

DETERMINATION OF THE STRUCTURE OF SOME
LYOTROPIC CHIRAL NEMATIC AND RACEMIC
NEMATIC PHASES BY SMALL-ANGLE X-RAY
SCATTERING

by
EROL AKPINAR

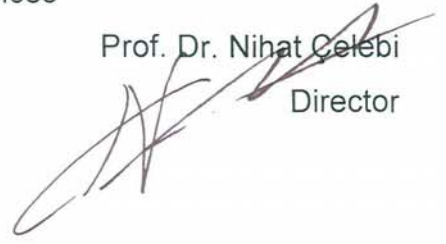
A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES OF
THE ABANT İZZET BAYSAL UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE
DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE DEPARTMENT OF CHEMISTRY

APRIL 2010

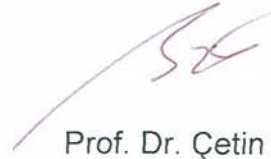
Approval of the Graduate School of Natural Sciences

Prof. Dr. Nihat Celebi

Director



I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.



Prof. Dr. Çetin Bozkurt

Head of Chemistry Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality as a thesis for the degree of Doctor of Philosophy.



Prof. Dr. Mahmut ACIMIŞ

Supervisor

Examining Committee Members

1. Prof. Dr. Mahmut ACIMIŞ

2. Prof. Dr. Çetin Bozkurt

3. Prof. Dr. Vural BÜTÜN

4. Prof. Dr. Veli DENİZ

5. Assist. Prof. Dr. Sedat ÇETİN



ABSTRACT

DETERMINATION OF THE STRUCTURE OF SOME LYOTROPIC CHIRAL NEMATIC AND RACEMIC NEMATIC PHASES BY SMALL- ANGLE X-RAY SCATTERING

Akpınar, Erol

Ph.D., Department of Chemistry

Supervisor: Prof. Dr. Mahmut Acımiş

April 2010, 213 pages

In this thesis, it was mainly aimed to make a contribution to the chiral induction mechanism of the chiral lyotropic nematic liquid crystals. For this purpose, the lyotropic nematic and chiral nematic liquid crystalline phases were produced using the racemic amphiphiles, potassium N-dodecanoyl-DL-alaninate (DL-KDDA) and DL-serinate (DL-KDDS) and their L-enantiomers, potassium N-dodecanoyl-L-alaninate (L-KDDA) and L-serinate (L-KDDS), respectively. Consequently, the different racemic nematic and chiral nematic phases were characterized by a polarizing light microscope, and their phase diagrams were constructed using laser light diffraction technique. In addition, in order to calculate the helical twisting powers (htp) of these chiral nematic phases, their pitches were determined as functions of concentrations of the

L-enantiomers and temperature. The results showed that the L-KDDA system had, in general, a higher helical twisting power than the L-KDDS system. The temperature dependence of the h_{TP} for both systems were also determined. Furthermore, our systems were investigated by the mass density and small-angle x-ray scattering techniques in order to determine the structural differences between the racemic micelles and the chiral micelles of the racemic and intrinsic chiral nematic phases. The L-enantiomers exhibited higher densities than their racemic mixtures, which imply that the intrinsic chiral nematic micelles are more compact than their corresponding racemic micelles. These results were interpreted in terms of the different molecular arrangements of the chiral amphiphiles in the micelles compared to the amphiphiles in the racemic micelles. Similar results were obtained from the small-angle x-ray scattering measurements. For instance, for a mole fraction of 2.50%, a micelle volume of 108 nm^3 for the L-KDDA and a micelle volume of 138 nm^3 for the DL-KDDA system were calculated whereas the micelle volumes of 221 nm^3 and 248 nm^3 were calculated for the L-KDDS and DL-KDDS systems, respectively. In addition, the aggregation numbers, N_{agg} , of the chiral and racemic micelles were calculated. The N_{agg} of the L-KDDA and DL-KDDA were found to be 181 and 231, respectively. For the KDDS system, the N_{agg} of L-KDDS and DL-KDDS were calculated as 356 and 407, respectively. Moreover, it was found that when the concentrations of the amphiphiles in both chiral nematic and racemic nematic phases increased, the N_{agg} values decreased. This result was interpreted as the increase of the anisotropic chiral interactions with the increase in the concentrations of the amphiphiles.

Increasing the mole fraction from 2.50% to 3.25%, the intermicellar distances decreased from 19.4 to 11.4 Å for the L-KDDA and from 21.8 to 14.0 Å for the DL-KDDA system, however, they changed from 26.6 to 17.4 Å for the L-KDDS and from 28.2 to 17.6 Å for the DL-KDDS systems. These results indicate that the intermicellar distances of the chiral micelles of L-KDDA and L-KDDS systems are shorter than those of the achiral micelles of DL-KDDA and DL-KDDS, respectively. Furthermore, the intermicellar distance of the L-KDDA is about ~6-7 Å shorter than that of the L-KDDS system. This means that the intermicellar chiral interactions between the micelles of the L-KDDA system are stronger than those of the L-KDDS system. This explanation is analogous with the h_{tp} s of these systems, i.e. the higher intermicellar chiral interactions indicate higher h_{tp} . Furthermore, the screw angle of the L-KDDA system was larger than that of the L-KDDS system at all studied temperatures. The screw angles of both L-KDDA and L-KDDS systems became smaller as the temperature was increased. This result explained why the h_{tp} s of the chiral nematic phases became smaller with the increase in the temperature.

On the other hand, the intermicellar interaction parameters k_H , which was determined from the viscosity measurements of the isotropic micellar solutions which are the precursors of the nematic phases, were calculated. The k_H values were found to be 0.75 and 0.68 for L-KDDA and DL-KDDA systems, respectively at 25 °C. These k_H values showed that the chiral interactions between the chiral micelles of the intrinsic chiral nematic phases were stronger than those of the achiral interactions between the racemic micelles of the nematic phases. Similar result was obtained for KDDS

system, i.e. the k_H value of the L-KDDS system (1.19) is higher than that of the DL-KDDS (0.85). The higher k_H values of L-enantiomers explain why the intermicellar distances between the chiral micelles of the chiral nematic phases were shorter than those between the achiral micelles of the racemic nematic phases. Furthermore, if the k_H values of KDDS systems were compared to those of KDDA systems, the KDDS system had higher k_H values because the KDDS amphiphiles contain a hydroxyl group in their head groups, which was discussed to hinder the rotation of the surfaces with respect to each other due to the hydrogen bonding at the rims.

According to our experimental results and the results on the induced chiral nematic phases in the literature, we proposed a new model on the chiral induction mechanism. This model indicates that there must be (i) a crucial distance and (ii) a critical micelle size in order to obtain chiral induction. In addition, the model shows that the chiral induction does not take place completely as was suggested by pairwise interaction or sterical interaction models in the literature, but through anisotropic chiral interactions via distorted micelles for which a crucial distance between the micelles and a critical micelle size are required.

Key words: Chiral induction model, Racemic nematic phase, Chiral nematic phase, DL-racemic mixture, L-enantiomer, Small-angle x-ray scattering, Mass density, Pitch, Helical twisting power, Racemic micelle, Chiral micelle, Intermicellar interaction, Huggins's constant, Viscosity.

ÖZET

BAZI LİYOTROPİK KİRAL NEMATİK VE RASEMİK NEMATİK FAZ YAPILARININ KÜÇÜK AÇI X-IŞINI SAÇILMASI YÖNTEMİYLE BELİRLENMESİ

Akpınar, Erol

Doktora, Kimya Bölümü

Tez Danışmanı: Prof. Dr. Mahmut Acımiş

Nisan 2010, 213 sayfa

Bu tezde, esas olarak liyotropik sıvı kristallerde kiral indüklenme mekanizmasına katkı sağlamak amaçlanmıştır. Bu amaçla, potasyum N-dodekanoil-DL-alaninat (DL-KDDA) ve DL-serinat (DL-KDDS) rasemik amfifilik molekülleri ile bunların L-enansiyomerleri olan potasyum N-dodekanoil-L-alaninat (L-KDDA) ve L-serinat (L-KDDS) amfifilik molekülleri kullanılarak, liyotropik nematik ve kiral nematik sıvı kristal fazlar hazırlandı. Bu farklı rasemik nematik ve kiral nematik fazlar polarize ışık mikroskobu ile karakterize edildi ve faz diyagramları lazer ışığı kırınım tekniği ile belirlendi. Bunun yanında, kiral nematik fazların heliksin döndürme güçlerini hesaplamak için, bu fazların heliks adım uzunlukları derişime ve sıcaklığa bağlı olarak ölçüldü. Sonuçlar, L-KDDA sisteminin genel olarak L-KDDS

sistemine göre daha büyük heliks döndürme gücüne sahip olduğunu göstermektedir. Her iki sistemin heliks döndürme gücünün sıcaklığa bağımlılığı da belirlenmiştir. Bu tezle ilişkili olarak, üzerinde çalıştığımız rasemik nematik ve kiral nematik fazların miselleri arasındaki yapısal farkların belirlenmesi için kütle yoğunluğu ve küçük açı x-ışını saçılması teknikleri kullanıldı. L-enansiyomerlerin, rasemik misellerden daha büyük yoğunluk değerine sahip oldukları görüldü ve bu durum saf kiral nematik misellerin rasemik misellerden daha sıkı olduğunu göstermektedir. Bu yoğunluk sonuçları, kiral amfifilik moleküllerin, rasemik moleküllerle karşılaştırıldığında, miseller içinde farklı moleküler dizilme (konfigürasyon) içinde oldukları şeklinde yorumlandı. Benzer sonuçlar küçük açı x-ışını saçılması ölçümlerinden de elde edildi. Örneğin, amfifilik moleküllerin faz içindeki yüzde mol oranları 2.50% olduğu durumda, L-KDDA sisteminde miselin hacmi 108 nm³ ve DL-KDDA sisteminde 138 nm³ iken, L-KDDS ve DL-KDDS sistemlerinde sırasıyla 221 nm³ and 248 nm³ olarak hesaplandı. Ayrıca, kiral ve rasemik misellerin kümelenme sayıları, N_{agg}, da hesaplandı. L-KDDA ve DL-KDDA misellerinin kümelenme sayıları sırasıyla 181 and 231 olarak bulunmuş olup KDDS sistemi içinse, L-KDDS ve DL-KDDS misellerinin kümelenme sayıları sırasıyla 356 ve 407 olarak hesaplanmıştır. Bunlara ek olarak, kiral nematik ve rasemik nematik fazların her ikisi için de, amfifilik moleküllerin derişimi artırıldıkça kümelenme sayılarının azaldığı bulunmuştur. Bu sonuçla, amfifilik moleküllerin derişimlerinin artırılmasıyla, miseller içindeki çekim kuvvetlerinin daha da arttığı ortaya çıkmıştır.

Amfifilik moleküllerin faz içindeki yüzde mol oranlarının 2.50%'den 3.25%'e artırılmasıyla, L-KDDA sisteminde misellar arası uzaklık 19.4 Å'den

11.4 Å'e ve DL-KDDA sisteminde 21.8 Å'den 14.0 Å'e düşerken, L-KDDS sisteminde 26.6 Å'den 17.4 Å'e ve DL-KDDS sisteminde 28.2 Å'den 17.6 Å'e değişmiştir. Bu sonuçlar, DL-KDDA ve DL-KDDS sistemlerinde akiral miseller arasındaki uzaklığın, sırasıyla L-KDDA and L-KDDS sistemlerindeki kiral miseller arasındaki uzaklıktan daha uzun olduğunu göstermektedir. Ayrıca, L-KDDA sistemindeki misellerarası uzaklık, L-KDDS sistemindekinden yaklaşık 6-7 Å daha kısadır. Bu sonuç, L-KDDA sisteminin miselleri arasındaki anizotropik kiral etkileşimlerin L-KDDS sisteminden daha kuvvetli olduğu anlamına gelmektedir. Bu açıklama, bu sistemlerin heliks döndürme güçleriyle paralellik göstermektedir, yani daha büyük misellerarası kiral etkileşimler daha büyük heliks döndürme gücüne neden olmaktadır. Ayrıca, çalışılan bütün sıcaklıklarda L-KDDA sisteminde heliks dönme açısının L-KDDS sisteminkinden daha büyük olduğu hesaplanmıştır. L-KDDA ve L-KDDS sistemlerinin her ikisinde de heliks dönme açılarının sıcaklık artışıyla küçüldükleri görülmüştür. Bu sonuç, kullandığımız sistemler için, sıcaklık artışıyla kiral nematik fazlarda heliks döndürme gücünün neden daha da küçüldüğünü açıklamaktadır.

Diğer taraftan, nematik fazların öncülü olan izotrop miselli çözeltilerin vizkozite ölçümlerinden, misellerarası etkileşim parametresi k_H hesaplandı. L-KDDA ve DL-KDDA sistemlerinin k_H değerleri 25 °C'de sırasıyla 0.75 ve 0.68 olarak bulundu. Bu k_H değerleri, saf kiral nematik fazların kiral miselleri arasındaki kiral etkileşimlerin, nematik fazların rasemik miselleri arasındaki akiral etkileşimlerden daha kuvvetli olduğunu göstermiştir. Benzer sonuç KDDS sisteminden de elde edilmiştir, yani L-KDDS sisteminin k_H değeri (1.19) DL-KDDS sisteminin k_H değerinden (0.85) daha büyüktür. L-

enansiyomerlerin büyük olan k_H değerleri, kiral nematik fazların miselleri arasındaki uzaklığın neden nematik fazların akiral miselleri arasındaki uzaklıktan daha kısa olduğunu açıklamaktadır. Ayrıca, KDDS sisteminin k_H değerleri KDDA sisteminin değerleriyle karşılaştırıldığında, KDDS sistemi daha büyük k_H değerine sahiptir. Çünkü, KDDS amfifilik molekülleri baş gruplarında bir hidroksil grubu içerir ve bu hidroksil grupları miselin yüzeyinde ve kenarlarında hidrojen bağı yaparlar. Bu olguyla, hidroksil gruplarının misel yüzeylerinin birbirlerine göre dönmelerini engellediği sonucuna varıldı.

Elde ettiğimiz deneysel sonuçlar ile literatürde indüklenmiş kiral nematik fazlar için verilen sonuçlar dikkate alınarak, kiral indüklenme mekanizması için yeni bir model önerildi. Bu model, kiral indüklenme elde edebilmek için, (i) miseller arasında belli bir uzaklığın ve (ii) kritik bir misel büyüklüğünün olması gerektiğini göstermektedir. Literatürde önerilen kiral indüklenmenin ikili etkileşim veya yapısal etkileşim modelleriyle tam olarak açıklanmadığını, indüklenmenin belli misel yaklaşması ve kıvrılmış miseller üzerinden anizotropik kiral etkileşimler sonucunda meydana geldiği görülmektedir.

Key words: Kiral indüklenme modeli, Rasemik nematik faz, Kiral nematik faz, DL-rasemik karışım, L-enansiyomer, Küçük açılı x-ışını saçılması, Kütle yoğunluğu, Adım uzunluğu, Heliksi döndürme gücü, Rasemik misel, Kiral misel, Misellerarası etkileşim, Huggins sabiti, Vizkozite.

to my wife and my daughter

ACKNOWLEDGEMENTS

First, I would like to thank my research advisor, Professor Mahmut Acımiş for his help, patience and encouragement over the last eleven years.

I would also like to sincerely thank Prof. Dr. Frank Giesselmann for his support and guidance about small-angle x-ray scattering measurements and the staff in his research group in the University of Stuttgart/Germany.

I would like to thank the staff in the Department of Chemistry/Abant İzzet Baysal University for their helps and supports.

I would like to thank my parents, for their supports throughout my entire education.

Finally, I would like to thank my wife, İlknur. I will always be grateful for her support, patience and encouragement.

