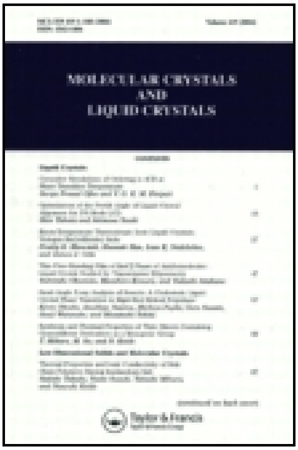

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Factors Governing the Stability of Micellar Nematic Phases

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FACTORS GOVERNING THE STABILITY OF MICELLAR NEMATIC PHASES

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Abstract The factors which govern the stability of lyotropic micellar nematic phases are delineated and then used to design mesogens which give rise to stable N_C and N_D phases on dissolution in water. The relationship between phase behaviour and the size and shape of the micelles in the caesium pentadecafluoroctanate/water system is examined. Small discoid micelles are shown to be stable at high concentrations due to the presence of a net attractive force. It is argued that this is the reason why the nematic phase in this system is stable over an exceptionally wide range of concentration.

INTRODUCTION

Twenty years ago (1967) Lawson and Flautt[1] demonstrated that a solution of sodium decylsulphate in water containing small amounts of decanol and sodium sulphate exhibited a microscopic texture and response to an applied magnetic field quite analogous to those of thermotropic nematics. These solutions were initially referred to as lyotropic nematic phases. Twelve years later Charvolin, Levelut and Samulski[2] showed that these phases were solutions of orientationally ordered anisometric micelles. There is currently considerable interest in the structure and properties of these 'micellar nematic phases'; especially in similarities to and differences from thermotropic nematics. A major constraint on this work is the complexity of the systems available to experimentalists.

To date, these phases have largely been found to occur over only narrow intervals of concentration in a small number of surfactant/water mixtures usually containing either a long chain alcohol or an inorganic salt.[3,4] It is, therefore, of vital importance to prepare nematic phases which are stable over wide concentration and temperature intervals, preferably in simple two component systems. The factors which govern the stability of such phases are first discussed. They are then applied to the design of novel amphiphilic mesogens which give rise to stable uniaxial N_C (columnar or rod-shaped micelles) and N_D (discoid micelles) phases on dissolution in water. It is demonstrated that nematic phases, stable over wide intervals of concentration and temperature, can be prepared from both ionic and non-ionic amphiphiles without addition of either salt or alcohol. The size of the micelles at high concentration is shown to be controlled by the intermicellar froces. It is concluded that it will not be possible to completely specify the criteria for the preparation of stable micellar nematic phases until these forces are properly understood.

PREPARATION OF NEMATIC PHASES

The object is to eliminate the alcohol and salt and maximise the concentration and temperature intervals over which the nematic phase is stable. It is generally

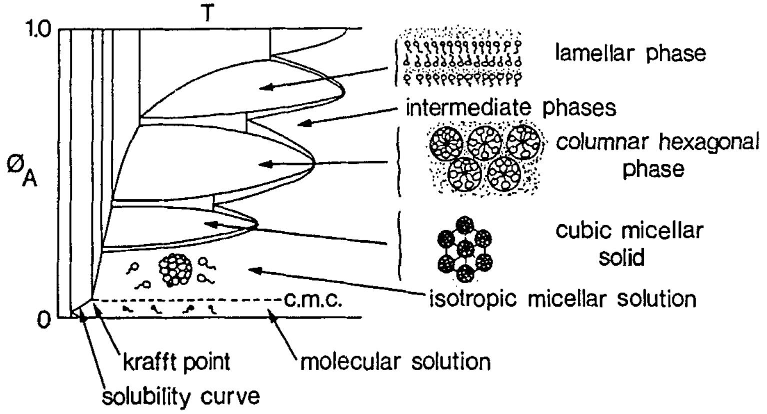

FIGURE 1 Schematic phase diagram (volume fraction of amphiphile $Ø_A$ versus temperature T) for a conventional lyotropic mesogen in water.

