\left[c_t + c_1^M \exp\left(M \frac{\mu_1^{(0)} - \mu_M^{(0)}}{T}\right)\right] \tag{9}$$

as a function of the total concentration of the amphiphile c_t. Using the notation

$$x \equiv f c_1, \quad y \equiv f c_t, \quad p_{osm} \equiv \frac{\tilde{\pi} T}{f}, \quad f \equiv \exp\left(\frac{\mu_1^{(0)} - \mu_M^{(0)}}{T}\right),$$

we shall write relations (8) and (9), which determine in an implicit form the functional dependence $p_{osm}(c_t)$,

$$\tilde{\pi} = x + f x^M, \quad y = x + M f x^M. \tag{10}$$

The function $x = x(y)$, defined by the second of these equations, is a smooth function for real x for any finite M. However, in the complex $x(y)$ plane, it has $M - 1$

singular points. As M increases, the number of poles increases and, in addition, two of them approach the real axis from the side of the upper and lower half-planes, respectively, near the point

$$x \approx x_c = (fM^2)^{-1} (fM^2)^{-1/(M-1)}.$$

At $M = \infty$, the distance between the singularities in the complex plane, decreases arbitrarily. This situation is analogous, in a certain sense, to the distribution of zeros of the partition function of a ferromagnetic material.[48] We introduce instead of x the variable ξ defined as

$$x = x_c \left(1 + \frac{\xi}{M}\right).$$

We expand Eq. (10) in inverse powers of the aggregation number with $x \approx x_c$; retaining only terms linear with respect to M^{-1}, we obtain

$$y(x) \approx y(x_c) + x_c M^{-1} (\xi + e^\xi - 1),$$
$$\tilde{\pi}(y) \approx \tilde{\pi}(x_c) + x_c \xi M^{-1}.$$

From here, we find the slope and curvature of the curve $\pi(y)$:

$$\frac{d\tilde{\pi}}{dy} = \frac{1}{1 + e^\xi}, \quad \frac{d^2\tilde{\pi}}{dy^2} = -\frac{M}{x_c} \frac{e^\xi}{(1 + e^\xi)^3}. \tag{11}$$

It follows from (11) that the characteristic change in the concentration of the amphiphile, at which the slope of the osmotic pressure changes, constitutes $\Delta c_t \approx c^* M^{-1}$ and, in addition, the curvature of the curve $p_{osm}(c_t)$ increases arbitrarily as $M \to \infty$.

We note that analogous results were obtained in Ref. 47 for some more complicated models of micellar solutions, containing micelles with different aggregation numbers.

b) Micelle structure in dilute solutions

If the dimensions of the aggregates are small compared to the wavelength of light, then the intensity of the radiation scattered at an angle θ relative to the direction of propagation of the incident beam is given by the expression[49,50]

$$I(\theta) = I_0 \frac{2\pi^2 \tilde{n}_0^2}{\lambda^4 N_A} \left(\frac{\partial \tilde{n}}{\partial c_t}\right)^2 c_t (1 + \cos^2 \varphi) \left(\frac{1}{M_W} + 2Bc_t\right)^{-1}, \tag{12}$$

where I_0 is the intensity of the incident light, λ is the wavelength of the light, $\tilde{n}_0$ is the index of refraction of the pure solvent, M_W is the molecular weight of the aggregate, N_A is the Avogadro number, B is the second virial coefficient, and c_t is the total concentration of the AP substance. Measurements of the quantities $I(\theta)$ and $\tilde{n} = \tilde{n}(c_t)$ permit determining M_W and the second virial coefficient from Eq. (12). According to (12), the quantity $R(\theta) = I(\theta)(1 + \cos^2\theta)^{-1} I_0^{-1}$ does not depend on the scattering angle θ. Taking into account the finiteness of the particle sizes leads to the appearance of dissymmetry in the scattering, which is usually expressed in the form

$$\frac{Kc_t}{R(\theta)} = \frac{1}{M_W P(\theta)} + 2Bc_t. \tag{13}$$

The form of the function $P(\theta)$ depends on the geometrical shape of the particles in the solution. Thus, for spherical particles of radius R, $P(\theta)$ was calculated by Rayleigh and has the form[50]

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$$P(\theta) = \left[\frac{3}{z^3}(\sin z - z\cos z)\right]^2, \quad z = \frac{4\pi R\tilde{n}_0}{\lambda}\sin\frac{\theta}{2}; \qquad (14)$$

for rod-shaped particles of length L, greatly exceeding the diameter,

$$P(\theta) = \frac{2}{y}\int_0^y \frac{\sin t}{t}\,dt - \left[\frac{\sin(y/2)}{y/2}\right]^2, \quad y = \frac{4\pi L\tilde{n}_0}{\lambda}\sin\frac{\theta}{2}. \qquad (15)$$

Thus the measurement of the dissymmetry of scattering and comparison with Eqs. (14) and (15) permit drawing a conclusion concerning the geometrical dimensions of the aggregates. For small z and y, i.e., for $\lambda \gg R$, L, or for low angles θ, the function $P(\theta)$ can be expanded in a series:

$$P(\theta) = 1 - \frac{1}{3}R_g^2\left(\frac{4\pi\tilde{n}_0}{\lambda}\right)^2\sin^2\frac{\theta}{2}. \qquad (16)$$

The quantity R_g, called the radius of gyration, in this expression is a convenient experimentally observed characteristic of the aggregates. If the particles are spherically shaped, then $R_g^2 = (3/2)R^2$; for a flattened ellipsoid of revolution with semiaxes a and b ($a>b$), $R_g^2 = (2/5)a^2 + (1/5)b^2$; for a rod of length L with diameter D, $R_g^2 = (L^2/12) + (D^2/8)$.

Experimental investigations of the elastic scattering of light established the presence of aggregates of AP molecules in solutions containing, in some cases, several hundreds of particles;[51-54] in addition, values of the radius of gyration obtained in this case agree with the conjectured appearance of rod-shaped micelles, possibly, partially deformed. The size and shape of the aggregates greatly depend on the composition of the solution. Thus the sphere-cylinder transition can be initiated by the addition of an inorganic salt to the solution (Fig. 11). The section of the dependence $M_w = M_w(c_s)$, corresponding to the smaller slope, agrees with spherical micelles with aggregation number $N \sim 10^2$, while the section with large slope corresponds to CM. The longest micelles, obtained in Ref. 54, correspond to the values $\overline{N} = 986$, $L = 597$ Å ($M_w = 284{,}000$, $R_g = 172$ Å).

An independently measured characteristic of the aggregate is its hydrodynamic radius R_h, which is related to the coefficient of diffusion of micelles $\tilde{D}$ by Einstein's relation
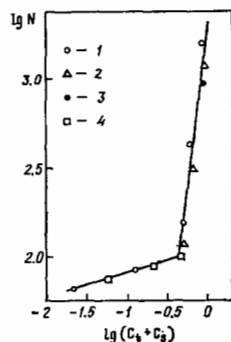
$$R_h = \frac{T}{6\pi\eta\tilde{D}}, \qquad (17)$$

where η is the viscosity and T is the temperature of the solution.

The quantity $\tilde{D}$ can be measured, for example, with the help of quasi-elastic scattering of light.[52,53]

It is demonstrated in Refs. 52 and 53 that in a SDS solution with NaCl concentration $c_s > 0.6$ M, aggregates with $R_h > 100$ Å and aggregation number $N \approx 10^3$ can appear. The angular dependence of the scattered light agrees with the assumption of large cylindrical micelles.

The magnitude of the coefficient of viscosity of a micellar solution η is related with its value η^* corresponding to CMC, by the relation

$$\eta = \eta^*(1 + \nu\varphi), \qquad (18)$$

where φ is the volume fraction of the solution occupied by the micelles, the coefficient of the "characteristic viscosity" ν depends on the shape of the particles:[49] $\nu = 2.5$ for a sphere and $\nu = 16\,J/15 \arctan J$ for a flattened ellipsoid of revolution with semiaxes $a > b$ ($J = a/b$), and

$$\nu = \frac{J^2}{15(\ln 2J - 1.5)} + \frac{J^2}{5(\ln 2J - 0.5)} + \frac{14}{15}$$

for an elongated ellipsoid of revolution with $J > 10$. Figure 12 shows a graph of the dependence $\nu = \nu(N)$ for a solution of dodecylammonium chloride.[56,57] The slope of the curve for aggregation numbers in the range $N = 10^3$–10^4 corresponds to CM (deformed). In Ref. 56, the decrease in slope for $N > 10^4$ was interpreted as a transition of the micelles into a coiled state, analogous, for example, to the helix-coil transition in DNA.[58] It should be noted, however, that the slope of the curve $\nu(N)$ for large N can also be brought into agreement with the assumption of the appearance of disk-shaped micelles in the solution, for which, as also for coils, $\nu \sim \sqrt{N}$. For this reason, the conclusion that coiled states of large micelles appear must be confirmed by investigations of the internal structure of aggregates, for example, with the help of NMR[59] or with the use of fluorescence probes.[5,60]

The change in the conformation of hydrocarbon chains within micelles accompanying the sphere-cylinder transition leads to a sharp change in the NMR spectra (see Sec. 4c), which was observed by Tiddy and Staples[59] for a SDS solution. In Ref. 60, the change in the conformation of fatty tails accompanying the sphere-cylinder transition at the point $c = c^{**}$ led to a change in the fraction of pyrene molecules (fluorescence probe) in the dimerized state within the hydrocarbon nucleus of the micelles.

FIG. 11. Dependence of the aggregation number of micelles in an aqueous solution of SDS on the concentration of NaCl.[54] 1) 25 °C; 2) 30 °C; 3) 35 °C; 4) data in Ref. 55.
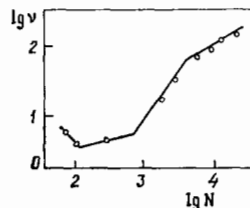

FIG. 12. Dependence of the coefficient of the characteristic viscosity of a solution of dodecyldimethylammonium chloride on the aggregation number of micelles.[57]

Measurements of the fluorescence intensity at frequencies corresponding to the dimerized state also led to the conclusion that CM arise in the solution.

c) Models of the sphere-cylinder structural transition

We shall first discuss the general characteristics of SM-CM and SM-DM transitions and we shall show that, in general, they must occur abruptly.[51] We introduce the quadrupole moment tensor of a micelle

$$Q_{\alpha\beta} = \left\langle \sum_i \left(r_{i\alpha} r_{i\beta} - \frac{1}{3} \delta_{\alpha\beta} r_i^2 \right) \right\rangle, \tag{19}$$

where r_α are the coordinates of the atoms in AP molecules in the micelle, and the brackets indicate averaging over the states of the micelle with a fixed aggregation number N. Assuming that Q is small near the transition point, we expand the chemical potential of the AP molecules in powers of Q

$$\mu_N(Q_{\alpha,\beta}) = \mu_N(0) + \frac{1}{2} a \, Sp \, Q^2 + \frac{1}{3} b \, Sp \, Q^3 + \dots. \tag{20}$$

The coefficient a in this expression vanishes at some critical value $c = c^{**}$ of the amphiphile concentration (or the electrolyte concentration, temperature, etc.) and b may be assumed to be constant. Expression (20) formally coincides with the Landau–de Gennes expansion in the theory of thermotropic nematics[6,62] and, in general, the coefficient b, as in Ref. 6, differs from zero. Indeed, substituting the tensor $Q_{\alpha\beta}$ in the "uniaxial" form

$$Q_{\alpha\beta} = Q \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}_{\alpha\beta}$$

into (20), we obtain

$$\mu_N(Q) = \mu_N(0) + 3aQ^2 - 2bQ^3 + dQ^4 + \dots. \tag{21}$$

Since the case $Q > 0$ corresponds to DM, while the case $Q < 0$ corresponds to the case CM, there is no basis for assuming that $\mu_N(Q) = \mu_N(-Q)$. Therefore, $b \neq 0$ and sphere-cylinder or sphere-disk transitions, in general, occur abruptly[3] and, in addition, Q changes from 0 to the value $Q_c = b/d$. In analogy with thermotropic nematics,[62,64-67] it may be expected that the minimum of expression (20), in some range of parameters of the solution in which the magnitude of the coefficient b is anomalously small, will be achieved with pair-wise different principal values of the tensor $Q_{\alpha\beta}$, i.e., the biaxial form of the micelle may turn out to be more advantageous than the uniaxial form. The transition of uniaxial micelles into biaxial micelles can proceed smoothly.

Biaxial micelles are structural units of tetragonal mesophases C and K,[1,3] and, apparently, of biaxial nematics as well.

The use of the phenomenological expansion (20), just as in the general theory of phase transitions,[68] permits

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[3] A particular case of this assertion is the result of the well-known Rayleigh problem concerning stretching of a charged metallic drop,[63] where the sphere-ellipsoid transition also occurs abruptly. We note that the drop stretches as the charge on it increases, while the micelle stretches as the charge on it decreases (see below).

studying the loss of symmetry by aggregates of AP molecules, as a result of which there arises the possibility of the formation of anisotropic liquid-crystalline phases in solutions. We shall consider in greater detail the interactions between amphiphilic molecules responsible for the structural transformations of micelles.

