

# Effect of the thickness of the hydrophobic bilayer on the helical twisting power in micellar nematic liquid crystals

M. Acımiş,\* Ç. Ocak, Ş. Özacar and K. Göçmen

Abant İzzet Baysal University, Faculty of Arts and Sciences, Department of Chemistry 14280, Bolu, Turkey. E-mail: mahmut@ibu.edu.tr

Received (in London, UK) 18th September 2001, Accepted 15th November 2001

First published as an Advance Article on the web 12th March 2002

The effect of the thickness of the hydrophobic bilayer of host nematic phases on the helical twisting power (HTP) of some chiral guests has been investigated. The thickness of the hydrophobic bilayer of the host nematic phases was varied with varying chain length from C<sub>8</sub> to C<sub>12</sub> in the alkylammonium chloride series and from C<sub>12</sub> to C<sub>16</sub> in the alkyltrimethylammonium bromide series. The chiral guests were L-alanine esters with C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub> and C<sub>10</sub> hydrocarbon chains, mandelic acid (MA) and hexahydromandelic acid (HHMA). In the host chiral nematic phases of the alkylammonium chloride series, the HTPs of the chiral alanine ester guests increased as their chain length was increased and the thickness of the hydrophobic bilayer was extended. In both series, similar behaviour was observed for the chiral guests MA and HHMA, but in general, the HTPs of HHMA were larger than those of MA. Accordingly, the chirality transfer from the chiral guest to the achiral micelle was interpreted to be more effective if the chiral guest has a “certain fitting and orientation” in the micelle.

## Introduction

Micelles, with their ionic or hydrophilic surface consisting of head groups attached to long hydrocarbon chains in the interior, offer an interesting structure to accommodate solute molecules. In the nematic state under constant concentration and temperature conditions, micelles exhibit an average micelle size and a certain order in the hydrophobic and ionic regions. Any small amount of solute added may cause a modification in both regions, which reflects itself, for example, in increases or decreases in the nematic–isotropic phase transition temperature, density and flow properties.<sup>1,2</sup>

Recently, we have investigated the effect of the structure of two chiral solutes with the same hydrophilic group but different hydrophobic parts, mandelic acid (MA), C<sub>6</sub>H<sub>5</sub>CHOH-COOH, and hexahydromandelic acid (HHMA), C<sub>6</sub>H<sub>11</sub>CHOHCOOH, on the induced pitch in two achiral nematic host phases.<sup>1</sup> The difference between the helical twisting powers (HTP) of the chiral guests, MA and HHMA, in a decylammonium chloride nematic host phase was extremely large, but that in a DL-serine hydrochloride decylester nematic host phase was insignificant.<sup>1</sup>

The chiral induction in thermotropic liquid crystals is explained on the basis that the chirality is mapped onto the nematic phase, whereby a chiral nematic phase is induced.<sup>3</sup> This mapping was also described by a theory for inherent dissymmetric molecules which assumes that the liquid crystal environment is deformed by the “structure of the surface” of the inducing chiral guest.<sup>4,5</sup> The effect of the chiral guest on the nematic phase, *i.e.* the phase chirality, is expressed by two quantities, the helical twisting power and handedness, according to the working equation  $\beta = \pm p^{-1}/x$ , where  $\beta$ ,  $p^{-1}$  and  $x$  indicate the HTP, reciprocal pitch and molar fraction of the chiral guest, respectively. The plus or minus signs denote a right or left-handed helix.

$\beta$ , the helical twisting power, is a quantity determined from the measurement of the pitch in an anisotropic state and expresses the interaction of an oriented chiral molecule with its achiral anisotropic environment, built up of oriented achiral molecules. Therefore, it can be expected that the measured  $\beta$

will depend on the orientational distribution of the chiral molecules in the anisotropic phase.<sup>3</sup>

Since the smallest unit in thermotropic liquid crystals is the molecule, but that in lyotropics is the micelle, which consists of an average of a hundred amphiphilic molecules<sup>6</sup> in the nematic state, the question arises as to what degree the above explanations concerning the chirality transfer are applicable to micellar nematic systems, *i.e.* how can the chirality of a molecule be mapped onto an individual micelle, which exhibits an ionic cover attached to a hydrophobic core in the interior? Furthermore, it is worth bearing in mind that the dominant forces between the molecules in thermotropic liquid crystals are van der Waals type, but those between micelles consisting of surfactants are Coulombic.