considered that the role of these additives is to stabilise the characteristically small discrete micelles (the axial ratio is typically in the range 2-4 in N_C phases and 0.25 to 0.5 in N_D phases) against 'explosive' growth into infinite columns/rods (columnar/hexagonal phases) or bilayers (lamellar phases).[5-8] Their role is, however, more likely to be connected with the manner in which they modify the underlying phase behaviour (Figure 1) characteristic of conventional lyotropic amphiphilic mesogens (soap and synthetic detergents). This can be understood by considering the concentration-temperature domain where nematic phases occur. Nematic phases are to be found intermediate to isotropic micellar solutions and smectic phases[9] (Figure 2), in the concentration interval ca. 0.1 to 0.5 volume fraction of amphiliphile ϕ_A, and below ca. 350 K.[10] The role of the additive seems to be

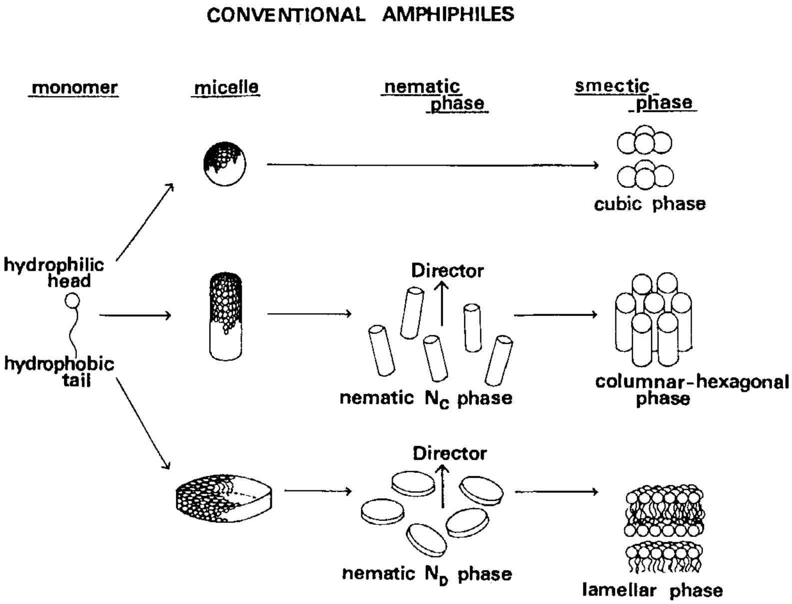

FIGURE 2 Schematic representation of possible structures of aggregates and their associated mesophases formed by conventional amphiphiles in water. The concentration of amphiphile should be read as increasing from left-to-right and top-to-bottom.

to bring the relevant smectic to isotropic transition line into this concentration-temperature domain. To obtain extensive nematic phases it is also necessary to constrain the structure of the aggregate to a single kind across, at least, this concentration window.

The shape and size of the aggregate depends upon both the structure (geometry) of the amphiphile and the inter-aggregate forces. The influence of the latter on the shape of the aggregate, though not necessarily its size, can be suppressed by designing amphiphiles which can only

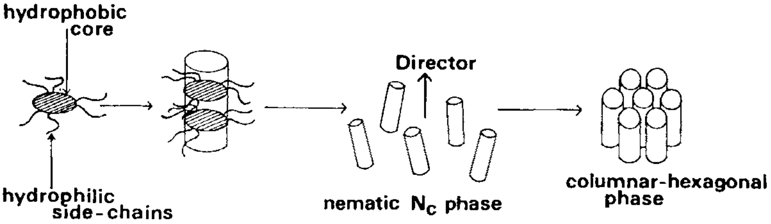

FIGURE 3 Schematic of structures of aggregates and mesophases formed by discoid amphiphiles in water with volume fraction of amphiphile increasing from left-to-right.

form aggregates of a particular structure. Thus, to optimise the stability of N_C phases it is necessary to choose an amphiphile which can only assemble into columnar aggregates. This requires a discoid amphiphile consisting of a hydrophobic core which is latteraly surrounded by hydrophilic groups (Figure 3). An example of such a discoid mesogen is 2,3,6,7,10,11-hexa-(1,4,7-trioxa-octyl)-triphenylene (Figure 4), abbreviated to

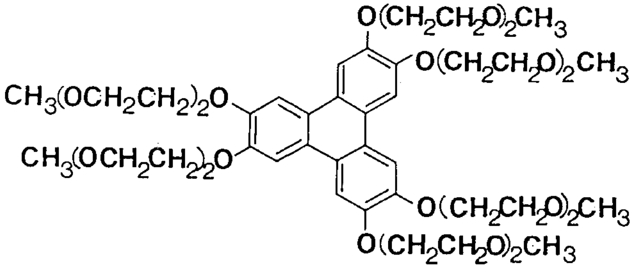

FIGURE 4 Structure of 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)-triphenylene [TP6EO2M].

