TABLE V: NaTDC Molality, m (mol kg⁻¹), the Relaxation Frequency, f_r (MHz), the Relaxation Amplitude, $10^{17}A$ (cm⁻¹ s²), and the Ultrasonic Absorption at Infinite Frequency, $10^{17}B$ (cm⁻¹ s²), of the High-Frequency Relaxation Processes

m	25 °C			35 °C			45 °C		
	f_r	$10^{17}A$	$10^{17}B$	f_r	$10^{17}A$	$10^{17}B$	f_r	$10^{17}A$	$10^{17}B$
0.1007	105	42	23	145	30	20	190	24	16
0.2566	75	110	30	85	85	27	100	67	25
0.3007	70	150	32	80	124	30	90	100	28
0.4089	50	260	38	60	230	35	68	167	33

Figure 8. Dependence of the ultrasonic absorption coefficient, α/f^2 (cm⁻¹ s²), on the NaTDC molality, m , at 25 (●) 35 (▲), and 45 °C (■) at 15 MHz.

become more marked in the less concentrated solutions.

The asymmetry of the curves $\mu_{\text{exc}} = \mu - \mu_B$ vs. $\log f$, Figure 7, is further evidence that several kinetic processes play a role in the ultrasonic absorption of these bile salt solutions.

One process, with f_r lower than 15 MHz, occurs at lower frequency with higher surfactant concentration and could be related with the change of primary micelles into flexible superaggregates via hydrogen bonds²² or via hydrophobic interactions.²³

Other processes, with f_r higher than 50 MHz, should be ascribed to reactions between dispersed monomers, S, and aggregates, S_n:

An analysis, by eq 7, of the ultrasonic results in the range 50–300 MHz gave relaxation frequencies decreasing as the surfactant concentration increases (Table V). This feature is inconsistent with bimolecular reactions 8 and could be a strong indication that several overlapping processes, with relaxation times close each other, are responsible for the ultrasonic absorption above 50 MHz.

The dependence of sound absorption on the composition of the solutions does not seem monotonic (Figure 8). For instance, at 15 MHz, plots of α/f^2 against molality show an inflection at about 0.3 mol kg⁻¹. Although the experimental points are too few to draw any quantitative conclusion, however, the phenomenon, with some differences, is evident at each temperature; moreover, it occurs in the same critical range of concentrations observed for viscometric anomalies, i.e., where rodlike micelles are supposed to exist.

The hypothesis that inflections in the functions of $\alpha/f^2(m)$ could be related with aggregation changes of the solute was previously considered by Zana.²⁴

Registry No. Sodium taurodeoxycholate, 1180-95-6.

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Liquid Crystal Phase Transitions in a Solution of Rodlike and Disklike Particles

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The Onsager theory for the isotropic–anisotropic phase transition in a solution of rodlike particles is extended to solutions that contain a mixture of rodlike and disklike particles. Dependent on the total concentration of the particles and the fraction of rods and disks, one finds, in addition to the isotropic phase, two uniaxial nematic phases and a biaxial nematic phase.

I. Introduction

Zocher^{1–3} discovered that solutions of highly anisometric colloidal particles exceeding a critical concentration undergo an orientational order–disorder transition from an isotropic phase to an uniaxial lyotropic liquid crystal phase. Onsager⁴ first explained this phase transition as the result of the competition between the orientational entropy that favors disorder and the entropy effect associated with the orientation-dependent excluded volume of anisometric particles that favors order. Recently Yu and Saupe^{5,6} for the first time presented conclusive evidence for

the existence of a biaxial nematic phase. The system they studied consists of a mixture of surfactants (soap + long-chain alcohol) in water in which both rodlike and disklike micelles occur. Motivated by these experimental findings, we felt it worthwhile to extend the simple Onsager theory to solutions of rodlike and disklike particles to study the phase transitions in these systems. Dependent on the total concentration of the particles and the fraction of rods and disks a biaxial phase is indeed predicted to occur.