We shall begin with an analysis of the simplest model of a micelle.[46,49,70] In this model, it is proposed that the hydrocarbon tails within the aggregate are in a "melted" state and the state of AP molecule in a micelle is characterized by a specific volume v_0 and specific area s_0 per polar head. Experimental data[56] show that v_0 varies insignificantly with an increase in the aggregation number from 10^2 to 10^4, so that it may be assumed that $v_0 \approx$ const. The specific area s_0 is determined from the condition that the interaction energy for AP molecules interacting with one another and with the solvent is minimum:

$$\mu_N^{(0)} = \mu_1^{(0)} + \alpha s + \frac{2\pi e^2 r_D}{\varepsilon s} + g, \tag{22}$$

where the first term represents the energy of interaction of water with the hydrocarbon nucleus of the micelle and α is the coefficient of surface tension at the oil-water interface, while the second term is the Coulomb repulsion energy of the heads in a medium with dielectric permittivity ε, approximately equal to the energy stored in the field of a capacitor whose gap-size is of the order of the Debye radius r_D. The quantity g in (22) represents the gain in the free energy of hydrophobic interaction, arising with the displacement of the hydrocarbon tail from the polar medium into the fatty medium. Since g is proportional to the number of carbon atoms in the tail of the AP molecule, expression (22) leads to a linear dependence of $\ln c^*$ (see (6)) on the number n in agreement with the experimental data.[5] Minimizing (22), we find

$$s_0 = \sqrt{\frac{2\pi e^2 r_D}{\alpha \varepsilon}}. \tag{23}$$

The radius of the spherical micelle R and the aggregation number N are determined by the relations

$$R = \frac{3v_0}{s_0}, \quad N = \frac{4\pi}{s_0} \sqrt{\frac{3v_0}{s_0}}, \tag{24}$$

obtained from the condition that all AP molecules in the aggregate have a constant specific volume v_0 and specific area s_0 (23).

From geometrical considerations, it follows that expressions (23) and (24) make sense if the radius of the spherical micelle R is less than the length of a completely extended AP molecule l_0, i.e.,[45]

$$s_0 > s_c = \frac{3v_0}{l_0}. \tag{25}$$

Thus, in the model examined, the transition to nonspherical aggregates accompanying the breakdown of condition (25) is related to the packing of hydrocarbon chains within a micelle. Different forms of nonspherical aggregates, which are possible for $s_0 < s_c$, are examined in Ref. 46. Apparently, the strongest assumption made in this reference was the requirement that the specific area be constant for all constituent molecules of the micelle.[71] At the same time, from physical considerations, it may be expected that the area per

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polar head, for example, on the end and lateral surfaces of CM, will be different. An indirect confirmation of this is given by NMR data, obtained with oriented specimens of lyotropic nematics (LN), which are examined in Sec. 4c. For this reason, we shall examine a model of structural transformations of micelles, which permits the appearance of groups of AP molecules with different specific area per polar head within a single aggregate.[61]

As before, we shall assume that the quantity s_0 depends uniquely on the pressure, temperature, and composition of the solution, but not on the size of the aggregate. This is valid if the Debye screening radius is small compared with the dimensions of the micelles. In addition, the region occupied by the polar heads of the amphiphiles, interacting with one another and with the solvent, can be viewed as a separate two-dimensional phase, whose equation of state depends on the temperature and concentration of the solution. In studying the structural transformation of micelles, initiated by a change in the ionic strength of the solution, it is convenient to use another quantity instead of the electrolyte concentration: the fraction p of unionized polar heads of AP molecules. For ionic AP of the type AOT or SDS, the quantity p is close to one for low salt concentrations in the solution c_s and decreases with increasing c_s. Depending on p and T, the two-dimensional "liquid if polar heads" (TLH) can be in different states, differing by the magnitude of the specific area per polar head s. Since the specific volume of AP molecules v_0 is nearly independent of the shape of the micelles, this being related to the high conformational flexibility of hydrocarbon tails, a change in s must lead to a change in the curvature of the surface of the aggregates.

In general, the phase diagram of TLH will consist of regions corresponding to a single phase with a definite value of the specific area per polar head as well as to "two-phase" regions, in which groups of polar heads, differing by the specific area and, therefore, the curvature of the given section of the aggregate surface, are present on the surface of a micelle. If the system also contains co-surfactants, for example, alcohol, which affect the state of the TLH, then "three-phase" regions can appear in the phase diagram. We note that different phases of TLH can likewise be distinguished by the mutual orientation of the polar groups of molecules on the surface of micelles.

The case of a single phase is apparently realized for "classical" TLH: cubic I_1, hexagonal $H_{1,2}$, and lamellar L_α mesophases. The case of two-phase TLH corresponds to $I_{C,D}$ and $N_{C,D}$, as well as complex hexagonal H_C and tetragonal C and K phases. In the case of biaxial nematics N_{bx}, the TLH is apparently a three-phase liquid.

In the simplest case, when it is possible to neglect the change in the free energy of the fatty tails with a change in the curvature of the surface of the aggregate, the sequence of changes in the shape and size of micelles is determined by the requirement that the length of the line separating the TLH phases be minimum.[61]

Indeed, we shall examine the section of the phase diagram that includes the two-phase region of TLH, illustrated in Fig. 13. In a certain temperature range, when a fraction of uncharged heads $p = p_1$ is reached, a section with the high temperature L-phase will appear on the surface of a micelle. For $p - p_1 \ll p_1$, the L-phase must arise in the form of a circular spot on a spherical micelle, which in this case assumes a "disk-shaped" form. As p increases and, therefore, the fraction of the surface occupied by the L-phase increases as well, the CM phase in which the low-temperature phase is concentrated on the end-faces of the cylinder, becomes more advantageous. In this case, the length of the boundary separating the phases is practically independent of the length of CM, equal approximately to

$$\frac{L}{D} \approx \frac{s_L}{s_C} \frac{p - p_1}{p - p_2}.$$

This explains the fact that micelles with large aggregation numbers usually have a cylindrical shape (see above). When the value $p = p_2$ is reached, the length of CM increases, leading in concentrated solutions to the formation of nematic or hexagonal phases.

If the differences of the free energies of the hydrocarbon tails differ in cylindrical and disk-shaped micelles, then the alternating order, indicated above, of the structural transformations of micelles can break down,[61] and large disk-shaped aggregates, forming nematic and lamellar phases, can appear.

A decrease in the specific area per polar head of the amphiphile on the surface of micelles with increasing concentration of the solution is a manifestation of a general law observed in the analysis of all lyotropic mesophases: the number of water molecules bound to the hydrophilic surface of the aggregates decreases with the addition of amphiphile, inorganic salts, etc. to the solution. A change in the specific area, as indicated above, leads to a change in the shape and dimensions of micelles, and, under certain conditions, to phase transformations between different liquid-crystalline modifications.

d) Stratification of micellar solutions

As the concentration of AP molecules in solution increases, together with the change in the shape of the aggregates, the long range order in the position of the centers of gravity of the micelles can also change. The simplest phenomenon of this type is separation of a micellar solution into two isotropic phases, which is often observed, for example, for nonionic AP substances such as dodecyloxyethylene glycol monoether:
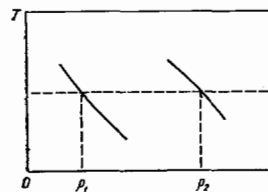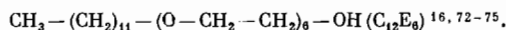
$$CH_3 - (CH_2)_{11} - (O - CH_2 - CH_2)_6 - OH \; (C_{12}E_6)$$ [16, 72-75].

FIG. 13. Section of the phase diagram of a two-dimensional "fluid of polar heads."[61]

The phase diagram of the system $H_2D/C_{12}E_6$, illustrated in Fig. 14, has a lower critical point of stratification with parameters $c_0 = 12.5$ mg/cm³ and $T_c = 50.35$°C.[17] As the critical point is approached, light scattering increases strongly,[72,74] which indicates the appearance of inhomogeneity in the solution with dimensions comparable to the wavelength of visible light. An investigation of the conformation of hydrocarbon tails, performed using the NMR method,[59] shows that in this case the state of the fatty tails within the micelles does not change significantly. This indicates that the aggregates of AP molecules arising in a solution of $C_{12}E_6$ are clusters consisting of several spherical micelles bound together either by van der Waals forces or by means of polyvalent ions, which could be present in the solution in small numbers.[76]

Light-scattering measurements in the critical region[17] showed that the scattering intensity satisfies the Ornstein-Zernike relation for critical opalescence[77]:

$$I(\theta) = \frac{I(\theta=0)}{1+k^2\tilde{\xi}^2}, \qquad k = \frac{4\pi\tilde{n}}{\lambda}\sin\theta,$$

and, in addition, $I(\theta = 0)$ and ξ as functions of $\varepsilon = (T_c - T)/T_c$ in the region $10^{-1} > \varepsilon > 10^{-3}$, $c = c_0$ behave in accordance with the predictions of the "classical" theory of the critical point

$$\gamma = -\frac{d\ln I(\theta=0)}{d\ln\varepsilon} = 0.97 \pm 0.05, \quad \nu = -\frac{d\ln\xi}{d\ln\varepsilon} = 0.53 \pm 0.05.$$

Measurements of the temporal correlation function of the scattered light gave, for the hydrodynamic radius R_h (17), the value $R_h \approx 0.9\xi$.

4. LYOTROPIC NEMATICS

a) Orientational ordering in solutions of rigid rod-shaped molecules

Nematic phases are the most symmetrical of all LC phases and are characterized by the presence of a distinguished direction of orientation of the long axes of molecules in the system.[6-8] Apparently, the simplest systems in which orientational ordering can appear are solutions of rigid rod-shaped particles of biological origin: the mosaic tobacco virus (MTV) or desoxyribonucleic acid (DNA) or synthetic polymers such as PBG.[11,13] The MTV particles are cylindrically-shaped protein aggregates with a length of $L = 300$ Å and a diameter of $D = 200$ Å, while the DNA molecules ($D = 20$ Å, $L = 10^4-10^5$ Å) and PBG molecules ($D = 20$ Å, $L = 10^2-10^4$ Å) are long hydrogen-bond-stabilized helices.[50,58]

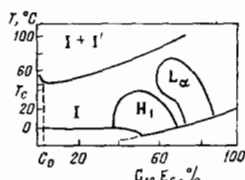The simplest model predicting the appearance of nematic ordering in a system of rigid rods was examined

FIG. 14. Phase diagram of an aqueous solution of dodecylhexaoxyethylene glycole monoether $(C_{12}E_6)$.[16] $I_1 + I_1'$ indicates the two-phase region.

by Onsager[78] (see also Ref. 6), and the phase diagram of a two-component system, containing anisotropic particles, was constructed by Flory with the help of a lattice-model calculation.[79,80]

We shall discuss a model of orientational order in a solution of anisotropic rigid particles which is analogous to the model examined by Meier and Saupe[81-83] (see also Refs. 6-8).

The thermodynamic potential of the homogeneous solution, containing N solvent molecules and $f(a)$ particles, whose distinguished axes are oriented along the unit vector a, can be written up to second-order terms in the concentration in the form

$$\Phi = N\mu_L + T\int do_a f(a)\ln\left(\frac{f(a)}{eN}\right) + \frac{1}{2N}\int do_a \int do_{a'} f(a) f(a') U(a, a'),$$
(26)

where μ_L is the chemical potential of the pure solvent. The scalar function $U(a, a') \equiv U(a \cdot a')$ depends on the temperature and pressure of the solution and the angle between the vectors a and a'. We shall expand $U(a \cdot a')$ in Legendre polynomials and, in addition, for simplicity, we shall retain only the first two terms:

$$U(aa') = \sum_{l=0}^{\infty} U_l P_l(aa') \approx U_0 + U_2 P_2(aa').$$
(27)

We shall determine the regions of stability of the isotropic and nematic phases on the temperature-concentration diagram. For this, we shall write out the conditions for I–N equilibrium, i.e., equality of the chemical potentials of the solvent and of the solute in contiguous phases. Using (26) and (27), we obtain the following system of equations:

$$Tc_I + \frac{1}{2}U_0 c_I^2 = Tc_N + \frac{1}{2}U_0 c_N^2 + \frac{1}{2}c_N^2 s U_2,$$
(28a)

$$f_N(an) = \frac{c_I}{4\pi}N\exp\left[\frac{U_0}{T}(c_I-c_N) - \frac{U_2}{T}c_N s P_2(an)\right],$$
(28b)

where we have introduced Tsvetkov's order parameter[84]

$$s = \int do_a P_2(an) f_N(an) / \int do_a P_0(an) f_N(an).$$
(29)

In (28) and (29), n is a unit vector oriented along the distinguished axis in the nematic (director) and $c_{I,N}$ are the total particle concentrations in the isotropic and nematic phases. Substituting (29) into (28b), we obtain an equation for the order parameter s, analogous to that studied in Refs. 81–83 and 6:

$$m = \xi\left(-\frac{1}{2}+\frac{3}{2}\frac{\partial}{\partial m}\ln z\right), \quad z = \int_0^1 dx e^{mx^2},$$

$$m = -\frac{3}{2}\frac{U_2 c_N s}{T}, \quad \xi = -\frac{3}{2}\frac{U_2 c_N}{T}.$$
(30)

For small ξ, the only solution of this equation is $s = 0$, which corresponds to a stable isotropic phase. If $V_2 < 0$, then for some value of ξ a solution with $s \neq 0$ appears. Equality of the thermodynamic potentials of the phases $\Phi_I = \Phi_N$ corresponds to the value $\xi = \xi_c \approx 0.33$, i.e.,

$$c_N = \frac{2\xi_c}{3}\frac{T}{|U_2|};$$
(31)

in this case, the order parameter in the nematic phase $s = s_c \approx 0.44$. We determine the jump in concentrations accompanying the transition $I \rightleftharpoons N$ from (28a):

$$\frac{c_I - c_N}{c_N} \approx -\frac{\xi_c s_c^2}{3\left(1+\frac{U_0}{|U_2|}\frac{2\xi_c}{3}\right)} \approx -\frac{2\cdot10^{-2}}{1+\frac{U_0}{|U_2|}\cdot\frac{2\xi_c}{3}}.$$
(32)

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In this expression, it is assumed that the condition of stability of the isotropic solution relative to stratification is satisfied,[68]

$$\frac{\partial \mu'}{\partial c_I} = \frac{1}{c_I} T + U_0 > 0, \tag{33}$$

which guarantees that the denominators in (32) are positive.

