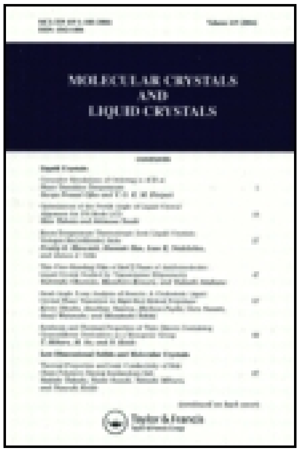

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Influence of Lyotropic Nematic Host Phases on the Twisting Power of Chiral Dopants

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Influence of Lyotropic Nematic Host Phases on the Twisting Power of Chiral Dopants

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The twisting power of several chiral dopants in two host phase classes is investigated under the viewpoint of its dependence on chain length and size of the headgroups of the surfactants. The results are explained qualitatively, using a simple model of intramicellar chiral induction, which is sensitive to flexibilities and lengths of the surfactant chains. Additional hints for this model are given by the temperature dependence of the pitch. It is shown that $p(T)$ of "solid" micelles can be described by a model/formula valid for thermotropic liquid crystals and that deviations become larger if the micelles become more flexible. To interpret the observed temperature dependences, it is speculated that a change of dominance occurs, from sterical chiral interactions to dispersive ones.

Keywords: Lyotropic nematic phases; chiral induction; helical twisting power; host phase influence

1 INTRODUCTION

A lyotropic liquid crystalline state is characterized by a long-range orientational order of anisometric building blocks in a solvent (in this paper: disk-like micelles in water). In the literature certain phases have been classified as nematic from the observation of typical textures and/or alignability by magnetic fields. Nevertheless, the criterion of the nematic state should be a structural one, namely the long-range orientational order, in general associated with the absence of long-range positional order.

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The amphiphilic molecule, as well as the aggregate shape, can be described by the packing parameter which was defined by Israelachvili [1]. The hydrophilic tail of an amphiphilic molecule is geometrically characterized by its volume v and its alltrans length l_C of the hydrocarbon chain. The headgroup of the molecule requires a certain area a_0 within a hydrophilic/hydrophobic interface. The packing parameter is defined as the ratio of the apparent cross-section of the hydrophobic tail (v/l_C) to the headgroup area a_0:

$$\Pi = \frac{v}{a_0 \cdot l_C} \tag{1}$$

As a rule of thumb, every aggregate shape corresponds to a certain range of Π. One possibility to change the shape of a micelle is the addition of further components, so-called co-surfactants, to the system. A co-surfactant is an amphiphilic material, which mixes with the surfactant in the micelle, these are often molecules with a small polar head, e.g. long chain alcohols. The addition of such co-surfactants reduces the mean headgroup area and a rod-like micelle may transfer into a disk-like one [2].

The director field of a nematic phase (N) may become chiral by obtaining a helical superstructure, i.e. the preferred orientation twists spontaneously around a helix axis. This state of matter has been called 'cholesteric' for historical reason, a more appropirate term is 'chiral nematic' (N^*). The chiral superstructure within the long-range orientational order of anisometric micelles is characterized by the pitch p (or its inverse, the twist p^{-1}) and the handedness of the twist, right or left. Figure 1 shows the helical arrangement of disk-like micelles (N_L^*), the helix axis aligns parallel to the glass-

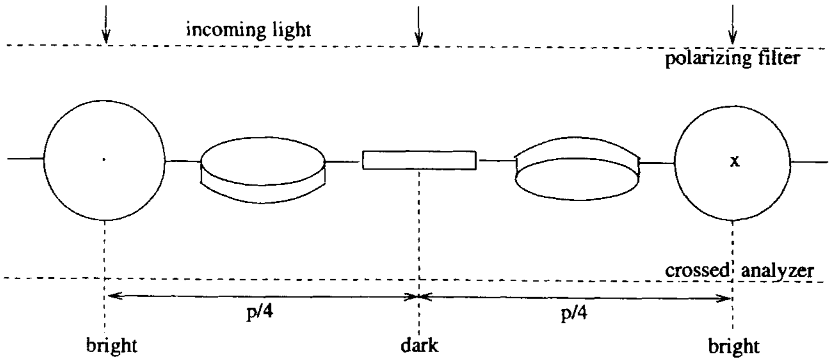


FIGURE 1 Helical arrangement of disk-like micelles and formation of the fingerprint-texture.

surface. Because of this alignment there are regions where the polarised light passes the sample and regions where the light is reflected. One observes a so-called fingerprint-texture. The distance between adjacent stripes is then, for lyotropic systems, equivalent to half of the pitch [3,4], which is a very easy method to measure the pitch of the helix.

A phase chirality can arise either from the chirality of the aggregates [3,5] or from the chirality of the solvent. Both can be achieved by the use of the chiral surfactants or chiral solvents, or can be induced by the solubilization of chiral dopants within solvent and/or micelle [6,7]. This report deals only with the latter case.

Two models for the origin of lyotropic phase chirality were proposed in 1978 by Radley and Saupe [7]: (1) a sterical interaction model and (2) a chiral dispersion interaction model.