In section II the extension of the Onsager theory to solutions of rodlike and disklike particles is given. The predictions that follow from this theory for the concentrations, compositions, and

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order parameters of the isotropic–uniaxial and uniaxial–biaxial phase transition are presented in section III. Finally in section IV the present calculations are discussed and compared to related theories.

II. Onsager Theory for Liquid Crystal Phase Transitions in a Solution of Rodlike and Disklike Particles

The starting point of the Onsager theory⁴ for the phase separation in a solution of N long hard rods of length L and diameter D ($L \gg D$) is the Helmholtz free energy of the solution in dialytic equilibrium with the solvent at temperature T .

$$\frac{\Delta F}{Nk_B T} = \frac{F(\text{solution}) - F(\text{solvent})}{Nk_B T} = \frac{\mu^0(T, \mu_0)}{k_B T} - 1 + \ln c + \sigma(f) + bc\rho(f) \quad (1)$$

Here $\mu^0(T, \mu_0)$ represents the standard chemical potential of the particles at temperature T in a solvent with chemical potential μ_0 , $c = N/V$ is the number density, $b = (\pi/4)L^2D$ is the average excluded volume of two long rods with random orientations, and σ and ρ stand for the following functionals of the distribution function $f(\vec{a})$ of the axes $\vec{a}$ of the rodlike particles

$$\sigma(f) = \int f(\vec{a}) \ln 4\pi f(\vec{a}) d\Omega \quad (2)$$

$$\rho(f) = (4/\pi) \int \int \sin \gamma(\vec{a}, \vec{a}') f(\vec{a}) f(\vec{a}') d\Omega d\Omega' \quad (3)$$

Here $\gamma(\vec{a}, \vec{a}')$ is the angle between $\vec{a}$ and $\vec{a}'$. The free energy of the solution of thin hard disks with diameter D is given by exactly the same expression as (1) with now $b = (\pi^2/16)D^3$. Note that in the free energy (eq 1) concentration contributions of order c^2 and higher order have been neglected (second virial approximation). This approximation can be justified for long hard rods since for these systems $B_3/B_2^2 \ll 1$ (B_2 and B_3 are the second and third virial coefficient). As already noted by Onsager⁴ this is not the case for thin hard disks. Consequently, the approximation in the free energy (eq 1) will be more serious when applied to disks than to rods. This is made evident by a recent Monte Carlo study of a system of thin hard disks.⁷

The appropriate extension of the free energy (eq 1) to a solution of N_1 long hard rods of length L_1 and diameter D_1 ($L_1 \gg D_1$) and N_2 thin hard disks of length L_2 and diameter D_2 ($D_2 \gg L_2$) in dialytic equilibrium with the solvent at temperature T is given by

$$\frac{\Delta F}{Nk_B T} = \frac{F(\text{solution}) - F(\text{solvent})}{Nk_B T} = \frac{(1-x)\mu_1^0(T, \mu_0) + x\mu_2^0(T, \mu_0)}{k_B T} - 1 + \ln c + (1-x) \ln(1-x) + x \ln x + (1-x)\sigma_1 + x\sigma_2 + c\{(1-x)^2 b_{11}\rho_{11} + 2x(1-x)b_{12}\rho_{12} + x^2 b_{22}\rho_{22}\} \quad (4)$$

Here $N = N_1 + N_2$ is the total number of particles, $c = N/V$ is the total number density, $(1-x) = N_1/N$ is the fraction of rods, $x = N_2/N$ is the fraction of disks, μ_1^0 and μ_2^0 are the standard chemical potentials of the rods and the disks at temperature T in a solvent with chemical potential μ_0 , and b_{11} , b_{12} , and b_{22} are the average excluded volumes of two rods, a rod and a disk, and two disks with random orientations.

$$b_{11} = (\pi/4)D_1 L_1^2 \quad b_{12} = (\pi/16)L_1 D_2^2 \quad b_{22} = (\pi^2/16)D_2^3 \quad (5)$$

In the following we relate the various excluded volumes to b_{11} by using the notation

$$b_{11} = b \quad b_{12} = qb \quad b_{22} = rb \quad (6)$$

Figure 1. Orientation axes of the rodlike (a) and disklike (b) particles.

