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Mass density measurements as a tool to distinguish between micelle size and shape in nematic and chiral nematic phases

M. Acımış* and E. Akpınar

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

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The relative alteration in micelle size and micelle shape brought about by two sets of specific solutes have been investigated by mass density measurements at constant composition and temperature. The mass density of the first set of solutes, phenol, benzene, cyclohexanol and cyclohexane, was measured in the same host phase and found to change in the order: phenol > cyclohexanol > benzene > cyclohexane. The contribution of the solutes to the mass density of the host phase was interpreted to arise from the capability of the hydrophilic group and the hydrophobic part of the solutes to interact with the corresponding region of the host micelle. The second set consisted of racemic amphiphilic mixtures and their enantiomers, decyl- and dodecyl-esters of serine and alanine. It was found that the mass density increases in the serine phases but decreases in the alanine ones as the DL-racemic amphiphiles of the nematic phases were replaced by their L-isomers. These phenomena were shown to arise from a definite arrangement of the head groups in the racemic nematic and intrinsic chiral nematic phases. Furthermore, on the basis of the mass density difference between the achiral/induced chiral nematics and the racemic/intrinsic chiral nematics, a distinction between the induced chiral nematic phases and the intrinsic chiral ones is possible.

Introduction

Amphiphilic molecules, on dissolution in water, self-assemble to form micelles and liquid crystals as their concentration is increased. Among the various liquid crystalline structures, we concentrate on nematic and chiral nematic liquid crystalline phases. The nematic phase region exists between the borderlines of the totally ordered lamellar or hexagonal phase and the totally disordered isotropic micellar solution and in general can be achieved either from lamellar or hexagonal phases by increasing the temperature[1,2] or as usual at constant temperature and certain concentrations of the host amphiphile, water and other additives. The geometry of the building units, *i.e.* the shape of the micelles in the nematic region was revealed to be discotic (D), cylindrical (C) or biaxial (B) and designated N_D, N_C or N_B, respectively, where N stands for nematic. Although macroscopically there is no apparent difference between nematic phases (achiral nematic phases) obtained from the host amphiphiles *e.g.* decylammonium chloride (DACl), or sodium decylsulfate (SDS) and the racemic nematic phases derived for instance from DL-serine hydrochloride decylester (DL-SDE), or DL-alanine hydrochloride dodecylester (DL-ADDE), we wish to introduce both terms for later discussion.

Chiral nematic phases can primarily be obtained either by adding a suitable chiral solute to an achiral nematic phase or by using an amphiphilic enantiomer *e.g.* L-serine hydrochloride decylester (L-SDE), with water and a salt. As a result, an induced chiral nematic phase and an intrinsic chiral nematic phase can be produced, respectively, where we emphasize the difference between them as we will show in this paper. As nematic phases, the chiral nematic phases are also designated Ch_D, Ch_C or Ch_B, where Ch stands for cholesteric, and the subscript letters indicate the shape of the micelles, being discotic, cylindrical or biaxial.

Micelle size and shape in both nematic and chiral nematic phases have been of fundamental interest and investigated by some research groups.[3–5] In the frame of this paper we confine ourselves to discotic (disc-like) micelles and in order to have an estimate, we depict some literature values of SDS and DACl nematic phases: the discs of a particular SDS nematic phase were found to possess a diameter of ≈57 Å and a thickness of ≈20 Å,[3] but for the DACl nematic phase a diameter of ≈90 Å and a thickness of ≈40 Å were given.[6]

Another important property of the liquid crystals is their preferred alignment, *i.e.* the alignment of the director (optical axis) of the phase with respect to a given direction, *e.g.* magnetic field direction. This quantity can be assessed by diamagnetic susceptibility anisotropy ($\Delta\chi$) or optical anisotropy (Δn). Particularly, it is easy to determine the sign of Δn by using a polarizing light microscope to obtain conoscopic measurements for N_D phases which align with their director perpendicular to the magnetic field direction,[7] Fig. 1a. Such N_D phases possess a positive Δn, but a negative $\Delta\chi$, then Δn and $\Delta\chi$ are opposite in sign for amphiphilic liquid crystals.[7]

The shape of the micelle of the induced chiral phase was also of fundamental interest, and small angle X-ray diffraction studies could not differentiate between the shapes of chiralized micelles and achiral micelles,[4,8] however, we have inferred from our investigations on chiral induction[9] and the results in the literature[10] that a chiral micelle would possess a screw-like shape, Fig. 1c and d. The nematic and chiral nematic phases can easily be recognized by a polarizing light microscope from their schlieren (threaded) textures and the finger print texture, respectively.[11] The nematic state can then be visualized as a dispersion of anisometric micelles of finite size in water with long range orientational order but with no positional order. The chiral nematic state, however, can, in a first approximation, be considered as a nematic state in which the