1. The sterical interaction model assumes that the rod- or disk-like micelles of the appropriate nematic phase are deformed into a chiral shape by the influence of the solubilized chiral guest molecules. Due to thermal motion, the micelles frequently collide with each other and thus chirality information can be transferred sterically from one aggregate to its neighbours.
2. An alternative model for the induction of phase chirality proposes a direct pairwise interaction between chiral molecules, resident in different micelles. A chiral dispersion interaction can be understood theoretically by means of the multipole expansion of the dispersion interaction energy if at least a dipole/quadrupole term is present (Goossens theory [8]).

We want to contribute to a further understanding of the mechanisms of the chiral induction in lyotropic liquid crystals.

There is some literature reporting on the correlations between the molecular structures of chiral dopants and their twisting efficiency [9,10,11,12,13]. Our study deals with the correlations between the twisting efficiency and properties of the nematic host phases [9,10]; therefore we vary the length of the alkyl-chain and the bulkiness of the headgroup, which influences the chemical nature of the headgroup, too, for one cationic as well as for one anionic surfactant series.

2 EXPERIMENTAL

2.1 Nematic Host Phases

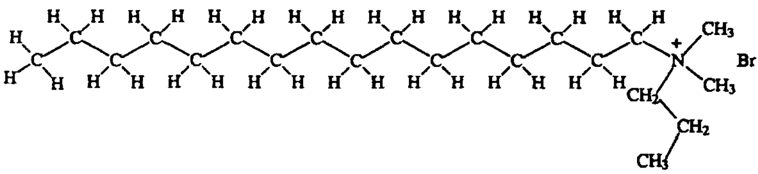
Our nematic host phases were (1) mixtures of N,N-dialkyl-N,N-dimethylammonium-bromides with *n*-decanol and water [2] and (2) binary mixtures of perfluorinated surfactants with water [14, 15, 16] (see Tabs. I, II and Fig. 2). They all form disk-like micelles and in all investigated host phases exists a lamellar phase (L_α) at lower temperatures, neighboured to the nematic phase.

TABLE I *N*,*N*-dialkyl-*N*,*N*-dimethylammoniumbromides; *n*: number of CH_2-groups in the long alkyl-chain, *R*: short alkyl-chain (see Fig. 2)

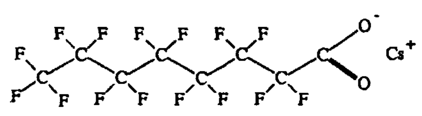
hostphase	*n*	*R*	*surf.*	*dec.* [*weight-%*]	H_2O
$C_{14}C_1$	13	CH_3^-	30.2	4.9	64.9
$C_{14}C_2$	13	$C_2H_5^-$	36.2	6.0	57.8
$C_{16}C_1$	15	CH_3	23.1	3.6	73.3
$C_{16}C_2$	15	$C_2H_5^-$	28.3	4.3	67.4
$C_{16}C_3$	15	$C_3H_7^-$	31.5	4.3	64.2

TABLE II Perfluorosurfactants; *n*: number CF_2-groups, X^+: counterion of the head group (see Fig. 2)

hostphase	*n*	X^+	*surf.* [*weight-%*]	H_2O
A-C_8	6	NH_4^+	40,50	60,50
A-C_9	7	NH_4^+	40	60
C_5-C_7	5	C_5^+	60	40
C_5-C_8	6	C_5^+	40,50,60	60,50,40
C_5-C_9	7	C_5^+	40	60



N,N-Dialkyl-N,N-dimethylammoniumbromides (CmCn); example: C16C3



Perfluorosurfactants (PF); example: Cs-C8

FIGURE 2 Host phase classes.

The perfluorinated surfactants exhibit some advantages. First, no co-surfactant is needed to form disk-like micelles and second, the nematic phase is stable about a wide surfactant concentration range, therefore the surfactant concentration dependence of the twisting power could be investigated, too.

$C_{14}C_1$ and $C_{16}C_1$ (for abbrevations see Tabs. I, II and Fig. 2) were purchased from Fluka ($>98\%$) and $C_{16}C_2$ from Merck ($>98\%$) and were used without further purification. $C_{14}C_2$ and $C_{16}C_3$ were synthesized by reaction of the long-chained N, N-dimethylamine (which were gifts of Hoechst, Gendorf) with the corresponding alkyl-bromide (Aldrich) in acetonitril. The products were recrystallized from ethylacetate with 10% ethanol. $C_{18}C_2$ has also been synthesized, but in this system no discotic nematic phase, but only a lamellar phase could be observed, when decanol was continuously added to the calamitic system $C_{18}C_2$/water. This can be explained by the inhomogeneous distribution of the co-surfactant in the micelles [17]. The decanol is solubilised mostly in the plain parts of the micelles and so the packing parameter II cannot be changed sufficiently.

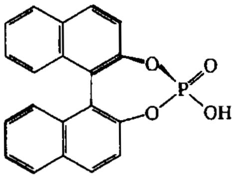
The perfluorinated surfactants were prepared by neutralizing perfluoroacid with the suitable hydroxides; A-C_8 was purchased from Fluka. All salts were recrystallized from a mixture of *n*-hexane and *n*-butanol.

The required amounts of each component were weighed into a flask and homogenized by stirring the mixtures during 2 days at about 40°C in a waterbath.