Having the above considerations in mind, the aim of the present report was directed toward understanding the effect of varying the thickness of the hydrophobic bilayer of the nematic host phases as well as the chain length of the chiral guests on their HTP. Host mesophases with varied hydrophobic bilayer thickness were obtained from the alkylammonium chloride series CH<sub>3</sub>-(CH<sub>2</sub>)<sub>*n*</sub>-NH<sub>3</sub>Cl with C<sub>8</sub>, C<sub>10</sub> and C<sub>12</sub> hydrocarbon chains, and the chiral guests were the esters of L-alanine CH<sub>3</sub>-(CH<sub>2</sub>)<sub>*n*</sub>-OOCCH(NH<sub>3</sub>Cl)CH<sub>3</sub>, with C<sub>4</sub>, C<sub>6</sub>, C<sub>8</sub> and C<sub>10</sub> hydrocarbon chains. In addition, we have studied the host phases of the alkyltrimethylammonium bromide series CH<sub>3</sub>-(CH<sub>2</sub>)<sub>*n*</sub>-N(CH<sub>3</sub>)<sub>3</sub>Br with C<sub>12</sub>, C<sub>14</sub> and C<sub>16</sub> hydrocarbon chains, using the chiral guests MA and HHMA. Since the head groups of guests and hosts, as well as the chemical constituents of the host phases, have the same chemical identity, this choice of chiral guest and host phases allows us to interpret the effect of the location or orientational distribution of the chain length or hydrophobic parts of the chiral guests on the helical twisting power in various thicknesses of hydrophobic bilayer.

## Experimental

Octylammonium chloride (OACl), decylammonium chloride (DACl) and dodecylammonium chloride (DDACl) were obtained by neutralizing the corresponding amines with dilute

hydrochloric acid in ethanol. The crude materials were purified by recrystallization from petroleum ether (40–60 °C)–chloroform mixtures (~4:1). The esters of L-alanine, L-alanine hydrochloride butylester (L-ABE), L-alanine hydrochloride hexylester, (L-AHE), L-alanine hydrochloride octylester (L-AOE) and L-alanine hydrochloride decylester (L-ADE), were synthesized by esterification of L-alanine with the corresponding alcohol, as described previously.<sup>7</sup> The dodecyltrimethyl ammonium bromide (DDTABr), tetradecyltrimethylammonium bromide (TDTABr) and hexadecyltrimethylammonium bromide (HDTABr) of 99% purity were purchased from Merck and Aldrich. Before use, they were recrystallized from petroleum ether (40–60 °C)–chloroform mixtures (~3 : 1). n-Decanol is abbreviated to DeOH. The initial compositions of liquid crystalline phases are given as molar fractions for each component in Table 1.

In order to prepare the liquid crystalline samples, appropriate amounts of ingredients (Table 1) were weighed into a test tube which was flame-sealed. The mixture was then homogenized by heating in a water bath (~50 °C) and centrifuging occasionally. For microscopic investigations, microslides of 0.2 and 0.3 mm thickness (CamLab, UK) were used. Pitch lengths were measured with a polarising light microscope on the fingerprint texture. The distance between three parallel stripes corresponds to the pitch of the helix (*P*).

## Results and discussion

Two series of micellar host phases have been used to investigate the effect of the thickness of the hydrophobic bilayer on

the HTPs of chiral guests with different chain lengths and structures.

### (A) The HTPs of the first series

In this series, the host amphiphiles, OACl, DACl and DDACl, with the salt, Na<sub>2</sub>SO<sub>4</sub>, and water, were used to prepare micellar liquid crystalline phases with varying hydrophobic bilayer thicknesses. From each achiral host phase, chiral nematic (cholesteric) phases were induced, using L-alanine hydrochloride esters with varying chain length from C<sub>4</sub> to C<sub>10</sub> (n-butyl, n-hexyl, n-octyl, n-decyl esters) abbreviated as L-ABE, L-AHE, L-AOE and L-ADE, respectively, as chiral guests. The compositions of the achiral phases, phase structures and the chiral nematic–isotropic phase transition temperatures (CH–I) are presented in the Experimental, and as can be seen from Table 1, the composition of each phase had to be adjusted with respect to the addition of the chiral guest.

By adding the chiral guests (L-ADE, L-AOE, L-AHE) to the micellar nematic host phases, chiral nematic phases with fingerprint texture were obtained, from which the pitch was measured.<sup>8,9</sup> The chiral guest L-ABE, however, showed a striking effect, as it was added to the nematic phases, it turned them into isotropic phases. Suitable chiral nematic phases were then obtained by adding L-ABE to lamellar phases. So, the statement “addition of a suitable chiral solute to a nematic phase induces a chiral nematic phase in a thermotropic liquid crystal” has to be extended in lyotropics to nematic and lamellar phases. A similar effect, a strong lowering of the CH–I phase transition temperature, was also observed for the chiral guest L-AHE, particularly in the DDACl host phase. The lowering

**Table 1** The compositions of the constituents of the investigated phases in molar fractions in the two series. The heading “phase” indicates the initial phase type without addition of the chiral guest. The notation Tr/°C includes two phase transition temperatures; the first number is the nematic–isotropic phase transition temperature (N–I), whereas the second indicates the cholesteric–isotropic phase transition temperature (CH–I).