Figure 15 shows the experimental phase diagram of a PBG/DMP solution (N, N-dimethylformamide).[11] Evidently, at high temperatures the model under study describes qualitatively correctly the mutual distribution of phases, but at low temperatures ($T < 20\,°C$), there is considerable disagreement. Namely, as T decreases, a phase with finite shear moduli arises in the solution.[11] This suggests the formation of a three-dimensional network, formed by the rod-shaped particles of PBG, which can be either periodic as, for example, the cubic phase illustrated in Fig. 9b, or disordered similar to polymer gels.[12] The details of the structures arising in the PBG/DMF system for $T < 120\,°C$ are still not clear.

b) Three types of nematics in solutions of amphiphilic molecules

The greater complexity in the case of nematics arising in solutions of AP molecules, as compared with the simple picture examined in the preceding section, is related to the change in the sizes and shapes of micelles accompanying the phase transition $I \rightleftharpoons N$. This circumstance is characteristic for LLC, in which a phase transformation is usually the result of the restructuring of aggregates of molecules and complicates the interpretation of the experimental data.

We shall discuss the results of some experimental work on the investigation of the internal structure of LN. The following methods are most widely used:

a) Investigation of the orientation of specimens in a magnetic field;

b) NMR spectroscopy;

c) Birefringence and scattering of light; and,

d) X-ray diffraction.

The first specimens of LLC, capable of aligning in a magnetic field of several kilogauss over a time of about one hour, were obtained by Lawson and Flault[31] in the four-component system $NaC_{10}/C_{10}H_{22}O/H_2O/Na_2SO_4$. Later, LLC, aligning in a magnetic field over a time of $1-10^3$ s, were obtained in a number of three- and
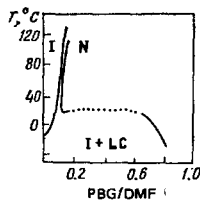
FIG. 15. Phase diagram of a solution of PBG in N, N-dimethylformamide.[11]

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[4])See also the review in Ref. 200.

four-component systems.[33,35,4)] As is well known, it is precisely this property that is characteristic of nematic mesophases.[6-8]

Investigation of the optical properties showed that LN are uniaxial (with the exception of the biaxial phase discovered by Yu and Saupe[37]); in addition, there are at least two types of nematics that are distinguished by the sign of the diamagnetic anisotropy and the index of refraction[35]

$$\chi_a = \chi_{\parallel} - \chi_{\perp}, \quad n_a = \tilde{n}_{\parallel} - \tilde{n}_{\perp}, \tag{34}$$

where the indices $\parallel$ and $\perp$ refer to the directions along the distinguished axis and an axis perpendicular to it, respectively. Namely, the distinguished axis of type N_C specimens is oriented along the applied magnetic field, i.e., $\chi_a^c > 0$ and, in this case, $n_a^c < 0$. On the other hand, type N_D specimens are oriented perpendicular to the field; in this case, $\chi_a^D < 0$ and $n_a^D > 0$. This behavior agrees with the proposition that N_C phases consist of cylindrical micelles, while N_D phases consist of disk-shaped micelles (which is reflected in the notation). To clarify this assertion, we shall write down the free energy of interaction for a dilute solution of anisotropic particles (uniaxial ellipsoids) in a magnetic field:

$$F_M = -\frac{1}{2}\int d^3r\, m(r)\, H(r), \tag{35}$$

where $m(r)$ is the magnetic moment per unit volume. For the solvent, we have

$$m(r) = \chi_L H(r), \tag{36}$$

for points within micelles, oriented along the principal axis a,

$$m(r) = \tilde{\chi}_{\perp} H + (\tilde{\chi}_{\parallel} - \tilde{\chi}_{\perp})\, a\, (Ha), \tag{37}$$

where $\tilde{\chi}_{\perp,\parallel}$ are the transverse and longitudinal magnetic susceptibilities of the particles. Substituting (36) and (37) into (35) and averaging over the orientations of a, we obtain an expression for the diamagnetic susceptibility tensor of the solution:

$$\chi_{ik} = \delta_{ik}\left[\chi_L + \Phi\left(\frac{1}{3}\tilde{\chi}_{\parallel} + \frac{2}{3}\tilde{\chi}_{\perp} - \chi_L\right)\right] + \Phi(\tilde{\chi}_{\parallel} - \chi_{\perp})s_{ik}, \tag{38}$$

where Φ indicates the fraction of the volume of the solution occupied by micelles, and the tensor order parameter[6] is

$$s_{ik} = \left\langle a_i a_k - \frac{1}{3}\delta_{ik}\right\rangle. \tag{39}$$

Lining up the z axis of a Cartesian coordinate system with the direction of the director n, we obtain

$$s_{ik} = \frac{1}{2}s\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}_{ik},$$

where the quantity s coincides with the order parameter (29). Thus the anisotropy of the permeability of the solution is proportional to the parameter describing the ordering of the axes of anisotropic particles.

At the present time, there are no experimental data on the absolute magnitude of χ_a for LN. In a model in which the interior of a micelle is an isotropic medium with permeability χ_0, differing from χ_L, the appearance of anisotropy of the susceptibility is related with the difference in the demagnetizing factors $\varkappa_{\parallel,\perp}$ parallel and transverse to the axes of the particle. Here

$(\mu_L = 1 + 4\pi\chi_L)$

$$\tilde{\chi}_{\parallel} - \tilde{\chi}_{\perp} = \frac{4\pi(\chi_0 - \chi_L)^2(\varkappa_{\perp} - \varkappa_{\parallel})}{(\mu_L + 4\pi\varkappa_{\perp}(\chi_0 - \chi_L))(\mu_L + 4\pi\varkappa_{\parallel}(\chi_0 - \chi_L))} \quad (40)$$

$$\approx 4\pi(\chi_0 - \chi_L)^2(\varkappa_{\perp} - \varkappa_{\parallel}). \quad (40a)$$

For CM with $L \gg D$, $\varkappa_{\parallel} = 0$ and $\varkappa_{\perp} = 1/2$ (Ref. 63), i.e.,

$$\chi_a = \pi(\chi_0 - \chi_L)^2 \Phi s > 0, \quad (41a)$$

while for DM with $D \gg 2l_0$, $\varkappa_{\parallel} = 1$ and $\varkappa_{\perp} = 0$, i.e.,

$$\chi_a = -2\pi(\chi_0 - \chi_L)^2 \Phi s < 0. \quad (41b)$$

However, in view of the smallness of the diamagnetic permeability of substances ($\chi \sim 10^{-5}$–10^{-6}) the absolute value of χ_a according to (41), is extremely small, so that the anisotropy of the magnetic properties of the hydrocarbon nuclei of CM or DM, related to the presence of a definite packing order of the fatty tails of the molecules, can make a large contribution to χ_a. This is confirmed by NMR data.[35] In this case, the quantity χ_a will be determined by the difference between the susceptibilities of CH_2 groups parallel to and perpendicular to the C–C bonds $\chi_{C-C}^{\parallel, \perp}$ and the degree of ordering of the orientations of these bonds s_{C-C} relative to the axis of the micelle:

$$\chi_a = \frac{1}{2} s_{C-C} \Phi(\chi_{C-C}^{\parallel} - \chi_{C-C}^{\perp}). \quad (42)$$

For CM, $s_{C-C} < 0$ and for DM, $s_{C-C} > 0$. Since the absolute magnitude of $\chi_{C-C}^{\perp}$ is greater than the absolute magnitude of $\chi_{C-C}^{\parallel}$, as in (41), $\chi_a > 0$ for cylinders and $\chi_a < 0$ for disks.[5]

The anisotropy of the dielectric permittivity of the solution at optical frequencies, when the wavelength of light exceeds the size of a micelle, can be described by expressions analogous to (38)–(40) (we neglect the anisotropy of the dielectric permittivities of the hydrocarbon nuclei of the micelles):

$$\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp} = \frac{1}{2}\varphi s \frac{(\varepsilon_0 - \varepsilon_L)^2(\varkappa_{\perp} - \varkappa_{\parallel})}{[\varepsilon_L + \varkappa_{\perp}(\varepsilon_0 - \varepsilon_L)][\varepsilon_L + \varkappa_{\parallel}(\varepsilon_0 - \varepsilon_L)]}, \quad (43)$$

i.e., $\varepsilon_a > 0$ for CM and $\varepsilon_a < 0$ for DM. The value of ε_a for $\varepsilon_L \gg \varepsilon_0$ equals $\varepsilon_a = (1/2)\varphi s(\varkappa_{\perp} - \varkappa_{\parallel})$, from where we obtain an expression for the anisotropy of the index of refraction:

$$n_a = \frac{\varkappa_{\parallel} - \varkappa_{\perp}}{4\sqrt{\varepsilon_L}}\varphi s. \quad (44)$$

Thus N_C type LN must have negative birefringence and N_D type LN must have positive birefringence. For $\varphi \sim 0.1$, it follows from (44) that $|n_a| \sim 10^{-3}$, which agrees with the experimental value of this quantity.[33]

The assumption of disk-shaped micelles in N_D and cylindrically-shaped micelles in N_C is confirmed by x-ray diffraction measurements for magnetic-field aligned specimens.[85] The Bragg reflections turn out to be diffuse, indicating the absence of ordering of the centers of gravity of micelles and some orientational disordering of their axes.

In the biaxial nematic phases N_{bx}, obtained by Yu and

Saupe,[37] the dielectric permittivity and magnetic permeability tensors have three different values. An analysis of the lattice model of a fluid consisting of anisotropic particles shows[66] that the biaxial phase can be thermodynamically stable if the dimensions of the molecules in the three directions satisfy certain relations. For example, for molecules in the form of rectangular parallelepipeds with sides $L_1 > L_2 > L_3$ for $L_1 = 10L_3$, the biaxial phase arises only if $L_2^* < L_2 < L_2^{**}$, where $L_2^* \approx 2.5L_3$ and $L_2^{**} = 5L_2^*$. For $L_2 < L_2^*$, the N_C nematic phase is the thermodynamically stable phase, while the N_D mesophase is thermodynamically stable for $L_2 < L_2^{**}$.

c) NMR spectroscopy of lyotropic liquid crystals[6]

In the NMR method, the absorption of high-frequency electromagnetic radiation by nuclear spins, precessing in an external magnetic field, is measured. In principle, any isotopes with nonzero spin can be used for this purpose; the most widely used spins for investigations of LLC are ^{1}H, ^{2}D, ^{13}C, ^{23}Na, ^{31}P, and others.[1-3] The Hamiltonian, describing the interaction of spins with an external magnetic field H parallel to the z axis and with neighboring atoms, has the form

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_D + \mathcal{H}_Q. \quad (45)$$

Here, $\mathcal{H}_z$ describes the Zeeman splitting of levels in a magnetic field:

$$\mathcal{H}_z = \hbar\gamma \sum_i \hat{I}_z^i,$$

$\mathcal{H}_D$ is the dipole-dipole interaction of spins on different nuclei:

$$\mathcal{H}_D = -\frac{1}{2}(\hbar\gamma)^2 \sum_{i\neq j}\left(\frac{1}{|r_{ij}|^5}3(\hat{I}^i r_{ij})(\hat{I}^j r_{ij}) - \frac{\hat{I}^i\hat{I}^j}{|r_{ij}|^3}\right), \quad (46)$$

where $\hat{I}^i$ is the spin operator of the ith nucleus, $\hbar\gamma\hat{I}^i$ is its magnetic moment, and r_{ij} is a vector connecting the ith and jth spins. The last term in (45) $\mathcal{H}_Q$ describes the interaction of nuclei with $I \geq 1$, having a quadrupole moment, with a nonuniform electric field:

$$\mathcal{H}_Q = \frac{1}{6}\sum_i \hat{Q}_{\alpha\beta}^i \frac{\partial^2\varphi_i}{\partial x_\alpha \partial x_\beta}, \quad \hat{Q}_{\alpha\beta}^i = \int d^3r \hat{\rho}_e^i(3r_\alpha r_\beta - r^2\delta_{\alpha\beta}). \quad (47)$$

Here $\varphi_i(r)$ is the electric field potential in which the ith nucleus is located, $\hat{\rho}_e^i(\mathbf{r})$ is its charge density, $Q_{\alpha\beta}^i$ is the electric quadrupole moment tensor related to $\hat{I}^i$ by the relation[86-89]

$$\hat{Q}_{\alpha\beta}^i = \frac{3Q}{2I(2I-1)}\left[\hat{I}_\alpha^i\hat{I}_\beta^i + \hat{I}_\beta^i\hat{I}_\alpha^i - \frac{2}{3}\delta_{ik}I(I+1)\right]. \quad (48)$$

Neglecting $\mathcal{H}_D$ and $\mathcal{H}_Q$, the spectrum of eigenvalues of (45) has $2I+1$ equidistant levels. Correspondingly, the absorption spectrum for an alternating electromagnetic field will have a single line at the frequency

$$\omega_0 = 2\hbar\gamma H.$$

The dipole-dipole and quadrupole terms in (45) lead to splitting of the NMR lines. For typical thermotropic nematics, the dipole term (46) makes the main contribution to the splitting,[6,90] since in this case the resonance is observed on nuclei coupled to the rigid part of the mesogen. On the other hand, for lyotropic systems, when AP molecules do not have rigid parts, the

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[5] Mesophases in solutions of amphiphiles, whose fatty tails contain one or several aromatic rings, are examined in Ref. 201. In this case, the sign of the anisotropy of the magnetic susceptibility can change.