TABLE OF CONTENTS

ABSTRACT.....	iii
ÖZET.....	vii
ACKNOWLEDGEMENTS.....	xii
TABLE OF CONTENTS.....	xiii
CHAPTER	
1. INTRODUCTION AND STATEMENT OF THE PROBLEM.....	1
2. THEORY OF LIQUID CRYSTALS.....	4
2. 1 What are liquid crystals?.....	4
2.1.1 .Structures of lyotropic liquid crystals.....	6
2.1.1.1 Lamellar phases.....	7
2.1.1.2 Hexagonal phases.....	9
2.1.1.3 Cubic phases.....	10
2.1.1.4 Nematic phases.....	11
2.1.1.5 Chiral nematic (cholesteric) phases.....	15
2.2 Optical and magnetic properties of nematic and chiral nematic phases.....	18
3. EXPERIMENTAL TECHNIQUES.....	23
3.1 Polarizing light microscope.....	23
3.2 Small-angle x-ray scattering.....	25
3.3 Laser light diffraction.....	30
3.4 Mass density method.....	31

3.5	Viscosity method.....	33
4.	EXPERIMENTAL.....	34
4.1	Instruments and chemicals.....	34
4.2	Synthesis of amphiphilic molecules (surfactants).....	35
4.3	Preparation of liquid crystal samples for microscopic, mass density, laser diffraction and SAXS measurements.....	46
4.4	Experimental procedure for isotropic micellar solutions.....	51
4.4.1	Mass density measurement.....	51
4.4.2	Viscosity measurement.....	51
4.5	Phase compositions.....	52
5	RESULTS AND DISCUSSION.....	66
5.1	Polarising light microscopic investigations of racemic nematic and chiral nematic phases.....	66
5.1.1	The lyotropic nematic phases.....	66
5.1.2	The lyotropic chiral nematic phases.....	68
5.2	The phase diagrams of potassium N-dodecanoyl-alaninate and potassium N-dodecanoyl-serinate systems.....	70
5.3	The pitches of the chiral nematic phases and their temperature dependences.....	73
5.3.1	The system potassium N-dodecanoyl-L-alaninate.....	76
5.3.2	The system potassium N-dodecanoyl-L-serinate.....	79
5.4	The helical twisting powers of the chiral nematic phases and their temperature dependences.....	80
5.5	Mass density measurements of lyotropic nematic and chiral nematic phases.....	84

5.5.1	The system potassium N-dodecanoyl-DL and L-alaninate.....	85
5.5.2	The system potassium N-dodecanoyl-DL and L-serinate.....	90
5.6	Determination of micelle sizes of the racemic nematic and chiral nematic phases from small-angle x-ray scattering measurements.....	95
5.6.1	The racemic and chiral nematic phases of potassium N-dodecanoyl-alaninate.....	96
5.6.2	The racemic and chiral nematic phases of potassium N-dodecanoyl-serinate.....	121
5.7	Comparison of the effect of the temperature on the twist angle and the helical twisting powers of the chiral nematic phases.....	137
5.8	The effect of the concentration of the L-enantiomers on the twist angle and the helical twisting powers of the chiral nematic phases.....	141
5.9	The viscosities of the studied systems in isotropic micellar solutions.....	143
5.10	A new model for the chiral induction mechanism.....	147
6.	CONCLUSIONS.....	155
	REFERENCES.....	159

LIST OF TABLES

TABLE

1. FT-IR data of DL/L-KDDA and DL/L-KDDS.....	38
2. Elemental analysis results of racemic amphiphilic molecules and their L-enantiomers.....	39
3. ¹ H-NMR results of DL/L-KDDA amphiphiles according to the spectrum in Figure 25. Splittings are in good agreement with the n+1 rule where n is number of H-atom bounded to the neighbour C-atom. These amphiphiles include one mole of water per each amphiphile and two hydrogen atom in water (labelled as 9) molecule give one signal because they are equivalent.....	42
4. ¹ H-NMR results of DL/L-KDDS amphiphiles according to the spectrum in Figure 26.....	44

5. The compositions of the individual racemic nematic and chiral nematic phases obtained from (a) alanine and (b) serine amides in the mixtures of Na_2SO_4 , n-decanol (DeOH) and water in mole percent. The transition temperatures, $T_{N\phi}$ from nematic to turbid phases, ϕ , are also given. These phase compositions were used for the characterization of the phases under polarising light microscope, mass density and SAXS measurements. The temperature was controlled with an accuracy of $\pm 0.1^\circ\text{C}$ by using a thermostat.....54

6. The concentrations of the components in mole percent for mass density and SAXS measurements on going from the racemic nematic phase to its intrinsically chiral nematic phases for (a) KDDA and (b) KDDS.....56

7. The compositions of the chiral nematic phases of L-KDDA in mole percent. The phase types are given at room temperature. T_{CN^*} and $T_{N^*\phi}$ represent the phase transition temperatures from crystalline phase to chiral nematic phase and from chiral nematic phase to turbid phase, respectively. These phases were used for (i) the construction of the partial phase diagram, (ii) the determination of the effect of the temperature on the pitch and (iii) also calculate the helical twisting power and its temperature dependence.....57

8. The pitch values of the L-KDDA systems whose compositions and phase codes were given in Table 7. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat. The standard deviations of the measured pitches were 3-5% with respect to their average values.....	58
9. The compositions of the chiral nematic phases of L-KDDS in mole percent. The phase types are given at room temperature. T_{CN^*} and $T_{N^*\phi}$ represent the phase transition temperatures from crystalline phase to chiral nematic phase and from chiral nematic phase to turbid phase, respectively. These phases were used for (i) the construction of the partial phase diagram, (ii) the determination of the effect of the temperature on the pitch and (iii) also calculate the helical twisting power and its temperature dependence. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat.....	61
10. The pitch values of the L-KDDS systems whose compositions and phase codes were given in Table 9. The standard deviations of the measured pitches were 4-6% with respect to their average values.....	62
11. The temperature dependence of the https of L-KDDA and L-KDDS.....	82

12. The mass density results for KDDA at 25 °C on going from the racemic nematic phase to its intrinsically chiral nematic phases whose phase compositions were given in Table 6a.....	85
13. The mass density results of the racemic nematic phases and their intrinsically chiral nematic phases for KDDA at 25 °C, keeping the concentrations of DL-mixtures and L-enantiomers to be equal to each other. The phase compositions were given in Table 5a.....	88
14. The mass density results on going from the racemic nematic phase to its intrinsically chiral nematic phases for KDDS at 25 °C. The phase compositions were given in Table 6b.....	90
15. The mass density results of the racemic nematic phases and its intrinsically chiral nematic phases for KDDS at 25 °C, keeping the concentrations of DL-mixtures and L-enantiomers to be equal to each other. The phase compositions were given in Table 5b.....	94
16. The Bragg's values of KDDA system on going from racemic mixture to intrinsically chiral nematic phase at 25°C. The phase compositions were given in Table 6a.....	109
17. The Bragg's values for different compositions of DL-KDDA and L-KDDA.....	110

18. The parameters obtained from the SAXS measurements for KDDA on going from DL-KDDA to L-KDDA.....	114
19. The parameters obtained from the SAXS measurements for DL- KDDA and L-KDDA, for different concentrations.....	114
20. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , on going from DL-KDDA to the intrinsically L-KDDA where the mole fraction of the total amphiphile ($X_{DL-KDDA+L-KDDA}$) was 0.0252. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} was calculated as 2.19 according to the phase compositions in Table 6a.....	116
21. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , for DL-KDDA and L-KDDA phases where the mole fraction of DL-KDDA and L-KDDA were equal to each other. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} were calculated as 2.19, 2.41, 2.64 and 2.87 for the mole fractions of 0.0252, 0.0275, 0.0300 and 0.0325, respectively, according to the phase compositions in Table 5a.....	118

22. The Bragg's values of KDDS system on going from racemic mixture to intrinsically chiral nematic phase at 25 °C. The phase compositions were given in Table 6b.....	130
23. The Bragg's values for different compositions of DL-KDDA and L-KDDA. The phase compositions were given in Table 5b.....	131
24. The parameters obtained from the SAXS measurements for KDDS on going from DL-KDDS to L-KDDS.....	132
25. The parameters obtained from the SAXS measurements for DL- KDDS and L-KDDS, for different concentrations.....	132
26. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , on going from DL-KDDS to the intrinsically L-KDDS where the mole fraction of the total amphiphile ($X_{DL-KDDS+L-KDDS}$) was 0.0251. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} was calculated as 2.15 according to the phase compositions in Table 6b. The molar volumes and volumes of a single KDDS molecule were determined from the mass density measurements as described for KDDA system: DL-KDDS= $277.4 \text{ cm}^3/\text{mol}=460.6 \text{ \AA}^3$, L-KDDS= $284.9 \text{ cm}^3/\text{mol}=473.1 \text{ \AA}^3$, 24.7%L= $463.7 \text{ \AA}^3$, 50.1% L= $466.9 \text{ \AA}^3$, 73.3%L= $469.7 \text{ \AA}^3$	133

27. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , for DL-KDDS and L-KDDS phases where the mole fraction of DL-KDDS and L-KDDS were equal to each other. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} were calculated as 2.15, 2.36, 2.59 and 2.81 for the mole fractions of 0.0251, 0.0275, 0.0300 and 0.0325, respectively, according to the phase compositions in Table 5b.....	135
28. The comparison of the $d_{\perp}$, $W_{\perp}$, pitch, n_{mic} , θ and htp values for (a) L-KDDA (%X=2.52) and (b) L-KDDS (%X=2.51) phases at 25-45 °C. The temperature was controlled with an accuracy of ± 0.1 °C using a thermostat.....	139
29. The comparison of the $d_{\perp}$, $W_{\perp}$, pitch, n_{mic} , θ values for (a) L-KDDA and (b) L-KDDS phases at 25 °C as a function of the increase in the L-enantiomers.....	141
30. The evaluated k_H values according to the Huggins's equation in the temperature range of 25 and 45 °C. The temperature was controlled with an accuracy of ± 0.1 °C using a thermostat.....	145
31. The important experimentally determined parameters for KDDA and KDDS systems.....	152

LIST OF FIGURES

FIGURE

1. (a) In the solid state molecules have certain positions in the crystal lattice and they perfectly align. (b) In the liquid crystal state molecules align with certain angles to a preferred direction which is called director, n . As seen in (c), molecules in liquid state orient in all directions.....5
2. Schematic representation of an amphiphilic molecule, DL-alaninehydrochloride dodecylester. **1** and **2** correspond to the hydrophobic (long alkyl chain) and hydrophilic (polar or ionic head group) parts of the amphiphile, respectively.....6
3. The schematic representation of the lamellar phase. Water molecules exist between two adjacent layers. In the lamellar phase, there exists one dimensional repeating order perpendicular to the lamellae which is represented by red arrow.....7
4. The schematic representation of the hexagonal phase. The arrows represent two-dimensional repeating order in this phase.....9

5. The schematic representation of the cubic phase.....	10
6. The schematic representation of a N_D phase. The director shows the preferred alignment of the micelles.....	12
7. The schematic representation of a N_C phase. The director indicates the preferred alignment of the micelles in this phase.....	12
8. The schematic representation of a biaxial micelle in the N_B phase. The micelle has three axes: axis 1 is perpendicular to the large surface of the micelle and axes 2 and 3 , which are equivalent, are perpendicular to it.....	13
9. The schematic representation of the alignment of the director of nematic phases with respect to the magnetic field, $\vec{B}$. OA indicates the optical axis (director) of the nematic phase.....	14
10. Schlieren texture of a nematic phase.....	14
11. The schematic representation of a chiral nematic phase and the occurrence of a helical structure. $\vec{B}$ is the direction of magnetic field.....	16
12. The fingerprint texture of a chiral nematic phase.....	17

13. Double refraction of the polarized light in a liquid crystal sample.....	18
14. The pseudo-isotropic texture (extinct area) of the nematic phase. The white areas at the sides of the microslide are not yet aligned sections of the phase.....	19
15. An interference figure (cross dark brushes) of a nematic phase, indicating a perfect alignment of the optical axis of a nematic phase.....	20
16. Interference colors of nematic phases for (a) $\Delta n > 0$ and (b) $\Delta n < 0$ as a $\frac{1}{4} \lambda$ retardation plate is inserted in the light path of the polarizing light microscope.....	20
17. This figure shows the configuration of polarizing light microscope.....	24
18. The Fourier transformation of the pair distance distribution function to the intensity distribution function. FT represents the “Fourier transformation”.....	26
19. The figure shows the pair distance distribution functions of a lyotropic disc phase for the Bragg's values, $d_{\perp}$ and $d_{\parallel}$	27

20. The alignment of the disc-like micelles with their directors with respect to the incident x-ray beam: director (a) perpendicular and (b) parallel to the x-ray beam.....	29
21. An experimental set-up of laser diffraction. h is the distance between the light source and diffraction pattern.....	30
22. The schematic representation of the oscillating U-tube and the some other parts of density meter.....	32
23. FT-IR spectrum of DL/L-KDDA.....	36
24. FT-IR spectrum of DL/L-KDDS.....	37
25. ^1H -NMR of DL/L-KDDA. The spectrum of DL-KDDA was similar as that of L-KDDA. NMR spectra were taken in CD_3OD	40
26. ^1H -NMR of DL/L-KDDS. The spectra of DL-KDDS was same as that of L-KDDS. NMR spectra were taken in CD_3OD	43
27. The molecular structures of (a): (i) DL-KDDA, (ii) L-KDDA and (b): (i) DL-KDDS, (ii) L-KDDS.....	45

28.	The experimental set-up for determination of phase transitions temperatures from microscopic investigations. This set-up was placed on the rotating stage of the polarizing light microscope. The holes, on the cap and the one below the microslide, were closed when no measurement was performed.....	47
29.	A schematic drawing of the measuring cell. The liquid crystal sample was covered with a cover slip.....	48
30.	The measuring holder produced from brass was used to determine pitch length by laser diffraction. This set-up has two places where the measuring cell can be placed, so that laser diffraction measurements of two different liquid crystal samples can be made at the same time.....	48
31.	A schematic representation of SAXS experiment. X-ray beam coincides with the x-axis. The choice of direction of axes is arbitrary.....	50
32.	The position of the cylindrical capillary including the chiral nematic phase in a magnetic field of 1.1 T. By this way, the helix axis of the chiral nematic phase is aligned parallel to the magnetic field direction and long capillary axis. B represents the magnetic field direction.....	50

33. A falling ball viscometer.....	52
34. A characteristic schlieren texture obtained from racemic nematic phases, DL-KDDA or DL-KDDS. The thickness of microslide was 0.2 mm. The photograph was taken approximately 15 minutes after the sample was transferred into the microslide. Magnification was 50x.....	66
35. The pseudo-isotropic texture of DL-KDDA. The similar texture was also observed for DL-KDDS. The thickness of the microslide was 0.2 mm and the magnification was 25x.....	67
36. The conoscopic investigation of the homeotropically aligned textures of DL-KDDA and DL-KDDS.....	68
37. The fingerprint texture of the chiral nematic phase of L-KDDA. The thickness of te microslide was 0.2 mm and the magnification was 100x.....	69
38. The fingerprint texture of the chiral nematic phase of L-KDDS. The thickness of the microslide was 0.2 mm and the magnification was 50x.....	69

39. The partial phase diagram of (a) KDDA and (b) KDDS. C, N* and ϕ represent solid, chiral nematic and turbid phases, respectively.....	70
40. The phase separation of the chiral nematic phases of L-KDDS (%X=2.51). The temperature was ~60-61 °C. The completely dark areas are water phase. The isotropic phase regions include the droplets. The thickness of the microslide was 0.2 mm and the magnification was 25x.....	72
41. The change in the pitch of the chiral nematic phases of L-KDDA and L-KDDS systems with the concentrations of the L-enantiomers at 25 °C.....	73
42. The occurrence of the twisted micelle, resulting through torques caused by the chiral amphiphiles at opposite surfaces.....	74
43. The temperature dependences of P (●) and P ⁻¹ (O) for the phase LA-5 (%X=2.52).....	76
44. The schematic representation of the intermicellar distance, d, and the twist angle along the helix axis.....	77

45. The temperature dependences of P (●) and P^{-1} (○) for the phase LS-6 (%X=2.51).....	79
46. The temperature dependence of the twist for L-KDDA system at 25 °C.....	81
47. The temperature dependence of the twist for L-KDDS system at 25 °C.....	81
48. The temperature dependence of the h_{tp} for L-KDDA and L-KDDS.....	82
49. The change in the mass density of KDDA system on going from the racemic nematic phase to the intrinsically chiral nematic phase.....	86
50. The molecular arrangement in the micelles of (a) racemic nematic and (b) chiral nematic phases of KDDA, where the volume of the racemic micelles appear to be larger than that of the intrinsically chiral micelles. The arrangements of these molecules were derived from stick models.....	87
51. The concentration dependence of the mass densities of DL-KDDA and L-KDDA at 25 °C.....	89

52. The change in the mass density of KDDS system on going from the racemic nematic phase to the intrinsically chiral nematic phase at 25 °C.....	91
53. The molecular arrangement in the micelles of (a) racemic nematic and (b) chiral nematic phases of KDDS. The arrangements of the molecules were drawn according to stick models.....	92
54. The change of the mass densities of DL-KDDS and L-KDDS at 25 °C, as their concentrations were increased.....	94
55. Observation of the schlieren texture at the edges of the capillary and the pseudo-isotropic texture at the center along the long axis of the capillary of the racemic N _D -phase of DL-KDDA. The microphotographs were taken at room temperature (~25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.....	96
56. SAXS diffraction pattern of the racemic N _D - phase of DL-KDDA (%X=2.52) system in a cylindrical capillary of 0.7 mm in diameter at 25 °C. The shadow in the center is the beam-stop. The arrow shows the direction of the phase director ($\vec{n}$).....	97