(a)										
$X_{\text{OACl}}$	$X_{\text{DACl}}$	$X_{\text{DDACl}}$	$X_{\text{Na}_2\text{SO}_4}$	$X_{\text{H}_2\text{O}}$	$X_{\text{ABE}}$	$X_{\text{AHE}}$	$X_{\text{AOE}}$	$X_{\text{ADE}}$	Phase	Tr/°C
0.1150	—	—	0.0271	0.8579	added	—	—	—	$L_\alpha$	~ 78–28
0.1053	—	—	0.0245	0.8701	—	added	—	—	$N_D$	~ 47–37
0.0992	—	—	0.0234	0.8774	—	—	added	—	$N_D$	~ 27–35
0.1028	—	—	0.0239	0.8773	—	—	—	added	$N_D$	~ 41–30
—	0.0829	—	0.0086	0.9085	added	—	—	—	$L_\alpha$	~ 77–26
—	0.0706	—	0.0067	0.9227	—	added	—	—	$N_D$	~ 45–26
—	0.0641	—	0.0062	0.9297	—	—	added	—	$N_D$	~ 37–26
—	0.0623	—	0.0060	0.9317	—	—	—	added	$N_D$	~ 34–29
—	—	0.0384	0.0026	0.9590	added	—	—	—	$L_\alpha$	~ 60–27
		0.0384	0.0027	0.9590	—	added	—	—	$L_\alpha$	~ 60–27
		0.0329	0.0022	0.9649	—	—	added	—	$L_\alpha$	~ 50–57
		0.0247	0.0013	0.9740	—	—	—	added	$N_D$	~ 34–26

(b)										
$X_{\text{OACl}}$	$X_{\text{DACl}}$	$X_{\text{DDACl}}$	$X_{\text{Na}_2\text{SO}_4}$	$X_{\text{H}_2\text{O}}$	$X_{\text{MA}}$	$X_{\text{HHMA}}$	Phase		Tr/°C	
0.1054	—	—	0.0024	0.8706	added	—	$N_D$		~ 43–58	
0.1013	—	—	0.0023	0.8762	—	added	$N_D$		~ 30–63	
—	0.0658	—	0.0063	0.9279	added	—	$N_D$		~ 38–26	
—	0.0576	—	0.0058	0.9365	—	added	$N_D$		~ 28–37	
—	—	0.0230	0.0012	0.0756	added	—	$N_D$		~ 35–28	
—	—	0.0220	0.0010	0.9770	—	added	$N_D$		~ 29–26	

(c)											
$X_{\text{DDTABr}}$	$X_{\text{TDTABr}}$	$X_{\text{HDTABr}}$	$X_{\text{Na}_2\text{SO}_4}$	$X_{\text{DeOH}}$	$X_{\text{H}_2\text{O}}$	$X_{\text{MA}}$	$X_{\text{HHMA}}$	Phase		Tr/°C	
0.0436	—	—	0.0097	0.0142	0.9325	added	—	$N_D$		~ 40–25	
0.0421	—	—	0.0094	0.0134	0.9351	—	added	$N_D$		~ 27–59	
—	0.0215	—	0.0104	0.0075	0.9606	added	—	$N_D$		~ 54–25	
—	0.0157	—	0.0074	0.0054	0.9715	—	added	$N_D$		~ 28–40	
—	—	0.0095	0.0049	0.0036	0.9819	added	—	$N_D$		~ 44–26	
—	—	0.0061	0.0032	0.0023	0.9884	—	added	$N_D$		~ 27–29	

of the CH-I phase transition temperatures as L-ABE or L-AHE was added to a lamellar or nematic host phase is represented in Fig. 1. The effect of other guests, L-ADE and L-AOE, on the CH-I phase transition temperature was observed to be similar, however, it was not striking as the effect of L-ABE or L-AHE.