[6] For a more detailed discussion of the problems touched upon here, see Refs. 86–88.

rapid relative motion of neighboring nuclei, characteristic of liquids, decreases the contribution of the dipole-dipole forces[7] and the quadrupole Hamiltonian (47) makes the main contribution to the splitting of NMR lines. In a field that is axially symmetric with respect to the z axis, we have[89]

$$\frac{\partial^2\varphi}{\partial x^2} = \frac{\partial^2\varphi}{\partial y^2} \equiv a, \quad \frac{\partial^2\varphi}{\partial z^2} = -2a,$$

while the displacement of levels is given by the expression

$$\Delta E = \frac{aQ}{2I(2I-1)}[I(I+1) - 3I_z^2],$$

where Q is the electric quadrupole moment of the nucleus. The splitting of the NMR line equals ($I = 1$)

$$\Delta\nu = \left|\frac{3aQ}{2\hbar}\right|. \tag{49}$$

This quantity for different nuclei varies in the range $10^2 - 10^5$ Hz. If there is a spread in the directions of the distinguished axes of micelles relative to the direction of the magnetic field, then instead of (49) we have

$$\Delta\nu = \left|\frac{3aQs}{2\hbar}\right|. \tag{50}$$

We note that the long time for reorientation of LN permits performing measurements on rotating specimens.[31] Yu and Saupe[37] investigated the splitting of the NMR line in N_{bx}, which have no axial symmetry.

Figure 16 shows an example of the dependence of the magnitude of the quadrupole splitting of the NMR line of deuterium, which is a constituent of heavy water, added to a KL solution.[91] In this case, only molecules of water directly coupled to the hydrophilic surface of the micelles by hydrogen bonds (1–2 molecular layers) contribute to the splitting and, in addition, depending on the temperature and the degree of ionization of the polar heads of the AP molecules, the amount of "bound" water and the degree of its orientation can vary.[1,3] Let us examine the upper curve in Fig. 16. For a concentration of potassium laurate exceeding 40%, the solution is in the hexagonal phase (Fig. 17), i.e., the given axes of the micelles are completely ordered: $s \equiv 1$. The decrease in $\Delta\nu$ in Fig. 16 indicates a change in the inhomogeneity of the electric field leading to splitting of the line [the parameter "a" in (49)
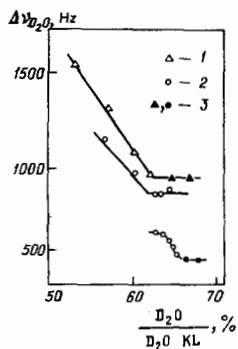

FIG. 16. Variation of the magnitude of the quadrupole splitting of the NMR spectrum. 1) KL/D_2O; KL/D_2O+2% KCl, $T = 30.3$°C; 3) two-phase region.

[7]This weakening, in particular, gives rise to the well-known narrowing of NMR lines in liquids and gases.[86]
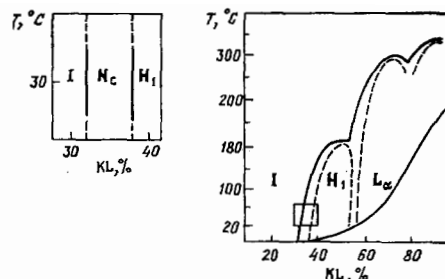

FIG. 17. Change of a portion of the phase diagram of an aqueous solution of potassium laurate in the presence of 2% KCl.

and (50)]. The appearance of a second doublet in the NMR line with the addition of 2% KCl salt to the solution indicates that new groups of water molecules, whose degree of orientation differs from the orientation on the lateral surfaces of the cylinder, appear on the surface of the micelles. We can conjecture (and this proposition is confirmed by data on the orientation of specimens in a magnetic field and investigations of the textures and x-ray diffraction patterns) that the second doublet originates with the water molecules bound on the end-faces of the CM.

d) Structural transformations of nematics

Figure 17 illustrates schematically the change in the section of the phase diagram of a water solution of potassium laurate caused by the addition of 2% KCl to the system,[91] from which it is evident that the formation of the nematic phase with the addition of an amphiphile to the system precedes the appearance of ordering of the centers of gravity of micelles. It may be assumed that nematic ordering appeared in this case due to the increase in the length L of CM, caused by the addition of the electrolyte. Indeed, according to (31), the fraction of the volume of the solution occupied by micelles, for which the nematic phase arises, is given by the expression

$$\varphi_N = \frac{\pi D^2 L}{4v_L} c_N = \frac{3\pi}{8\xi_0} \frac{T}{|U_2|} \frac{D^2 L}{v_L}, \tag{51}$$

where v_L is the specific volume of the solvent molecules. For $C_N \ll 1$, the long-range van der Waals forces make the main contribution to U_2. In this case, $|U_2| \sim L^2$, i.e., $\varphi_N(L) \sim L^{-1}$, if the average distance between micelles exceeds L and $|U_2| \sim L$, i.e., $\varphi_N(L) \approx \varphi_N(\infty) = $ const, if the distance between the cylinders is small compared to L. Thus the critical concentration of an amphiphile in (51) is a decreasing function of the length of the CM. A qualitatively analogous behavior of the function $\varphi_N(L)$ was obtained in calculations by Flory.[79,80] The experimental curves, obtained for a solution of PBG in dioxane, are illustrated in Fig. 18.

In the experimental situation being studied,[91] $\varphi_{N,I} \approx 30\%$, while with the addition of salt, the length of CM $L = L(c_s)$ increases (see Secs. 3 b and c and Fig. 11). The transition $I_D \rightleftharpoons N_D$, initiated by the addition of a certain electrolyte to the system, occurs in an analogous manner.[91]

Yu and Saupe[34] and Forrest and Reeves[36] observed the

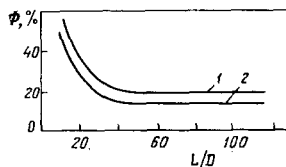A. A. Vedenov and E. B. Levchenko   760

FIG. 18. Critical volume fraction of PBG in dioxane[92]:
1) $\Phi_N(L)$; 2) $\Phi_I(L)$.

phase transition $N_C \rightleftharpoons N_D$, initiated by the addition of an inorganic salt or (and) a cosurfactant (decanol) to the system. The phases N_C and N_D can coexist, for example, in the region of the phase diagram illustrated in Fig. 19, since in this region, the lines separating the phases H_1 and I_C, I_C and I_D, and I_D and L_α converge. The addition, for example, of a salt, as we saw above, increases the sizes of aggregates and the possibility of orientational ordering.

The appearance of a biaxial nematic phase deserves special attention.[37] Figure 20 shows a section of the phase diagram of the system $KL/D_2O/decanol$, which contains a narrow N_{bx} region. Yu and Saupe reported in Ref. 37 that they also observed an analogous phase in a SDS solution. An investigation of a lattice model shows that the biaxial nematic phase is thermodynamically stable, if the sizes of the particles in the system fall into a certain range[66] (see also Sec. 4b). For this reason, one result of Ref. 37 is a proof of the thermodynamic stability of triaxial micelles. This fact can apparently be related to the influence of alcohol on the dimensions and shape of aggregates in solutions of amphiphiles.

Molecules of alcohols dissolve not only in the polar medium surrounding the head of the AP molecules, but also in the hydrocarbon nucleus of micelles; in this case, the energy of the interface between the polar and fatty media decreases strongly.[93] Thus the presence of alcohol, generally speaking, facilitates the formation of large aggregates in solutions of AP molecules. Experimental data on quasi-elastic light scattering show that the addition of alcohol can indeed lead to the appearance of large disk-shaped micelles and, in addition, the cosurfactant is distributed in them nonuniformly: the alcohol density is higher at the perimeter of the disk and lower in the plane of the lamellae.[5,94] This is apparently related to the presence of voids in the packing of AP molecules near the curved surface, which are filled by the hydrophobic parts of the cosurfactant.

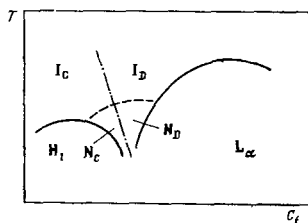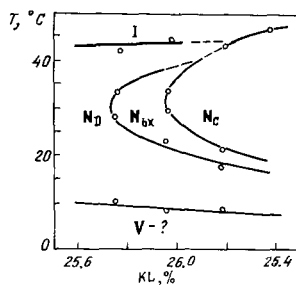Two situations can arise when alcohol is added to a

FIG. 20. Portion of the phase diagram of an aqueous solution of KL containing 6.24% decanol.[37]

solution containing CM. First of all, the cylinders can restructure into DM, which has been observed in a number of systems[1-3]; in particular, the transition $N_C \rightleftharpoons N_D$, initiated by the addition of alcohol, was observed in Refs. 34 and 36. Second, a circular cylinder can flatten into a biaxial aggregate, which in its turn can lead to the formation of LLC with low symmetry of the type N_{bx}. The latter case was apparently realized in Ref. 37.

In concluding this section, we note that clarification of conditions of the appearance of such phases as N_{bx}, C, K, and H_C in solutions is of great significance both for the physics of LLC in itself and for the study of the mechanisms of self-assembly of different supermolecular structures of living cells. In particular, some sections of the surface of aggregates in structures of the type $V_{1,2}$ illustrated in Fig. 9b and in analogous so-called microtrabecular cellular structures (Fig. 21) have very different curvatures. The thermodynamic stability of such formations is apparently ensured, just as in the mesophases mentioned, by the nonuniform distribution of cosurfactant and (or) charges of the polar heads on the surface of the aggregates.

The same thing can be said of vesicles (see Fig. 2f), myelin figures, and other formations, examined in the literature as models of biomembranes.[4,96,97] Usually metastable, aggregates of this type can be thermodynamically stable under certain conditions.

e) Energy of elastic distortions

In the presence of external fields, the state of a nematic in which the director n at each point is parallel to a fixed direction is, generally speaking, incompatible with the conditions imposed on n by the walls bounding the specimen, as a result of which the field of the director becomes distorted: $n = n(r)$. In the macro-

FIG. 19. Portion of a phase diagram clarifying the formation of nematic phases (see text).

FIG. 21. Schematic diagram of the microtrabecular structure of a live cell.[95]

scopic continuous approach, the energy of the distorted state of a uniaxial nematic is described by the Oseen-Frank free energy[6-8]:

$$F_d = \frac{1}{2} \int d^3r \{ K_1 (\text{div } n)^2 + K_2 (n \text{ rot } n)^2 + K_3 [n \text{ rot } n]^2 \}. \quad (52)$$

The first term in (52) describes transverse bending (splay), the second term describes twisting (twist), and the third term describes longitudinal bending (bend). An expression for the energy of elastic distortion of biaxial nematics is obtained in Ref. 98.

The elastic constants K_1, K_2, and K_3 are usually determined from measurements of the critical field H_C, giving rise to reorientation of the director in a specimen with fixed dimensions: Frederiks effect[6-8,99]; in this case, the magnitude of the anisotropy of the diamagnetic susceptibility must be determined from independent experiments. At the present time, there are no data on χ_a; according to preliminary estimates,[33,100] $|\chi_a| \sim 10^{-8}$.

On the surface of glass, AP molecules align along the normal to the glass surface. For this reason, in the space between two glass plates, LN of the type N_C form a planar texture, in which the director is parallel to the surface of the plates, while N_D type LN form a homeotropic texture (the director is oriented along the normal; Fig. 22). If an external magnetic field, which has a component along the normal to the plates, is now imposed on the specimen, then for $H > H_C$, a reorientation of the director will occur in the interior of the specimen. This orientation can be observed by optical methods. The magnitude of H_C is inversely proportional to the gap size d between the plates and is related to Frank moduli entering into (52). Saupe et al.[100] measured $H_C d$ for N_D in a system of decylammonium chloride NH_4Cl/H_2O and determined the values of $K_1/|\chi_a|$ and $K_3/|\chi_a|$ as a function of the temperature of the specimen (Fig. 23). Assuming that $|\chi_a| \sim 10^{-8}$, the data in Ref. 100 lead to the estimate $K_{1,3} \sim 10^{-6}$ dynes, which agrees in order of magnitude with analogous quantities for thermotropic nematics.[6-8]

Estimates based on an investigation of the dynamics of the Frederiks effect (see the next section) show that for LN of the type N_C, the Frank moduli can be one to two orders of magnitude smaller: $K \sim 10^{-7} - 10^{-8}$ dynes. It is interesting to compare this value with the bending energy of CM, which can be determined from the data in Ref. 57, if it is assumed that the break in the dependence of $\log \nu$ plotted against $\log N$ with $N \sim 10^4$ (see Fig. 12) is indeed related to the formation of a coiled state of CM in the solution.

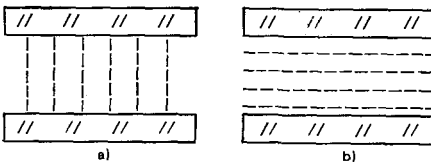The energy of the weakly deformed state of CM is given by the expression[68]

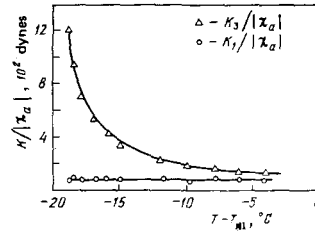FIG. 22. Homeotropic (a) and planar (b) texture of nematics.