- 57.** The intensity versus 2θ for the racemic N_D - phases of DL-KDDA (%X=2.52) at 25 °C. // and $\perp$ represent the scattering intensities obtained from the periodicity along and perpendicular to the phase director, $\vec{n}$, respectively. The curves were fitted to Lorentzian function and were found to be in good agreements with it.....98
- 58.** The fingerprint texture of the N_D^+ of L-KDDA (%X=2.52) in the cylindrical capillary. The microphotographs were taken at room temperature (~ 25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.....99
- 59.** Schematic representations of the orientation of the cholesteric stripes and the helix axis in the intrinsically N_D^+ phase of L-KDDA in a cylindrical capillary.....100
- 60.** SAXS diffraction patterns of the intrinsically N_D^+ phase of L-KDDA (X%=2.52) system in a cylindrical capillary of 0.7 mm in diameter without applying a magnetic field at 25 °C. The shadow in the center is the beam-stop.....101
- 61.** The diffraction of the x-ray beam from the rims and centers of the micelles. The z-axis is perpendicular to the plane of the page. The intense arcs along the z-axis, Figure 60, may correspond to the diffraction from the rims of the micelles.....102

- 62.** The intensity versus 2θ for the intrinsically non-aligned N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter without applying a magnetic field at 25 °C. The curves were fitted to Lorentzian function.....103
- 63.** The fingerprint texture of the N_D^+ phase of L-KDDA ($X\%=2.52$) in the cylindrical capillary obtained when the magnetic field direction was parallel to the long axis of the capillary. The microphotographs were taken at room temperature (~ 25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.....104
- 64.** Schematic representation of the possible orientation of the helix axis of an N_D^+ phase when x-ray is perpendicular to the helix axis.....105
- 65.** SAXS diffraction pattern of the intrinsically N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter with a magnetic field of 1.1 T at 25 °C. The shadow in the center is the beam-stop.....105
- 66.** The intensity versus 2θ for the intrinsically N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter with a magnetic field of 1.1 T at 25 °C. The curves were fitted to Lorentzian function.....106

67. The SAXS patterns of the DL/L-KDDA mixtures: (a) 75.3% DL-KDDA; 24.7% L-KDDA, (b) 49.9% DL-KDDA; 50.1% L-KDDA and (c) 26.7% DL-KDDA; 73.3% L-KDDA.....	107-108
68. The Bragg's values of KDDA system on going from pure DL-KDDA to pure L-KDDA.....	109
69. The concentration dependence of the Bragg's values for KDDA systems at 25 °C.....	111
70. The schematic representation of the “naked” disc-like micelle (blue one) and surrounding water (vacancy). Here h and D represent the thickness and the diameter of the naked micelle, respectively.....	112
71. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of L-KDDA in the mixtures of DL/L-KDDA according to the data in Table 20.....	117
72. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of KDDA for DL-KDDA racemic nematic phases and L-KDDA chiral nematic phases according to the data in Table 21.....	119

- 73.** Observation of the schlieren texture at the edges of the capillary and the pseudo-isotropic texture at the center along the long axis of the capillary of the racemic N_D-phase of DL-KDDS. The microphotographs were taken at room temperature (~25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.....121
- 74.** SAXS diffraction pattern of the racemic N_D- phase of DL-KDDS system in a cylindrical capillary of 0.7 mm in diameter at 25 °C. The shadow in the center is the beam-stop. The arrow shows the direction of the phase director ($\vec{n}$).....122
- 75.** The intensity versus 2θ for the racemic N_D- phase of DL-KDDS (%X=2.51) at 25 °C. // and $\perp$ represent the scattering intensities obtained from the periodicity along and perpendicular to the phase director, $\vec{n}$, respectively. The curves were fitted to Lorentzian function.....123
- 76.** The fingerprint texture of the L-KDDS (%X=2.51) in the cylindrical capillary. The microphotographs were taken at room temperature (~25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.....124

- 77.** SAXS diffraction pattern of the intrinsically $N_{D^+}^*$ phase of L-KDDS (X%=2.51) system in a cylindrical capillary of 0.7 mm in diameter without a magnetic field at 25 °C. The shadow in the center is the beam-stop.....125
- 78.** The intensity versus 2θ for the intrinsically $N_{D^+}^*$ phase of L-KDDA (X%=2.51) system in a cylindrical capillary of 0.7 mm in diameter without applying a magnetic field at 25 °C. The curves were fitted to Lorentzian function.....126
- 79.** The fingerprint texture of the phase of L-KDDS (%X=2.51) in the cylindrical capillary. The microphotographs were taken at room temperature (~25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.....127
- 80.** SAXS diffraction pattern of the intrinsically $N_{D^+}^*$ phase of L-KDDS (X%=2.51) system in a cylindrical capillary of 0.7 mm in diameter with applying a magnetic field of 1.1 T at 25 °C.....128
- 81.** The intensity versus 2θ for the intrinsically $N_{D^+}^*$ phase of L-KDDS (X%=2.51) system in a cylindrical capillary of 0.7 mm in diameter with applying a magnetic field of 1.1 T at 25 °C. The curves were fitted to Lorentzian function.....129

82. The Bragg's values of KDDS system on going from pure DL-KDDS to pure L-KDDS.....	130
83. The concentration dependence of the Bragg's values for KDDS system at 25 °C.....	131
84. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of L-KDDS in the mixtures of DL/L-KDDS according to the data in Table 26.....	134
85. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of KDDS for DL-KDDS racemic nematic phases and L-KDDS chiral nematic phases according to the data in Table 27.....	136
86. The figure shows the illustration of the twist angle.....	138
87. The concentration dependences of η_{sp}/C for DL-KDDA and L-KDDA system at 25 °C.....	144
88. The concentration dependences of η_{sp}/C for DL-KDDS and L-KDDS system at 25 °C.....	144
89. The schematic representation of a pairwise interaction between two chiral dopants in adjacent micelles.....	147

90. The schematic representation of the distortion of a micelle by the influence of an added chiral dopant.....	147
91. Top: The stripes of the fingerprint texture of the chiral nematic phase. Bottom: The arrangement of the micelles along the helix axis and the interaction of the incident polarized light with the micelles. The helix axis is parallel to the glass surface.....	149

ABBREVIATIONS

Tlc	Thermotropic liquid crystal
Llc	Lyotropic liquid crystal
N	Nematic phase
N*	Chiral nematic phase
N _D /N _D *	Nematic/Chiral nematic disc phase
N _C /N _C *	Nematic/Chiral nematic cylindrical phase
N _B /N _B *	Nematic/Chiral nematic biaxial phase
L _α	Lamellar phase
H	Hexagonal phase
I	Cubic phase
V	Bicontinuous cubic phase
P	Helical pitch
P ⁻¹	Reciprocal of the pitch or twist
htp	Helical twisting power
$\vec{B}$	Magnetic field
AE	Amphiphilic enantiomer
Δn	Optical anisotropy or birefringence
M	Magnetization
χ	Magnetic susceptibility

$\Delta\chi$	Diamagnetic susceptibility anisotropy
SAXS	Small-angle x-ray scattering
$p(r)$	Pair distance distribution function
$\Delta\rho(r)$	Scattering density difference
$\Delta\tilde{\rho}^2(r)$	Convolution square of the scattering density difference
$I(q)$	Scattering intensity distribution function
q	Magnitude of the scattering vector q
θ_s	Scattering or diffraction angle
λ	Wavelength of the incident x-ray beam or laser light
$d_{\perp}$	The Bragg's value when the scattering intensity is in the direction of the periodicity where it is perpendicular to the director of the micelles
$d_{//}$	The Bragg's value when the scattering intensity is in the direction of the periodicity where it is parallel to the director of the micelles
n	Director of the phase
DL-KDDA	Potassium N-dodecanoyl-DL-alaninate
L-KDDA	Potassium N-dodecanoyl-L-alaninate
DL-KDDS	Potassium N-dodecanoyl-DL-serinate
L-KDDS	Potassium N-dodecanoyl-DL-serinate
ϕ	Distortion angle
θ	Twist/screw angle
V_p	Periodic volume of a micelle
V_{mic}	Volume of a "naked" micelle

D	Diameter of a “naked” micelle
h	Thickness of a “naked” micelle
N_{agg}	Aggregation number of a micelle
v_a	Volume of a single amphiphilic molecule
ρ	Density of a liquid crystalline phase
ρ_s	Density of a surfactant (amphiphilic) molecule
ρ_w	Density of water
ρ_{sol}	Density of an isotropic solution
ρ_{DeOH}	Density of n-decanol
W_s	Weight fraction of surfactant in a liquid crystalline phase
W_w	Weight fraction of water in a liquid crystalline phase
W_{DeOH}	Weight fraction of n-decanol in a liquid crystalline phase
ϕ_{mic}	Volume fraction of micelles in a liquid crystalline phase
$W_{\perp}$	Water layer between the micelles of a liquid crystalline phase along the diameter of the micelles
$W_{//}$	Water layer between the micelles of a liquid crystalline phase along the thickness of the micelles
d	Intermicellar distance
n_{mic}	Number of micelles along the helix axis
η_{sp}	Specific viscosity
$[\eta]$	Intrinsic viscosity
k_H	Huggins’s constant which describes intermicellar interaction parameter

1. INTRODUCTION and STATEMENT OF THE PROBLEM

Lyotropic liquid crystals (llcs) are a class of liquid crystals in addition to thermotropic one. Their building blocks are anisometric micelles which are agglomerations of amphiphilic molecules in a suitable solvent (typically water). Although the llcs exhibit different phase structures, depending on both concentration of the amphiphilic molecules in the solvent and temperature [1-3], we only concentrate on the nematic phases, N, and the chiral nematic phases, N*.

The most definite property of the N and N* phases is that they exhibit a long-range orientational order and a short-range translational order without a positional order [4-8]. The N phases can be formed by dissolution of either an achiral amphiphilic molecule [9,10] or a racemic mixture in water [11]. In general, the N* phases can be produced by adding a chiral solute (dopant) to a nematic phase (induced N*) [12-17] or by using optically active amphiphiles (intrinsic N*) [11,18-21]. The micelles in both N and N* phases may have different shapes. In the literature, the micelle shapes are described to be discotic (oblate), cylindrical (prolate) or biaxial which are designated as N_D , N_C or N_B where the subscript letters, D, C and B indicate the individual micelle shape, being discotic, cylindrical or biaxial, respectively [22,23]. The N* phases are also classified in terms of the micellar shape similarly, e.g. N_D^* , N_C^* or N_B^* [24-26]. Under polarising light microscope, the N and N* phases are characterized by the schlieren and the fingerprint textures, respectively.

In both chiral nematic phases, induced and intrinsic N* ones, the chiral dopant or pure L-enantiomer transfers its molecular chirality to the whole phase to induce a macroscopic structure, so-called “helix”, which is characterized by the pitch and its handedness. The quantity, helical twisting power (htp), is used as a chirality measure for the dopant or L-enantiomer which is obtained from the pitch measurements [19-21].

Up to the present, although there are some studies in the literature related to the understanding of chiral induction mechanism, this mechanism is not understood well yet. In 1978, Radley and Saupe suggested two basic models for the chiral induction mechanism [27]. The first model is known as “a chiral dispersion interaction model”. In this mechanism, a chiral dispersion interaction occurs as a result of a direct pairwise interaction between one dopant (or L-enantiomer) existing in a micelle and a dopant in another micelle. The formation of this dispersion interaction is based on Goosen’s theory [28]. The second model, so-called a chiral sterical interaction model, proposes that when a chiral dopant is added to a nematic phase, it causes a distortion of the achiral micelles of the nematic phase. Then, because the distorted or chiralized micelles are in thermal motion, they mostly collide with each other and thus chirality information can be transferred to the whole phase sterically from one micelle to its neighbours [14,29]. Consequently, in both two models, the spatial arrangement of chiralized micelles and intermicellar interactions serve to transmit the chirality to form the helical structure.

Racemic nematic phases obtained from DL-amphiphiles and their intrinsic chiral nematic phases derived from the pure L-enantiomers appear

to be very important in studying phase properties. For this purpose, we selected two racemic amphiphilic molecules, potassium N-dodecanoyl-DL-alaninate (DL-KDDA) and serinate (DL-KDDS), and their L-enantiomers (L-KDDA and L-KDDS) because there were enough information about their liquid phases in the literature [19,21,30-36]. In general, these N and N* phases are four component systems, amphiphile, salt, n-alkanol (especially n-decanol) and water. They exhibited disk, cylindrical and biaxial nematic and chiral nematic phases, depending on the concentrations of the constituents in the sample and salt type. Nevertheless, we chose the nematic phases exhibiting N_D phases only.

In the frame of this thesis we were interested in answering the following questions: (i) Are the micelle sizes of the racemic nematic phases different from those of their intrinsic chiral phases derived from their L-enantiomers?, (ii) is there any relation between the micelle sizes and the η_{sp}/c of the L-enantiomers? and (iii) can the Huggins's constant k_H , which will be determined from the viscosity measurements of the micellar isotropic solutions (precursors of the racemic and intrinsic chiral nematic phases), be interpreted as chiral interactions? Consequently, the aim of this thesis is to make a fundamental contribution to the chiral induction mechanism by answering the above questions. In order to answer the posed questions, small-angle x-ray scattering studies, pitch, viscosity and mass density measurements were performed.

2. THEORY OF LIQUID CRYSTALS

2.1 What are liquid crystals?

A liquid crystal phase is a distinct state of matter, which is observed between crystalline solid and liquid states, and exhibits properties similar to both, i.e. a liquid crystal material is strongly anisotropic in some of its properties and has a certain degree of fluidity [37,38]. The liquid crystalline behaviour was firstly observed towards the end of the 19th century by Reinitzer [39] and Lehmann [40].

In order to understand what liquid crystals are, they can be compared with solid and liquid states. In solid state, molecules perfectly arrange to build up the crystal lattice and they have certain position and orientation in long range scale. This means that there are *long-range positional* and *orientational order* in the solid state, Figure 1a. If a solid forms a liquid crystal phase, molecules lose most of their positions but still have the long-range orientational order, Figure 1b. Finally, the molecules in liquid state move in any directions randomly and they have no positional and orientational orders, Figure 1c.

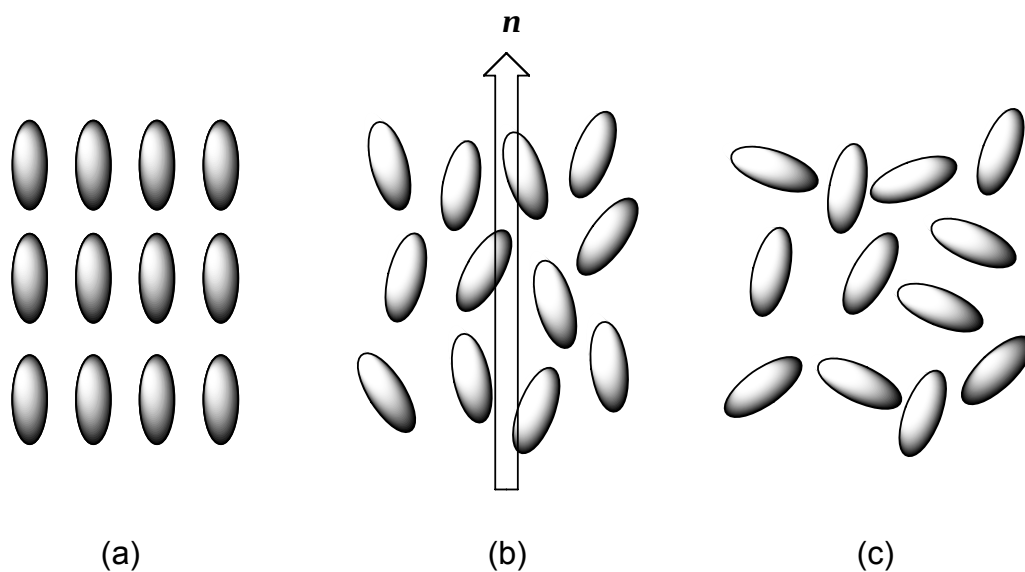


Figure 1. (a) In the solid state molecules have certain positions in the crystal lattice and they perfectly align. (b) In the liquid crystal state molecules align with certain angles to a preferred direction which is called director, n . As seen in (c), molecules in liquid state orient in all directions.

Liquid crystals are mainly divided into two types: (i) thermotropic and (ii) lyotropic liquid crystals, tlcs and llcs, respectively. In general, tlcs can be formed by heating a suitable crystalline solid, but nowadays some materials form tlcs at and below room temperature. The second type of the liquid crystals, llcs, are obtained by dissolution of an amphiphilic molecule, Figure 2, in a suitable solvent such as water. The phase transitions of tlcs take place by adding or removing heat [1,41-45], while those of llcs take place by changing of both temperature and concentration.