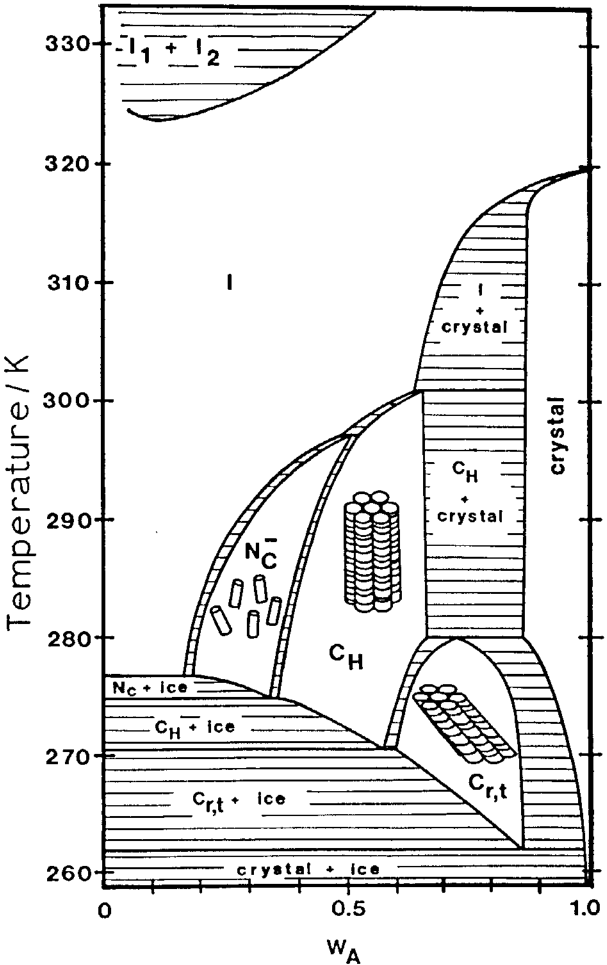

FIGURE 5 Phase diagram of the TP6EO2M/^2H_2O system. Nomenclature: I, I_1, I_2, isotropic micellar solution phases; N_C^-, nematic phase with negative diamagnetic anisotropy and columnar micelles; C_H, columnar phase with hexagonal arrangement of aggregates - there is no long range transitional order along the axes of the columns; $C_{r,t}$, columnar rectangular phase with the planes of the triphenylene rings tilted with respect to the axes of the columns.

TP6EO2M.[10,11,12] In water this amphiphile exhibits a mesomorphism (Figure 5) which is quite analogous to that of thermotropic mesogens with discoid molecules,[13] but with increasing volume fractions of water taking on the role of increasing length of the aliphatic side chains.

Similarly, to optimise the stability of N_D phases it is necessary to choose an amphiphile which can only form discoid micelles or bilayer aggregates. There are two possibilities, as depicted in Figure 6. The first is an amphiphile with a rigid rod-shaped hydrophobic moiety.

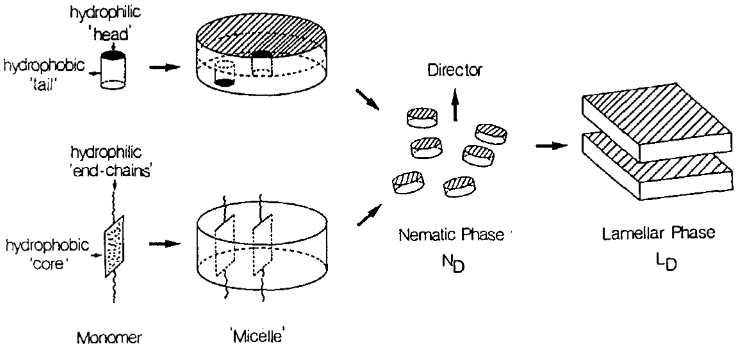

FIGURE 6 Schematic of structures of aggregates and mesophases formed by rod-shaped or lath-shaped amphiphiles in water with volume fraction of the amphiphile increasing from left-to-right.