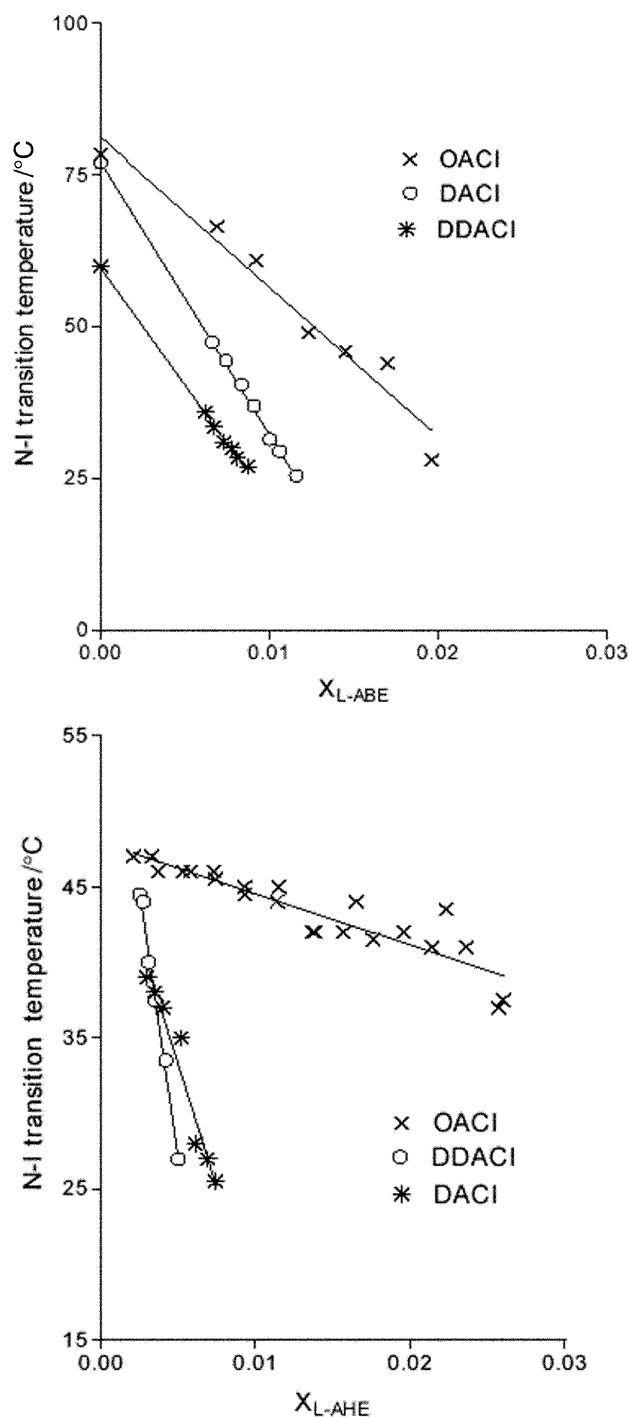
All the investigated nematic host phases exhibited a positive optical anisotropy ( $\Delta n$ ) as determined from oriented liquid crystalline samples with a polarizing light microscope, *i.e.* pseudoisotropic texture with positive  $\Delta n$  indicates a disc-like micelle structure which orients perpendicular with its optical axis to an applied magnetic field.<sup>8,9</sup> In the microscope samples of the induced cholesteric phases, beside the fingerprint texture, Grandjean texture develops as well, occasionally from which  $\Delta n$  of the chiral nematic phase was measured to be negative. Consequently, the induced cholesteric phases align with their optical axis parallel to the applied magnetic field.<sup>8,9</sup>

The HTPs of the chiral guests (L-ADE, L-AOE, L-AHE and L-ABE) were determined from the slope of plots of the reciprocal pitch ( $P^{-1}$ ) versus molar fraction of the chiral solute according to the equation  $P^{-1} = \beta x$ , given in the Introduction, for each host phase. As can be seen from Fig. 2, the plots of the reciprocal pitch  $P^{-1}$  versus molar fraction of the chiral guests (L-ADE, L-AOE and L-AHE) in an OACI host phase are not linear, but that of the chiral guest L-ABE is. The HTPs for L-ADE, L-AOE and L-AHE were then determined from the first five data where a straight line between  $P^{-1}$  and  $x$  of the chiral guest exists (Fig. 2). The plots of  $P^{-1}$  versus the molar fractions of the chiral guests in DACI and DDACI host phases gave straight lines for each chiral solute, and because the appearance of both plots was similar, only the plot for the DDACI host phase is represented as an example in Fig. 3. Throughout our series, since the plot of  $P^{-1}$  versus molar fraction of alanine esters gave straight lines or nearly straight lines, we have concluded that there were no rotamers of the chiral guests, which would contribute to an opposite chirality for the induced cholesteric phases, as discussed by Radley and co-workers for L-proline hydrochloride decylester<sup>10</sup> and L-ADE<sup>11</sup> in some micellar liquid crystalline phases.