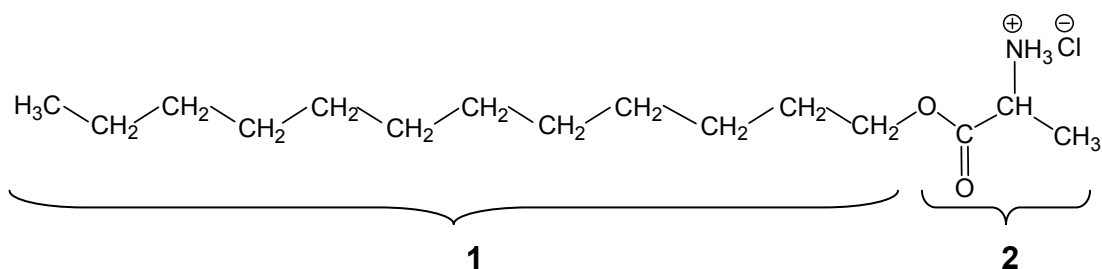


Figure 2. Schematic representation of an amphiphilic molecule, DL-alaninehydrochloride dodecylester. **1** and **2** correspond to the hydrophobic (long alkyl chain) and hydrophilic (polar or ionic head group) parts of the amphiphile, respectively.

In the tlcs, the structural units are molecules and in the llcs they are micelles, so the llcs are also called “micellar liquid crystals, mlcs”. Since the subject of this thesis is concerned with llcs, the tlcs will be not further discussed here.

2.1.1 Structures of lyotropic liquid crystals

Llcs are mainly classified as lamellar, hexagonal, cubic, nematic and chiral nematic (cholesteric) phases. In this thesis, though we will mainly concentrate on the nematic and chiral nematic structures, some introductory informations on the lamellar, hexagonal and cubic phase structures will be presented.

2.1.1.1 Lamellar phases, L_α

Lamellar or neat phases are produced at high amphiphile concentration where the amphiphile prefers to built up disc-like micelles at low amphiphile concentration [41]. In the lamellar phase, water molecules are sandwiched between the polar head groups of adjacent layers while the hydrocarbon chains are in a non-polar environment, Figure 3 [37]. The lamellae in the lamellar phases can consist of bilayers of monomers, thus this gives a layer thickness of about or somewhat less than twice the molecular length [41,46].

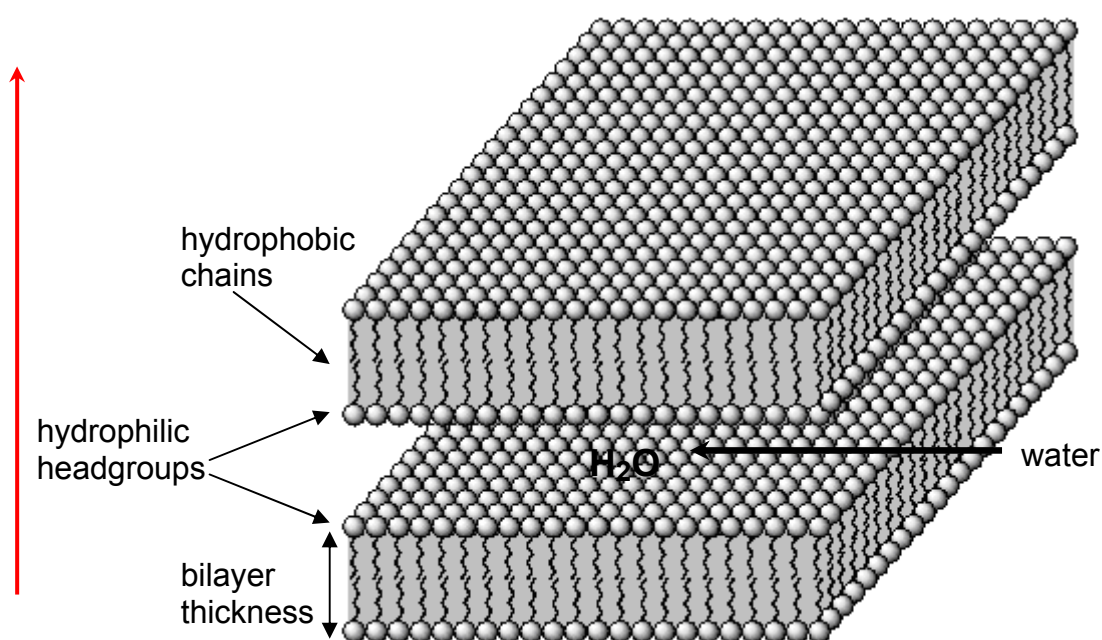


Figure 3. The schematic representation of the lamellar phase. Water molecules exist between two adjacent layers. In the lamellar phase, there exists one dimensional repeating order perpendicular to the lamellae which is represented by red arrow.

Lamellar phases possess a repeating order in one-direction perpendicular to the lamella. These phases are denoted by the symbols L_α and L_β where L represents lamellar phase, the indices α and β refer to the state of the hydrocarbon chains of the amphiphiles within the micelles: α and β stand for liquid-like disordered chains and solid-like ordered chains, respectively, i.e. the liquid-like hydrocarbon chains contain lots of different conformations while the solid-like chains are in all-trans conformations. The phases with solid-like hydrocarbon chains are called “gel phases” which are characterized with very high viscosity or viscoelasticity [41].

2.1.1.2 Hexagonal phases, H

A hexagonal or middle phase is similar to the lamellar phase, except that it is formed by amphiphiles which built up the rod-like micelles. In the hexagonal phase, the layers are rolled up the rods or cylinders and the cylindrical units of indefinite length are arranged parallel to one another in a hexagonal array, Figure 4 [37].

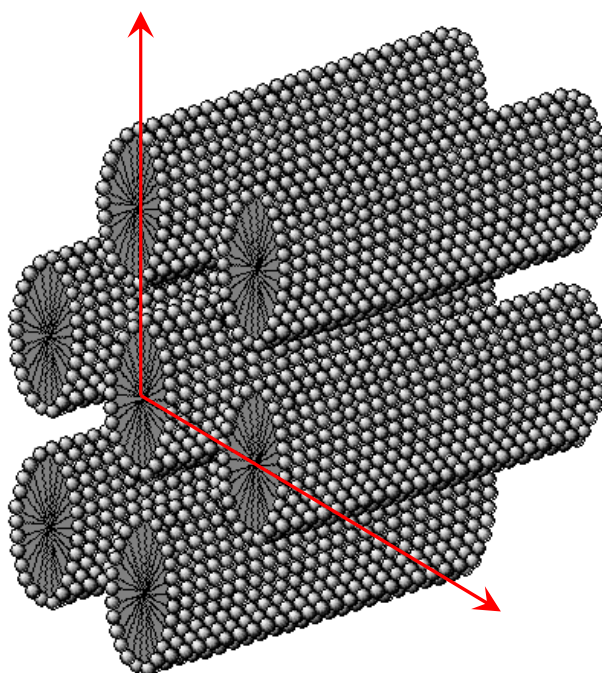


Figure 4. The schematic representation of the hexagonal phase. The arrows represent two-dimensional repeating order in this phase.

As the rod-like micelles arrange in a two-dimensional hexagonal lattice, a long-range positional order occurs in addition to the long-range orientational order of the rods. In the hexagonal phase, there exists two-dimensional repeating order which is represented by red arrows in Figure 4. The normal hexagonal phase is denoted as H.

2.1.1.3 Cubic phases, I

Cubic phases consist of spherical micelles where the polar head groups lie on the surface of the sphere and the hydrophobic chains fill up its interior [37]. In the cubic phases, a body-centered cubic arrangement is formed [47] and water molecules take up the space between the units, Figure 5.

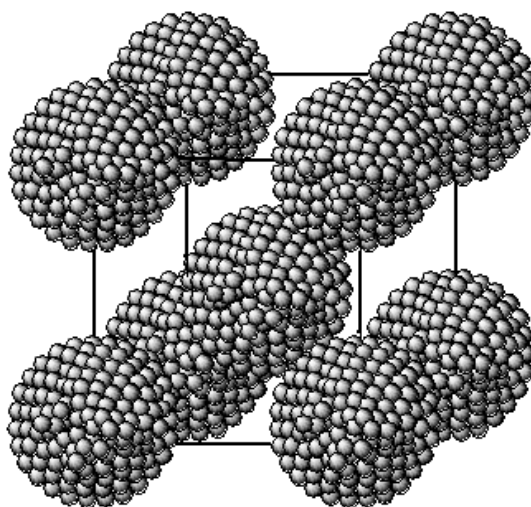


Figure 5. The schematic representation of the cubic phase.

Bicontinuous cubic phases, V, as well as normal cubic phases, I, have been also reported in the literature [48]. Because the cubic phases have the properties of isotropic media in many respects, they are also known as “viscous isotropic phases” [37,41].

2.1.1.4 Nematic phases, N

Lyotropic nematic phases, formed by mixtures of amphiphilic compounds and water, were first reported by Lawson and Flautt [9] and Rosevear [10]. They are classified as nematics on the basis of their microscopic textures [10,27] and spontaneous alignment in magnetic fields [9,12,49]. According to experimental results, the micelles in the nematic phase are of finite size and exhibit a long-range orientational order with a short-range translational order. The lyotropic nematic phases may be classified according to their micelle shapes, optical and magnetic properties. As reported in the literature, the micelle shapes may be discotic (oblate), cylindrical (prolate) or biaxial which are designated as N_D , N_C or N_B where the letter N stands for nematic and the subscript letters, D, C and B, indicate the individual micelle shape, being discotic, cylindrical or biaxial, respectively [50-54]. In the Figures 6-8, the N_D , N_C and N_B phases and the alignment of the micelles in each phase are shown, respectively.

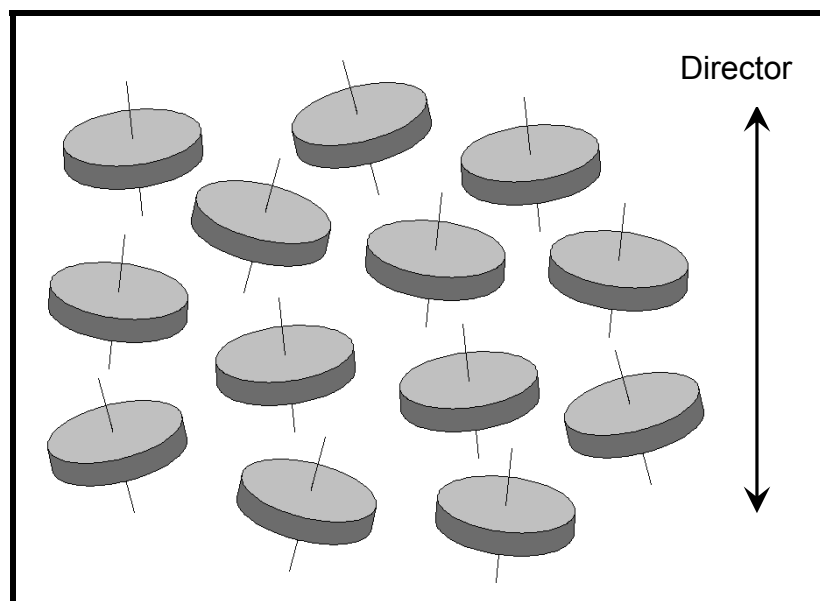


Figure 6. The schematic representation of a N_D phase. The director shows the preferred alignment of the micelles.

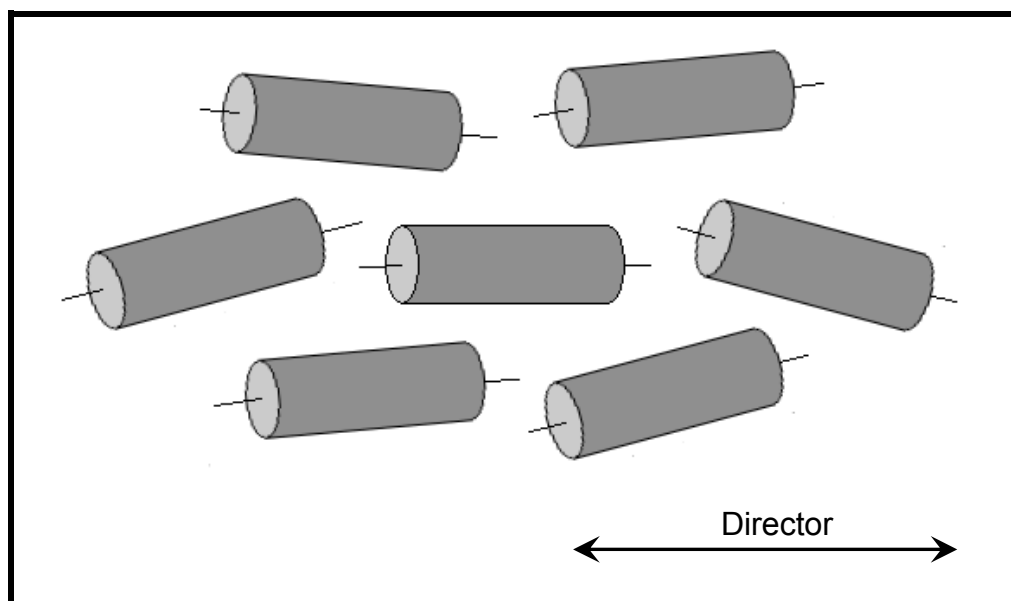


Figure 7. The schematic representation of a N_C phase. The director indicates the preferred alignment of the micelles in this phase.

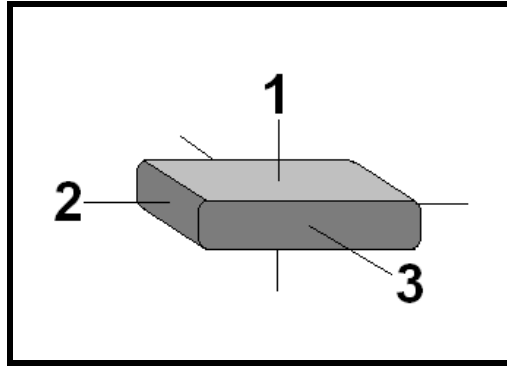


Figure 8. The schematic representation of a biaxial micelle in the N_B phase. The micelle has three axes: axis **1** is perpendicular to the large surface of the micelle and axes **2** and **3**, which are equivalent, are perpendicular to it.

The second parameter that is used to classify lyotropic nematic phases is the diamagnetic susceptibility anisotropy, $\Delta\chi$, (see section 2.2). If the director of the nematic phase aligns parallel to the magnetic field direction, it is denoted as N_D^+ or N_C^+ , where $\Delta\chi > 0$, Figure 9. If the director of the nematic phase orients perpendicularly with respect to magnetic field, it is assigned as N_D^- and N_C^- , where $\Delta\chi < 0$ [50], Figure 9.

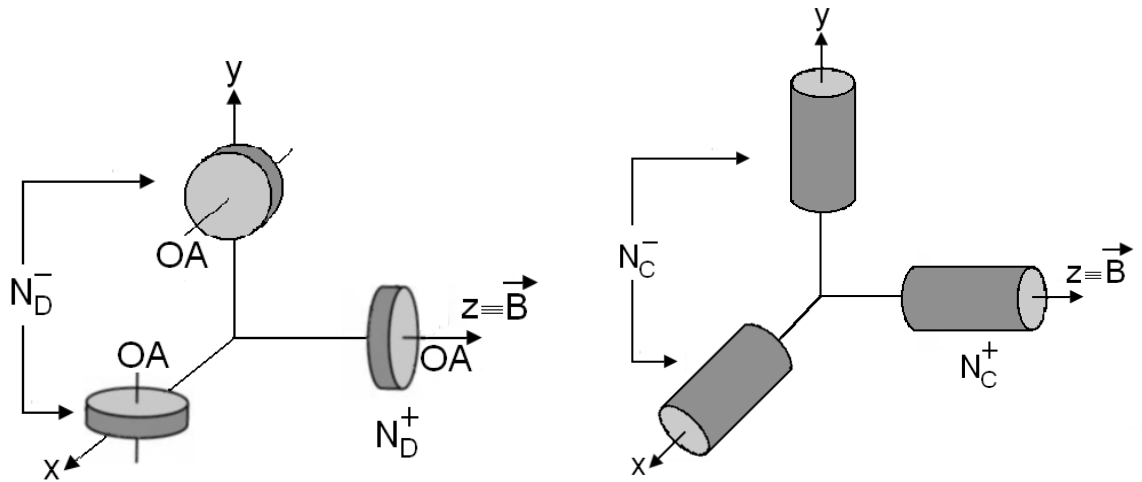


Figure 9. The schematic representation of the alignment of the director of nematic phases with respect to the magnetic field, $\vec{B}$. OA indicates the optical axis (director) of the nematic phase.