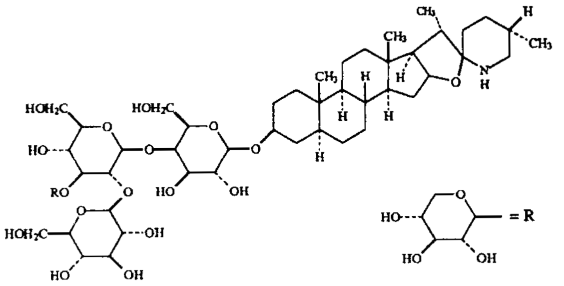
2.2 Chiral Dopants

As chiral dopants we used two α-hydroxy carboxylic acids (MA, HHMA) (for structures and abbreviations see Fig. 3) which differ in their polarizability, bulkiness and rigidity of the ring groups. Furthermore, two sterically demanding molecules (BNDHP, tomatine) were investigated. BNDHP is a dopant molecule without any chiral carbon but with an inherent dissymmetry. This often leads to a high twisting power [13], as observed in thermotropics as well [18]. Tomatine is a glycoalkaloid of the aglycon tomatidine and the tetrasaccharide β-lycotetraose, and it is the main alkaloid of the tomato (see Fig. 3). Tomatine was only used with the perfluorinated systems, because in the ammoniumbromides it induces a lamellar phase instead of a chiral nematic phase due to its bulkiness. All dopants, except MA (Merck) are products of Fluka and were used without further purifications.

R(-)-Mandelic acid (MA)   R(-)-Hexahydromandelic acid (HHMA)



R(-)-1,1'-Binaphthalene-2,2'diyl-hydrogen-phosphate (BNDHP)



Tomatine

FIGURE 3 Chiral dopants.

2.3 Chiral Nematic Phases

The chiral nematic phases were obtained by weighing the required amounts of dopants and host phase into 4 ml sample vials (Neolab) and rotating the vials slowly for 2 days at about 40°C. The dopant concentration x was defined as molar fraction of aggregated material. To achieve fingerprint textures the chiral nematic samples were filled into microslides (Camlab) of 0.4 mm layer thickness and annealed in a heating stage until an equilibrium texture was observed. The microslides were sealed with parafilm (a flexible, self-sealing, and thermoplastic laboratory film) for use at lower temperatures. For use at more than 50°C they were sealed with an epoxy glue

(UHU plus). The formation of fingerprints of constant width takes some minutes with tomatine and BNDHP or even many hours (with MA as dopant), which gives first hints of the twisting efficiency of these dopants.

The pitch versus the dopant concentration measurements were usually performed at a constant difference of 3°C below the clearing temperature to obtain best possible comparability within the different systems (see section 3.3). The pitches of the chiral nematic samples were determined using the distance between a couple of stripes of the fingerprint texture (see Fig. 1) by use of a camera with measure cross-hairs (Leitz Latimet). Each measurement was carried out ten times and averaged. The measuring errors of the 3σ-interval were in most cases smaller than 10%.

3 RESULTS AND DISCUSSION

3.1 Concentration Dependence of the Clearing Temperatures and the Twist

The addition of a further component to a host phase affects the thermodynamic stability of its lyotropic liquid crystalline state. Therefore, first the influence of the dopants on the chiral nematic to isotropic phase transition was checked. The clearing temperature T_C of the induced phases increases with increasing dopant concentration for all dopants, except of MA, which is a small and hydrophilic dopant.

In the case of HHMA and BNDHP, at higher dopant concentrations a two-phase region (isotropic/lamellar) between the chiral nematic and isotropic phase becomes visible, whereas with MA as dopant always sharp clearing points could be detected. Tomatine can only be used at low concentrations because of its poor solubility; it induces no biphasic region. The dopant concentration x could be increased up to a certain maximum value, because further doping led to the loss of the chiral nematic phase and a lamellar phase, induced by the dopant, appeared instead.

The influence of the dopant solubilisation on the clearing temperature can be explained in terms of micelle size variation enforced by the guest molecules. Small and more hydrophilic dopants (like MA) will prefer locations in the outer, polar shell of the aggregates, whereas the more hydrophobic ones will solubilize in the inner, less polar regions of the micelles. The solubilization of dopants in the outer shell of the micelles leads to a stronger curvature of the aggragate surface and also to a smaller mean packing parameter. Smaller aggregates with a reduced anisometry will be formed resulting in the observed reduction of the clearing temperature. Vice versa it is obvious that solubilization in the inner regions of the micelles leads to larger aggregates with increased anisometry.

For induced chiral nematic phases it is known that the twist (i.e. the inverse pitch) is a function of the dopant concentration x. At infinite dilution (i.e. $x \to 0$) the absolute value of p^{-1} increases linearly with x. The helical twisting power (*htp*) δ is defined as [19]:

$$\delta = \left(\frac{\partial p^{-1}}{\partial x}\right)_{x \to 0} \tag{2}$$

Often, the htp is constant over some concentration range. In our study we always found deviations from linearity (with the exception of tomatine) (see Figs. 4–7). Anyway, even more than in the thermotropic case, no linearity may be expected at higher dopant concentrations, because lyotropic systems behave like non-ideal mixtures due to aggregate size variations. It can be shown [13] that approximately:

$$p^{-1} \propto \frac{x}{v_M} \tag{3}$$

(v_M = volume of the micelle).