The amphiphile caesium pentadecafluorooctanoate, abbreviated to CsPFO, is an example of such an amphiphile. It has a fairly rigid rod-shaped fluorocarbon chain which, together with the low hydration energy of the caesium ion, favours the formation of bilayer aggregates. It forms an N_D^+ phase over a wide range of concentration (0.225 to 0.632 weight fraction CsPFO) and temperature (285.3 to

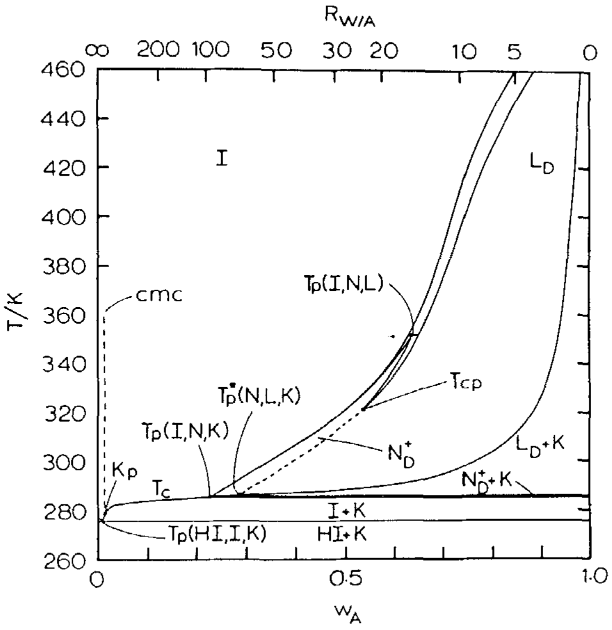

FIGURE 7 Phase diagram for the CsPFO/^2H_2O system. Nomenclature: K, crystal; L_D, lamellar phase; $N_D{}^+$, nematic phase with positive diamagnetic anisotropy and discoid micelles; I, isotropic micellar solution; HI, heavy ice; Tcp, the lamellar-nematic tricritical point; Tp(I,N,L), the isotropic micellar solution - nematic - lamellar triple point; Tp^*(N,L,K), the apparent nematic - lamellar - crystal 'triple' point; Tp(I,N,K), the isotropic micellar solution - nematic - crystal triple point; Tp(HI,I,K), the heavy ice - isotropic micellar solution - crystal triple point; K_P, the Kraft point; T_c, the solubility curve for CsPFO.

351.2 K) (Figure 7).[14,15] The aggregates are discrete discoid micelles in all of the three phases.[16,17] The isotropic micellar solution to nematic to lamellar

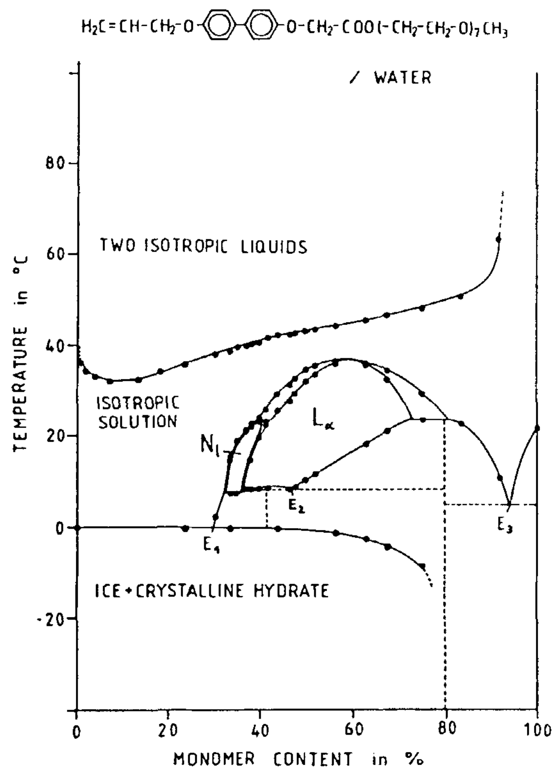

FIGURE 8 Phase diagram for the 3,6,9,12,15,18,21-Heptaoxydocosyl-(4'-allyloxy)-4-biphenyloxyacetate [by courtesy of B. Lühmann and H. Finkelmann, Coll. and Polym. Sci., 264, 189 (1986)].