As the name nematic was derived from thread like appearance, a characteristic threaded (schlieren) texture of nematic phases is observed when investigated under polarizing microscope, Figure 10 .

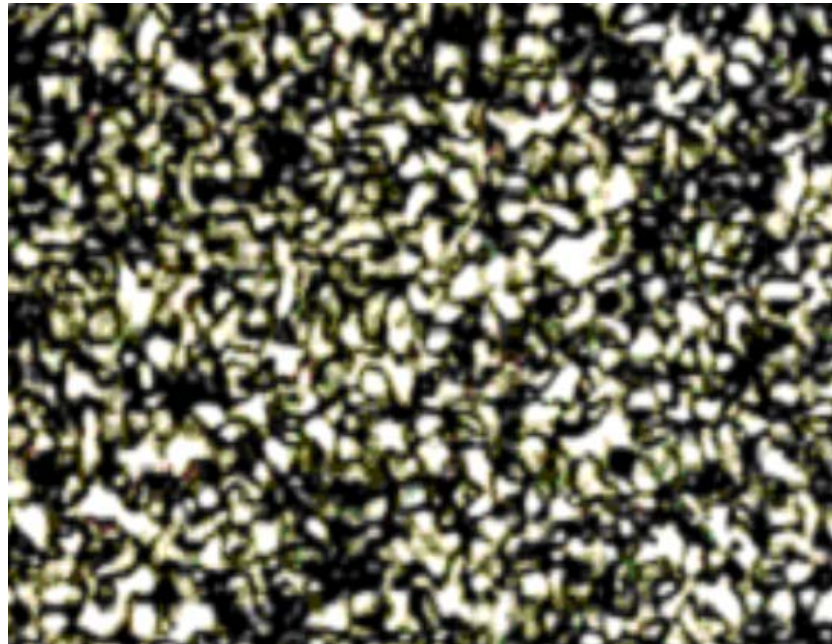


Figure 10. Schlieren texture of a nematic phase.

2.1.1.5 Chiral nematic phases, N*

In general, lyotropic chiral nematic phases can be formed by three ways:

- (a) adding a suitable chiral solute (dopant) to a micellar nematic phase [12-17],
- (b) using suitable purely amphiphilic enantiomers [11,18-21],and
- (c) using chiral solvent [55].

The lyotropic chiral nematic phases obtained by the method (a), which are called *induced chiral nematic phases*, were widely reported in the literature whereas lyotropic nematic liquids crystals prepared by method (b) using purely amphiphilic enantiomers (*intrinsic chiral nematic phases*) have not. The third method (c) is rarely used. In 1980, Acımiş and Reeves found that while enantiomers of an amphiphilic compound give the lyotropic chiral nematic phase, N*, their racemates give a lyotropic nematic phase [11]. The intrinsic N* systems may be more advantageous than the induced N* phases because no phase modifications (phase separation or phase transition) are caused when the concentration of the enantiomers are increased within the N* region.

In a lyotropic chiral nematic phase, as in the lyotropic nematic phase, there is a long-range orientational order with a short-range translational order. The director varies by a constant angle coming from one layer to the next that leads to a helical structure as described in Figure 11. A 2π rotation of the director is necessary for the director to regain its original direction. The linear distance traveled by this 2π rotation of the director is called the pitch

(P), Figure 11 [56,57]. Consequently, a chiral nematic phase is characterized by its pitch and handedness.

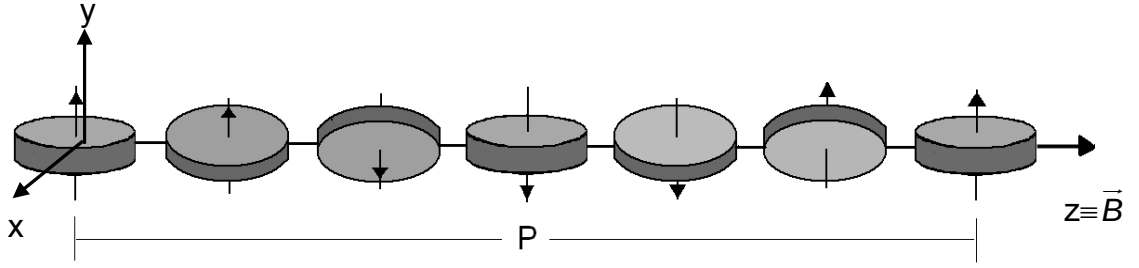


Figure 11. The schematic representation of a chiral nematic phase and the occurrence of a helical structure. $\vec{B}$ is the direction of magnetic field.

Three types of chiral nematic phases have been identified according to the orientation from their parent nematics. They are N_D^* , discotic chiral nematics, N_C^* , cylindrical nematics and N_B^* , biaxial chiral nematics. It is also possible to classify them as $N_{D^+}^*$, $N_{D^-}^*$, $N_{C^+}^*$, $N_{C^-}^*$ and N_B^* with respect to perpendicular or parallel orientation of the helix axis in a magnetic field [58].

When chiral nematic phases are investigated under polarizing microscope, the characteristic fingerprint texture, in which successive dark and bright lines appear, can be observed, Figure 12. The colour of the lines in this texture can vary depending on the birefringence of the phase. The pitch then corresponds to a perpendicular distance measured between three dark and bright lines which can be determined easily by polarizing microscope or laser diffraction techniques.

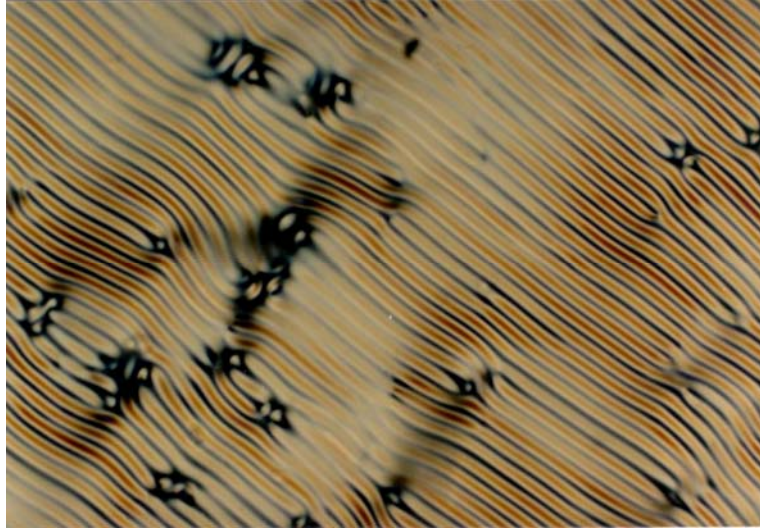


Figure 12. The fingerprint texture of a chiral nematic phase.

In the lyotropic chiral nematic phases, induced or intrinsic, the chirality of the phase is given by the microscopic helical twisting power (htp), i.e. htp can be considered as a measure for the chirality of the dopant or the enantiomer. The htp is given by the following equation quantitatively:

$$\text{htp} = \pm(P.x.r)^{-1} \quad (1)$$

where P is the helical pitch of the phase produced by the amphiphilic enantiomer, AE, or the dopant, and x and r are the molar fraction of the AE or dopant and their enantiomeric purity, respectively [59]. The signs (+) and (-) indicate a right- and left-handed helix, respectively. The values of the htps of the AEs or chiral dopants are determined from the slope of the straight line obtained by plotting the twist, the reciprocal pitch (P^{-1}), versus molar fraction of the AEs or dopant by using Eq. (1):

$$P^{-1} = (\text{htp}).x.r \quad (2)$$

The last equation is verified by many research groups for chiral nematic phases in thermotropic [59-61] and also lyotropic [11,13,62,63] where r is taken as equal to one for pure AEs or dopants.

2.2 Optical and Magnetic Properties of Nematic and Chiral Nematic Phases

When a polarized light beam is passed through the anisotropic liquid crystal sample, the beam splits into two plane-polarized rays that travel with different velocities, corresponding to two different refractive indices. The electric field vectors of the two rays (ordinary and extraordinary rays) vibrate in perpendicular directions to each other inside the liquid crystal material, Figure 13. This phenomenon is called birefringence or double refraction. The electrical vectors of the ordinary and extraordinary rays vibrate perpendicular and parallel to the optical axis of the liquid crystal, respectively. If the refractive indices for these rays are labeled n_o and n_e , the birefringence or optical anisotropy (Δn) is given by the equation,

$$\Delta n = n_e - n_o = n_{//} - n_{\perp} \quad (3)$$

The sign of the optical anisotropy can be greater than zero (in this case, liquid crystal has a positive birefringence, $\Delta n > 0$) or less (a negative birefringent material, $\Delta n < 0$).

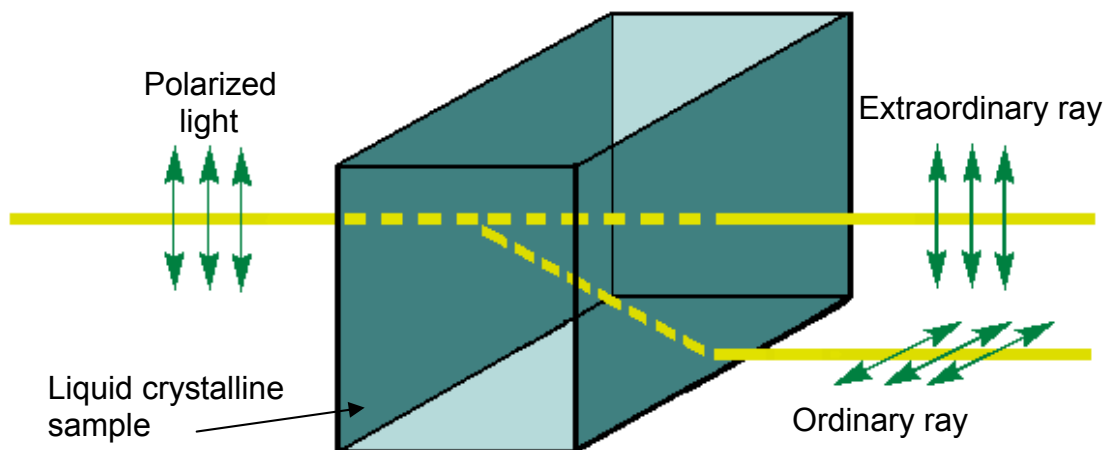


Figure 13. Double refraction of the polarized light in a liquid crystal sample.

In practice, it is found that $n_{//} > n_{\perp}$ (positive Δn), and Δn varies from values close to zero to about 0.4 [64,65]. It is noted that while nematic liquid crystals have a positive birefringence, chiral nematic ones a negative [64].

The sign of the optical anisotropy can be determined by conoscopic investigations of the nematic phase under a polarizing microscope. When a nematic liquid crystal sample with $\Delta\chi < 0$ is placed into a microslide and is equilibrated long enough time or put in a magnetic field at room temperature, it gives a pseudo-isotropic or homeotropic texture, Figure 14.



Figure 14. The pseudo-isotropic texture (extinct area) of the nematic phase. The white areas at the sides of the microslide are not yet aligned sections of the phase.

The conoscopic investigations of pseudo-isotropic textures show characteristic cross dark brushes, Figure 15.

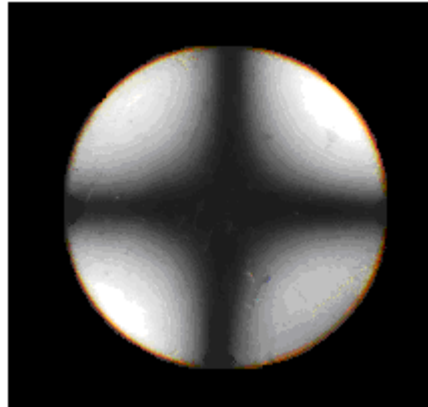
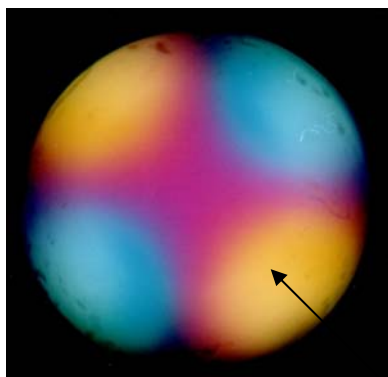


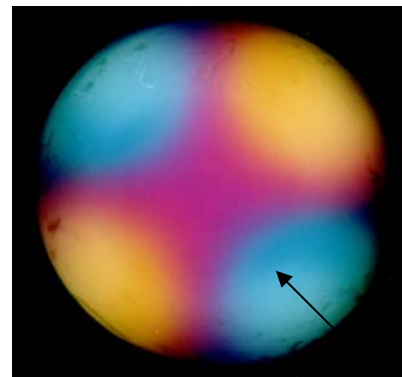
Figure 15. An interference figure (cross dark brushes) of a nematic phase, indicating a perfect alignment of the optical axis of a nematic phase.

When a $\frac{1}{4} \lambda$ retardation plate is introduced into the optical path of the microscope, a characteristic colors in the direction of the plate and in the perpendicular direction to the plate are observed, Figure 16a and b.



Direction of the retardation plate

(a)



Direction of the retardation plate

(b)

Figure 16. Interference colors of nematic phases for (a) $\Delta n > 0$ and (b) $\Delta n < 0$ as a $\frac{1}{4} \lambda$ retardation plate is inserted in the light path of the polarizing light microscope.

The behaviour of materials on application of a magnetic field is an important physical property. There are three main types of magnetic materials, i.e. diamagnetic, paramagnetic and ferromagnetic. Liquid crystals are diamagnetic like most organic materials. The magnetization M for diamagnetic materials is proportional to the magnetic field strength H ,

$$M = \chi H \quad (4)$$

where χ is the magnetic susceptibility and for diamagnetic materials χ is always negative.

For liquid crystals, which are anisotropic liquids, the difference between the components of magnetic susceptibilities measured with respect to the direction of the applied magnetic field, determines the sign of the magnetic susceptibility. If the applied magnetic field is parallel to the optical axis of the phase, the resultant magnetic susceptibility is indicated as $\chi_{//}$. If the application of the magnetic field is perpendicular to the optical axis of the phase, it is indicated as $\chi_{\perp}$. The diamagnetic susceptibility anisotropy $\Delta\chi$ of a liquid crystal can be characterized by these two susceptibilities $\chi_{//}$ and $\chi_{\perp}$ with the following equation

$$\Delta\chi = \chi_{//} - \chi_{\perp} \quad (5)$$

When a liquid crystalline sample has a positive diamagnetic susceptibility anisotropy ($\Delta\chi > 0$) that means the optical axis of the liquid crystal aligns parallel to the applied magnetic field direction. When it is negative ($\Delta\chi < 0$), the direction of the optical axis is perpendicular to the direction of magnetic field. When it equals to zero, the system is isotropic.

As the sign of the diamagnetic susceptibility anisotropy, the optical anisotropy (Δn) is also a criterion for characterization of nematic phases, i.e.

in general Δn and $\Delta\chi$ have opposite signs. For instance, if the optical axis of a nematic liquid crystal sample aligns perpendicular to an applied magnetic field, $\Delta\chi < 0$ but $\Delta n > 0$, and vice versa.

3. EXPERIMENTAL TECHNIQUES

3.1 Polarizing Light Microscope

Polarizing light microscope is an essential tool to characterizing the textures and alignment of the optical axes of the liquid crystal phases. A polarizing light microscope mainly consists of a light source, a mirror, convex lenses which together constitute the condenser, a polarizer, an analyzer, an objective and an eyepiece, Figure 17. In the polarizing light microscope, the incident unpolarized light whose electrical vector vibrates in all directions passes through polarizer and it is converted to the polarized light of which electrical vector vibrates in one direction. The polarized light is refracted in anisotropic media and the two-plane polarized rays produced by double refraction are analyzed by the analyzer, which is placed between the objective and the eyepiece. The observed texture is characteristic of the anisotropic sample, e.g. schlieren texture, fingerprint texture. In order to determine the optical axis of a liquid crystalline phase, the director of the phase has to be aligned parallel to the propagation direction of the plane polarized light. When the microscope is used in conoscopic configuration, the optical axis and sign of the liquid crystalline phase may be determined, as in Figures 15 and 16. The Nikon Optiphot2-Pol polarizing light microscope was used in our studies.