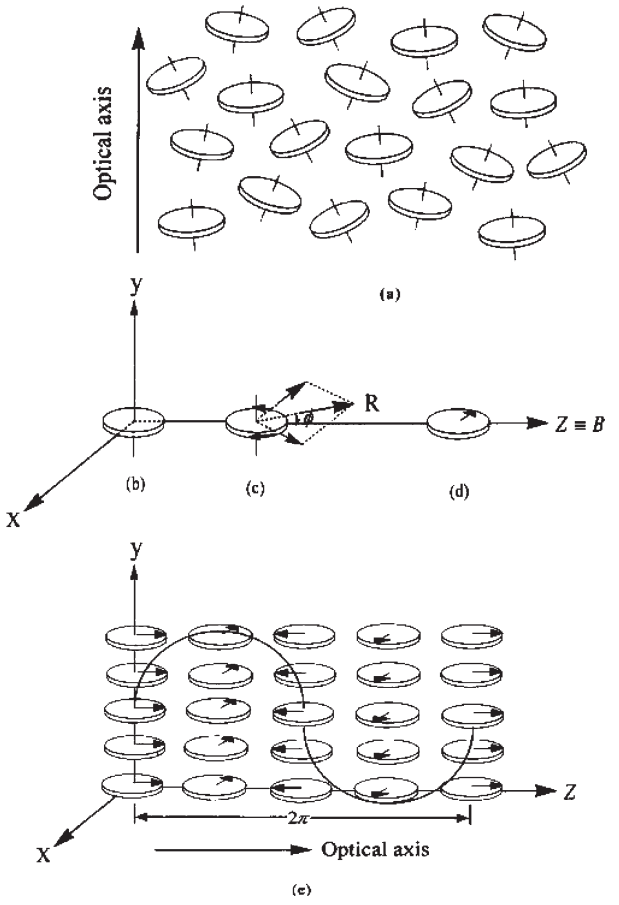

Fig. 1 (a) A schematic representation of the nematic disc-like phase, N_D, and the alignment of its optical axis with respect to magnetic field (B). When a discotic micelle (b) is chiralized, it takes a screw-like shape (c), indicated by two arrows that give a resultant vector, R, with respect to the magnetic field, B. For simplicity, R is drawn on the surface of the skewed micelle (d). (e) A schematic representation of the fingerprint texture, arising from stacked micelles with different rotation to complete the 2π distance.

chiralized micelles are arranged in a helicoidal structure, Fig. 1e. The 2π distance corresponds then to the pitch (P) of the chiral phase, Fig. 1e.

From the preceeding picture of nematic and chiral nematic phases it is easy to conceive that micelle structure may be extremely sensitive to the addition of solute molecules. Some solutes may increase the volume of the micelle but some decrease it, which is reflected in the flow properties of the phase and changing the nematic–isotropic phase transition.[10,12,13] Particularly of interest is the modification observed if the DL-amphiphile mixture of a racemic nematic phase is replaced by its L-enantiomer. Therefore, it is important to capture such changes by an easily applicable method, mass density measurements, which give us insight into the phenomena taking place in the micelle on addition of any solute.

In a recent communication we have shown for the first time, by a few examples, that mass density measurements may be used to detect relative changes in micelle size and micelle shape in a racemic nematic/L-isomer mixture and we have delivered some qualitative results on the effect of solutes on the host phases.[14] The present investigation is designed to show (i) quantitatively the effect of specifically chosen achiral solutes on the micelle dimension of the host phase, (ii) to extend the studies of racemic nematic/L-isomer mixtures to newly developed racemic nematic phases and their enantiomers and discuss why intrinsically chiral micelles can have smaller or larger densities than their racemic micelles. Furthermore, we will show, in contrary to common belief, that a distinction between induced chiral nematics and intrinsic chiral nematics is possible.

Experimental

Chiral amphiphilic molecules and their racemates were obtained by esterification of the amino acids, serine and alanine, with n-decanol and n-dodecanol according to the procedure given in reference 11. It was found that the yield of serine esters was better when the mole ratio of serine to alcohol 1 : 7 was chosen. In this way, L- and DL-serine hydrochloride decylesters (L-SDE and DL-SDE), L- and DL-serine hydrochloride dodecylesters (L-SDDE and DL-SDDE), and the corresponding esters of alanine, L- and DL-alanine hydrochloride decylesters (L-ADE and DL-ADE) as well as L- and DL-alanine hydrochloride dodecylesters (L-ADDE and DL-ADDE) were synthesized. Because n-dodecanol in the reaction mixtures solidifies at room temperature, it was removed from the crude esters by extraction using diethyl ether. The esters were obtained in purest form by recrystallizing them four times from ethylacetate which was distilled over a fractinating column prior use. Decylammonium chloride (DACl) was prepared by neutralizing n-decylamine with dilute hydrochloric acid in ethanol. After removing the solvent, the crude material was recrystallized four times from a mixture of petroleum ether (bp 40–60 °C) and chloroform (4 : 1). All other materials, cyclohexane, benzene, cyclohexanol, phenol, mandelic acid (MA) and hexahydromandelic acid (HHMA) were purchased at high purity (> 99.5%) and used without further purification.