Finally, σ_j and ρ_{jk} stand for the following functionals of the distribution functions $f_1(\vec{a})$ and $f_2(\vec{a})$ of the axes $\vec{a}$ of the rods and disks (see Figure 1):

$$\sigma_j = \int f_j(\vec{a}) \ln 4\pi f_j(\vec{a}) d\Omega \quad j = 1, 2 \quad (7)$$

$$\rho_{jj} = (4/\pi) \int \int \sin \gamma(\vec{a}, \vec{a}') f_j(\vec{a}) f_j(\vec{a}') d\Omega d\Omega' \quad j = 1, 2 \quad (8)$$

$$\rho_{12} = 2 \int \int |\cos \gamma(\vec{a}, \vec{a}')| f_1(\vec{a}) f_2(\vec{a}') d\Omega d\Omega' \quad (9)$$

The orientational distribution functions $f_1(\vec{a})$ and $f_2(\vec{a})$ are determined by minimizing the free energy with respect to variations of these distribution functions. This leads to the following coupled integral equations:

$$\ln 4\pi f_1(\vec{a}) = C_1 - (8/\pi)bc(1-x) \int \sin \gamma(\vec{a}, \vec{a}') f_1(\vec{a}') d\Omega' - 4bqc \int |\cos \gamma(\vec{a}, \vec{a}')| f_2(\vec{a}') d\Omega'$$

$$\ln 4\pi f_2(\vec{a}) = C_2 - 4bqc(1-x) \int |\cos \gamma(\vec{a}, \vec{a}')| f_1(\vec{a}') d\Omega' - (8/\pi)brc \int \sin \gamma(\vec{a}, \vec{a}') f_2(\vec{a}') d\Omega' \quad (10)$$

where C_1 and C_2 are constants that are determined by applying the appropriate normalization conditions

$$\int f_j(\vec{a}) d\Omega = 1 \quad j = 1, 2 \quad (11)$$

Once the minimization problem has been solved, the compositions and concentrations of the coexisting phases are found by solving the coexistence conditions, i.e., the equality of the osmotic pressure Π and the chemical potentials μ_1 and μ_2 of the dissolved particles in the two coexisting phases:

$$\Pi = -(\partial \Delta F / \partial V)_{T, \mu_0, N_1, N_2} = k_B T c \{1 + c[(1-x)^2 b\rho_{11} + 2x(1-x)bq\rho_{12} + x^2 br\rho_{22}]\} \quad (12)$$

$$\mu_1 = (\partial \Delta F / \partial N_1)_{T, \mu_0, V, N_2} = \mu_1^0 + k_B T \times \{\ln c + \ln(1-x) + \sigma_1 + 2c[(1-x)b\rho_{11} + x bq\rho_{12}]\} \quad (13)$$

$$\mu_2 = (\partial \Delta F / \partial N_2)_{T, \mu_0, V, N_1} = \mu_2^0 + k_B T \{\ln c + \ln x + \sigma_2 + 2c[(1-x)bq\rho_{12} + x br\rho_{22}]\} \quad (14)$$

At this point it is convenient to introduce dimensionless variables. In the following c denotes the dimensionless concentration bc , Π the dimensionless osmotic pressure $b\Pi/(k_B T)$, and μ_j the dimensionless chemical potentials $[(\mu_j - \mu_j^0)/(k_B T)] + \ln b$. Using these dimensionless variables and taking into account that in the isotropic phase $\sigma_j = 0$ and $\rho_{jk} = 1$ we can write the coexistence