Polarized Light Microscope Configuration

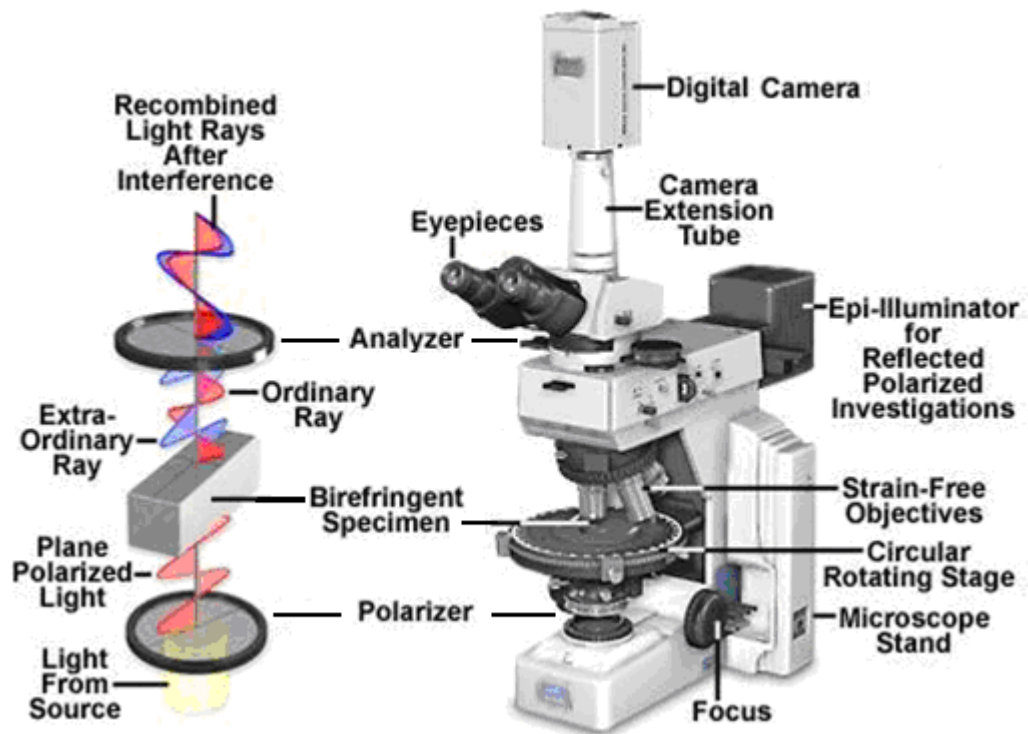


Figure 17. This figure shows the configuration of polarizing light microscope.

3.2 Small-angle x-ray scattering (SAXS)

Because the wavelength of x-ray beam is in the order of the micellar size, it is used as a tool to investigate the micellar size and structure. This method is called small-angle x-ray scattering (SAXS) technique. This technique can provide useful information on the micelles and their organization in the lyotropic liquid crystalline phases [66].

In this technique, the x-rays are sent to the sample and they are scattered from the micelles. The scattered x-rays are detected by the detector and the small-angle x-ray data are analyzed by Fourier transformation of the pair distance distribution function, $p(r)$. This function is independent of particle shape and is given by

$$p(r) = r^2 \Delta \tilde{\rho}^2(r) \quad (6)$$

where $\Delta \tilde{\rho}^2(r)$ is the convolution square of the scattering density difference, $\Delta \rho(r)$, averaged over all directions in space [67] and r is the distance of a selected point from the origin of the system [68] or intraparticle distance [69]. The Fourier transformation of $p(r)$ then gives the intensity distribution function $I(q)$ which is mostly called scattering intensity. Mathematically, the relationship between the $p(r)$ and $I(q)$ is given by

$$I(q) = 4\pi \int_0^\infty p(r) \frac{\sin(qr)}{qr} dr \quad (7)$$

where q is the magnitude of the scattering vector $\mathbf{q}$ [67,69]. The q is related to the scattering or diffraction angle, θ_s , by the following equation

$$q = \frac{4\pi}{\lambda} \sin \theta_s \quad (8)$$

where λ is the wavelength of incident x-ray beam. As can be seen from the equation of the $p(r)$, this function is dependent on the r . It consists of several peaks at $r = nd$ where n is the order of the diffraction (n takes the values of 1,2,3,...) and d is the distance between repeating particles, Figure 18 [70]. Thus, the Fourier transformation of the $p(r)$ results

$$q = \frac{2n\pi}{d} \quad (9)$$

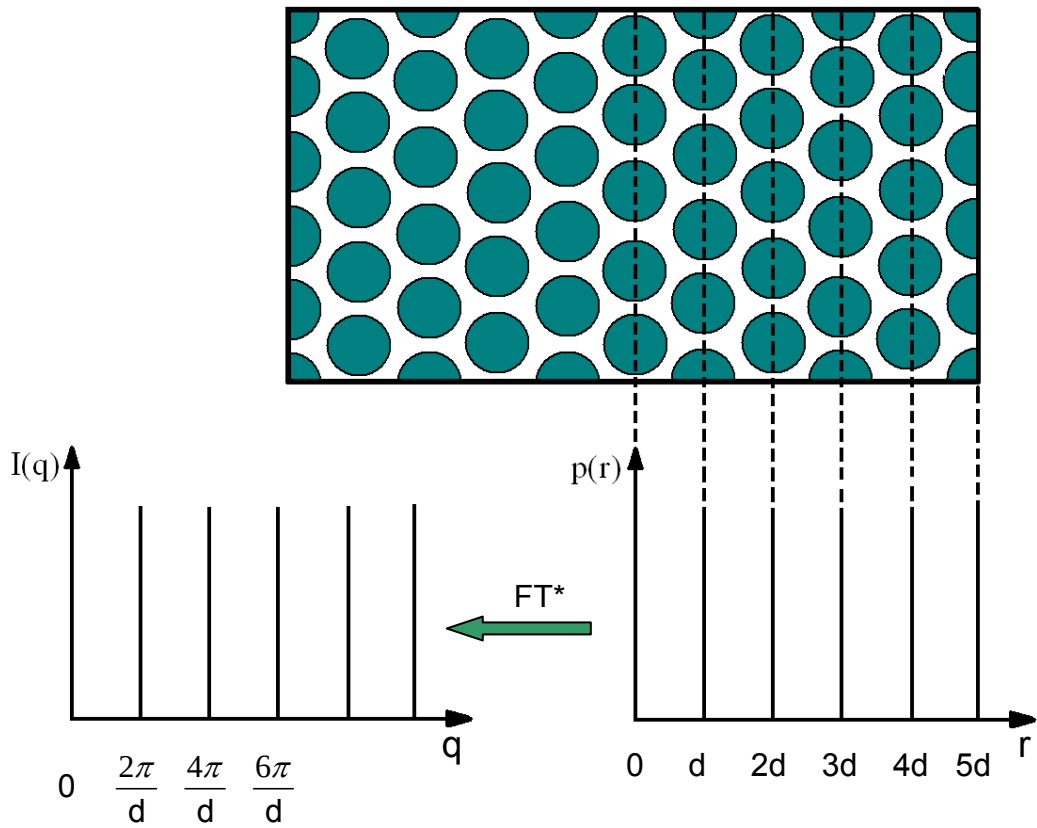


Figure 18. The Fourier transformation of the pair distance distribution function to the intensity distribution function. FT represents the “Fourier transformation”.

If the equation 8 is combined with the equation 9,

$$q = \frac{4\pi}{\lambda} \sin \theta_s = \frac{2n\pi}{d} \quad \text{and then}$$

$$n\lambda = 2d \sin \theta_s \quad (10)$$

The last equation, so-called Bragg's equation, was derived by W. L. Bragg in 1913 [71]. In this equation, d is also known as Bragg's value. In our case, in the lyotropic liquid crystalline state, the Bragg's value corresponds to the smallest distance between micelles.

In order to understand how the Fourier transformation occurs, the arrangement of atoms or molecules in a crystalline structure is imagined in the Figure 18. In that figure, each colored circle corresponds to an atom or a molecule. However, in the lyotropic liquid crystalline state, repeating units are

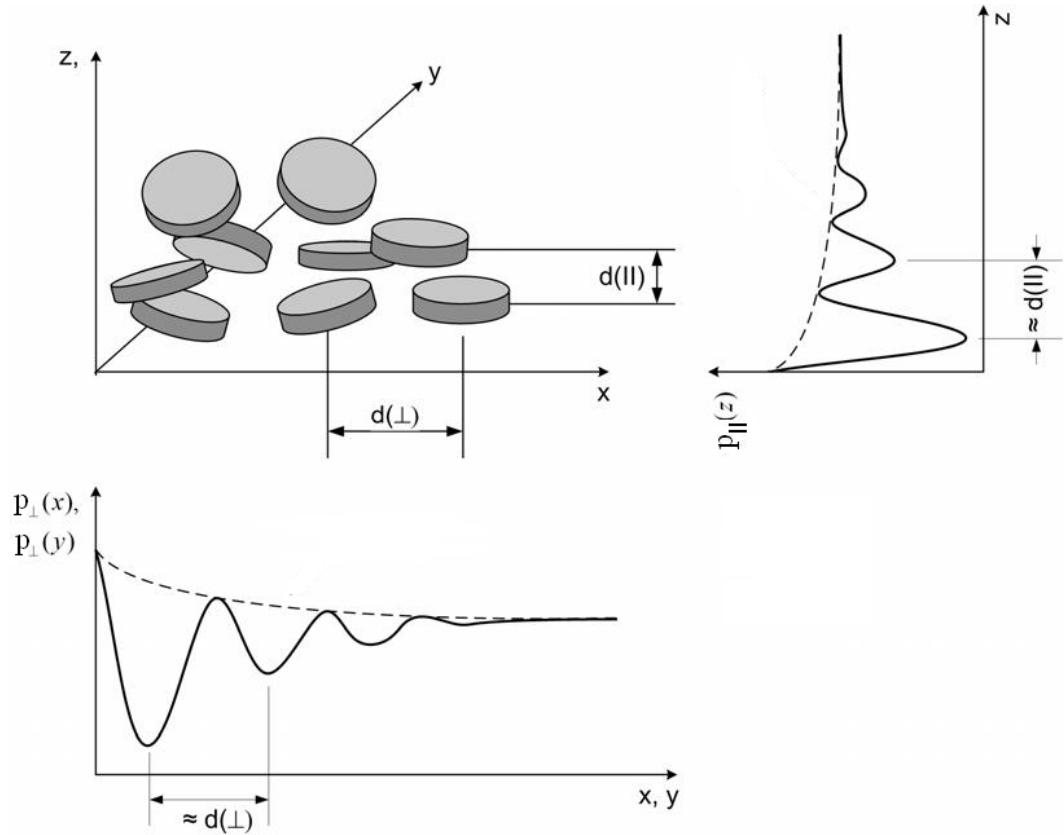


Figure 19. The figure shows the pair distance distribution functions of a lyotropic disc phase for the Bragg's values, $d_{\perp}$ and $d_{//}$ [70].

micelles and the Fourier transformation of the $p(r)$ should be made in three dimensions because of the periodicities in x, y and z-directions, Figure 19. The transformations in x- and y-directions are equivalent because the directors of the micelles are perpendicular to the periodicity in both directions, thus the scattering intensities in these directions lead to the Bragg's value $d_{\perp}$. By the same way, the transformation in z-direction gives the scattering intensity in the direction of the periodicity where it is parallel to the director of the micelles. Now, the Bragg's value is represented by the symbol $d_{\parallel}$. At this point, we should notice that the Fourier transformation of the $p(r)$ is a Lorentzian function as with liquids [72]

$$I(q) = \frac{a}{1 + \left(\frac{q - q_0}{b} \right)^2} \quad (11)$$

where a and b are constants.

The diffraction pattern obtained from the SAXS is dependent of the alignment of the director of the nematic phases with respect to the incident x-ray beam. Charvolin and Levelut suggested two possible measuring arrangements [73]. The director of the phase may be parallel and perpendicular to the x-ray beam. If the director of the lyotropic nematic disc phase is perpendicular to the x-rays, there will be a periodicity in the direction of the director which is a measure for the thickness of the micelle, Figure 20a, i.e. the Bragg's value $d_{\parallel}$ is used for evaluation of the micelle thickness. After rotation of the sample by 90° without the magnetic field, the x-ray becomes parallel to the director of the phase, Figure 20b. However, in this arrangement, the smallest distance between micelles corresponds to the periodicity in the diameter. Now, this periodicity is perpendicular to the

director, and the Bragg's value $d_{\perp}$ is used in the calculation of the diameter of the micelles.

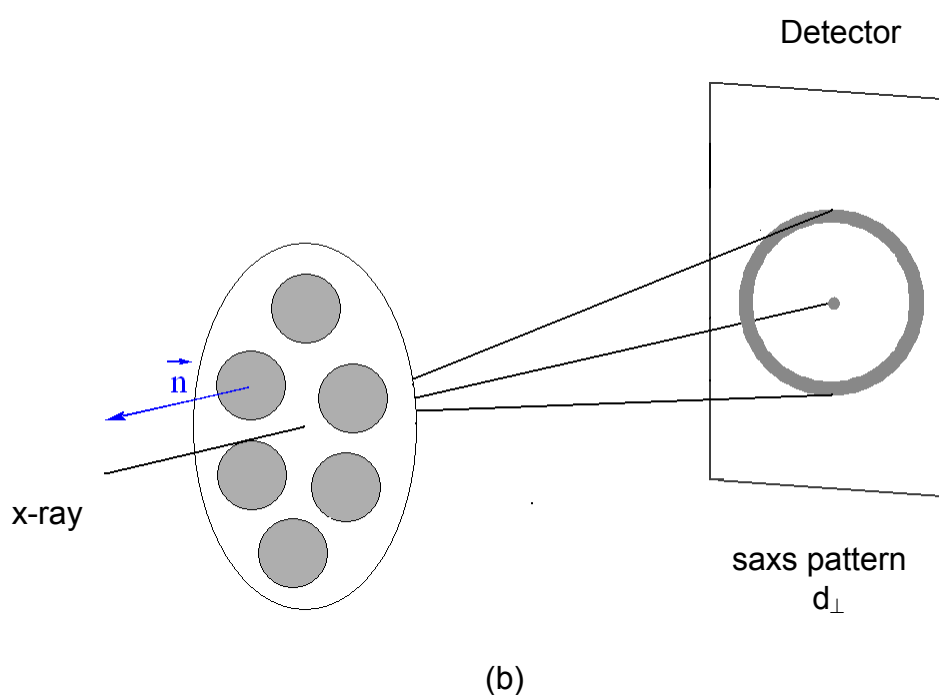
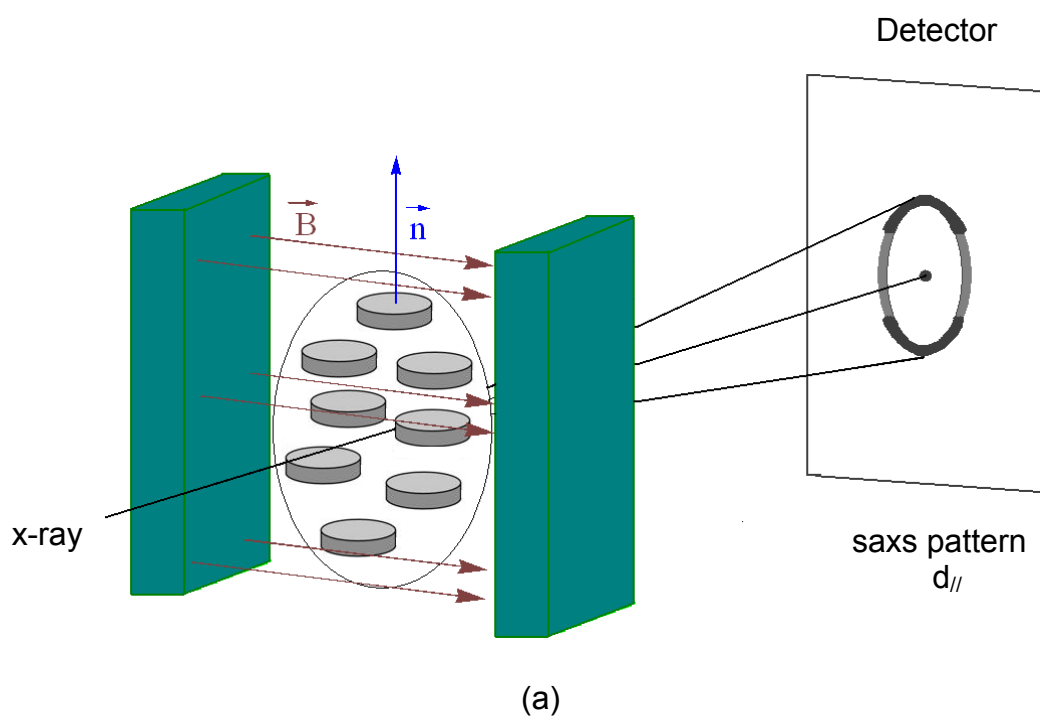


Figure 20. The alignment of the disc-like micelles with their directors with respect to the incident x-ray beam: director (a) perpendicular and (b) parallel to the x-ray beam.