FIG. 23. Temperature dependence of Frank's moduli of the N_D phase (7.57% decylammonium chloride, 2.73% NH_4Cl, 89.70 molar % H_2O).[100]

$$f_d = \frac{a}{2} \int_a^L dl \left[\left(\frac{d\theta_1}{dl} \right)^2 + \left(\frac{d\theta_2}{dl} \right)^2 \right], \quad (53)$$

where $\theta_{1,2}$ are the angles of rotation of the axis of CM relative to the unperturbed state. The mean-square distance between the ends of the CM equals

$$\overline{R^2} = 2 \frac{a}{T} \left(\frac{LT}{a} - 1 + e^{-LT/a} \right). \quad (54)$$

For $L \ll L_C \equiv a/T$, $\overline{R^2} \approx L$, and for $L \gg L_C$, $\overline{R^2} \approx 2LL_C$. The quantity L_C and, therefore, a are determined from Fig. 12: $L_C \approx 1600$ Å. If it is assumed that the distance between CM in N_C is $r \approx 200$ Å, then the elastic constant of LN, related to bending of CM, constitutes

$$K_d = \frac{a}{\pi r^2} = \frac{L_C T}{\pi r^2} \approx 5 \cdot 10^{-8} \text{ dynes}. \quad (55)$$

Thus, in general, the possibility of deformation of CM must be taken into account in calculating the energy of elastic distortions. We note that an analogous situation arises for LLC in solutions of polymers.[101]

Aside from smooth distortions, for which $n(r)$ varies continuously from point to point, when observing LN in a polarizing microscope, singular lines (nuclei of disclinations) are observed.[6-8] The structure of these defects of the director field in LM is the same as in the case of thermotropic nematics, i.e., nuclei with integer and half-integer Frank indices are possible. In the biaxial phase N_{bx},[37] disclinations with integer Frank index were not observed. We note that topological considerations indicate that linear defects in N_{bx} can have a more complicated structure than in uniaxial nematic mesophases,[102] but this problem has not yet been studied in detail experimentally.

f) Relaxation processes in lyotropic nematics

The investigation of the dynamic properties of LN at the present time is only beginning. Of the five coefficients of viscosity, which, as is well known,[6-8] enter into the equations of nematodynamics, data are available only for the coefficient of rotational viscosity γ_1, measured for solutions of several compositions by Fujiwara and Reeves[103] (N_C) and Haven et al.[100] (N_D).

Fujiwara and Reeves[103] investigated the reorientation of the director in an external magnetic field, described by the equation[6]

$$-\gamma_1 \dot{\theta} = \frac{1}{2} \chi_a H^2 \sin 2\theta, \quad (55')$$

where θ is the angle between n and the direction of the field H. Measurements of the angle θ as a function of

time from NMR data, performed in Ref. 103, gave the following values for the N_C phases: $\chi_a/\gamma_1 = 5.89 \cdot 10^{-13}$ $s \cdot cm^{-2}$ for $D_2O/KL/KCl$ (64, 56; 33, 22; 2, 21) and $\chi_a/\gamma_1 = 1.80 \cdot 10^{-12}$ $s \cdot cm^{-2}$ for $D_2O/LaC_{10}/Na_2SO_4$ (55, 69; 39, 77; 4, 54), where the numbers in parentheses indicate the weights of the corresponding components. From the data presented, for $\chi_a \sim 10^{-8}$, we obtain $\gamma_1 \sim 10^4$ poise. The value of γ_1, obtained in Ref. 100 in the N_D nematic phase from investigations of the dynamics of the Frederiks transition, is much smaller: $\gamma_1 \sim 1$ poise.

The appearance of convective instability in the N_C phase (40.5% NaC_{10}, 7.1% decanol, and 52.4% water), accompanying the application of an external magnetic field perpendicular to the initial direction of the director of the planar texture (Fig. 24), was observed in Ref. 104. As a result of the instability, vortex motions arise in the nematic layer; the size of the vortices in a field $H = 15$ kG is about 80 μm along the y axis and is independent of the thickness of the specimen for $d > 100$ μm. The distance between the vortices in the x, z plane (see Fig. 24) equals the thickness of the specimen. We note that an analogous instability was investigated for thermotropic nematics.[105]

A superstructure in the spacing of DM in the N_D phase with a period of 10–20 μm was discovered in Ref. 106 (from the diffraction of helium-neon laser light). One possible reason for the appearance of this structure, as in Ref. 104, could be the convective instability of a nematic in a magnetic field.

The equations of hydrodynamics for biaxial nematics are discussed in Refs. 98 and 107–109.

In LLC, arising in solutions of AP molecules, the relaxation process (usually unimportant for thermotropic nematics) related to restructuring of the sizes of micelles to their equilibrium values, determined also by the local concentrations of the components of the system, could be important. The time for this process may be comparable to other characteristic relaxation times, for example, the reorientation time of the director on the application of a magnetic field. According to NMR data, obtained for dilute micellar solutions,[5,110] the order of magnitude of the restructuring time of micelles for amphiphiles such as SDS is about 1 s with $C = C^*$ and decreases rapidly as more amphiphile is added to the solution. For this reason, complete local equilibrium of all degrees of freedom may not be achieved, even in quite slow processes. The relaxation process indicated is especially important when concentration and temperature gradients are present in the system.
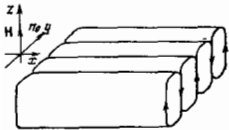

FIG. 24. Schematic diagram of convective flows initiated in a nematic by application of a magnetic field.[104]

5. LAMELLAR PHASES

a) Thermodynamics of formation of lamellar phases in solutions

Phenomenologically, the formation of a layered structure of lamellar phases (see Fig. 6) can be viewed as the appearance of a density wave in the spatial distribution of AP molecules[6,110]:

$$\rho(r) = \rho_0 + \rho_1 \cos q_0 z. \qquad (56)$$

In this expression, ρ_1 represents the modulus of the order parameter, differing from zero in the smectic phase. In lyotropic systems, the structural transition into the L_α phase could be initiated by a change in the temperature as well as by a change in the composition of the solution (see, for example, Figs. 3, 4, 7, 8, 14, and 17). From purely symmetry considerations,[6,68] it follows that the appearance of the wave (56) could be due to a second-order phase transition. However, the interaction of the order parameter ρ_1 with other degrees of freedom, for example, with fluctuations of the director accompanying the transition $N_D \rightleftharpoons L_\alpha$,[62,112,113] leads to a first-order transition. On experimental phase diagrams, the region of the L_α phase is usually separated from the isotropic solution or LN by a two-phase region.

X-ray diffraction and NMR data show[36] that near the transition into the L_α phase, the size of micelles in an I_D, N_D solution increases. Thus, in a N_D nematic, near an interface with I_D, the diameter of DM is $D = 300–500$ Å, while as the L_α region is approached, the diameter reaches approximately 2000 Å. In observations under a polarizing microscope, embryos of the lamellar phase ("small bars") are visible near the interface between the phases $I_D–L_\alpha$ in an isotropic solution. The growth of micelles leads to an increase in Frank's modulus K_3 (Fig. 23)[100] and, probably, K_2, as occurs in the case of thermotropic nematics.[6,7]

The thermodynamic potential of an inhomogeneous weak solution of rigid anisotropic particles has the form [compare (26)]

$$\Phi = N\mu_L + T \int do_a \int d^3r \rho(r, a) \ln \frac{\rho(r, a)}{eN}$$
$$+ \frac{1}{2N} \int d^3r \int d^3r' \int do_a \int do_{a'} \rho(r, a) \rho(r' a') u(r-r', a, a'), \qquad (57)$$

where $\rho(r, a)$ is the density of particles (cm^{-3}), whose distinguished axis is oriented along the unit vector a, and $u(r - r', a, a')$ is the correlation function of the uniform solution. Expression (57) corresponds to the assumption, usually made in the Kirkwood-Monroe theory of crystallization,[114,115] that the lamellar phase forms via a first-order phase transition, close to a second-order transition (the jump in ρ_1 at the transition point is small). In this case, the magnitude of the wave vector q_0 in (56) is determined from the condition that the Fourier component of the correlation function

$$u(q, a, a') = \frac{1}{V} \int d^3r e^{-iqr} u(r, a, a')$$

is maximum. As also in the analysis of the transition I–N, we shall represent the expression for $u(r, a, a')$ in the form of an expansion in $\cos(mq_0 z)$ and $P_l(a \cdot a')$ and we shall retain only the first few terms of the series

[compare (27)]:

$$u(\mathbf{r}, \mathbf{a}, \mathbf{a}') \approx u_0 + u_1 \cos q_0 z P_2(\mathbf{aa}') + u_2 P_2(\mathbf{aa}'); \qquad (58)$$

where, $u_{0,1,2}$ are functions of the coordinates. Minimizing (57) keeping the number of particles fixed, we obtain

$$\rho(z, \mathbf{a}) = A \exp\left[-\frac{1}{T} V(z, \mathbf{a})\right], \qquad A = \text{const}, \qquad (59)$$

where the self-consistent potential acting on a particle at the point $\mathbf{r}$, taking (56) and (58) into account, has the form

$$V(z, \mathbf{a}) = \frac{1}{N} \int d\mathbf{o_a} \int d^3 r' \rho(r'_a a') u(\mathbf{r} - \mathbf{r'}, \mathbf{aa'})$$
$$\approx c \left[U_0 + U_2 s P_2(\mathbf{an}) + U_3 \sigma \cos q_0 z\right]. \qquad (60)$$

Here, s is Tsvetkov's parameter

$$s = \langle P_2(\mathbf{an})\rangle \qquad (61)$$

and σ is the MacMillan parameter, describing the appearance of the density wave:

$$\sigma = \langle P_2(\mathbf{an})\cos q_0 z\rangle. \qquad (62)$$

Expressions (59)–(62), obtained in Refs. 111 and 116, for $U_{2,3} < 0$, describe both the nematic–smectic transition and the nematic–isotropic-solution transition. Figure 25 shows the phase diagram of a solution of rigid anisotropic particles in the $(\tilde{\alpha}, T)$ plane, where $\tilde{\alpha} = U_3 / U_2$, obtained as a result of a numerical solution of Eqs. (59)–(62). If it is assumed that $\tilde{\alpha}$ increases with increasing sizes of micelles, which is apparently valid near the triple point I_D-N_D-L_α, when the distance between CM is of the same order of magnitude as their diameter, then the phase diagram of the solution in the (T, c_t) plane will be qualitatively analogous to the diagram illustrated in Fig. 25.

In thermotropic LC, the quantity q_0 is determined only by the length of the molecules $q_0 = 2\pi / l_0$ and remains practically constant in the region of existence of the liquid-crystalline phases.[6,7] In LLC, in solutions of AP molecules, the period of the lamellar structure can increase with the addition of water to the system from several angstroms to several tens and hundreds of angstroms, depending on the type of AP substance. For this reason, the forces of interaction between micelles, which determine the period of the lamellar structure, must be discussed in greater detail.

b) Interactions of micelles in solutions

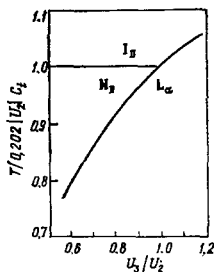The contributions of the following interactions between lamellae in solutions can be distinguished experi-

FIG. 25. Portion of the phase diagram of a solution near the triple point I_D-N_D-L_α.

mentally: van der Waals attraction of AP layers (F_{vdW}), repulsion of double electrical layers of plates (F_{DL}), and a specific interaction related to the distortion of the structure of the solvent in the gap between the lamellae (F_{ss}). The total repulsion force between AP plates per cm^2 is given by the sum

$$F = F_{vdW} + F_{DL} + F_{ss}. \qquad (63)$$

The van der Waals and electrostatic forces have been studied experimentally and theoretically for a long time, in particular, in connection with the problem of the stability of hydrophobic colloids[117,118] (see the somewhat more recent review in Ref. 119). The general method for calculating F_{vdW}, initially proposed by Lifshitz,[120] was later applied to bodies of different shapes[121-122]; for thick plates separated by a distance d_w, the following expression is obtained:

$$F_{vdw} = -\frac{A}{6\pi d_w^3}, \qquad (64)$$

where A is Hamaker's constant, which depends on the dielectric constants of the AP layers and of the solvent (in order of magnitude, $A \sim 10^{-13}$ erg). The magnitude of the electrostatic repulsion of double layers numerically equals the osmotic pressure of ions in a plane midway between the surfaces of the plates[123,117]:

$$F_{DL} = nT. \qquad (65)$$

The distribution of the potential in the gap is determined from Poisson's equation

$$\frac{d^2\psi}{dz^2} = -\frac{4\pi e n}{\varepsilon} e^{-e\psi/T} \qquad (66)$$

with the boundary condition[124]

$$n \int_0^{d_w/2} dz e^{-e\psi/T} = \frac{\alpha_i}{s_0}, \qquad (67)$$

from which the magnitude of the osmotic pressure (65) is determined. In (66) and (67), ε is the dielectric permittivity of the solvent, s_0 is the specific area per polar head of the amphiphile, and α_i is their degree of ionization. The dependence of α_i on the state of the solvent in the gap could play an important role.[125,126]

The solution of (66) and (67) has the form[124]

$$\psi = \frac{T}{e} \ln \cos^2 kx, \qquad k = \sqrt{\frac{2\pi n e^2}{\varepsilon T}}. \qquad (68)$$

The quantity n is determined from the relation

$$\frac{kd}{2} \text{tg} \frac{kd}{2} = \alpha_i \frac{n e^2 d}{\varepsilon T s_0} \qquad (69)$$

taking into account the expression for k (68).