TABLE I: Characterization of the Isotropic and Various Liquid Crystal Phases

phase	symbol	α_{11}	α_{12}	α_{21}	α_{22}	S_1	Δ_1	S_2	Δ_2
isotropic	i	0	0	0	0	0	0	0	0
uniaxial nematic	n(+)	>0	0	<0	0	>0	0	<0	0
uniaxial nematic	n(-)	<0	0	>0	0	<0	0	>0	0
biaxial	bx	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$	$\neq 0$

equations between the isotropic phase (i) and an anisotropic liquid crystal phase (a) as

$$c_i\{1 + c_i[(1 - x_i)^2 + 2x_i(1 - x_i)q + x_i^2r]\} = c_a\{1 + c_a[(1 - x_a)^2\rho_{11} + 2x_a(1 - x_a)q\rho_{12} + x_a^2r\rho_{22}]\} \quad (15)$$

$$\ln c_i + \ln(1 - x_i) + 2c_i[(1 - x_i) + x_iq] = \ln c_a + \ln(1 - x_a) + \sigma_1 + 2c_a[(1 - x_a)\rho_{11} + x_aq\rho_{12}] \quad (16)$$

$$\ln c_i + \ln x_i + 2c_i[(1 - x_i)q + x_i r] = \ln c_a + \ln x_a + \sigma_2 + 2c_a[(1 - x_a)q\rho_{12} + x_a r\rho_{22}] \quad (17)$$

The functionals σ_j and ρ_{jk} are functions of x_a and c_a since through the minimization of the free energy the orientation distribution functions depend on x_a and c_a . Note that in the three coexistence equations there appear four intensive thermodynamic variables, x_i , c_i , x_a , and c_a . This means that one variable can be freely chosen (in the actual calculations we will take this to be x_i).

III. Evaluation of the Composition, Concentrations, and Order Parameters of the Liquid Crystal Phases

1. Characterization of the Different Liquid Crystal Phases.

A systematic way to solve the minimization problem of the free energy is to start from the coupled integral equations (eq 10) and expand the kernels $\sin \gamma$ and $|\cos \gamma|$ in Legendre polynomials. For symmetry reasons only even Legendre polynomials appear in this expansion. To simplify the calculations we limit these expansions to the P_2 term

$$\sin \gamma = (\pi/4) - (5\pi/32)P_2(\cos \gamma) + \dots \quad (18)$$

$$|\cos \gamma| = (1/2) + (5/8)P_2(\cos \gamma) + \dots \quad (19)$$

For the case of long rods we have shown⁸ that the results of calculations involving the above type of approximation are definitely quantitatively not correct but qualitatively reliable. Substituting (18) and (19) in (10) and using the addition theorem of spherical harmonics one obtains

$$f_1(\vec{a}) = \exp[\alpha_{11}P_2(\cos \theta) + \alpha_{12}D(\theta, \varphi)]/Z_1$$

$$f_2(\vec{a}) = \exp[\alpha_{21}P_2(\cos \theta) + \alpha_{22}D(\theta, \varphi)]/Z_2 \quad (20)$$

Here Z_1 and Z_2 are normalization constants

$$P_2(\cos \theta) = \frac{3}{2} \cos^2 \theta - (1/2)$$

$$D(\theta, \varphi) = \sin^2 \theta \cos \varphi$$

where θ and φ are the polar angles characterizing the orientation of the axis $\vec{a}$. The coefficients α_{jk} characterizing the distribution functions are determined by the consistency equations

$$\alpha_{11} = (5/4)c\{(1 - x)S_1 - 2xqS_2\}$$

$$\alpha_{12} = (15/16)c\{(1 - x)\Delta_1 - 2xq\Delta_2\}$$

$$\alpha_{21} = (5/4)c\{-2(1 - x)qS_1 + xrS_2\}$$

$$\alpha_{22} = (15/16)c\{-2(1 - x)q\Delta_1 + xr\Delta_2\} \quad (21)$$

The quantities S_j and Δ_j are defined as

$$S_j = \int f_j(\vec{a})P_2(\cos \theta) d\Omega = (3/2)\langle a_z^2 \rangle_j - (1/2) \quad (22)$$

$$\Delta_j = \int f_j(\vec{a})D(\theta, \varphi) d\Omega = \langle a_x^2 \rangle_j - \langle a_y^2 \rangle_j \quad (23)$$

Figure 2. Lowest concentration for which a minimum appears in the free energy for a nematic phase: (—) $b_{12} = 0.75b$; (····) $b_{12} = b$; (---) $b_{12} = 1.50b$.