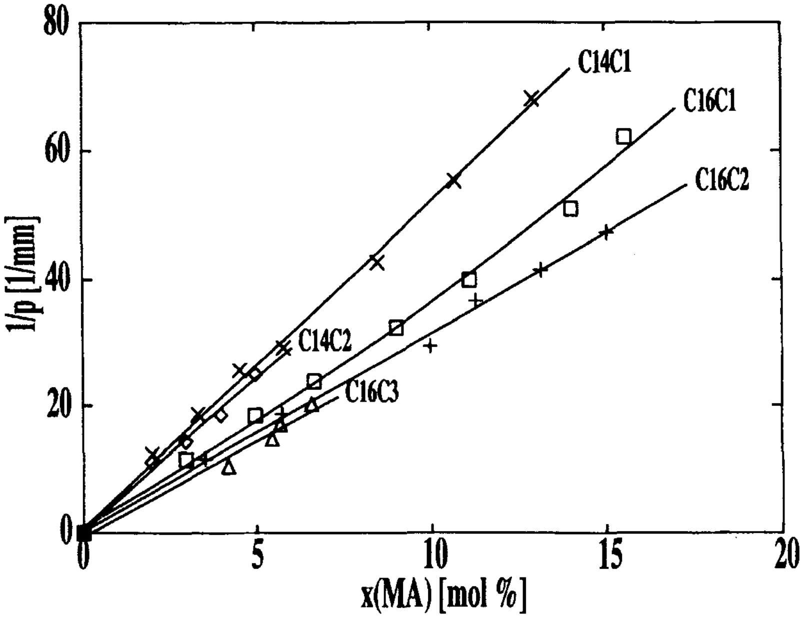


FIGURE 4 Twist vs. dopant concentration: MA in the ammoniumbromides.

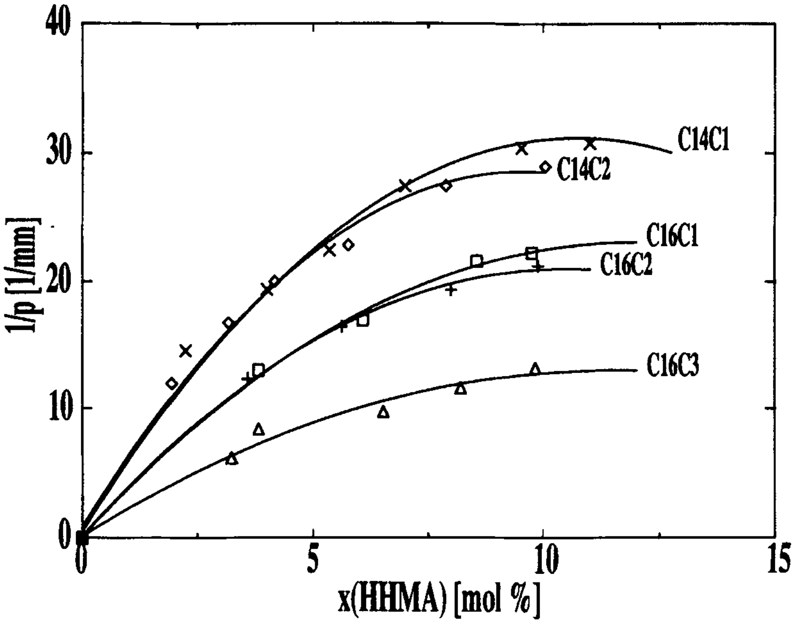


FIGURE 5 Twist vs. dopant concentration: HHMA in the ammoniumbromides.

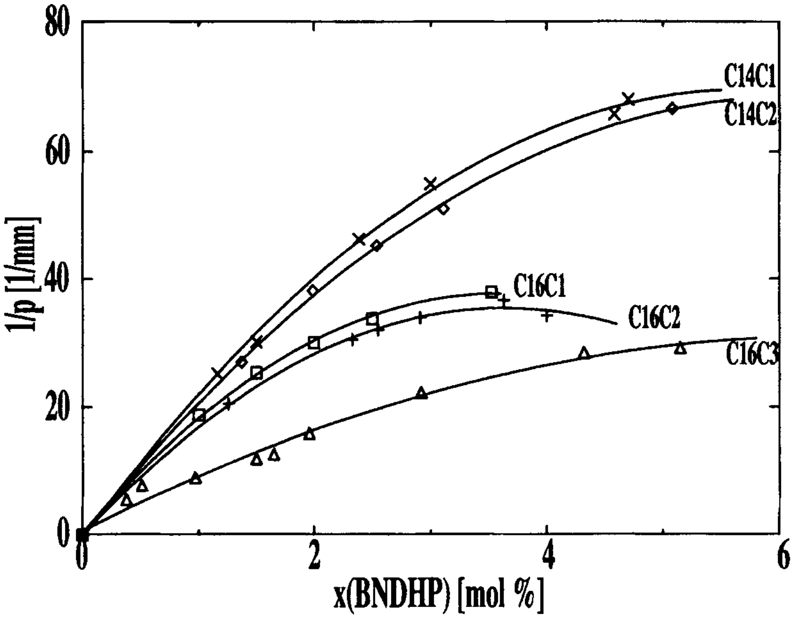


FIGURE 6 Twist vs. dopant concentration: BNDHP in the ammoniumbromides.