sequence of transitions is, therefore, quite analogous to the isotropic liquid to nematic to smectic sequence observed for thermotropic mesogens with lath shaped molecules. This brings us naturally to the second scenario depicted in Figure 6. That is to use an amphiphile consisting of a fairly rigid lath-shaped core to which is attached hydrophilic end-chains. An example of such a mesogen is 3,6,9,12,15,18,21-Heptaoxydocosyl-(4'-allyloxy)-4-biphenyloxyacetate which in water gives the phase behaviour shown in Figure 8.[18]

The above results demonstrate that neither salt nor alcohol are essential to stabilize nematic phases. These phases can be prepared using either ionic or non-ionic amphiphiles. We have shown that the geometry of these amphiphiles governs the shape of the aggregates they assemble into in water. But to obtain nematic phases it is also necessary that some factor be involved to inhibit the growth of the micelles at high concentrations. Indeed, one of the most significant implications of the occurrence of these nematic phases is that small micelles are stable to far higher concentrations than hitherto recognised. It is thus vitally important to understand the factors which govern the stability of these small micelles.

RELATIONSHIP BETWEEN PHASE BEHAVIOUR AND MICELLE SHAPE AND SIZE

The shape and size of the aggregates in the CsPFO/water (^2H_2O) system have been studied, using small angle X-ray scattering, as a function of concentration (0.25 to 0.65 weight fraction CsPFO) and temperature (293 to 350 K).[17,19] The aggregates are found to be discrete discoid micelles (axial ratio a/b is in range 0.23 to 0.55 with a = 2.2 nm) at all concentrations studied. The variation of the micelle size with concentration (Figure 9) is qualitatively the same at all temperatures. The average

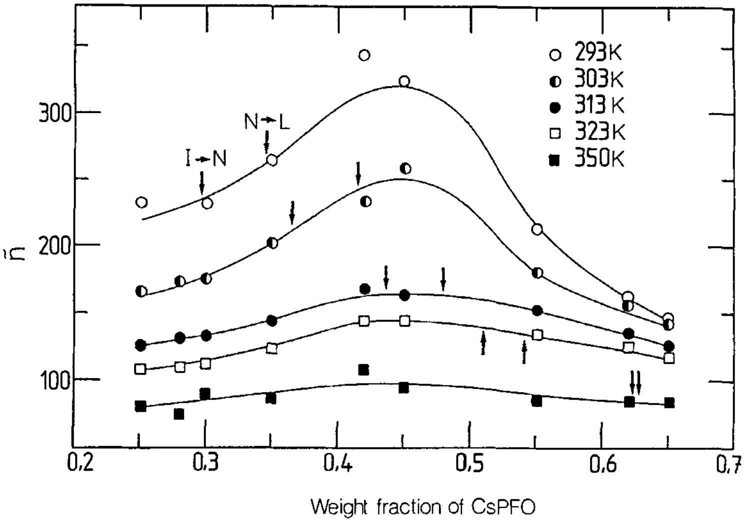

FIGURE 9 Average aggregation number $\bar{n}$ as a function of weight fraction of caesium pentadecafluorooctanoate at fixed temperatures. The vertical arrows denote the concentrations at which the isotropic to nematic and nematic to lamellar transitions occur.

aggregation number $\bar{n}$ initially increases with concentration, reaches a maximum at a weight fraction of CsPFO of approximately 0.45 (1.42 mol dm^{-3} CsPFO) and then decreases. The aggregation number is seen to decrease with increasing temperature at a rate which is roughly inversely proportional to the axial ratio of the micelle, that is, in a manner which is dependent upon the ratio of planar to curved interface. This has the effect of weakening the concentration dependence: in fact, the variation is only 20 per cent at 350 K.

There is only a small discontinuity in the value of $\bar{n}$ at the isotropic to nematic transition, as predicted by

Gelbart and co-workers,[6,7] but none is detected at the nematic to lamellar transition. The value of $\bar{n}$ along the lower boundary T_{NI} of the isotropic to nematic transition, summarised in Table 1, decreases markedly with increasing concentration. Above 360 K, $\bar{n} \simeq 75$ and, although the micelles are still discoid in shape, the strength of the anisotropic intermicellar interaction is now too weak to seed a nematic phase (Figure 7). We see that along the

TABLE 1 The average aggregation number $\bar{n}$, densities ρ and reduced densities $\rho^*_{NI} = \rho\tilde{\sigma}^3_{NI}$ along the lower boundary T_{NI} of the isotropic to nematic transition of CsPFO/^2H_2O solutions. The axial ratios a/b have been calculated assuming the micelle is a oblate elipsoid with a = 2.2 nm.