Using (22) and (23) and taking into account that $\vec{a}$ is a unit vector, one can write

$$\langle a_x^2 \rangle_j = (1/3) - (1/3)S_j + (1/2)\Delta_j$$

$$\langle a_y^2 \rangle_j = (1/3) - (1/3)S_j - (1/2)\Delta_j$$

$$\langle a_z^2 \rangle_j = (1/3) + (2/3)S_j \quad (24)$$

The parameters S_1 and S_2 describe the ordering of the orientation of the axes of the rods and disks with respect to the Z axis. The parameters Δ_1 and Δ_2 describe the ordering of the orientation of the axes in the XY plane. For random orientations (isotropic phase) $\langle a_x^2 \rangle = \langle a_y^2 \rangle = \langle a_z^2 \rangle = 1/3$ and then $S_1 = S_2 = \Delta_1 = \Delta_2 = 0$. A positive value of S_1 or S_2 means that the axes of the rods or disks are oriented preferentially along the Z axis whereas a negative value indicates that the axes lie preferentially in the XY plane. In the case that there is no preferred direction in the XY plane $\Delta_1 = \Delta_2 = 0$, whereas in the case that there is a preferred direction Δ_1 and Δ_2 are nonzero. Solving eq 21 self-consistently for a given concentration and composition, one obtains the parameters α_{jk} that determine the orientation distribution functions. Note that the isotropic state ($S_1 = S_2 = \Delta_1 = \Delta_2 = 0$) represents a (trivial) solution of eq 21 that is valid for all concentrations and compositions. In the calculations pertaining to anisotropic solutions the required integrals were calculated by Gaussian integration (relative error $\leq 10^{-8}$) and the set of eq 21 was solved with an algorithm that combines the Newton method and the method of steepest descent. In the actual calculations we have limited ourselves to the simple case $b_{22} = b_{11}$, i.e., $r = 1$, resulting in a phase diagram that is symmetric around $x = 1/2$. The influence of the rod-disk excluded volume b_{12} was studied by varying q

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TABLE II: Composition, Concentration, Order Parameters, and Orientation-Dependent Free Energy Terms of the Coexisting Isotropic and Uniaxial Nematic Phases for $b_{11} = b_{22} = b_{12}$

x_i	c_i	x_a	c_a	S_1	S_2	σ_1	σ_2	ρ_{11}	ρ_{12}	ρ_{22}
0.000	3.504	0.000	3.872	0.574		0.756		0.794		
0.050	3.296	0.078	3.564	0.497	-0.382	0.563	0.546	0.845	0.763	0.909
0.100	3.144	0.130	3.320	0.407	-0.344	0.377	0.407	0.896	0.825	0.926
0.150	3.022	0.172	3.124	0.311	-0.290	0.221	0.267	0.940	0.887	0.947
0.200	2.920	0.212	2.973	0.222	-0.226	0.114	0.149	0.969	0.937	0.968
0.250	2.838	0.256	2.864	0.153	-0.163	0.055	0.074	0.985	0.969	0.983
0.300	2.773	0.302	2.786	0.104	-0.113	0.026	0.034	0.993	0.985	0.992
0.350	2.725	0.351	2.731	0.070	-0.075	0.012	0.015	0.997	0.993	0.997
0.400	2.692	0.400	2.694	0.043	-0.045	0.005	0.005	0.999	0.998	0.999
0.450	2.673	0.450	2.674	0.022	-0.022	0.001	0.001	1.000	0.999	1.000
0.500	2.667	0.500	2.667	0.000	-0.000	0.000	0.000	1.000	1.000	1.000

Figure 3. Values of the order parameters S_1 and S_2 for which the minimum in the free energy appears: (—) $b_{12} = 0.75b$; (····) $b_{12} = b$; (---) $b_{12} = 1.50b$.

between 0.75 and 2.0. This corresponds with ratios L_1/D_2 between 0.75π and 2.0π . The coupled eq 10 give rise to three distinct types of nematic phases: two of uniaxial symmetry and one of biaxial symmetry. The distribution function coefficients and order parameters characterizing these phases are given in Table I.