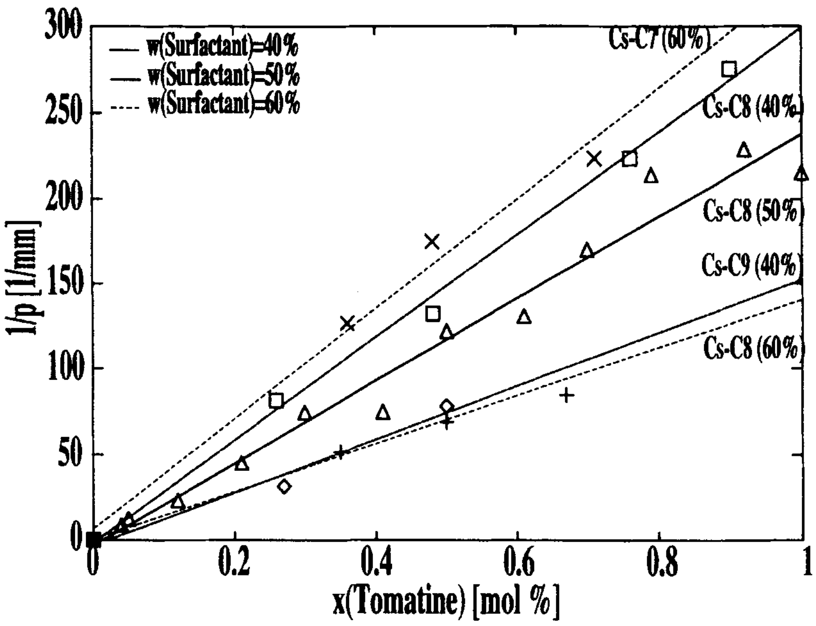


FIGURE 7 Twist vs. dopant concentration: tomatine in the cesium-perfluorosystems.

Hereby a qualitative explanation of the observations is possible: the htp of the small and rather hydrophilic MA increases with increasing dopant concentration. For the more hydrophobic HHMA and in addition more bulky BNDHP the opposite is true. For tomatine surprisingly no deviations from linearity are found although it is by far the bulkiest dopant we used.

Corresponding to the clearing temperature variations, the positive and negative deviation from linearity can be understood by micelle size variation. An over-proportional increase of the twist in the case of MA is obviously due to a decrease of the micelle size. When more and smaller micelles are formed the micelle number density increases and consequently the mean micelle distance is reduced, i.e. the chiral interaction between two micelles might increase. The opposite case of a decreasing htp with increasing dopant concentration is due to the respetice decrease of the micelle number density. The latter has been interpreted also as a pretransitional effect caused by the approach to the lamellar phase [7, 22]. Hydrophobic dopants like BNDHP and tomatine obviously increase the micelle size (as can be deduced from the clearing temperature increase) and the pitch is increased, too.

3.2 Measured htps and Model of Chiral Induction

For all data measured with the ammoniumbromides it was possible to achieve a good fit of the twist curves by polynomials of order two as a function of the dopant concentration. The first derivative of the fit polynomial provides the htp. With MA the curvature is so small that it is also possible to fit the data with linear functions in consideration of the measuring errors. In case of the perfluoro systems with tomatine the data can be also described as linear functions. In case of BNDHP the curvature at the graphs is so large that only polynomials of fourth order could fit the data. At high dopant concentrations the micelles become much bigger because of the voluminous BNDHP and therefore the decrease of the slope is more dramatic than with HHMA. In Tables III–V the htps at infinite dilution are listed and in Figures 4–7 the twists p^{-1} versus dopand concentration x are shown.

TABLE III Htps of the ammoniumbromide systems

hostphase	*htp MA*	*htpHHMA* [mm^{-1}]	*htp BNDHP*
$C_{14}C_1$	510	580	2460
$C_{14}C_2$	490	580	2230
$C_{16}C_1$	310	390	2090
$C_{16}C_2$	310	400	1950
$C_{16}C_3$	300	220	940

TABLE IV Htps of the perfluoro systems

hostphase	*% surf.*	*htp MA*	*htp HHMA* [mm^{-1}]	*htp BNDHP*
A-C_8	50	55	310	6900
C_5-C_8	50	55	180	6300

TABLE V Htps of the perfluoro systems with tomatine

hostphase	*% surf.*	*htp tomatine* [mm^{-1}]
A-C_8	40	26100
A-C_8	50	20400
A-C_8	40	17900
C_5-C_7	60	32200
C_5-C_8	40	30100
C_5-C_8	50	24100
C_5-C_8	60	14400
C_5-C_9	40	15500

One important result is, that with all of our dopants in the ammoniumbromides the htp increases in the same ranking: $C_{16}C_3 < C_{16}C_2 < C_{16}C_1 < C_{14}C_2 < C_{14}C_1$. In most cases the htps ($x \rightarrow 0$) are similar, but at higher dopant concentrations there are distinct differences in the twists. Two rules can be extracted from this series:

1. The longer the alkyl-chain of the surfactant, the smaller the twist.
2. The bulkier the headgroup of the surfactant, the smaller the twist.