At this point, it is interesting to compare the HTPs of the chiral guests in the different thicknesses of hydrophobic bilayer (Fig. 4). It is remarkable to note that the chiral guest, L-ABE, with four carbon atoms in the hydrocarbon chain exhibits almost the same HTP in the three different host phases (OACI, DACI and DDACI), Fig. 4. The HTP of the chiral guest, L-AHE, is nearly the same ( $3.58 \pm 0.12 \mu\text{m}^{-1}$ ) in the OACI and DACI host phases, but it differs slightly ( $4.7 \pm 0.18 \mu\text{m}^{-1}$ ) in the DDACI host phase. Similarly, the HTP of the chiral guest, L-AOE, is approximately the same in the OACI and DACI host phases ( $5.52 \pm 0.29 \mu\text{m}^{-1}$ ), but twice as large in the DDACI host phase ( $11.4 \pm 0.82 \mu\text{m}^{-1}$ ) as in the OACI and DACI host phases. Finally, the values of the HTP of the chiral guest L-ADE are different in the three host phases, with the highest HTP value ( $17.6 \pm 0.055 \mu\text{m}^{-1}$ ) in the DDACI host phase (Fig. 4). These results can be summarized as follows. (i) As the chain length of the chiral guest increases, the value of its HTP also increases, in each host phase, (ii) the HTP values of each chiral guest increases as the thickness of the host bilayer increases, and (iii) the most effective thickness of the hydrophobic bilayer is found to be the host phase with C<sub>12</sub> (DDACI phase) which produces the highest HTP with the chiral guest L-ADE.

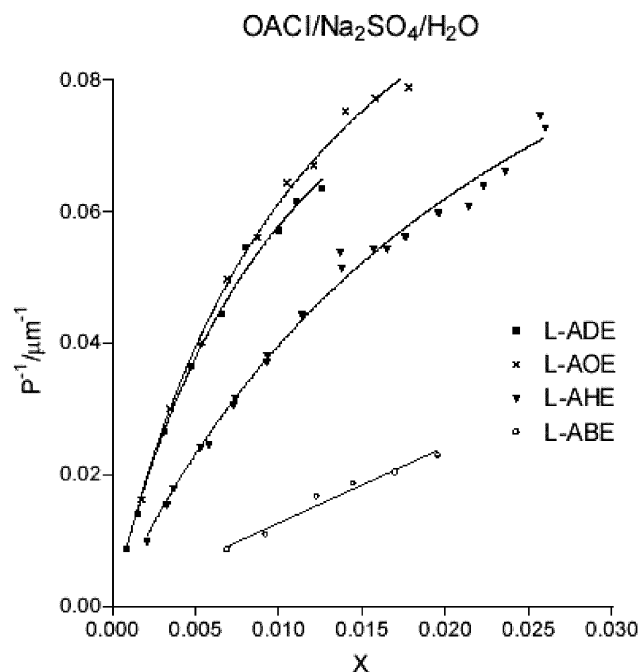
The size of the HTP may be regarded as a measure for the degree of chirality transfer from the chiral molecule to the achiral host phase. Our results suggest that the chirality transfer is determined by two factors, the orientational distribution of the chiral guest in the anisotropic achiral host phase and the thickness of the hydrophobic bilayer.

It is self-evident to imagine that the chiral guests with longer hydrocarbon chains reside with their chiral head group in the



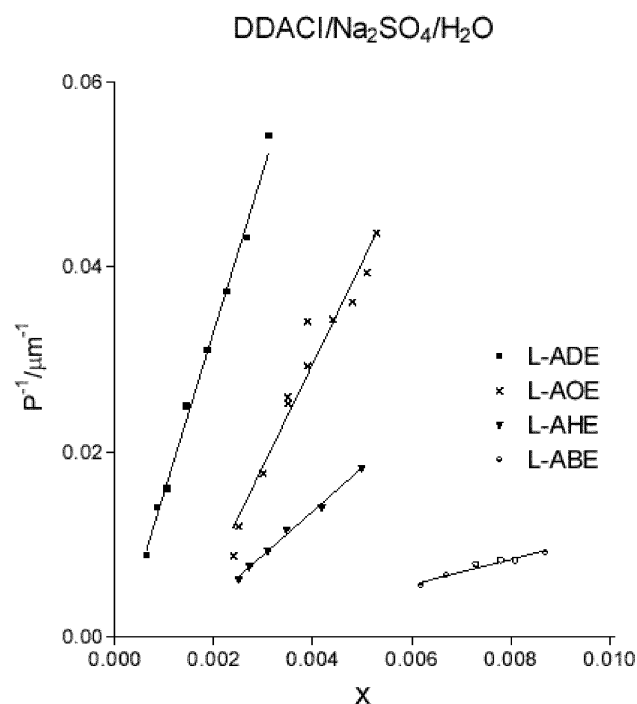
**Fig. 1** The effects of the addition of the chiral guests L-ABE and L-AHE on the chiral nematic-isotropic phase transition temperature in OACI, DACI and DDACI achiral host phases, respectively.