2. Isotropic-Uniaxial Nematic Phase Separation. To determine the phase transition between the isotropic phase and an uniaxial nematic phase one must first minimize the free energy by solving the consistency eq 21 and subsequently solve the coexistence conditions 15–17. In Figure 2 we display for various q values and as a function of composition the lowest density for which there occurs a minimum in the free energy for a $n(+)$ phase ($0 \leq x \leq 1/2$) and a $n(-)$ phase ($1/2 \leq x \leq 1$). In Figure 3 we give the values of the order parameters S_1 and S_2 for which these minima occur. First of all, we see that adding disks to rods or rods to disks substantially lowers the density at which this minimum occurs. Not surprisingly this depression of the density is the stronger the larger q , i.e., the bigger the rod-disk excluded volume is. Secondly we note that with the exception for $x = 1/2$ the minimum occurs for a finite value of the order parameters, i.e., we are dealing with a hard bifurcation. When x approaches $1/2$, the jump in the order parameters becomes smaller and vanishes completely for $x = 1/2$. This can be understood as follows. Assuming that the parameters α_{11} and α_{21} are infinitesimally small one obtains $S_1 = \alpha_{11}/5$ and $S_2 = \alpha_{21}/5$. When these values are substituted in (21) for $x = 1/2$ it follows that the coupled equations have a solution for

$$c = \frac{8}{1 + 2q}$$

with

$$\alpha_{21} = -\alpha_{11}$$

Figure 4. Π - x diagram for the case $b_{11} = b_{22} = b_{12}$.

Expanding the free energy in α_{11} and α_{21} one finds that for $x = 1/2$ and $\alpha_{21} = -\alpha_{11}$ the cubic terms just cancel and thus the hard bifurcation becomes a continuous bifurcation.

Having established that above a certain composition-dependent minimum concentration the free energy has a minimum for a $n(+)$ or $n(-)$ phase, we now consider the coexistence problem, i.e., those values of concentration and composition for which the free energy is minimized and for which coexistence conditions 15–17 are satisfied. In Table II we present the characteristic parameters of the coexisting phases for the equilibrium $i \leftrightarrow n(+)$ for the case $b_{11} = b_{22} = b_{12}$, i.e., $q = r = 1$. The results for the equilibrium $i \leftrightarrow n(-)$ are, due to the fact that $b_{11} = b_{22}$, exactly the same as for the equilibrium $i \leftrightarrow n(+)$. One only has to replace x_i by $(1 - x_i)$ and x_a by $(1 - x_a)$. The Π - x diagram for the $i \leftrightarrow n(+)$ and $i \leftrightarrow n(-)$ given in Figure 4 and the behavior of the order parameters S_1 and S_2 is presented in Figure 5. Note that the Π - x phase diagram has the form of a minimum azeotrope.

3. Biaxial Nematic Phase. We now consider the possibility of the occurrence of a biaxial phase, i.e., a phase for which $S_1 \neq 0$, $S_2 \neq 0$, $\Delta_1 \neq 0$, $\Delta_2 \neq 0$. We assume that the axes of the

Figure 5. Order parameters S_1 and S_2 in the nematic phase that coexists with the isotropic phase for the case $b_{11} = b_{22} = b_{12}$.