These results can be explained by the following simple model of chiral induction: The state of aggregated monomers in a micelle resembles a local orientational order. A chiral guest molecule within an orientationally ordered environment will act similarly as in thermotropic liquid crystals. Chiral dopants will twist the preferred orientation of its neighbouring achiral molecules. Then the surfactant long axes will tilt with respect to the symmetry axis of the micelle (the normal of the disk). This twist can extend without frustration into two dimensions towards the rim of the micelles (double twist). The micelles get an intrinsic chiral structure, which becomes "visible" also at the micelle surface. With regard to the intermicellar interactions, we can only speculate at the moment that also the charges on the shell of the micelles could take up a chiral formation. Also the electronic polarizability of the micelles adopts the same symmetry. Figure 8 shows a sketch of a disk-like micelle with tilted orientation of the surfactant molecules [13]. The tilted lines can be imagined also as an expression of the symmetry of the charge distribution and polarizability.

A simple explanation of our two rules is that the volume of the micelles influences the twist (see above). A longer alkyl chain leads to a larger

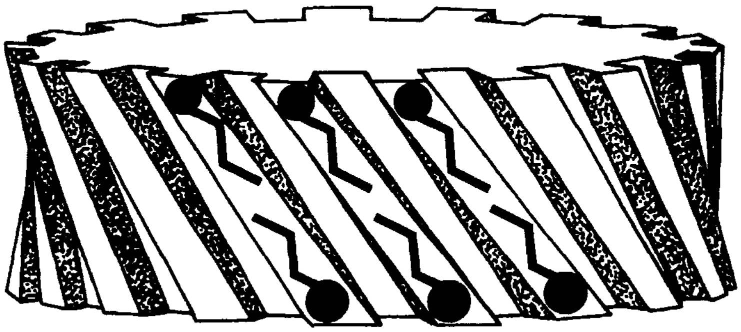


FIGURE 8 Sketch of a disk-like micelle with preferred tilted orientation of the surfactant molecules.

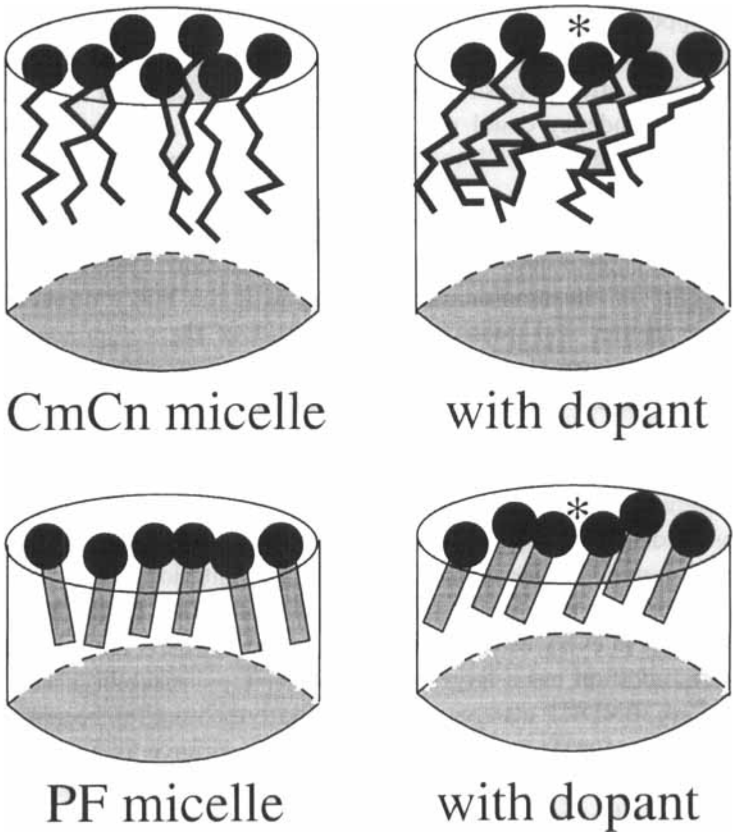


FIGURE 9 Schematical diagrams of the two micelle classes, with and without dopant molecule.

micelle volume and to an increase of the aggregation number $\tilde{n}$ [20] and therefore to a smaller twist and htp.

A further and new argument refers to our model of intramicellar twist sketched above: The longer the alkyl-chains, the harder it is for the dopant to twist them because of the principle of the lever. The hydrocarbon chains are quite flexible and so changes of conformation are possible and the chains could mesh with each other. Moreover, the chains could bend if they are tilted. The order of the chains decreases the longer they become. This has been shown by measuring the order parameter of partially deuterated alkyl chains [21].

If the headgroups are getting larger, i.e. the short alkyl-chain of the ammonium-bromides becomes longer, the distance between the alkyl-chains increases and the tilt decreases. If the headgroups become more voluminous hollows appear beneath them. The chains try to fill out these gaps and so the number of conformations increase and the order of the chains is lowered. Figure 9 a is an attempt to show these effects schematically. In the perfluoro systems this tendency could not be proved because only the counterion could be exchanged from C_5^+ to NH_4^+. Of course this influences a_0, too, but no uniform trend became obvious.