The existence of the last term in (63) was discovered by Parsegian et al. in experiments on swelling of lamellar phases of lecithin in a water solution of dexstran (polymer), coils of which with a diameter of about 40 Å do not penetrate into the gap between the lamellae, and their presence therefore affects only the osmotic pressure of the solution.[127,128,124] By measuring the osmotic pressure of the polymer solution that balances the repulsive force of the layers (63), it is possible to find the dependence of F_{ss} on the gap size. According to Refs. 127, 128, and 124, this dependence can be approximated by the expression

$$F_{ss} = F_0 e^{-d_w/a}, \quad F_0 = 1,0 \cdot 10^{11} \text{ dynes/cm}^2, \qquad (70)$$
$$a = 1,93 \text{ Å}.$$

Later on, the existence of a contribution to the interaction between bodies depending on the structure of the solvent was confirmed by direct measurements of the force of repulsion of mica plates by Izraelcehvili *et al.*[129-132] It was demonstrated in Ref. 130 that as the gap size changes, the interaction force acting between the plates oscillates with a period that approximately equals the diameter of the solvent molecule (Fig. 26). A review of research related to the measurement of F_{ss} can be found in Ref. 132.

We note that the qualitative difference between the results in Refs. 127 and 129 is apparently not accidental, but is related to the difference in the orienting effect of crystalline aluminosilicate surfaces of mica and amorphous AP plates on the solvent: in the latter case, the oscillations in the pressure are "smeared" due to the translational and rotational motion of AP molecules in the bilayer.

The role of long-range forces in biological systems is discussed in Refs. 133 and 134.

Attempts have been made to analyze the "solvation" forces theoretically with the help of computer calculations using the Monte Carlo method.[135] In Refs. 136–139, the quantity F_{ss} was obtained from an analysis and subsequent numerical calculation of the equation for the correlation function of an inhomogeneous liquid.[140] The calculations yielded an oscillatory dependence of the force of interaction between two surfaces, the gap between which is filled with a liquid, on the whole analogous to Fig. 26. It should be noted, however, that the number of oscillations in these papers (usually 2–3) is appreciably smaller than the number observed experimentally (7–10). This could be related to the fact that under the conditions in Refs. 130–131, some pretransitional effects are manifested (growth in the correlation radius of the solvent), related to the proximity of the point of crystallization of the liquid $(T - T_c)/T_c \sim 0.1$). A phenomenological theory, within the framework of which this phenomenon can be taken into account, was proposed by Mercelja *et al.*[142] in connection with experiments performed by Parsegian *et al.* (see Ref. 126). In Ref. 142, it is proposed that the interaction between the solvent molecules and the polar heads of AP molecules of the lamellae gives rise to the appearance of some ordering of its structure, which can be described by an order parameter η. At a temperature above the point of the liquid-crystal phase transition, examined as a first-order transition close to a second-order transition, the Landau expansion for the
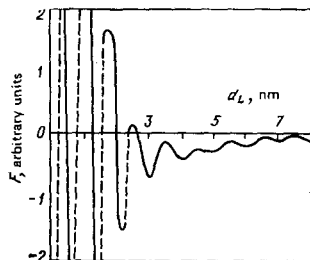

FIG. 26. Dependence of the force of interaction of two mica plates in the liquid $[(CH_3)_2SiO]_4$ on the gap size d_L.

free energy per cm² of area of the plates has the form

$$F = F_0 = \int_{-d_w/2}^{d_w/2} dx \left[\tilde{c} \left(\frac{d}{dx} \eta \right)^2 + \tilde{a} \eta^2 + \dots \right]. \quad (71)$$

The orienting action of the plates in this model is given by the boundary conditions

$$\eta \left(x = \frac{d_w}{2} \right) = -\eta \left(x = -\frac{d_w}{2} \right) = \eta_0. \quad (72)$$

Minimizing (71) and applying (72), we obtain

$$\eta(x) = \eta_0 \frac{sh(x/\xi_0)}{sh(d_w/2\xi_0)}, \quad F_{ss} = \frac{\tilde{a} \eta_0^2}{sh^2(d_w/2\xi_0)}, \quad \xi_0^2 = \frac{\tilde{c}}{\tilde{a}}. \quad (73)$$

It follows from this expression that near T_c, when the coefficient $\tilde{a}$ is small, the range of the solvation forces can increase considerably. In Ref. 142, the parameter η is interpreted within the framework of a molecular field theory, which is a generalization of Pople's model of the structure of water,[143] as a quantity proportional to the excess electrical polarization of the liquid in the gap.[8]

One of the internal inadequacies of the model[141,142] is the impossibility of explaining the oscillatory dependence of the pressure on the gap size and, what is more important, the absence of a transition from the hydrophilic to the hydrophobic surface of the plates. Indeed, the sign of the "solvation" interaction forces acting between hydrophobic surfaces in water, in contrast to hydrophilic surfaces, corresponds to attraction (for references and a discussion see, for example, Ref. 144), while the expression for F_{ss} (75) with $\tilde{a} > 0$, i.e. $T > T_c$, is always positive.[9] This disagreement can be eliminated if the entrainment of water into the region of the polar heads is taken into account explicitly.[126] We write the expression for the free energy of the solvent for $T \gtrsim T_c$ in the form

$$F = F_0 + \frac{1}{2} \int d^3r \int d^3r' \tilde{\rho}(r) K(r, r') \tilde{\rho}(r') + \int d^3r \varphi(r) \tilde{\rho}(r), \quad (74)$$

in which $\tilde{\rho}(r)$ represents the fluctuation of the density of the liquid and $\varphi(r)$ is the excess potential in which the water molecules in the gap between the plates are located. Minimizing (74), we obtain the equation

$$\int d^3r K(r, r') \tilde{\rho}(r') = -\varphi(r),$$
$$\tilde{\rho}(r) = -\int d^3r' K^{-1}(r, r') \varphi(r'). \quad (75)$$

It is convenient to separate explicitly the correlation function of the homogeneous liquid $-v(r - r')$ out of the expression for $K(r, r')$, after which the equation for $\tilde{\rho}(r)$ assumes the form

$$-\int d^3r' v(r - r') \tilde{\rho}(r') + \frac{T}{\rho_0} \tilde{\rho}(r) + \int d^3r' \varphi(r, r') \tilde{\rho}(r) = \varphi(r). \quad (75a)$$

In this expression, the last term on the left side differs from zero only in the region of the polar heads of AP molecules. We shall express the free energy of the liquid (74) in terms of the eigenvalues and eigenfunctions of the operator K:

$$F = F_0 - \frac{1}{2} \sum_n \frac{(\varphi \mid \psi_n)^2}{\lambda_n},$$
$$-\int d^3r' v(r - r') \psi_n(r') + \frac{T}{\rho_0} \psi_n(r) + \int d^3r \varphi(r, r') \psi_n(r') = \frac{\lambda_n}{\rho_0} \psi_n. \quad (76)$$

---

[8] An analogous interpretation of the order parameter was used in calculations of the solvation forces in Ref. 202.

[9] The force of attraction of hydrophobic surfaces in a polar solvent was recently measured directly by J. Israelachvili and P. Pashley.[203]

Near the point of crystallization of the liquid, the correlation function $v(q)$ has a sharp peak at $|q_x| = |q_y| = |q_z| = q_0$, where $2\pi/q_0$ is the period of the crystal lattice of the solvent for $T \lesssim T_c$. Substituting into (76) ψ_n in the form

$$\psi_n(\mathbf{r}) = \psi_n(x)\cos(q_0 y)\cos(q_0 z),$$

we obtain for $\psi_n(x)$ the equation

$$-\xi_0^2\left(\frac{d}{dz} - q_0\right)^2\psi_n(x) + \int dx' u(x, x')\psi_n(x') = \frac{\lambda_n - T + T_c}{T_c}\psi_n, \quad (77)$$

where we have used the relations

$$T - \rho_0 v(q)\,|_{q_y=q_z=q_0} \approx T_c\left[\frac{T-T_c}{T_c} + \xi_0^2(q_0 - q_x)^2\right],$$

$$u(x, x') = \frac{\rho_0}{T_c}\int dy \int dz \int dy' \int dz'\cos q_0 y\cos q_0 z\varphi(r, r')\cos q_0 y'\cos q_0 z'.$$

The integral term in (77) is negative near hydrophilic surfaces of AP plates, which corresponds to entrainment of water into the region of the polar heads of the amphiphiles, so that Eq. (77) can have solutions that are localized near the lamellae (analog of discrete levels in quantum mechanics, for example, in a Morse potential[89]). It is natural to interpret this part of the density of the liquid as "bound" water, which is the source of the NMR signal[1-3] of LLC (see Sec. 4b). If the magnitude of the last term in (77) is sufficiently large, then it is possible for the lowest eigenvalue λ_0 of the operator K to vanish, which corresponds to the point of crystallization of "bound" water.

We shall examine the case when (77) has only one discrete level with $\lambda_0 > 0$. The eigenfunction $\psi_0(x)$ at large distances from the AP plate has the following asymptotic behavior:

$$\psi_0(x) = \psi_0\cos(q_0 x)\exp\left(-\frac{x}{\xi_0}\sqrt{\frac{T-T_c-\lambda_0}{T_c}}\right). \quad (78)$$

The correction to the eigenvalue λ_0 related to the presence of a second surface situated at a distance d_w from the first one equals

$$\lambda_0(d_w) - \lambda_0(\infty) \approx 2T_c\langle\psi_0(x)\,|\,u(x, x')\,|\,\psi_0(d_w - x)\rangle$$

$$\approx 2T_c\psi_0\int dx\int dx'\psi_0(x)u(x, x')\cos q_0(d_w - x)$$

$$\times \exp\left(-\frac{d_w - x}{\xi_0}\sqrt{\frac{T-T_c-\lambda_0}{T_c}}\right). \quad (79)$$

Substituting (79) into (76) and differentiating with respect to d_w, we obtain an expression for the "solvation" component of the force

$$F_{\mathrm{CP}} = -\frac{\partial}{\partial d_w}\left\{\frac{\psi_0^2}{\lambda_0^2}\langle\psi_0\,|\,\varphi\rangle^2\exp\left(-\frac{2d_w}{\xi_0}\sqrt{\frac{T-T_c-\lambda_0}{T_c}}\right)\right.$$

$$\times \int dx\int dx' u(x, x')\cos q_0(x - d_w)\cos q_0(x' - d_w)$$

$$\left.\times \exp\left(\frac{x+x'}{\xi_0}\sqrt{\frac{T-T_c-\lambda_0}{T_c}}\right)\right\}, \quad (80)$$

which under the condition $\int dx\int dx'u(x,x')\psi_0(x)\cos q_0(d_w - x) < 0$ corresponds to repulsion between two hydrophilic surfaces.

c) Characteristics of swelling of lamellar phases. Gels

When water is added to a lamellar phase of LLC, two limiting cases of swelling are distinguished experimentally[145]:

1) All the added solvent penetrates into the space between the polar heads of AP molecules, increasing the specific area s_0 of the amphiphile. The period of the lamellar structure in this case remains approximately constant (Fig. 27a).

2) The value of d, proportional to the amount of added water, increases with the specific area per polar head remaining constant (Fig. 27b).

Intermediate types of swelling of lyotropic smectics is also possible, as is a change in the type of swelling accompanying a change in the composition of the solution (for example, with the addition of a cosurfactant).

The first type of behavior is observed for AP substances such as soap (sodium, potassium, and other salts of fatty acids), SDS, etc.[1,146] For LLC in solutions of these substances, there is a maximum amount of water, corresponding to a water gap between lamellae 15–20 Å thick, that can be pulled into the region of the polar heads of AP molecules. As this value is exceeded, the L_α phase goes over into an isotropic solution I_D or into a nematic N_D. With the addition of water, the specific area per polar head varies in the range from 25–30 to 40 Å² (in this case, the thickness of the lamellae decreases and the water gap increases in such a way that the total period of the lamellar structure of LLC remains constant).

Gel phases arising in solutions of such amphiphiles as monoglycerides (Fig. 28) also exhibit limited swelling. As the temperature decreases, the gel goes over into a crystalline state; in this case, the specimen may be both free of water entirely or contain some water.[27]

Substances such as AOT, monopalmitin, and others[1] exhibit the second type of swelling. The specific area per AOT molecule in the bilayer at 20 °C constitutes $s_0 = 68$ Å² and remains practically constant with the water content in the specimen varying from 25 to 80% (see Fig. 28).