The liquid crystalline samples were prepared by weighing appropriate amounts of the ingredients into test tubes which were flame-sealed immediately in order to avoid water loss. Homogeneous liquid crystalline samples were obtained by leaving the sealed test tubes in a water bath at 50 °C and centrifuging occasionally. Each liquid crystalline sample was left for 24 hours at room temperature prior to each density measurement. Approximately 3 grams of liquid crystalline sample was needed for the density and microscopic measurements. The water used was distilled 3 times over a 40-cm fractionating column. The compositions of the components, the phase type as well as the nematic–isotropic phase transition temperatures (T_{NI}) are presented in Table 1.

Great care must be taken when adding the liquid crystalline samples to the U-tube of the densitometer in order to avoid incuding air bubbles. For this purpose, the densitometer as well as the liquid crystalline samples were warmed to about 35 °C and then cooled to 20 °C. The mass density measurements were carried out on an Anton Paar DMA 5000 density meter which measures the density from the oscillation period of a U-tube. The density meter was calibrated with water at 20 °C, the temperature at which the liquid crystalline samples were measured. Each liquid crystalline sample was equilibrated at 20 °C for at least 2 hours before each measurement.

Each point of density was measured at least 3 times. The standard deviation of a point varied between 1.1×10^{-5} and 5.0×10^{-5} g cm^{-3}. In general, the deviations arise mainly from

Table 1 Compositions of the individual racemic nematic phases obtained from serine and alanine esters (hosts), salt and water in mole percent and their nematic–isotropic phase transition temperatures, T_{NI}

	NaCl	DACl	H_2O	T_{NI}/°C
DL-SDE, 5.553	3.589	–	90.858	≈34
DL-ADE, 4.415	3.712	2.211	89.662	≈34
DL-SDDE, 3.242	1.804	–	94.954	≈34
DL-ADDE, 4.072	1.936	–	93.992	≈31

random errors taking place at the weighing and filling stages for the samples. The accuracy of the density meter was given as 5×10^{-6} g cm^{-3}.

Results and discussion

The effect of solute structure on micelle size

The micelles, microscopically, are heterogeneous, consisting of an ionic and/or polar cover at the surface and a hydrophobic core in the interior, arising from the head groups and the long hydrocarbon chains, respectively. Inclusion of any solute, depending on its nature to interact with the ionic surface and the hydrophobic core of the micelle, may have a dramatic effect on the size and shape of the host micelle, which modifies the physical properties of the host phase. In general, the micelle size changes on addition of any solute, but here we consider strictly the relative changes in micelle size or shape brought about by a pair of molecules having the same head group but different hydrophobic parts (or *vice versa*) *e.g.* phenol/cyclohexanol and an amphiphilic racemic mixture and its enantiomer.

The different effect of the structure of some solute molecules was discussed in terms of the pitch induced in some host phases[12,13] and by measuring the mass density.[14] In the latter case, the mass density of two chiral dopants, mandelic acid (MA) and hexahydromandelic acid (HHMA), were measured in two different host phases and it is found that the chiral phases containing MA were more dense than those containing HHMA.[14] The density changes can be thought to arise from the contribution of the two parts of the solutes, the hydrophilic and the hydrophobic parts, phenyl and cyclohexyl, respectively. For instance, the solutes, MA and HHMA, to some extent, will become ionised in the micelle which can alter the counter-ion composition and hence the micelle size. Similarly, the hydrophobic parts, phenyl- and cyclohexyl-rings, of the solutes, are to be expected to reside in the hydrophobic region of the micelle and because they possess different shapes, they can affect the micelle size differently. The questions to be raised here are, how the two parts of the solute contribute to the density and whether they can be assessed. Indeed, in the previous communication some solutes were chosen and their mass densities were measured.[14] However, the density measurements were not complete and not discussed in detail and particularly the questions raised above were not answered. In order to have a clear picture of the effect of the structure of the solute molecules on the micelle size, it is important to study simple molecules from which the outcome may easily be perceived. The solute pairs, phenol/cyclohexanol and benzene/cyclohexane, were thought to be convenient and for comparison purposes, their mass densities were measured in the same host phase with the same composition and at constant temperature (20 °C), Table 2.