Our model of an intramicellar chirality caused by a double twist structure gives also an explanation why the htps in the perfluoro systems are larger than the htp of the ammonium bromides with the bulky dopants. The chains are shorter and quasi inflexible because of the voluminous fluoro atoms. The perfluoro-chains have all-trans conformation and cannot bend because the van der Waals radii overlap the chains (Fig. 9b) [23].

The tilt will become larger if the dopand molecule is solubilized in the inner regions of the micelles because then the intramicellar inter-molecular chiral interaction between dopants and surfactants is most intensive. MA, the most hydrophilic dopant, is solubilized in the shell region of the aggregates and cannot induce a large tilt. Chiral counterions show the same behaviour, because they are also located in the shell [20]. So the htp of MA is the smallest in every investigated host phase. HHMA is more hydrophobic (and in addition has a larger mean electronic polarizability). The result is a large htp. BNDHP also penetrates deep into the micelles; because of the bulky napthalene-rings and its unflexibility it can enforce an enormous tilt. The result is the largest htp in every ammonium alkyl host phase. This sequence was also found in C_5-C_8 (50%) and A-C_8(50%) with this three dopants. The same arguments as given above are also valid for tomatine in the perfluoro systems. The dopant can penetrate nearly the whole micelle with its fixed steroid-basic-scaffolding. Its htps are the highest in all investigated systems, but it must be emphasized that at the moment it is not clear how such a bulky molecule fits into the structure and geometry of the micelle.

3.3 Temperature Dependence of the Pitch

The first result is, that in the perfluoro systems every dopant qualitatively exhibits the same temperature dependence whereas in the ammoniumbromide systems every dopant shows a different course. In the perfluoro systems a nearly temperature independent pitch is found in the chiral nematic phase, in some temperature range close to the clearing point. With approach to the chiral nematic/lamellar phase transition the pitch increases (see Fig. 10). This behaviour is well known from thermotropic systems and it is possible

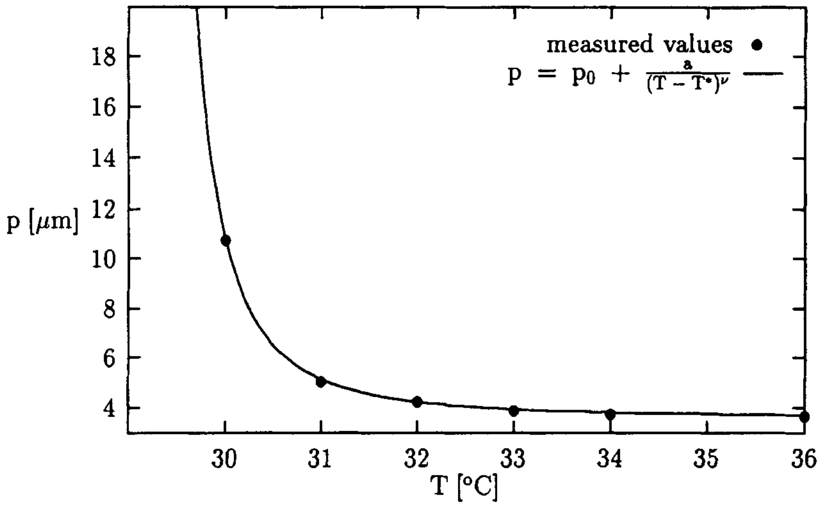


FIGURE 10 Example for the temperature depndence of the pitch in the perfluorosystems, C_5-C_8 (50%) with BNDHP.

to fit the measured pitches with an empiric "thermotropic formula" [24, 25]:

$$p = p_0 + \frac{a}{(T - T^*)^\nu} \tag{4}$$

(p_0, a: constants; T^*: transition temperature; ν: critical exponent (with thermotropics)).

For thermotropic liquid crystals this behaviour was intrepreted as a pretransitional effect of the arising smectic-A phase where the cholesteric helix unwinds with decreasing temperature just before the transition to the smectic phase. The anomalous increase of the pitch and of the elastic constants is proportional to the coherence length of the short-range smectic order in a cholesteric mesophase.

The similarities in the temperature dependence fits to the observation that the perfluoro systems can be well compared with thermotropic liquid crystals [26]; but in contrast to thermotropic systems, no real divergence of the pitch was found in all investigated cases [27] and therefore no critical exponent could be determined. As concluded in the last section, the micelles are rigid and inflexible and behave like hard disks.

The investigation of the ammonium bromides leads to a completely different picture. Only with BNDHP (see Fig. 11) as dopant there are some

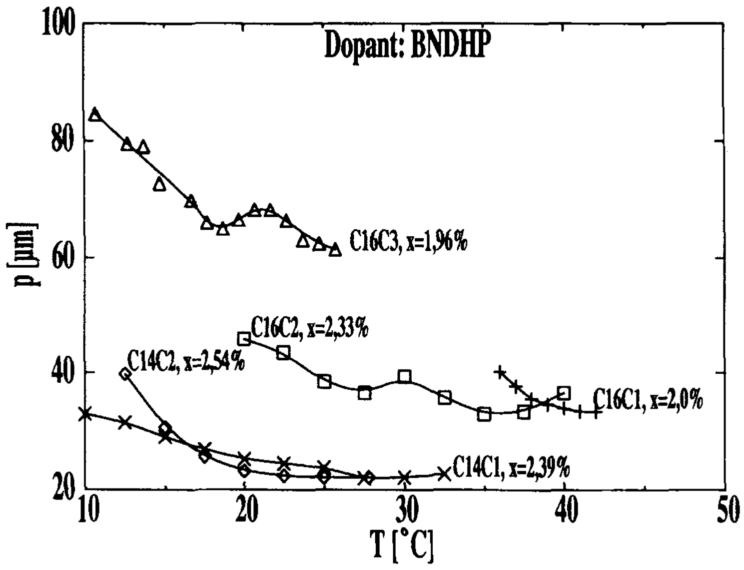


FIGURE 11 Temperature dependence of the pitch of BNDHP in the ammoniumbromides.