From these two possible measuring arrangements, the diffraction angle is determined from the maxima of the scattering intensity versus 2θ curve, respectively, which is fitted to the Lorentzian function, Eq. 11. After obtaining the diffraction angle, the values of $d_{\perp}$ and $d_{\parallel}$ are calculated using Eq. 10 and they help for the evaluation of the diameter and thickness of a micelle.

3.3 Laser light diffraction

The pitch of the lyotropic chiral nematic phases can also be measured using laser diffraction technique in addition to the polarising light microscopy [21,30-32]. The use of this technique is sometimes more convenient than polarizing light microscopy for the phases having small pitches. The experimental set-up of laser diffraction is shown in Figure 21.

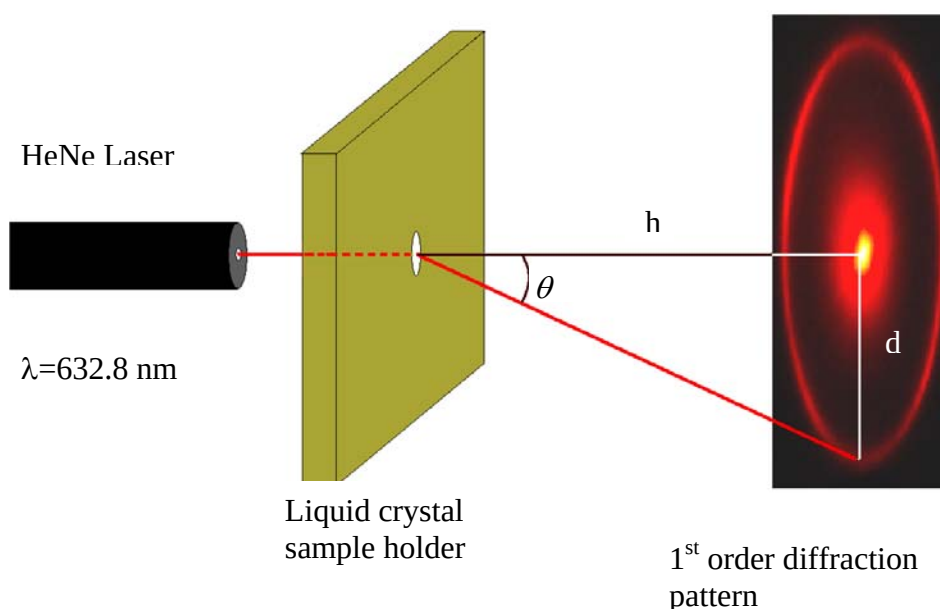


Figure 21. An experimental set-up of laser diffraction. h is the distance between the light source and diffraction pattern.

In laser diffraction technique, the twist (P^{-1}) is given by Bragg's law for diffraction as similar in the SAXS technique [33,34,74]

$$P^{-1} = \frac{\sin \theta}{2\lambda} \quad (12)$$

where λ is the wavelength of the incident light and θ is the angle of scattered light. To obtain the pitch, firstly the angle is determined by the following relation:

$$\tan \theta = \frac{d}{h} \quad (13)$$

The values of d and h can be easily determined by a ruler. λ is also known, then the pitch can now be calculated using Eq. 12.

3.4 Mass density method

Density measurements were carried out on Anton Paar DMA5000 density meter which measures the density from the oscillation period of a U-tube. The accuracy of the density meter was given by the manufacturer to be $5 \times 10^{-6} \text{ g cm}^{-3}$.

The U-tube oscillator is connected to a reference oscillator that provides a long-term stability of the density measurements. The density meter corrects the viscosity related errors of the sample by measuring the damping of the U-tube's oscillation caused by the viscosity of the filled-in sample. Furthermore, two integrated Pt 100 platinum thermometers provide a high accuracy of temperature control so that any temperature between 0 and 90°C can be measured to $\pm 0.001^\circ\text{C}$ of accuracy, Figure 22.

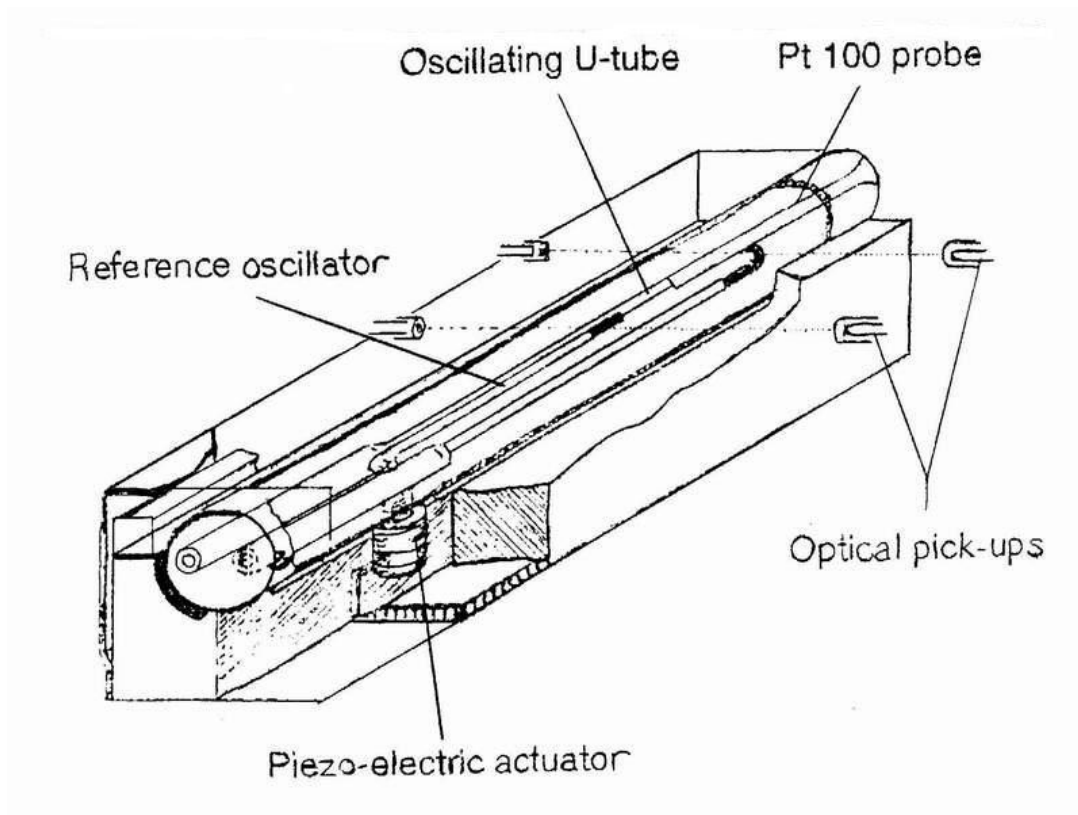


Figure 22. The schematic representation of the oscillating U-tube and the some other parts of density meter.

3.5 Viscosity method

Viscosity measurement is widely used to investigate polymer systems, for instance, the determination of the interactions between polymer blends and the intrinsic viscosity [75-80]. In addition, this method is also applied to the isotropic micellar solutions in order to determine the critical micelle concentration [81], the hydration number of micelles [82-85], the transition of micelle shape as a function of the surfactant concentration [86-88] or electrolyte type [89] and intermicellar interactions [90-93]. Among these, we deal with the intermicellar interactions because we may use them to investigate the interactions between micelles in the lyotropic nematic and chiral nematic phases. The intermicellar interactions can be evaluated from the Huggins equation [90-93]:

$$\frac{\eta_{sp}}{C} = [\eta] + k_H[\eta]^2 C \quad (14)$$

where η_{sp} is the specific viscosity, $[\eta]$ is the intrinsic viscosity, C is the surfactant concentration and k_H is Huggins constant which reflects the intermicellar interactions. The η_{sp} is determined from the viscosity measurement using the following equation:

$$\eta_{sp} = \frac{\eta_s}{\eta_o} - 1 \quad (15)$$

where η_s and η_o are the solution and solvent viscosities, respectively. Then, the intermicellar interaction parameter, k_H , can be determined from the slope of the graph of the η_{sp}/C versus C graph. We anticipate that the intermicellar interaction parameter, k_H , may give us some clue on the interactions between the micelles of our systems.

4. EXPERIMENTAL

4.1 Instruments and Chemicals

A Bruker AXS NanoSTAR small-angle x-ray scattering ($\text{Cu-K}_\alpha = 1.5418 \text{ \AA}$, Ni-filter) instrument equipped with a temperature control unit (metal -block) was used for the small-angle x-ray scattering measurements. The textures of the lyotropic liquid crystal phases were characterized by a Nikon Optiphot2-Pol polarizing light microscope attached with a Nikon D40 digital camera. The mass densities of the lyotropic liquid crystal samples and the isotropic micellar solutions were measured using an AntonPaar DMA5000 densitometer. In order to prepare the liquid crystalline samples, the constituents of the phases were weighed with a Mettler AT 261 balance having $\pm 0.01 \text{ mg}$ precision. A laser set-up was used for the pitch measurements where the wavelength of the laser light was 632.8 nm . For the temperature dependence of the pitch measurements, the stable temperatures were provided with $\pm 0.1 \text{ }^\circ\text{C}$ using a Polyscience 9106 refrigerator/heating circulator. Furthermore, other general laboratory equipments such as hot plates, a centrifuger, a rotatory evaporator, a vacuum pump and a vacuum oven were used.

The chemicals, DL-serine, L-serine, DL-alanine, L-alanine, n-decanol and n-lauroyl chloride were purchased from Merck of high purity ($>99\%$). The used common solvents, absolute ethanol, hexane, ethylacetate, diethylether and petroleum ether were of high purity (99.5%), except hexane (95%).

4.2 Synthesis of amphiphilic molecules (surfactants)

The amphiphilic molecules were synthesized as described in the literature [94]. Firstly, dodecanoyl (or lauroyl) chloride was distilled by vacuum distillation (bp. ~138-142 °C at 12-13 mmHg). 186 mL of an aqueous solution containing 23.82 g of DL-alanine and 14.98 g of KOH in a 600 mL beaker equipped with thermometer and pH electrode was put into an ice bath in order to keep reaction temperature between 0-4 °C until the reaction was completed. Then, 53 mL of freshly distilled dodecanoyl chloride was added dropwise (starting pH was ~11.45) to the DL-alanine solution. The pH of the reaction mixture was kept in the range of 9-12.5 by the simultaneous addition of aqueous 10% KOH solution. After the addition of acid chloride was completed, the reaction mixture was acidified with 30% sulfuric acid to a pH~2. The acid amide (N-dodecanoyl-DL-alanine) was filtered off in order to separate it from aqueous phase and then it was dissolved in ether. The ether phase was washed with water to neutrality and dried over anhydrous Na₂SO₄. The drying agent was filtered off and the ether was removed by rotatory evaporator. The product acid amide was dissolved in petroleum ether (bp. 60-80 °C) at room temperature in order to remove dodecanoic acid, which may be formed during the amidization reaction, then it was recrystallized from Hexane/EtAc (~4/1) and dried in vacuum. The potassium salt, potassium N-dodecanoyl-DL-alaninate (DL-KDDA), was prepared by dissolving the acid amide in water and neutralizing the solution with excess aqueous 10% KOH to a pH~7.5. After the water was evaporated on a hot plate (~80-85°C) by stirring with a magnetic stirrer during several hours, the last product DL-KDDA was dried completely in a vacuum oven (40°C). The

other potassium salts of N-acyl amino acids, potassium N-dodecanoyl-L-alaninate (L-KDDA), potassium N-dodecanoyl-DL-serinate (DL-KDDS), and potassium N-dodecanoyl-L-serinate (L-KDDS), were synthesized by the same way. DL- and L-KDDA were recrystallized from EtOH/Hexane (1/~3-4) three times and DL- and L-KDDS were recrystallized from EtOH three times.

The synthesized potassium salts of amides were characterized by FT-IR, elemental analysis and ^1H -NMR. The FT-IR spectra of DL-KDDA and DL-KDDS were given in Figures 23 and 24, respectively. The L-enantiomers gave the similar FT-IR spectra as their corresponding DL-racemic mixtures.

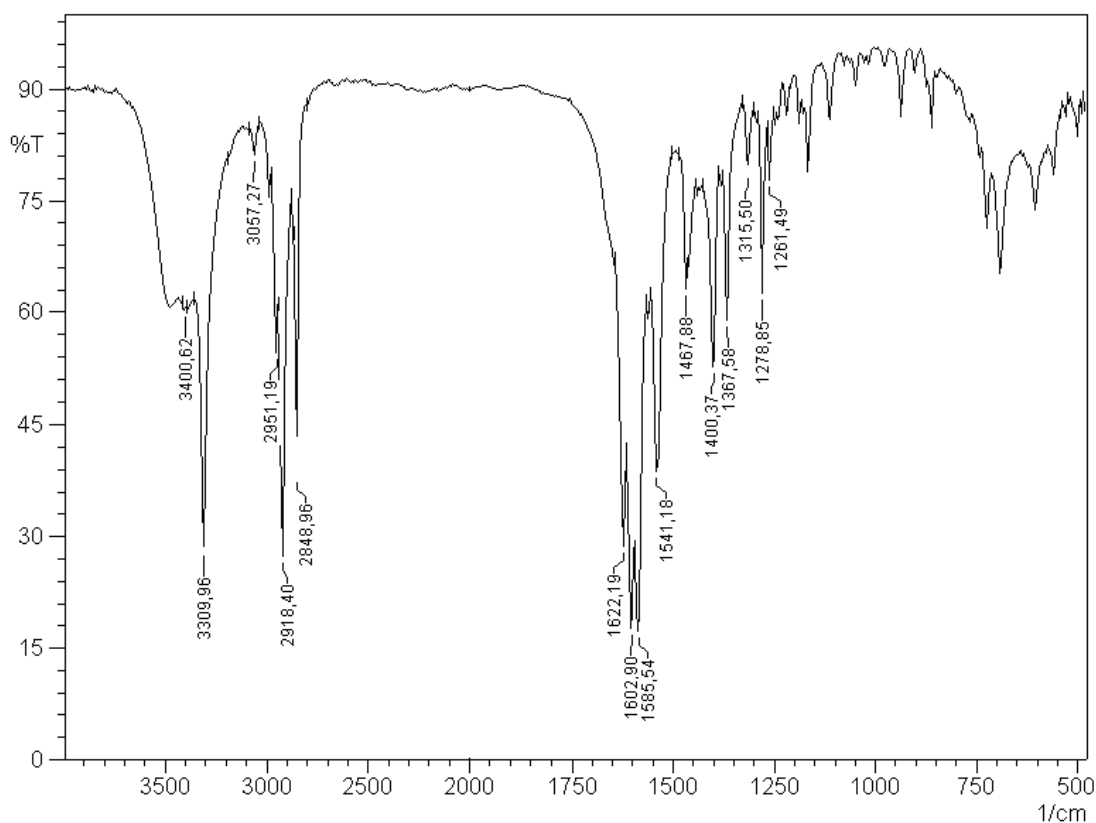


Figure 23. FT-IR spectrum of DL/L-KDDA.

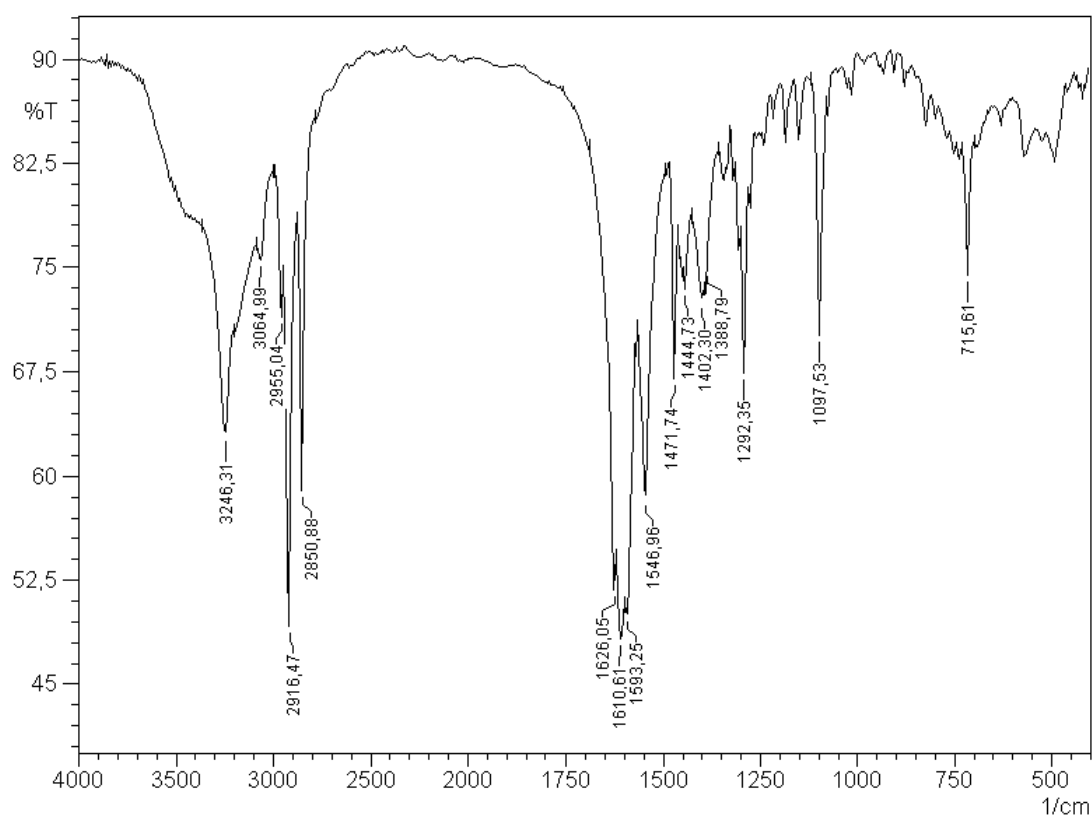


Figure 24. FT-IR spectrum of DL/L-KDDS.