W_A	ϕ_A	T_{NI}/K	$\bar{n}^a$	$\rho_{NI}/10^{24}m^{-3}$	ρ^*_{NI}	a/b
0.625	0.410	350.0	75	15.19	1.72	0.455
0.55	0.347	330.2	142	8.86	1.79	0.330
0.45	0.262	312.8	170	4.33	1.67	0.302
0.42	0.239	309.0	190	3.54	1.63	0.285
0.35	0.186	299.9	200	2.67	1.32	0.278
0.30	0.153	293.3	220	2.01	1.15	0.265
0.28	0.144	290.8	270	1.51	1.18	0.239
0.25	0.126	287.7	260	1.35	0.98	0.244

[a] ± 7.5 per cent.

nematic to isotropic transition line the value of ρ^*_{NI} is not constant, but, for the assumed ellipsoid micelle, it varies from 0.98 up to 1.72 as the weight fraction of CsPFO is increased from 0.25 to 0.625. These values are consistently smaller than the value of 4.07 obtained for an Onsager[20] hard disc model.[21] This result is hardly surprising. Short range orientational correlations of the micelles are absent, or relatively weak, in these solutions.[17] This means that the micelles are only loosely packed and undergo reorientation with little steric hinderance. Thus, hard particle interaction models do not seem appropriate.

To understand the variation of $\bar{n}$ with concentration it is necessary to extend to discoid micelles the recent theory of Gelbart and co-workers for the aggregation behaviour of amphiphiles into rod-shaped micelles.[7] Only the outline is given here, full details are presented elsewhere.

The average chemical potential of an amphiphile in a micelle (assumed to be monodisperse: $X_n = X$) of size n is written (in units of kT) as[7]

$$\tilde{\mu}_n = \tilde{\mu}_n^o + \frac{1}{n} \ln \frac{X}{n} + \tilde{\mu}_n^\ominus + \frac{1}{n} \sigma_n + \frac{1}{n} \chi_n. \qquad (1)$$

The first term represents the average chemical potential of an amphiphile in a micelle which has a particular orientation and is at a particular position in solution. It is conveniently expressed as

$$\tilde{\mu}_n^o = \tilde{\mu}_\infty^o + \delta/n^{\frac{1}{2}} \qquad (2)$$

where $\tilde{\mu}^{o}$ is the average chemical potential of an amphiliphile in the 'flat cap' of the micelle and δ is proportional to the difference between the chemical potential of an amphiphile in the 'curved rim' and the cap. The value of δ is determined by the interfacial tension. It is quite large for the CsPFO/water system and there is a strong tendency for the system to reduce curvature and for the micelles to grow. The second term is the entropy of mixing contribution, with X denoting the total mole fraction of surfactant incorporated into micelles. This term is negative and it will decrease as n increases. Consequently, it acts in oposition to the first term and provides a mechanism for keeping the micelles small in dilute solution. The third term $\tilde{\mu}^{\theta}_{n}$ represents contributions from the translational and rotational degrees of freedom of the micelle. It has the same functional form as the entropy of mixing term and reinforces the role of the latter in favouring small micelles in dilute solution. The fourth $\frac{1}{n}\,\sigma_{n}$ represents the contribution arising from the entropy loss due to the establishment of long range orientational order of the micelles at the isotropic to nematic transition. This term accounts for the small, yet detectable, increase in the size of the micelle at this transition (for a sample with weight fraction CsPFO of 0.55 the values of $\bar{n}$ are 88 at T_{IN} and 113 at T_{NI}).[17] But its effect is quite small compared with the overall effects of concentration and temperature (Figure 9). The last term $\frac{1}{n}\chi_{n}$ represents the contribution arising from interactions between micelles.