In Table 2, the densities of the pure solutes, the densities of the phases, the nematic–isotropic phase transition temperatures (T_{NI}), the phase type and compositions of individual components are presented. As seen from Table 2, the host phase is optically isotropic at 20 °C, and adding a certain amount of phenol transforms the host phase into the lamellar phase (L_α) with a density of 1.048733 g cm^{-3} which is smaller than the density of the isotropic host phase (1.048937 g cm^{-3}). On the other hand, the solute, cyclohexanol, added in the same amount as phenol does not transform the isotropic host phase into a liquid crystalline phase, but still exhibits a density of 1.046327 g cm^{-3}, smaller than the L_α produced by phenol and the isotropic host phase, Table 2. It is remarkable to compare the densities of the phenol/cyclohexanol pair with those of the benzene/cyclohexane pair. The latter pair is expected to reside completely in the hydrophobic region of the micelle. Phenol and benzene produce lamellar phases of comparable T_{NI} but of different densities, whereas the lamellar phase containing phenol is more dense than that containing benzene with a striking density difference of 0.003444 g cm^{-3}, Table 2. Nevertheless the solutes, cyclohexanol and cyclohexane produce an isotropic phase and a nematic phase, respectively. The isotropic phase containing cyclohexanol is more dense than that containing cyclohexane with a remarkable density difference of 0.003579 g cm^{-3}.

These results obtained from the DL-SDE system allow us to infer two different points, which can be attributed to the interactions of the solutes with the constituents of the host micelle. (i) The density of the isotropic host phase is higher than the phases containing the solutes, which means that the isotropic micelles of the host phase are packed more efficiently in the given volume than those containing solute molecules. (ii) The solute, phenol, produces a lamellar phase, but cyclohexanol an isotropic phase. We can think here of a concerted effect of the hydrophobic and hydrophilic parts of the solute molecules. Then, we can conceive that the hydrophobic rings of phenol and cyclohexanol are embeded in the hydrophobic region and the hydroxy groups are anchored at the hydrophobic–hydrophilic interface of the micelle. Therefore, the phenyl ring can be well accomodated in the micelle, so that the hydrophobic and hydrogen bonding interactions of phenol are fully utilized to form denser phases whereas the spacious cyclohexyl ring creates a disturbance (probably a hole) in the hydrophobic region of the micelle which may weaken the hydrophobic and the hydrogen bonding interactions, Fig. 2.

In summary, phenol and benzene transform the isotropic host phase into a lamellar phase, respectively, where the

Table 2 The composition of the host phase derived from DL-SDE, NH_4Cl and water without and with dopants, the phase types, nematic (N), lamellar (L_α) and isotropic (I) and the phase transition temperatures T_{NI}, and the corresponding mass densities. For comparison purposes the densities of the pure solutes also are given

	$X_{DL\text{-}SDE}$	X_{NH_4Cl}	X_{phenol}	$X_{cyclohexanol}$	X_{H_2O}	Phase type	T_{NI}/°C	d_{20}/g cm^{-3}
1	4.736	4.480	–	–	90.784	I	–	1.048937
2	4.703	4.449	0.697	–	90.151	L_α	≈51	1.048733
3	4.703	4.449	–	0.697	90.151	I	–	1.046327
	$X_{DL\text{-}SDE}$	X_{NH_4Cl}	$X_{benzene}$	$X_{cyclohexane}$	X_{H_2O}	Phase type	T_{NI}/°C	d_{20}/g cm^{-3}
1	4.736	4.480	–	–	90.784	I	–	1.048937
2	4.703	4.449	0.697	–	90.151	L_α	≈49	1.045289
3	4.703	4.449	–	0.697	90.151	N	≈34	1.042748
	Phenol	Cyclohexanol	Benzene	Cyclohexane				
d_{20}/g cm^{-3}	1.0576	0.9624	0.8765	0.7785				

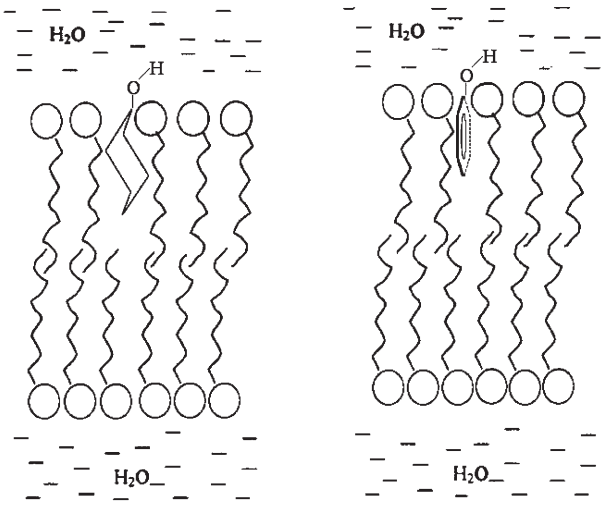

Fig. 2 A schematic representation of the locations of phenol and cyclohexanol in the micelle. For clarity the sketches are exaggerated.