ionic surface of the micelles whereas their hydrocarbon chains will be located in the hydrophobic regions of the achiral host phase, *i.e.* the longer the hydrocarbon chain of the chiral guest (*e.g.* L-ADE) the better it is anchored in the micelle. In this case, the chirality of the chiral guest can be mapped easily on the micelle and therefore a high HTP value is measured. Nevertheless, it is to be expected that the chiral guests with a shorter chain length (*e.g.* L-ABE or L-AHE), due to their high solubility in water, will be adsorbed at the hydrophobic-ionic interface and aqueous layer or they will be continuously drawn into and pushed out of the micelle. In this situation, the location or the orientational distribution of the guests with shorter chains will be different from those with longer chain length. In such a case, the chirality transfer from chiral guest to the

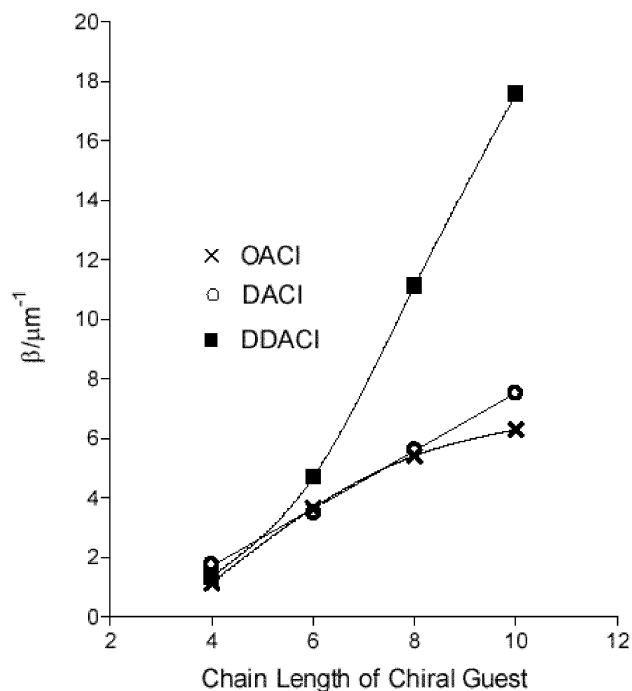


**Fig. 2** The non-linear behaviour of plots of the reciprocal pitch,  $P^{-1}$ , versus molar fraction of the chiral guests L-ADE, L-AOE and L-AHE in the OACl achiral host phase. Note the linear behaviour of L-ABE.

achiral micelle is not favoured, thus a small HTP is measured. The back and forth motion of the chiral guest molecule as presented above would also weaken the intramicellar attractive forces, which would explain the effect of the chiral guests L-ABE and L-AHE greatly lowering the CH-I phase transition temperature in these liquid crystalline systems. This explanation may be supported by considering water penetration, resulting in isotropic micellar solutions where it was found that



**Fig. 3** The linear behaviour of plots of  $P^{-1}$  versus molar fraction of the chiral guests L-ADE, L-AOE, L-AHE and L-ABE in the DDACl achiral host phase.



**Fig. 4** Plots of the helical twisting powers of the chiral guests, L-ADE, L-AOE, L-AHE and L-ABE, versus their chain lengths in the three achiral host phases, OACl, DACl and DDACl, respectively.

water penetrates the micelle until at least the first 7 of the 16 tail carbons.<sup>12</sup> Furthermore, Reeves *et al.* inferred from <sup>2</sup>H-NMR investigations that the location of the perdeuterated butanoic acid and its anion in two host phases could be explained by a time average of two conformations, all *trans* conformation (63%) and a *gauche* rotation of an  $\alpha$ - $\beta$  C-C bond (37%), both of which had a different orientation of the head group at the hydrophobic-ionic interface.<sup>13</sup>

The thickness of the hydrophobic bilayer appears to play a significant part in "feeling" the chiral potential of the chiral guest under the condition that the chiral guest, *e.g.* L-ADE, is accommodated well in the micelle with its hydrophobic and ionic parts. The HTP values of the chiral guest L-ADE in the three host phases OACl, DACl and DDACl, are  $6.3 \pm 0.28$ ,  $7.5 \pm 0.34$  and  $17.6 \pm 0.55 \mu\text{m}^{-1}$ , respectively. These results suggest that the greater the thickness the easier it is to twist in these systems, *i.e.* the most effective achiral host phase is the DDACl phase in this series. Similar results were found by Radley and Lilly in a study of the potassium dodecanoate achiral host phase with chiral potassium salts of acylated amino acids of different chain length, where it was observed that chiral L-KDDA (potassium dodecanoyl L-alaninate) with C<sub>12</sub> was the most effective host and chiral guest in inducing twist.<sup>14</sup>

#### (B) The HTPs of the second series

In this series, in addition to the nematic phases derived from OACl, DACl and DDACl, three nematic host phases were also prepared using the amphiphiles DDTABr, TDTABr and HDTABr. From these six nematic host phases, cholesteric phases were induced by the chiral guests MA and HHMA. These studies reinforce the results obtained from the first series with respect to the effect of the thickness of the hydrophobic bilayer and give the opportunity to compare the effect of the structure of the chiral guests MA and HHMA. In general, MA lowers the CH-I phase transition temperature, whereas the chiral guest HHMA increases it as they are added to the

**Table 2** The helical twisting powers of the chiral guests MA and HHMA depending on the varied thickness of the hydrophobic bilayer in OACl, DACl, DDACl, DDTABr, TDTABr and HDTABr host phases.