similarities to the perfluoro systems. In all cases a significant change of the pitch close to the phase transition N^*/L is observed, but in the chiral nematic phase there is no uniform course. From these first experimental datas, we speculate that BNDHP as a rigid and quite voluminous dopant stiffens the flexible ammoniumbromide micelles more than the other investigated dopants; the bulkier and more voluminous the dopant, the more rigid and inflexible the micelle and the smaller the deviations to the perfluoro systems.

How can these different temperature dependences be explained? A possible statement can be derived from a molecular statistical theory from Osipov [6]. Minimization of the elastic energy of a chiral nematic liquid crystal leads to:

$$\rho^{-1} \propto \frac{\Delta}{K_{22}} \tag{5}$$

(Δ: parameter of chirality; K_{22}: twist elasticity constant)

The theory considers sterical ("S") as well as dispersive ("D") interactions as a reason for the elasticity and also the helical structure of the chiral nematic liquid crystal. The expression of the temperature dependence of the pitch contains two parameters of chirality and two constants of twist elasticity.

$$p \propto \frac{K_{22}^{D} + kTK_{22}^{S}}{\Delta_D - kT\Delta_S} \tag{6}$$

Is $\Delta_D \gg \Delta_S$, i.e. if the sterical chiral interactions can be neglected, a linear course of the pitch as found with MA as dopant results. Vice versa, if $\Delta_S \gg \Delta_D$, and the dispersive chiral interactions are much smaller than the sterical ones the pitch decreases at a particular temperature like BNDHP in the perfluoro systems (see Fig. 12). So the changes in the temperature dependence of the pitch can be explained by changes in the predominating intermicellar interaction, if the micelles become flexible. In the case of inflexible micelles, there is no change and the temperature dependence seems to the independent from the used dopant.

One important aspect to mention is, that the Osipov theory only considers the **inter**micellar interactions but not the **intra**micellar ones. A complete description has to take into account both kinds of interactions and may be this could be a starting point to understand the different temperature dependences of the ammoniumbromides.

4 SUMMARY AND PREVIEW

Our investigations have shown that the htp depends on the chain-length of the surfactant molecule and also on the size of the headgroup in case of the

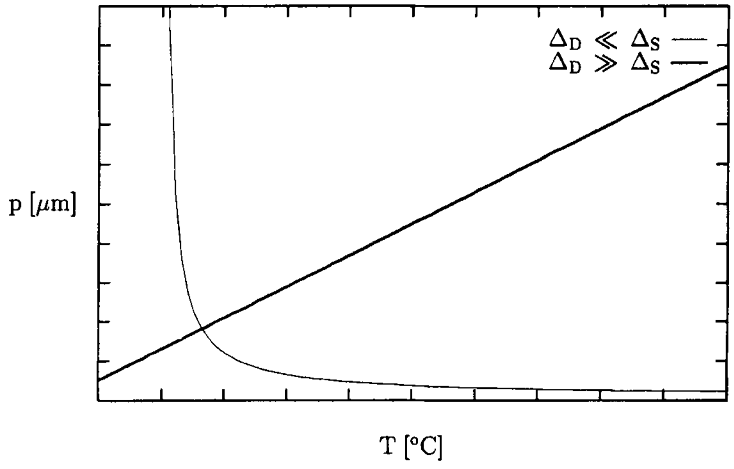


FIGURE 12 Sketch of the different possible temperature dependences after eq. (6).

ammoniumbromides. Within the perfluoro systems no headgroup influence could be detected as only the counterion has been changed. The micelles of the two host phase classes differ strongly in their flexibility. The voluminous perfluorinated chains have less tendency to undergo conformation changes and cannot bend when tilted. In the perfluorinated systems the phase chirality probably is enforced by sterical interactions as can be seen by the dependence $p(T)$. In the ammoniumbromide systems, it depends on the dopant if sterically or/and dispersive interactions are effecive. With small hydrophilic dopants the dispersive interactions predominate but with voluminous hydrophobic dopants the sterical interactions predominate like in the perfluoro systems.

One interesting topic to investigate in future is the behaviour of flexible **non-ionic** surfactants. There should predominate the dispersive interactions by use of hydrophilic dopants like MA in the ammoniumbromide systems but without charges it would be interesting to see on the one hand if the temperature dependence of the pitch is also linear and on the other hand if with bulky dopants there is also a contribution of sterical interactions. Another point is the molecualr statistical theory. As mentioned, only **inter**micellar interactions are considered but the **intra**micellar interactions must be considered, too. It is important to find out the place of residence of the dopant molecules in the micelles.

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