rods are oriented preferentially along the Z axis and the axes of the disks along the y axis. Then

$$\langle a_z^2 \rangle_1 > \langle a_x^2 \rangle_1 > \langle a_y^2 \rangle_1$$

$$\langle a_y^2 \rangle_2 > \langle a_x^2 \rangle_2 > \langle a_z^2 \rangle_2$$

Using (24) one finds the following:

$$S_1 > 0, \quad \Delta_1 > 0, \quad S_2 < 0, \quad \Delta_2 < 0$$

Note that we could have made other physically equivalent choices for the preferred orientations that would have led to different signs for the order parameters. One finds that for densities above the isotropic-uniaxial nematic transition the consistency eq 21 have a solution for a biaxial phase. The free energy corresponding to this biaxial phase is lower than the free energy corresponding to the uniaxial nematic phase at the same density. The osmotic pressures for which the biaxial phase occurs are indicated in Figure 4. The behavior of the order parameters is given in Figures 6 and 7. Note that the transitions $n(+) \leftrightarrow bx$ and $n(-) \leftrightarrow bx$ are second order, i.e., the order parameters Δ_1 and Δ_2 characterizing the biaxiality rise from zero in a continuous way. The reason for this is that $+\Delta$ and $-\Delta$ represent the same physical state and thus the free energy is even in Δ_1 and Δ_2 leading to a second-order phase transition. For $x = 1/2$ the biaxial phase arises at exactly the same concentration as that for which the transition isotropic-uniaxial occurs. Again this density can be calculated analytically. Assuming distribution functions with α_{jk} infinitesimal one obtains $S_1 = \alpha_{11}/5$ and $\Delta_1 = (4/15)\alpha_{12}$. Further for $b_{11} = b_{22}$ and $x = 1/2$ one has the following symmetry:

$$\langle a_z^2 \rangle_1 = \langle a_y^2 \rangle_2$$

$$\langle a_x^2 \rangle_1 = \langle a_x^2 \rangle_2$$

$$\langle a_y^2 \rangle_1 = \langle a_z^2 \rangle_2$$

From (24) it then follows that

$$S_2 = -(1/2) S_1 - (3/4) \Delta_1 = -(\alpha_{11}/10) - (\alpha_{12}/5)$$

$$\Delta_2 = -S_1 + (1/2) \Delta_1 = -(\alpha_{11}/5) + (2\alpha_{12}/15)$$

Substituting the above values for S_1 , Δ_1 , S_2 , and Δ_2 in consistency eq 21 one finds that these equations have a solution for

$$c = \frac{8}{1+2q}$$

This is indeed precisely the same concentrations for which the second-order transition $i \leftrightarrow n(+)$ and $i \leftrightarrow n(-)$ occur. For $c >$

Figure 6. Order parameters S_1 , Δ_1 , S_2 , Δ_2 in the biaxial phase for $x = 1/2$ and $b_{11} = b_{22} = b_{12}$ as a function of the concentration.

Figure 7. Order parameters S_1 , Δ_1 , S_2 , Δ_2 in the uniaxial and biaxial phase for $x = 0.4$ and $b_{11} = b_{22} = b_{12}$ as a function of the concentration.

$8/(1+2q)$ the free energy of the biaxial phase lies lower than that of the uniaxial phases.

IV. Discussion

In this work we have shown, using an extension of the Onsager theory, that solutions of rodlike and disklike particles depending on the concentration and composition exhibit three nematic liquid crystal phases: two of uniaxial symmetry and one of biaxial symmetry. Similar conclusions have been reached in previous

theoretical work.^{9,10} Alben⁹ considered a lattice model in which only three discrete orientations are allowed (*X*, *Y*, *Z*). This limitation is not present in the work of Rabin, McMullen and Gelbart¹⁰ who start from a free energy that implicitly contains powers of the concentration to all orders. In their treatment, however, they pay insufficient attention to the fact that the fractions of rods and disks in the coexisting isotropic and uniaxial nematic phase are not the same. Finally, Alben⁹ and Saupe, Boonbrahm, and Yu⁶ using a Landau expansion of the free energy find a phase diagram that qualitatively shows the same features as found here.

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A noteworthy feature is that the biaxial phase appears in a narrow gap between the *n*(+) and *n*(-) phase which may explain why it has been observed in some systems^{5,6} but not in other quite similar systems.¹¹ Finally, the systems where the biaxial phase has been observed^{5,6} have one inherent drawback: the rodlike and disklike particles are aggregates (micelles) the size, shape, and concentration of which depend on the physicochemical conditions of the system, e.g., by varying the temperature or overall surfactant concentration one also varies the characteristics of the aggregates. Therefore, it would be worthwhile to look for a biaxial phase in a solution of stable rodlike and disklike particles that keep their identity upon dilution. One might for example think of a mixture of vanadium pentoxide (rods) and clay platelets (disks).