lamellar phase of phenol is more dense than the one of benzene. This result implies that the micelle containing phenol at the ionic front and the hydrophobic region is shrunk, whereas the phase with benzene is compact at the hydrophobic region, but is loose at the ionic surface. The situation for cyclohexanol and cyclohexane, though the cyclohexyl and cyclohexane rings swell the micelle,[15] appears to parallel the case of phenol and benzene. The densities of the solutions change in the same order as the densities of the pure solutes, phenol > cyclohexanol > benzene > cyclohexane, which arises from the structure and interactions of individual solute with the corresponding parts of the host phase. Except for phenol, the densities of the pure solutes are much less than the densities in the liquid crystals, Table 2. In all cases the aggregate size increases upon addition of the solute molecules which is reflected in the density and T_{NI} changes.

It is important to mention that our density measurements have been performed only with one host phase and at one concentration. Although host phases with a C_{10} chain length such as DL-SDE give similar results with the solutes studied, it is interesting to make density measurements with different achiral and chiral host phases of different concentrations and chain lengths using the same and other organic solutes. Such measurements would allow us to make more accurate generalizations, and are the subject of our present research.

The origin of the change of mass density in racemic nematic and intrinsic chiral nematic phases

In a recent communication it was shown for one example that the mass density has increased as the racemic amphiphile (DL-SDE) in the racemic nematic phase was replaced by its L-enantiomer (L-SDE).[14] It is of fundamental interest to show whether this result can be generalized. Having been motivated by this aspect, and because there is very small choice on racemic/enantiomer amphiphiles we have synthesized amphiphilic molecules as decylesters and dodecylesters of the amino acids, alanine and serine. As a result, we have obtained two racemic amphiphilic molecules of alanine, DL-ADE and DL-ADDE, and their L-enantiomers, L-ADE and L-ADDE, and also two racemic amphiphilic molecules of serine, DL-SDE and DL-SDDE and their L-enantiomers, L-SDE and L-SDDE. It is of note that the racemic and intrinsic chiral nematic phases of DL-ADE and L-ADE were stabilized by adding a small amount of decylammonium chloride, DACl, as a co-surfactant. All the racemic nematic phases exhibited a positive optical anisotropy, Δn, indicating a disc-like structure N_D, and consequently, the intrinsic chiral nematic phases,N_D*, possessed a negative Δn.[7]

We have measured the changes in the density as the racemic amphiphilic molecules were replaced by their L-enantiomers at constant composition and temperature conditions. For the purpose of comparison we have represented the changes in density of serine and alanine decylesters in Fig. 3a and b, and the changes in density of serine and alanine dodecylesters in Fig. 4a and b. As seen from Figs. 3 and 4, the densities of the serine systems increase as the racemic amphiphiles are substituted by their L-enantiomers but those of the alanine systems decrease linearly. The change in density, as one goes from a racemic nematic phase to its intrinsic chiral one, may be attributed to a change in micelle size and structure, *i.e.* the symmetry of the disc-like micelle in the racemic phase ($D_{\infty h}$) is expected to change to C_2 or D_∞ in the chiral phase, Fig. 1c and d.

Now, we have to give a possible answer as to why the density, on passing from a racemic nematic phase to its intrinsic chiral one, increases in serine esters but decreases in alanine esters. Before answering this question, we have to state that it is not clear whether the average aggregation number changes as the racemic nematic system is converted into the intrinsic chiral nematic one. Any change in the average aggregation number, as the racemic amphiphile in the racemic nematic phase is substituted by its L-enantiomer may be investigated by X-ray[5] or neutron[16,17] diffraction studies.