First, we shall consider, in the light of Eq. (1), the growth in the micelle size observed at low concentrations. Here the micelles are sufficiently far apart to neglect the intermicellar interactions and so only the first three terms need be considered. This leads to $\bar{n} \propto X^p$ $(0 < p < 1.0)$ which is to be compared with the observed behaviour $\bar{n} \propto X^{0.4}_{CsPFO}$. The value $p = 0.4$ corresponds to quenching of the rotational degrees of freedom, but not the translational ones. It is difficult to decide whether this result has real significance! Nevertheless, the initial growth of the micelle with increasing concentration can be understood in terms of the interplay of the intramicellar interactions which cause the micelle to grow, and the various entropy terms all of which oppose its growth.

Next, we turn our attention to the diminution in the size of the micelles which occcurs at high concentrations. Here the term involving the intermicellar interaction becomes important. It can be shown that the sign of dn/dX is solely determined by that of $d\chi_n/dX$. If the force between the micelles is repulsive, χ_n becomes more positive upon increasing X and hence $d\chi_n/dX$ and, consequently, dn/dX are positive. Conversely, if the intermicellar force is attractive, then on increasing X, χ_n must become more negative so that $d\chi_n/dX$ and, consequently, dn/dX are negative. Figure 9 shows that at high concentrations dn/dX_{CsPFO} is negative, consistent with a net attractive force between the micelles. It could be argued that the same behaviour would obtain from a repulsive force which became less repulsive at higher concentrations. This behaviour would be expected if, for example, double layer coulombic repulsions enhance the excluded volume dimensions of the micelle:[22] at higher concentrations the Debye length would decrease resulting in a shorter range repulsive force. But such an interpretation is not consistent with the behaviour observed at low concentrations where there is no evidence for any initial rapid growth in $\bar{n}$ as would be required. Thus, it seems reasonable to conclude that at high concentrations the growth in size of the micelle, driven by the intramicellar interactions, is suppressed by a net attractive intermicellar force which appears to become stronger with increasing concentration. This attractive force is responsible for the stability of the small discoid micelles at high concentrations and hence the stability of the nematic phase over such a wide range of concentration.

This is the first observation of the existence of an attractive force between charged micelles. It is quite a surprising result as the micelles carry a net negative charge (55 per cent, or more, of the counterions are bound at the micelle/solution interface). The coulombic repulsion would have been expected to have dominated the intermicellar interaction. The nature of the attractive force is unclear. Sogami and Ise[23] have, however, recently proposed that the coulombic interaction in a macroionic system may become attractive at large particle separations. It is suggested that the interaction is mediated by the unbound counterions and gives rise to a secondary minimum in the intermicellar potential energy curve. The position of this minimum is determined by the Debye length of the macroions which would be consistent with the range of intermicellar separations in the CsPFO/-water system.

The effect of temperature on the size of the micelle can be understood in terms of its effect upon the arrangement of the Cs^+ ions bound at the micelle/solution interface. The simplest model[24] considers that the Cs^+ ions are distributed between two binding sites. In the lowest energy site, the Cs^+ ions are interposed between neighbouring negatively charged carboxylate groups, whilst in the higher energy site the ions are in a relatively diffuse layer atop these groups. The proportion of Cs^+ ions in the lower energy sites is expected to decrease as the temperature is raised; thus, there will be a concomitant increase in the average chemical potential of the amphiphile by an amount which is greater the lower the curvature of the interface. The net effect is to reduce the magnitude of the parameter δ in Eq. (2) and thereby effect a reduction in the size of the micelle. Clearly, the results show that the value of δ depends upon both the interfacial tension and the detailed arrrangement of the counterions at the micelle/solution interface. Little is known about how the latter varies with concentration and temperature, yet it is a subject of vital importance for understanding the stability of micellar solutions.

CONCLUSION

We have shown that to prepare stable nematic phases it is essential to consider both the intra- and inter-micellar interactions. The intramicellar interaction determines the shape of the micelle and also governs its growth in dilute solution. Both can be controlled by appropriate design of the amphiphilic molecule. The size of the micelle at high concentrations is controlled by the intermicellar force. In the case of the CsPFO/water system this force is attractive and it is responsible for the stability of the small discoid micelles at high concentrations and hence the stability of the nematic phase. It is important to establish whether the net intermicellar force is attractive in all nematic phase forming systems. It will not be possible to completely specify the criteria for the preparation of stable micellar nematic phases until these forces are properly understood.

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