	OACl	DACl	DDACl	DDTABr	TDTABr	HDTABr
$\beta_{MA}/\mu\text{m}^{-1}$	$2.98 \pm 0.03$	$6.76 \pm 0.07$	$30.25 \pm 0.52$	$4.13 \pm 0.10$	$7.33 \pm 0.09$	$15.96 \pm 0.40$
$\beta_{HHMA}/\mu\text{m}^{-1}$	$7.98 \pm 0.74$	$11.56 \pm 0.48$	$30.3 \pm 1.09$	$3.56 \pm 0.33$	$15.01 \pm 1.2$	$26.45 \pm 3.51$

achiral nematic host phases<sup>1</sup> (Table 1). Plotting  $P^{-1}$  versus molar fraction of the chiral guest MA gave in all the six host phases straight lines, whereas plots of the chiral guest HHMA yielded curved lines similar to those in Fig. 2 in DDTABr, TDTABr and HDTABr nematic host phases. Here again, the HTPs were determined from the first five data, where a straight line exists between the reciprocal pitch,  $P^{-1}$  and  $x$ , the molar fraction of HHMA.

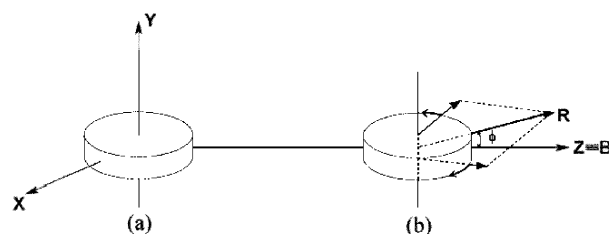
The experimentally determined HTPs of the chiral guests MA and HHMA in the six achiral nematic host phases are listed for comparison in Table 2. The results can be summarized as follows. In the host nematic phases of OACl, DACl and DDACl, the HTPs of MA and HHMA increase as the thickness of the hydrophobic bilayer increases. The values of the HTPs of the chiral guest HHMA are higher in OACl and DACl host phases than MA, but it is approximately the same in the DDACl host phase. The HTPs of the two chiral guests in the DDTABr, TDTABr and HDTABr host phases show a similar behaviour as in the series of OACl, DACl and DDACl phases, with one exception, the HTP of HHMA in the HDTABr phase is much larger than the HTP of MA. The HTPs of MA and HHMA in the DDACl host phase are greater than the corresponding HTPs in the alkyltrimethylammonium bromides phases, which imply a weak interaction of the chiral guests with the head group of the host in these systems (Table 2).

In general, one can say that the HTPs of the chiral guest HHMA with the cyclohexyl ring as hydrophobic part are higher than those of the chiral guest MA. These results may be explained again on the basis that MA is adsorped at the hydrophobic–ionic interface of the micelle and the aqueous layer, the solubility of MA in water is  $150 \text{ gL}^{-1}$  at  $20^\circ\text{C}$ , whereas HHMA is sparingly soluble. Consequently, one may expect that the phenyl ring of MA is continuously “being drawn into and pushed out of” the micelle. In this case, the chiral guest MA cannot fully transfer its chirality to the achiral host phase and, therefore, small HTPs are measured compared to the chiral guest HHMA whose cyclohexyl ring is expected to be located in the hydrophobic part of the micelle. The latter manifestation is supported by density measurements where it was found that the density of liquid crystal samples containing HHMA, cyclohexanol or cyclohexane rings, was less than those containing MA, phenol or benzene rings, respectively.<sup>2</sup> This result indicates that the chiral guest HHMA has the effect of swelling the micelle compared to the chiral guest MA and this is only possible if HHMA is well accommodated in the micelle.

Now, we have to answer the question of how the chirality of a molecule is transferred to an individual micelle. X-Ray diffraction studies do not differentiate between the micelles in the achiral nematic and the cholesteric phases, *i.e.* the one-dimensional periodicity “characteristic of a pseudolamellar ordering” found for achiral nematic phases was not changed by chiral dopants.<sup>15,16</sup>

Recently, we have shown that the chiral nematic phases can also be induced from doped lamellar phases or intrinsic chiral lamellar phases.<sup>9,17</sup> From the measurement of the optical anisotropy,  $\Delta n$ , in the phase sequence obtained by increasing the temperature,  $L_\alpha \rightarrow$  pseudoisotropic  $\rightarrow$  chiral nematic  $\rightarrow$  isotropic, we have concluded that the micelle shape changes from a disc shape with  $D_{\infty h}$  symmetry to a screw-like shape with  $D_\infty$

symmetry,<sup>9,17</sup> *i.e.* the surfaces of an individual micelle get rotated in opposite directions with respect to each other as the micelle is chiralized<sup>7</sup> (Fig. 5). The angle  $\phi$  was calculated roughly to vary between  $0.036$  and  $0.09^\circ$ . Consequently, our results suggest that the angle  $\phi$  can get large enough only if the chiral guest has a “certain fitting and orientation”, *i.e.* well accommodated with its hydrophobic and hydrophilic parts in the micelle so that it can fully convey its chiral potential to the achiral micelle.