In order to understand the striking change in density, we have constructed framework molecular models (FWM) of serine and alanine esters, then the density change clearly arises from the definite packing of the head groups in the racemic nematic and intrinsic chiral nematic phases, Figs. 5 and 6. In Fig. 5a, the racemic amphiphile, DL-SDE and in Fig. 5b, the intrinsic chiral amphiphile, L-SDE, are drawn according to the FWMs. As seen from Fig. 5a, if the D- and L-amphiphiles are placed as mirror images, the head groups are in a position to repulse each other because the equally charged groups, *e.g.* the ammonium group in the L-enantiomer experiences the charge of the ammonium group in the mirror image amphiphile. The same situation is valid for the carbonyl group. Other

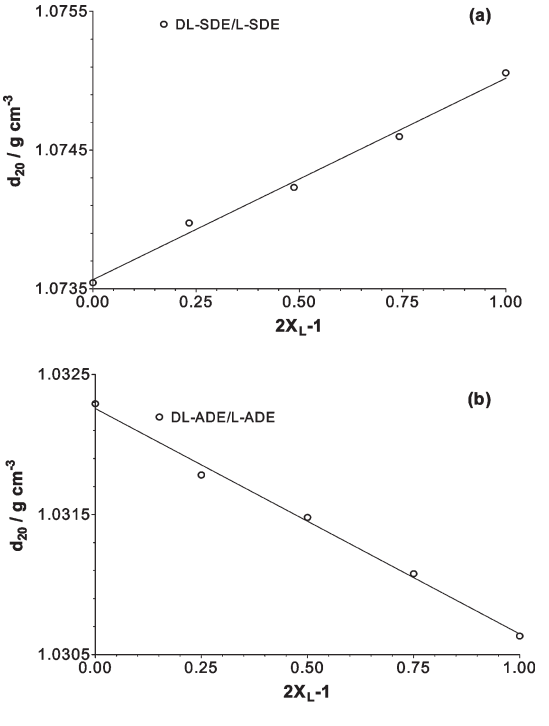

Fig. 3 The variation of mass density *versus* mole fraction when (a) DL-SDE and (b) DL-ADE in the racemic nematic phases were replaced by their enantiomers L-SDE and L-ADE, respectively.

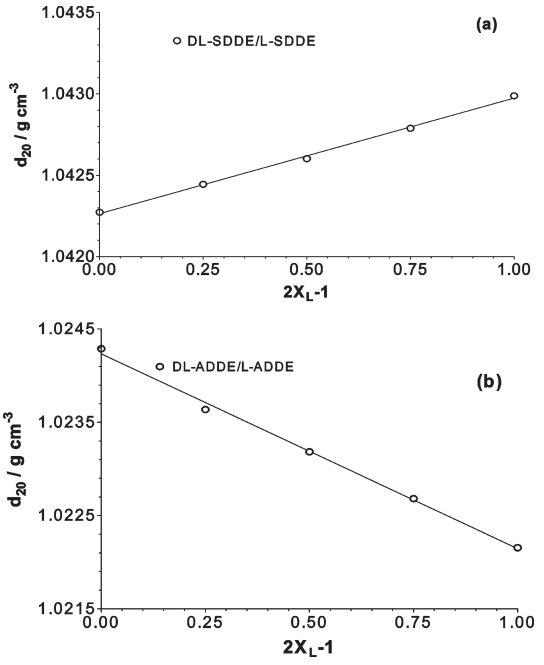

Fig. 4 The change of mass density with mole fractions as (a) DL-SDDE and (b) DL-ADDE in the racemic nematic phases were replaced by their L-enantiomers, L-SDDE and L-ADDE, respectively.

possible arrangements did not offer a favourable case where the groups could attract each other. If we have a pure enantiomeric amphiphile, however, as in the case of L-SDE, Fig. 5b, the ammonium groups and the carbonyl groups in adjacent molecules can attract each other which leads to efficient packing. From Figs. 5a and b, it is then easy to infer that the mass density has to increase as the DL-amphiphile of the racemic nematic phase is replaced by its enantiomer. Alanine ester phases, however, show exactly the opposite behaviour *i.e.* as DL-ADE or DL-ADDE in the racemic nematic phase is

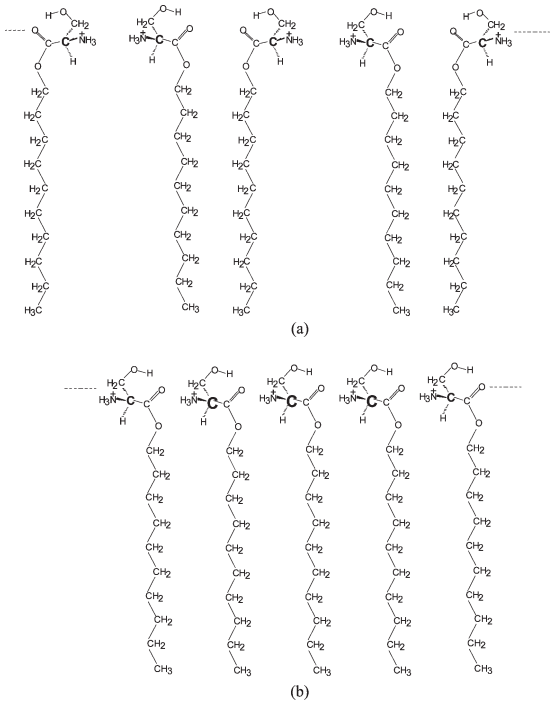

Fig. 5 Illustration of the arrangements of serine hydrochloride decylester (a) in the racemic nematic phase and (b) in the intrinsic chiral nematic phase.