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Rate Coefficients for Evaporation of Pure Liquids and Diffusion Coefficients of Vapors

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The reversed-flow gas chromatography sampling technique, reported earlier, is now used to measure the diffusion coefficient of vapors from a liquid into a carrier gas and at the same time to determine the rate coefficient for the evaporation of the liquid. The mathematical expression describing the elution curves of the sample peaks is derived and used to calculate the above parameters for the liquids *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, methanol, ethanol, propan-1-ol, butan-1-ol, and pentan-1-ol evaporating into the carrier gas helium. The values of diffusion coefficients found are compared with those calculated theoretically or reported in the literature. An alternative mathematical analysis based on equilibrium at the liquid-gas interphase leads to profound disagreement with the experimental findings.

Introduction

Reversed-flow gas chromatography is a new technique, first proposed for kinetic studies in heterogeneous catalysis,^{1,2} applied to the dehydration of alcohols³ and the deamination of primary amines.⁴ The method has been extended to the determination of diffusion coefficients in binary⁵ and in multicomponent⁶ gas mixtures, the variation of these coefficients with temperature,⁷ as well as to other measurements like those of adsorption equilibrium constants⁸ and of rate constants for removal of solvents from impregnated porous solids.⁹ Finally, the method was used to study the heterogeneous kinetics of a complicated reaction with two gaseous reactants, namely the oxidation of carbon monoxide with oxygen over Co₃O₄-containing catalysts.¹⁰ The reversed-flow gas chromatography has been reviewed recently.¹¹

This new method is carried out using simple gas chromatography instrumentation, and it is in reality a sampling technique based on perturbations imposed on the carrier gas flow. These perturbations consist of reversing the direction of flow of the carrier

gas from time to time. Each flow reversal creates perturbations on the chromatographic elution curve, having the form of extra peaks ("sample peaks"), and thus a slow rate process, taking place within the filled or the empty chromatographic column, is sampled at known times. The analytic mathematical dependence of the heights of the sample peaks on the time when the last reversal was made is given in the Theoretical Section. This function is used to calculate the relevant rate coefficient of the slow process being sampled.

In the present work the reversed-flow technique was used to measure simultaneously the rate coefficient for the evaporation of pure liquids and the diffusion coefficient of these vapors into a carrier gas passing over the surface of the liquids at a remote point (cf. Figure 1).

The liquids used were *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, methanol, ethanol, propan-1-ol, butan-1-ol, and pentan-1-ol, the carrier gas being helium.

Theoretical Section

The general chromatographic sampling equation, describing the elution curves which follow the carrier gas flow reversals, is⁷

$$c = c_1(l', t_0 + t' + \tau) u(\tau) + c_2(l', t_0 + t' - \tau) [1 - u(\tau - t')] \times \\ [u(\tau) - u(\tau - t_M')] + c_3(l', t_0 - t' + \tau) u(t_0 + \tau - t') \{u(t - t') [1 - \\ u(\tau - t_M')] - u(\tau - t') [u(\tau) - u(\tau - t_M')]\} \quad (1)$$

where *c* is the concentration of vapor at the detector, *c*₁(*l'*, ...), *c*₂(*l'*, ...), and *c*₃(*l'*, ...) are concentrations at the point *x* = *l'* (cf. Figure 1) for the times shown (*t*₀ = total time from placing the liquid in column *L* to the last backward reversal of gas flow, *t'* = time interval of backward flow, *τ* = *t* - *t*_M, *t* being the time from the last restoration of the carrier gas flow, and *t*_M the gas hold-up time of column section *l'*); finally, the various *u*'s are unit step functions for the arguments shown in parentheses and *t*_M' is the gas hold-up time in the section *l'*.

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