Qualitatively, the nature of the swelling does not depend on the length of the fatty tail in the homologous series of the given substance, but is determined only by the shape of the polar head of the AP molecule. By adding a third substance (usually an amphiphilic substance[1]) to a two-component system exhibiting type 1 swelling, it is possible to obtain a lamellar phase that exhibits unlimited swelling. In this case, the necessary
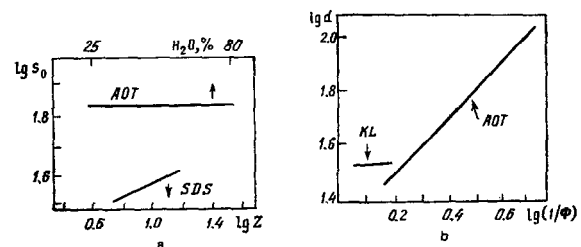
FIG. 27. Dependence of the area per polar head of the amphiphile on the water content of the specimen (a) (Z is the number of moles of water per mole of SDS) and of the period of the lamellar structure (b) of the L_α phase on the volume fraction of the amphiphile Φ.[1,146]
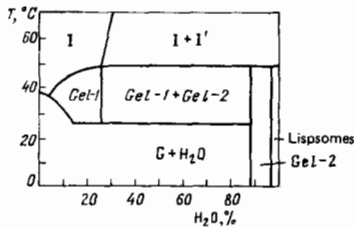
FIG. 28. Phase diagram of the tetradecylamine/water system.[27]

FIG. 30. Limited swelling of a monoglyceride gel with pH = 7 (1), unlimited swelling of the gel on addition of 1/60 part of sodium stearate (2).[27]

conditions for such a transition are: a) appearance of an interlayer of "unbound" water and b) weakening of the bond between the cations Na^+, K^+ and so on and the residues of the fatty acids.[1] The first of these conditions is checked by measuring the vapor pressure of water as a function, for example, of the alcohol content in the system (Fig. 29a). For a decanol concentration corresponding to a transition to unlimited swelling of the L_α phase (Fig. 29b), the vapor pressure rapidly approaches a value corresponding to the pure solvent. The second condition can be checked by measuring the width of the NMR line of the appropriate cations.[1,147] This same method can be used to observe the weakening of the bond between water molecules and the surface of lamellae at the time of the transition to unlimited swelling.[1,146]

The transition to unlimited swelling can also be initiated by the addition of a small amount of easily ionizable amphiphile, for example, soap, to the system (Fig. 30).[27]

A simple model of the characteristics of swelling of the lamellar phases of LLC is proposed in Ref. 125. We write the osmotic pressure of ions (65) in the form

$$nT = \frac{\alpha_i NT}{d_w}, \tag{81}$$

where N is the density of ions on the plates and α_i is the degree of dissociation. As the simplest assumption about the dependence $\alpha_i(d_w)$ we shall examine a model in which α_i decreases linearly with increasing average (over the water gap) order parameter:

$$\alpha_i = \alpha_0 - c_1 \bar\psi_0, \quad \psi_0 = \frac{1}{d_w} \int_{-d_w/2}^{d_w/2} dx\, \psi_0(x), \tag{82}$$

where [compare (78)]

$$\psi_0(x) \approx \psi_0 \frac{ch(x/\xi)}{ch(d_w/2\xi)}, \quad \xi = \xi_0 \left(\frac{T-T_c-\lambda_0}{T_c}\right)^{-1/2}. \tag{83}$$
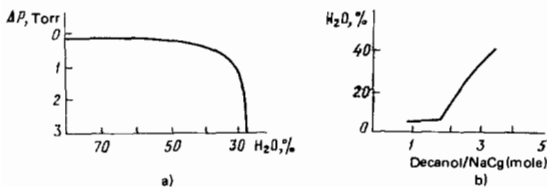
Substituting (83) into (82), we obtain

FIG. 29. Dependence of the osmotic pressure of the solution of sodium caprylate/decanol/water on the water content (a) and the dependence of the limiting content of the solvent in the L phase on the number of moles of decanol per mole of sodium caprylate (b).[1]
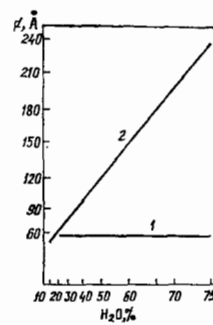
$$\alpha = \alpha_1 + c_1 \left[1 - \left(\frac{2\xi}{d_w}\right) th \left(\frac{d_w}{2\xi}\right) \right]. \tag{84}$$

In the model being examined, $\psi_0(x)$ (83) describes the ordering of the free water (outside the region of the polar heads of the AP layer), arising as a result of the interaction of the solvent with the surface of the micelles. Substituting (84), (81), (70), (65), and (64) into (63), we obtain an equation relating the equilibrium value of the thickness of the water gap d_w to the osmotic pressure of the external solution (or saturated vapor pressure) p':

$$\frac{NT}{d_w} \left[\alpha_0 + c_1 \left(1 - \frac{2\xi}{d_w} th \frac{d_w}{2\xi}\right) \right] + F_0 e^{-d_w/\xi} - \frac{A}{6\pi d_w^3} = p'. \tag{85}$$

This dependence is illustrated schematically in Fig. 31. The "shelves" on this curve are drawn in accordance with Maxwell's rule of areas. The nonuniqueness of the dependence $d_w(p')$ (85) for small d_w is related to the dependence of the degree of ionization of the polar heads on the order parameter in the water gap (84). As the osmotic pressure decreases, for values $p' = p_1'$, a phase transition occurs between the "quasicrystalline" and "liquid-crystalline" states. Inclusion of the oscillations of the pressure F_{ss} (Fig. 26) leads to the possibility of the existence of several "quasicrystalline" phases for $p' = p_1'$, differing by the water content.[125,126] With the addition of water, i.e., with $p' < p_1'$, two cases are encountered. If the first term in (85) is sufficiently small ($N < N_c$), then with $p' = p_2'$ a phase transition occurs, as a result of which a mesophase is formed with a high water content, for example, I_D or N_D[10] (shown by the dashed line in Fig. 31). For large N ($N > N_c$), the swell-
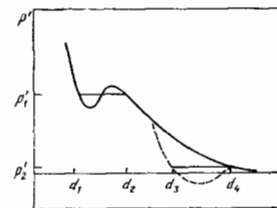

FIG. 31. Theoretical curve of the dependence of the osmotic pressure of water in the L phase on the period of the lamellar structure.

[10]According to Ekwall,[1] a lamellar mesophase of the type "B," whose properties and position on the phase diagram are close to the N_D nematic phase, can arise at this point.

ing will be continuous up to large magnitudes of the water gap d_w. The value of the parameter $N = N_c$ has a meaning analogous to the critical liquid-vapor temperature.

The quantity N can be changed by adding an ionic amphiphile[27] or alcohol, which weakens the strength of the bond between the cations and the bilayer.[1] Thus the model described above qualitatively describes many characteristics of swelling of LLC, observed experimentally.

Solidification of paraffin chains accompanying the formation of gels is usually accompanied by a decrease in the thickness of the lamellae and, correspondingly, an increase in the specific area per polar head.[24,149] This transformation, which has been widely investigated, in particular, in phospholipid membranes with an excess of water (vesicles), represents a collective phenomenon of a phase-transition type, which is manifested as an abrupt change in the thermodynamic functions of the system.[24,150,151] NMR data show[152] that cooperative tilting of the axes of molecules in a lamella occurs near the gel-formation point. A change in the pH of the solution, addition of inorganic salts, etc. have a considerable effect on the transition temperature.[153,154] For additional references concerning this problem see Refs. 97 and 155–159.

d) Structural defects. Permeation

In preparing specimens, different types of damage to the ideal packing of the lamellae—defects—appear in them. Some of the defects can be removed by the action of shear stresses, a magnetic field, etc. on the specimen; removal of the remaining defects requires displacement of macroscopic quantities of matter and, for this reason, they can exist practically indefinitely under normal conditions. A specimen with defects that have not been removed is in a metastable state. There is a profound relation between the characteristic remaining defects, arising in a liquid-crystalline phase, and the topological structure of the region of variation of the corresponding order parameter (in the case of a uniaxial nematic, for example, this region represents a sphere with unit radius with equivalent diametrically opposite points: the projective surface),[102,160–162] so that the study of the structure of defects in a specimen, for example, with the aid of an optical or an electron microscope,[163] is a convenient method for distinguishing LC phases. The textures of different mesophases are compared for LLC in Refs. 164 and 165 (see also Refs. 1, 4, 163, 166).

In the case of L phases, the period of the lamellar structure is determined by the conditions determining a minimum of the thermodynamic potential, so that the lowest energy will correspond to deformations of the structure for which the magnitude of the water gap is constant and equal to its equilibrium value (with the exception of some special lines). This condition is satisfied by edge dislocations and different confocal domains,[163] of which the simplest are myelin figures.[167] The energy of distortions, related to the formation of the latter, is discussed in Ref. 166 within the frame-

work of Helfrich's model.[168]

The presence of edge dislocations in L phases, of which there can be at least two types in lyotropic smectics (Fig. 32), leads to the formation of so-called Granjean terraces,[6] observed in optical and electron microscopes.[163] A technique for direct observation of dislocations in L phases is proposed in Ref. 169.

Distortions of the lamellar structure can appear at the point of gel formation $L_\alpha \rightleftharpoons L_\beta$. Indeed, the tilting of molecules in the L_β phase decreases the thickness and, therefore, increases the area of the lamellae. Since the time of the corresponding relaxation process is large, it may be expected that a Helfrich-Juro type wave-like deformation, observed in thermotropic smectics,[6] will occur. In lyotropic systems, such distortions have indeed been observed in studying the x-ray diffraction patterns and electron-microscope data.[22,151,164] A mechanism is proposed in Ref. 171 for the appearance of a two-dimensional inhomogeneous structure of phospholipid layers, caused by a cooperative tilting of the molecules in the lamellae. As a result, a two-dimensional monoclinic lattice is formed with two different periods, which corresponds to the data.[22,151] A simple model for the appearance of wave-like modulation, which is a generalization of the Marčelja and Radič approach[141] (see Sec. 5b) is examined in Ref. 172. An analogous transformation can occur in liposomes (bubbles of the type illustrated in Fig. 2f, but with a multilayered wall). In this case, an initially spherical aggregate assumes the form of a regular polygon: a dodecahedron or an icosahedron.[171] We note that liposomes in the form of dodecahedra have been observed experimentally.[170]

The structure of defects in lamellar phases of AP molecules depends greatly on the water content of the specimens. Thus, with a 24% water content in the L phase of lecithin, the texture of the specimen is observed to change sharply.[163] The coefficient of diffusion of ions changes sharply at the same point.[173,174] One reason for this behavior could be the dependence of the sizes of DM, forming the lamellar phase, on the concentration of AP substance and ions in the solution (see Secs. 3 and 4).

The investigation of nonequilibrium properties of LLC is only beginning.[174] We shall consider only the measurements of the so-called coefficient of permeation of the smectic λ_p in the L phase.[169] The concept of "permeation" was introduced by Helfrich[175] to describe transport of matter of smectic and cholesteric LC in which the spatial position of the layers and of the helices remains unchanged. By definition,[6] λ_p represents a kinetic coefficient, relating the macroscopic flow of matter accompanying deformation of the layered struc-
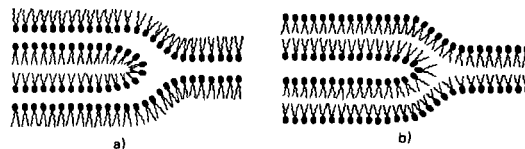

FIG. 32. Two types of edge dislocations in lyotropic smectics.[169]

ture:

$$\dot{u} - v_z = \lambda_p \left(C \frac{\partial \theta}{\partial z} + B \frac{\partial^2 u}{\partial z^2} \right), \quad \dot{\theta} + \frac{\partial v_z}{\partial z} = 0. \tag{86}$$

Here $\dot{u}$ is the rate of displacement of the layers in the direction of the normal, chosen along the z axis; v_z is the component of the macroscopic velocity; θ is the volume compression of the medium; and B and C are the moduli of elasticity; for more details see Ref. 6. The coefficient λ_p determines the damping decrement of the wave perturbations in the L phase with wave vector parallel to the z axis. For $\theta = 0$, we obtain from (86)

$$\frac{1}{\tau} = \lambda_p B q^2. \tag{87}$$

The relaxation process of "quenching" of dislocations in the lecithin–water system, which includes the coalescence of dislocation loops in the same gap between the lamellae, as well as the penetration of "excess" lamellae through infinite bilayers, was studied in Ref. 169. If it is assumed that it is precisely the latter process that determines the duration of the relaxation of a newly prepared specimen in a state with a regular system of edge dislocations with period d/φ, then, assuming in (87) $q \approx \pi/d$ and $\tau = 10^6$ s and using for the modulus of elasticity the value $B = 2 \cdot 10^{10}$ erg/cm^3 (Ref. 176), we obtain $\lambda_p = 10^{-30}$ cm^2/poise ($T = 37\,°C$). The characteristic permeation time is apparently determined by the process of exchange of AP molecules between lamellae in the case of the dislocations in Fig. 32a and by the "flip-flop" process (exchange of molecules between two layers of a single lamella) in the case of the dislocation in Fig. 32b.

6. HEXAGONAL AND SOME OTHER MESOPHASES. APPLICATIONS TO BIOLOGICAL SYSTEMS

a) Hexagonal and related phases

As the concentration of the solution containing CM increases, i.e., I_c or N_c, the latter usually transforms into a state in which the centers of gravity of the micelles are packed into a two-dimensional crystalline lattice, while the long axes of the micelles are oriented perpendicular to the plane of ordering.

The phases that are encountered most often among LLC with two-dimensional periodicity are the so-called hexagonal phases H_1 and H_2 (see Fig. 3, 4, 7, 8, and others). LLC of the type H_1 are formed from CM with a circular cross section, packed into a two-dimensional hexagonal lattice (Fig. 5a). The presence of periodicity in the spatial distribution of micelles leads to the appearance of distinct Bragg reflections in the x-ray diffraction patterns, which is one of the main indications of this type of phase. In the optical range, H_1 is transparent and birefringent. The viscosity of H_1 phases is greater than the viscosity of cubic LLC and lower than the viscosity of lamellar phases: 20–45 poise.[11),1]

The volume fraction of amphiphile in solution for which hexagonal phases are formed is a decreasing function of the ratio of the axes of the CM, qualitatively analogous to that illustrated in Fig. 18. The phase transition I_c–H_1 occurs when the anisotropy parameter of the micelles L/D reaches some critical value, which corresponds to the theories of Flory or Meier-Saupe

(see Sec. 4). The extension of MacMillan's model[116] to the case of the appearance of two-dimensional ordering in a plane perpendicular to the direction of the long axes of CM can apparently give a more detailed picture of the behavior near the triple point I_c–N_c–H_1.