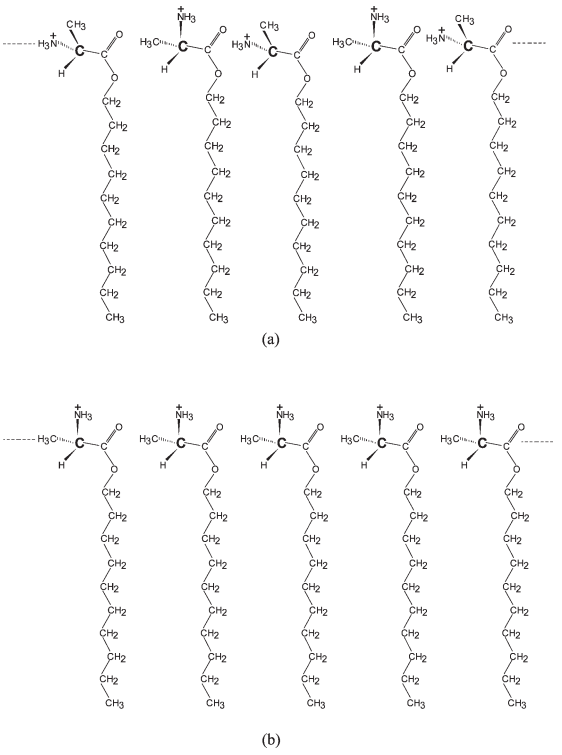

Fig. 6 Representation of the arrangements of alanine hydrochloride decylester (a) in the racemic nematic phase and (b) in the intrinsic chiral phase.

substituted by its L-enantiomer, the mass density decreases, which means that in the racemic nematic phases attraction forces, but in the intrinsic chiral nematic ones repulsion forces, are dominant. This situation is shown in Figs. 6a and b. In Fig. 6a, from left to right the ammonium group of the D-enantiomer is close to the carbonyl group of the L-enantiomer, which continues in the neighbouring pairs, therefore a close packing of the head groups is possible. This situation, however, is reversed if we consider the pure enantiomer, Fig. 6b, where oppositely charged groups can not approach each other closely enough due to methyl groups in the adjacent molecules. So, close packing does not take place, and therefore the mass density decreases as the DL-amphiphile of alanine in the racemic nematic phase is substituted by its L-enantiomer.

In summary, the change in mass density, as a DL-amphiphile of a racemic nematic phase is replaced by its L-enantiomer, depends on the packing of the head groups of the amphiphilic molecules in the racemic nematic and intrinsic chiral nematic ones which is predominantly determined in our case by specific attraction or repulsion forces of groups attached to the chiral centre of the amphiphilic molecules. Since the disc-like micelles in the racemic nematic phase change symmetry from $D_{\infty h}$ to D_{∞} or C_2 on replacing the DL-amphiphile by its L-enantiomer, the shape and size of the micelles are expected to change. Although mass density measurements give valuable insight into what takes place in the micelle, for quantitative determination of micelle size, X-ray or neutron diffraction studies are required. Such studies are envisaged.

Is a distinction between the induced chiral nematic and intrinsic chiral nematic phases possible?

As pointed out in the introduction, X-ray diffraction studies could not differentiate clearly between the achiral nematic phases of sodium decylsulfate (SDS)[4] and potassium laurate (KL)[8] and their induced chiral nematic ones obtained by brucine sulfate doping. So, we have asked ourselves the basic

Table 3 The compositions of the achiral nematic pases of DACl in mole percent containing DL-ADE/L-ADE, DL-SDE/L-SDE and DL-MA/S-MA, respectively, the pitch of the induced chiral phases, (P), the T_{NI} and the corresponding mass densities are represented