**Fig. 5** (a) A schematic representation of the “idealized” achiral disc micelle with  $D_{\infty h}$  symmetry and (b) the chiralized micelle with  $D_\infty$  symmetry.  $R$  represents the resulting vector with respect to a direction, *e.g.* magnetic field direction ( $B$ ), when the surfaces of the micelle are rotated with respect to each other by the action of the chiral guests.

## Conclusions

Two series of achiral host phases have been investigated to understand the effect of the varied thickness of the hydrophobic bilayer on the HTP.

In the first series, the HTPs of the chiral guests (L-ABE, L-AHE, L-AOE and L-ADE) increased as their chain length increased in each host phase (OACl, DACl and DDACl). The chiral guest L-ADE and the host phase DDACl were found to be most effective in producing a large HTP.

The HTPs of the chiral guests MA and HHMA in the second series (OACl, DACl, DDACl, DDTABr, TDTABr and HDTABr) increased too, as the thickness of the hydrophobic bilayer increased. The increase of the HTPs of MA and HHMA in the DDACl host phase with  $C_{12}$  was larger than those of the alkyltrimethylammonium bromide phases with  $C_{12}$ ,  $C_{14}$  and  $C_{16}$ . In general, the HTPs of the chiral guest HHMA were larger than those of MA.

These results and those in the literature suggest that the mapping of the chirality of a chiral molecule on an achiral micelle will be more effective if the chiral solute adopts a “certain fitting and orientation” in the micelle.

## Acknowledgements

We are grateful to the Research and Development Foundation of Abant İzzet Baysal University (71/27.03.2001) and the Volkswagen Foundation (I/67579/1992) for supporting this work. M. A. also wishes to thank B. Altıntaş for help with the graphics and Professor Kuball, Kaiserslautern University, Germany, for valuable discussions during his recent stay in Bolu.

## References

- 1 Ç. Ocak, M. Acımiş, E. Akpınar and A. Gök, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5703.
- 2 E. Akpınar, M. Acımiş and Ç. Ocak, *Phys. Chem. Chem. Phys.*, 2001, **3**, 645.
- 3 H.-G. Kuball and O. Türk, *Pol. J. Chem.*, 1999, **73**, 209.
- 4 F. Ferrarini, P. L. Nordio, P. V. Shibaev and V. P. Shibaev, *Liq. Cryst.*, 1998, **24**, 219.
- 5 A. Ferrarini and P. L. Nordio, *J. Chem. Soc., Perkin Trans.*, 1998, **2**, 455.
- 6 M. C. Holmes, D. J. Reynolds and N. Boden, *J. Phys. Chem.*, 1987, **91**, 5257.
- 7 M. Acımiş and L. W. Reeves, *Can. J. Chem.*, 1980, **58**, 1533.
- 8 A. M. Figueiredo Neto, L. Liebert and A. M. Levelut, *J. Phys. (Paris)*, 1984, **45**, 1505.
- 9 M. Acımiş, E. Dorr and H.-G. Kuball, *Liq. Cryst.*, 1994, **17**, 299.
- 10 K. Radley and N. McLay, *J. Phys. Chem.*, 1994, **98**, 3071.
- 11 K. Radley, N. McLay and K. Gicquel, *J. Phys. Chem. B*, 1997, **101**, 7404.
- 12 F. M. Menger *Acc. Chem. Res.*, 1979, **12**, 111.
- 13 B. J. Forrest, L. Hecker and L. W. Reeves, *Mol. Cryst. Liq. Cryst.*, 1980, **58**, 223.
- 14 K. Radley and G. J. Lilly, *Mol. Cryst. Liq. Cryst.*, 1993, **231**, 183.
- 15 A. M. Figueiredo Neto and M. E. Marcondes Helene, *J. Phys. Chem.*, 1987, **91**, 1466.
- 16 M. E. Marcondes Helene and A. M. Figueiredo Neto, *Mol. Cryst. Liq. Cryst.*, 1988, **162B**, 127.
- 17 M. Acımiş, A. Agar and A. Gök, *Liq. Cryst.*, 1998, **24**, 369.