The critical value of the ratio L/D for CM is very sensitive to the degree of hydration of the polar heads of the AP molecules: the H_1 phase in a solution of cetyltrimethylammonium bromide arises for a volume fraction of the amphiphile $\varphi_N \approx 25\%$ and $L/D \sim 58$, while the micelles of cetyltrimethylammonium chloride remain practically spherical right up to the transition point with $\varphi_N \sim 40\%$.[1,177] A small deformation of spherical micelles is also observed in solutions of some nonionic amphiphiles. A model of the structure of the hexagonal phase, in which the anisotropic aggregates form chains consisting of several spherical micelles, is discussed in Ref. 178.

As the content of the solvent in the specimen increases, the period of the hexagonal lattice of H_1 increases and, in addition, in the region of highest water content, the distance between the cylinders increases approximately proportionately to the square root of the solvent concentration, which corresponds to swelling of LLC without a change in the CM structure. In this range of parameters in the specimen, in addition to water bound to the hydrophilic surfaces of the micelles, there is some "free" water.

The specific area per polar head of AP molecule on the surface of CM in the H_1 phase is smaller than the analogous quantity for spherical micelles and greater than for lamellae. Figure 33 shows the dependence of s on the water content of the specimen.[1,146] We note that the points corresponding to AP molecules with identical polar groups, fall on a single straight line independent of the length of the hydrocarbon tail. This circumstance corresponds to the fact, already mentioned in the preceding section, that the nature of the swelling of LLC is determined primarily by the structure of the polar heads of the AP molecules.

The hexagonal phases with inverted micelles H_2 in two-component solutions usually arise in cases when the amphiphile contains several fatty tails: for example, two hydrocarbon chains in the case of AOT (see Fig. 3) or four chains in the case of cardiolipin.[179] Although H_2 mesophases have not yet been studied adequately at the present time, the general characteristics of the swelling of the LLC being studied, on the whole,
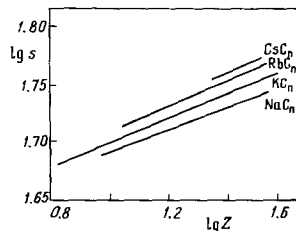

FIG. 33. Dependence of the specific area per the polar head of soaps in the H_1 phase on the water content (Z is the number of moles of water per mole of soap).[146]

correspond to the picture presented above. Namely, the period of the crystalline structure and the specific area per polar head of amphiphile decrease with increasing amphiphile concentration in the system.[1] The magnitude of the area s in H_2 is less than in the lamellar phase; for example, for AOT $s = 50-60$ Å^2, while in the L_α phase, $s = 86$ Å^2. The transition $L_\alpha \to H_2$ can be initiated by the addition to the system of ions binding easily to polar heads of the amphiphile and decreasing the degree of their hydration. In the case of cardiolipin, such ions are bivalent calcium ions.[179]

Hexagonal phases with inverted micelles can also arise in three-component solutions, containing, in addition to water and the amphiphile, a certain amount of cosurfactant, for example, decanol.[1]

At the present time, the important problem of the structure of the phases found in equilibrium with H_1 from the side of large concentrations of the amphiphile is not clear. Apparently, in the case of some nonionic amphiphiles,[178] such a phase could be a cubic phase, formed by weakly deformed spherical micelles packed into a face-centered lattice. For ionic AP substances such as soaps, the structure illustrated in Fig. 9b[29] or Scriven's[30] bicontinuous model, which is close to it, is more likely.

b) Cholesterics

Helical twisting of the director, arising in solutions of rigid chiral particles, has been most completely studied at the present time for synthetic PBG polypeptides.[11,180] There are only several papers concerning solutions of AP molecules with a cholestric superstructure.

In a lyotropic system, a cholosteric mesophase can be obtained either by dissolving chiral molecules in a nematic[39] or by using a nonracemic mixture of levo- and dextrorotary AP molecules.[40] According to the number of nematic mesophases, three types of cholestrices can, in principle, exist: N_c^*, N_D^*, and N_{bx}^*, of which the first two have been obtained experimentally in solutions of a certain composition.[34,36,39-41]

In the case of cholesterics of the type N_c^*, the magnitude of the optical rotation can apparently be calculated in a model developed in Ref. 181 for solutions of PBG polymers (a review of other theories for the appearance of cholesteric ordering in liquid crystals is given in Ref. 182). In this model, the helical twisting of the director is due to the long-range van der Waals forces, whose magnitude, as is well known,[120-122] is expressed in terms of the permittivities of the solvent and of the solute. Chiral molecules added to the micellar solution are dissolved in the hydrocarbon nuclei of the micelles, the symmetry of their susceptibilities relative to mirror reflections is lost, and the form of CM is probably distorted. Within the framework of the model in Ref. 181, solutions containing CM not having the indicated element of symmetry differ only quantitatively from solutions containing PBG type molecules.

The distortions of the structure of CM, caused by the addition of chiral molecules to the system, have not

been studied experimentally. The textures of the N_c^* mesophases are analogous to the textures of PBG solutions.[39] It is demonstrated in Ref. 40 that the cholesteric helix of a N_c^* specimen can be untwisted in an external magnetic field.

The structure of N_D^* cholesterics is apparently most similar to chiral smectics arising in thermotropic systems.[6] In this case, the most probable reason for the helical twisting of the field of the director (normal to DM) is the appearance of a screw distortion of DM, caused by the addition of chiral molecules. In contrast to thermotropic smectics, such a deformation is allowed in N_D^* due to the finite dimensions of DM.

Similar to the manner in which a change in the composition of a solution can lead to the structural transformation $N_c \rightleftharpoons N_D$ (see Sec. 4), the addition of a certain amount of cosurfactant to a N_c^* mesophase gives rise to the formation of a LLC of the type N_D^*.[34]

Data are not presently available on the appearance of a helical structure in other types of LLC, for example, in lamellar or hexagonal phases.

c) Three-component water-amphiphile-oil systems. Microemulsions

When a small amount of hydrophobic substance, such as oil, is added to a micellar solution, the molecules of the hydrophobic substance are distributed in the hydrocarbon nuclei of the micelles, i.e., they are solubilized. There is an extensive literature, reviewed in Ref. 183, on this process, which is of great importance in different applications. We shall discuss only the results of some experimental work on the phenomenon of inversion of microemulsions, studied in detail by Shinoda, Friberg, and others.[93,184-188]

With solubilization of oil, the radius of the micelles increases, reaching in some cases several hundreds of angstroms.[167] Micellar solutions, in this case, are called microemulsions, following MacBain. The capability of micelles to swell in oil is usually limited and when some critical concentration is reached, the latter separates in the form of a separate phase. The radius of the micelles, corresponding to this value of the concentration, can be estimated from a model analogous to that examined in Sec. 3c. In particular, we shall represent a micelle in the form of a spherical drop of oil, whose surface is covered by a single layer of amphiphile. The surface area of the water-amphiphile interface, per polar head $s_{w/s}$, is determined from the condition that the free energy of interaction of the amphiphile with the water be minimum, while the specific area of an AP molecule $s_{o/s}$ on the amphiphile-oil interface minimizes the energy of interaction of the surfactant with the oil. The quantities $s_{w/s}$ and $s_{o/s}$ depend on the temperature and composition of the solution, and their ratio characterizes the so-called hydrophilic-lipophilic balance of the given AP substance. Since, in general, $s_{w/s} \neq s_{o/s}$, the radius of curvature of the micelle surface must be finite. Assuming that the dimensions of the polar and nonpolar parts of the molecule are approximately equal, which is valid for a number of

nonionic amphiphiles of the type $C_{12}E_6$, we obtain the limiting value of the radius of a micelle

$$R \approx \frac{\sqrt{s_{o/s}} + \sqrt{s_{w/s}}}{\sqrt{s_{w/s}} - \sqrt{s_{o/s}}} l_0, \qquad (88)$$

where l_0 is the total length of the AP molecule. The quantity $\sqrt{s_{w/s}} - \sqrt{s_{o/s}}$ depends on the temperature and composition of the solution and, for some values of the parameters, its sign can change. In this case, the sign of the curvature of the micelle surface changes, i.e. a transformation of the emulsion of the type O/w → w/O occurs ("oil in water"–"water in oil"). In the work by Shinoda et al.,[184-186] the inversion of the emulsion occurred at some critical temperature, called the phase inversion temperature, (T_{pl}). Near this temperature, the turbidity of the solution increases sharply and the phenomenon of critical opalescence can be observed.[189,190] The appearance of liquid-crystalline phases, one of which (the anisotropic phase) is lamellar with alternating layers of oil, amphiphile, and water, while the second is optically isotropic, was observed in a narrow temperature range near T_{pl}. The conditions for the appearance of these phases and their structural models are discussed in Ref. 187.

In the first papers of Shinoda et al., nonionic AP substances with polyoxyethylene polar heads, whose interaction with water has a number of specific characteristics related to the structure of the polar groups, were used. However, in later work by Shinoda, Friberg, et al., the inversion of the emulsions was observed in solutions of other amphiphiles,[93,188] for example, in the system $C_8NH_3Cl/C_8NH_2/H_2O$/oxylene (Fig. 34). In Ref. 188, it is also reported that the behavior of a solution analogous to Ref. 34 was observed with the addition of alcohol and salt to the SDS/water system. These facts establish a relation between the properties of the ionic and nonionic substances.

d) Liquid crystals in biology

As already mentioned in the introduction, the interest in liquid-crystalline structures arising in solutions of AP molecules is related primarily to biological applications. It was noted a long time ago that the molecular organization of many organelles inside cells and living tissue of organisms is close to the structure of liquid crystals: smectics, cholesterics, and others.[2,4,191]
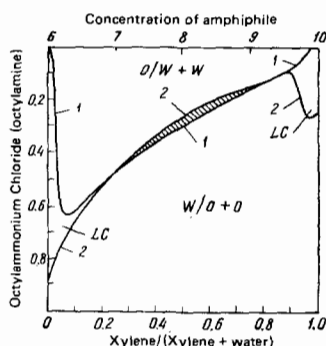

FIG. 34. Phase diagram of a solution of octylammonium chloride/octylamine/water/xylene.[188] The shaded area is the three-phase region.

Moreover, the term "liquid crystal" itself was introduced in connection with investigations of the optical properties of the cholesterol ether, a substance of biological origin.

In recent years, the self-assembly of different biological structures has been studied intensively[192]; here, the term "self-assembly" reflects the fundamental fact that a number of supermolecular aggregates in living cells do not require the expenditure of energy for support of their existence, but arise spontaneously in solutions with an appropriate composition (at a certain temperature), similar to micelles in solutions of AP molecules (see Sec. 3). From this point of view, the formation of DM lamellae in solution represents a model of self-assembly of a lipid membrane, playing the most important role in the functioning of the organism.[193,194] The investigation of the physicochemical properties of artificial membranes and, in particular, their interaction with proteins,[95] which in living organisms catalyze biochemical reactions, plays an important role in the study of the activity of cells. A number of cellular organelles are organized according to the lamellar phases of LLC. These include, in particular, chloroplasts, mitochondria, and others.

As already indicated in Sec. 4a, nematic LLC can arise in solutions of rod-shaped particles of biological origin: MTV, DNA, and others. Buligan investigated the packing of DNA in chromosomes and he showed that the latter represents a drop of cholesteric liquid crystal and, in addition, the process of chromosome splitting in cell division is related to the motion of screw dislocations.[191]

An important direction in these investigations is the study of the appearance of liquid crystals in the human organism as a result of some diseases: artherosclerosis, cholelithiasis, and others.[4,196,197] For example, the appearance of artherosclerosis can be interpreted as resulting from the breakdown of metabolism, as a result of which the concentration of cholesterol in the cell membranes of blood vessels reaches a level at which the liquid-crystalline phase begins to separate out. The precipitation of stones in cholepithiasis has an analogous explanation.[196]

A possible relationship between the liquid-crystalline state of cell membranes and, in particular, phase transitions in them, which change the form of cells with the appearance of cancer is discussed in Ref. 198.

7. CONCLUSIONS

The existence of a variety of liquid-crystalline structures in solutions of amphiphilic molecules, described above, is ultimately related to the appearance of two parts with very different properties—hydrophilic and lipophilic—in the makeup of AP molecules. To emphasize this property, AP molecules are also called diphilic. In principle, it is possible to obtain substances whose molecules contain a large number of different sections, for example, block copolymers with three and more blocks per chain. The appearance of liquid-crystalline phases (cubic, hexagonal, and lamellar) can

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likewise be observed in solutions of block copoly-mers.[199] The limiting case of this class of substances are copolymers, each link of which has a definite de-gree of solubility in water and oil—proteins. In living organisms, proteins are constructed from twenty "canonical" amino acids, whose sequence in the chain is determined genetically. The properties of amino acids vary from extremely hydrophilic to hydrophobic, including intermediate cases. For this reason, a pro-tein placed in a water solution forms a configuration that ensures minimum contact of the hydrophobic amino acids with the water and, in addition, a rearrangement or replacement of even one amino acid can lead to a change in this configuration or, as it is said, to a ter-tiary structure of the protein and a change in its cataly-tic properties. The investigation of these and other properties of proteins in solutions is an extremely com-plicated and biologically important problem, which must be solved in order to understand and control the vital processes occurring in living organisms.

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