X_{DACl}	X_{NaCl}	X_{H_2O}	$X_{DL\text{-}ADE}$	$X_{L\text{-}ADE}$	$P/\mu m$	$T_{NI}/°C$	$d_{20}/g\ cm^{-3}$
6.454	1.258	91.815	0.473	–	N_D	≈31	$0.984642 \pm 5.56 \times 10^{-5}$
6.454	1.258	91.815	–	0.473	29.55	≈31	$0.984613 \pm 1.21 \times 10^{-5}$
X_{DACl}	X_{NaCl}	X_{H_2O}	$X_{DL\text{-}SDE}$	$X_{L\text{-}SDE}$	$P/\mu m$	$T_{NI}/°C$	$d_{20}/g\ cm^{-3}$
6.307	1.173	92.084	0.436	–	N_D	≈29	$0.986399 \pm 3.57 \times 10^{-5}$
6.307	1.173	92.084	–	0.436	67.74	≈29	$0.986483 \pm 1.60 \times 10^{-5}$
X_{DACl}	X_{NaCl}	X_{H_2O}	$X_{DL\text{-}MA}$	$X_{L\text{-}MA}$	$P/\mu m$	$T_{NI}/°C$	$d_{20}/g\ cm^{-3}$
6.626	1.286	91.314	0.774	–	N_D	≈30	$0.992072 \pm 1.21 \times 10^{-5}$
6.626	1.286	91.314	–	0.774	15.82	≈30	$0.992055 \pm 1.60 \times 10^{-5}$

question: can density measurements verify these results? If yes, then it can be concluded that the micelle size would not change appreciably, but micelle shape has to change due to symmetry change. In order to have a clear picture on this subject, we have developed achiral nematic and induced chiral nematic phases of the DACl host amphiphile using the dopant pairs, DL-ADE/L-ADE, DL-SDE/L-SDE and DL-MA/S-MA, respectively, and their densities were measured. The results are summarized in Table 3. In Table 3 the composition of the individual components, the type of achiral nematic phase (N_D), the induced pitch (P), the T_{NI} and the mass densities are represented. As can be seen for the three phases the difference in mass density between the achiral nematic and induced chiral nematic phases is within the limit of measurement error. These results indicate that the micelle size in the achiral nematic phase and the induced chiral nematic phase of the DACl host amphiphile for the three dopant pairs remains essentially unchanged, but micelle shape changes from disc-like micelle ($D_{\infty h}$) to screw-like micelle (C_2 or D_∞), Fig. 1b and c. Nevertheless, the situation of the intrinsic chiral nematic phase is different. Then, we know that there is a striking mass density difference *e.g.* 0.00213 g cm^{-3} for the ADDE phase, between the racemic nematic and its intrinsic chiral one, Figs. 3 and 4. Consequently, the intrinsic chiral micelle in our studied systems has two quantities, the shape and the size, different from the racemic micelle. These results allow us to conclude that the induced chiral nematics and the intrinsic chiral nematics are different. Pictorially, the induced chiral nematic phase can be thought to consist of a hollow screw-like pipe, whereas the intrinsic chiral nematic phase also exhibits a screw-like pipe, but it is different in spatial structure, Fig. 7a and b. The spatial structure arises from the special packing of the chiral centres of the pure enantiomers in the intrinsic chiral nematic phase as in Figs. 5 and 6.

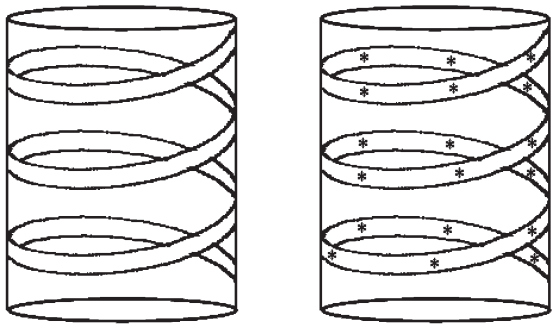

Fig. 7 (a) The screw-like pipe considered as a model for the induced chiral nematic phase, (b) the same model having a spatial structure indicated by asterisks.

Conclusions

The effect of the solute structure on the micelle size and shape has been investigated by mass density measurements employing two specific sets of guest molecules. The first set consisted of the achiral solutes, phenol, benzene, cyclohexanol and cyclohexane, whose mass densities were measured in a host phase of DL-serine hydrochloride decylester. The mass density measurements indicate clearly that the hydrophobic parts and the hydrophilic groups are important in changing the mass density where the effect of the hydrophilic groups outweighs the one of the hydrophobic parts. In the second set, it was established that the mass density may decrease (alanine ester phases) or increase (serine ester phases) when the racemic amphiphilic molecule in a racemic nematic phase is substituted by its L-enantiomer. These phenomena were shown to arise from the specific arrangements of the head groups in the racemic nematic and intrinsic chiral nematic phases. In addition, we have inferred from mass density differences between the achiral nematic and their induced chiral phases, and the racemic nematics and their intrinsic chiral ones, that the induced chiral nematics and the intrinsic chiral phases have to be different in spatial structure.

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