According to the FT-IR spectra given in the Figures 23 and 24, the vibrational band positions were presented in Table 1 as they were compared with the theoretical values.

Table 1. FT-IR data of DL/L-KDDA and DL/L-KDDS.

Type of vibration	Wavenumber/cm ⁻¹	
	A(experimentally)	B (theoretically)[95]
N-H symmetric stretching		
DL/L-KDDA	3310	3350-3180
DL/L-KDDS	3246	
N-H·····O=C stretching		
DL/L-KDDA	3057	3330-3060
DL/L-KDDS	3065	
Aliphatic C-H stretching		
DL/L-KDDA	2951, 2918, 2849	3000-2840
DL/L-KDDS	2955, 2916, 2851	
C=O stretching of amide		
DL/L-KDDA	1626	~1640
DL/L-KDDS	1622	
N-H bending (1) and C-N stretching (2)		
DL/L-KDDA	1541 (1) , 1279 (2)	1570-1515 (1) , ~1250 (2)
DL/L-KDDS	1547 (1) , 1292 (2)	

The second method for the characterization of the synthesized amphiphiles was the elemental analysis technique. The analysis results were given in Table 2. As seen from this table, the calculated values are very close to the experimentally found results. Furthermore, the results showed that as the DL-KDDA and L-KDDA molecules had one mole of water per one mole of these amphiphiles, the potassium salts of serine amides, DL-KDDS and L-KDDS, did not.

Table 2. Elemental analysis results of racemic amphiphilic molecules and their L-enantiomers.

Compound name	C%		H%		N%		Moles of H ₂ O
	Calc.	Found	Calc.	Found	Calc.	Found	
DL-KDDA	55.01	55.37	9.23	9.23	4.28	4.21	1
L-KDDA	55.01	54.63	9.23	9.19	4.28	4.16	1
DL-KDDS	55.35	55.27	8.67	8.57	4.30	4.22	0
L-KDDS	55.35	55.13	8.67	8.63	4.30	4.25	0

The last analysis technique was ¹H-NMR. The NMR data were taken by dissolving each amphiphiles in CD₃OD, separately. The strong broad peaks at ~4.80 ppm in both NMR spectra of KDDA, Figure 25, and KDDS, Figure 26, correspond to the peak of ¹H of CD₃OD, because CD₃OD has very low amount of CH₃OH which gives a strong singlet peak at ~4.87 ppm theoretically.

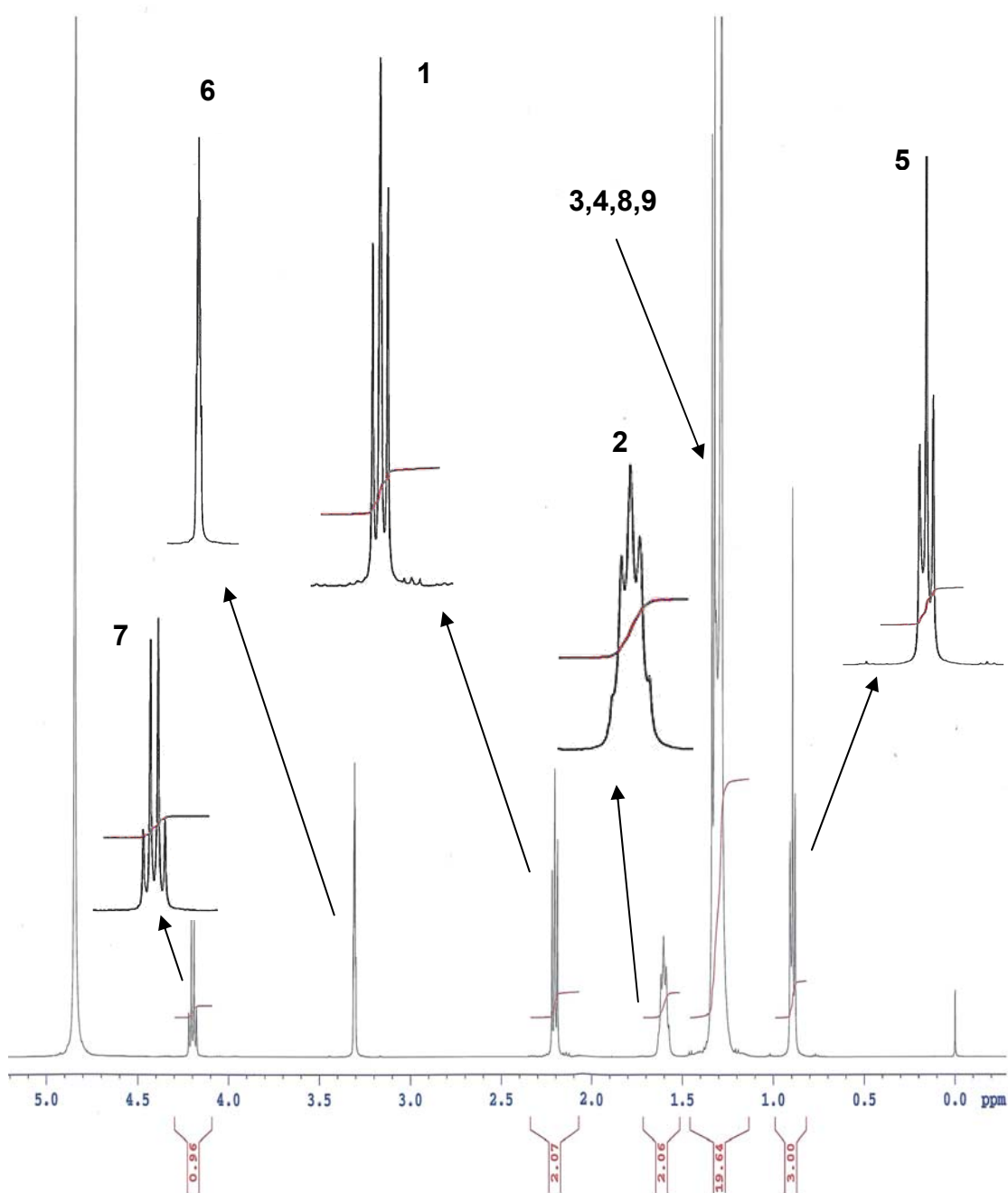
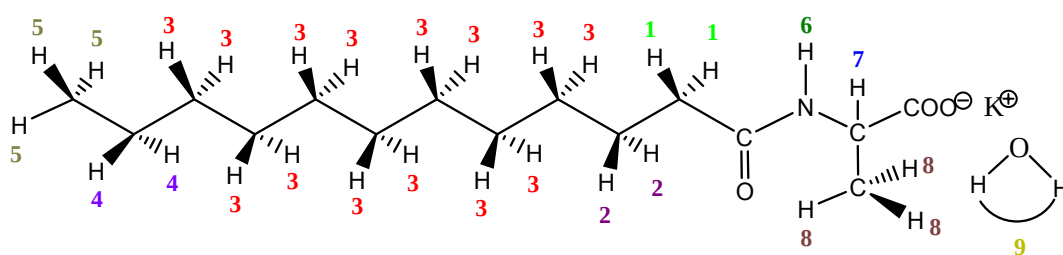


Figure 25. ^1H -NMR of DL/L-KDDA. The spectrum of DL-KDDA was similar as that of L-KDDA. NMR spectra were taken in CD_3OD .



The analysis of ^1H -NMR spectrum of a compound is based on the “n+1” rule where n is the number of the hydrogen atom bounded to the adjacent carbon atom. The peak of three terminal hydrogen atoms (5) was splitted into three (triplet) because there are two H-atoms (4) bounded to the adjacent carbon atom. By the same way, the peaks of the H-atoms (1), (2), (4) and (7) were splitted into three (triplet), five (multiplet), six (multiplet) and four (quartet), respectively. The amidic H-atom (6) gave one broad peak. The elemental analysis results showed that the alanine amides include one mole of water molecule per one mole of amphiphilic molecule. Because the two H-atoms (9) of water are equivalent, they gave only one peak. However, the peaks of these H-atoms and also the H-atoms (4) and (8) were overlapped with the peaks of the H-atoms (3), thus the peak at 1.29 ppm was multiplet and strong. The ^1H -NMR analysis results of DL- or L-KDDA were summarized in Table 3 where the numbers in the paranthesis are the estimated chemical shifts predicted from the computer program ChemDraw Ultra 8.0.

Table 3. ^1H -NMR results of DL/L-KDDA amphiphiles according to the spectrum in Figure 25. Splittings are in good agreement with the $n+1$ rule where n is number of H-atom bounded to the neighbour C-atom. These amphiphiles include one mole of water per each amphiphile and two hydrogen atom in water (labelled as 9) molecule give one signal because they are equivalent.

^1H no	Splitting	Total number of ^1H	δ/ppm (**)
1	T	2	2.21 (2.18)
2	M	2	1.61 (1.57)
3	M	14	1.29 (1.29)
4	M	2*	1.29 (1.33)
5	T	3	0.90 (0.96)
6	BS	1	3.31 (rough)
7	Q	1	4.20 (4.63)
8	---	3*	1.29 (1.41)
9	---	1*	1.29 (rough)

T: Triplet, Q: Quartet, M: Multiplet, BS: Broad singlet

* The signals of the H-atoms labelled as 4, 8 and 9 overlap with the signals of the H-atoms 3.

** The numbers in the paranthesis are the estimated chemical shifts predicted from the computer program ChemDraw Ultra 8.0.

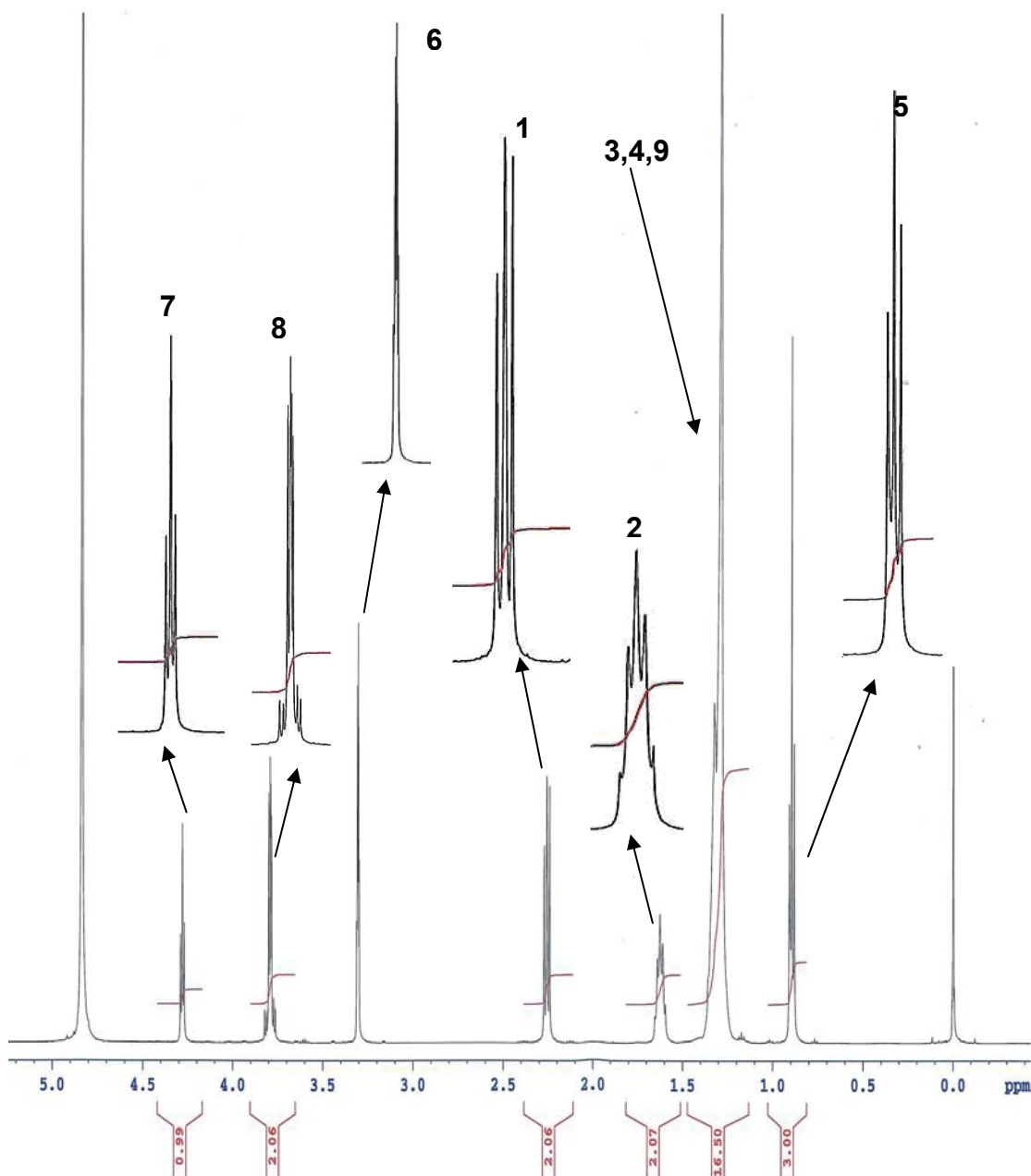
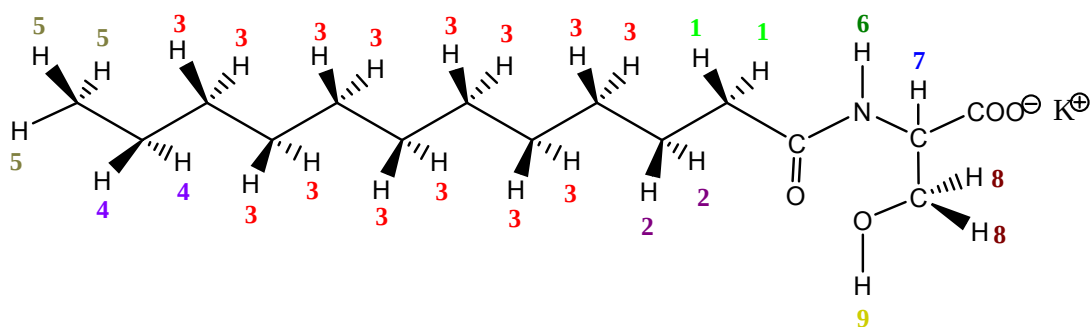


Figure 26. ^1H -NMR of DL/L-KDDS. The spectra of DL-KDDS was same as that of L-KDDS. NMR spectra were taken in CD_3OD .



The ^1H -NMR of DL/L-KDDS spectrum was analyzed as we did for KDDA amphiphiles. Hence, we only gave the results in Table 4.

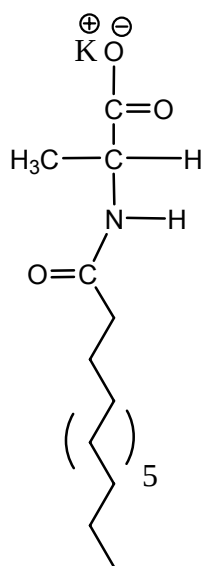
Table 4. ^1H -NMR results of DL/L-KDDS amphiphiles according to the spectrum in Figure 26.

^1H no	Splitting	Total number of ^1H	δ/ppm (**)
1	T	2	2.26 (2.18)
2	M	2	1.63 (1.57)
3	M	14	1.29 (1.29)
4	M	2*	1.29 (1.33)
5	T	3	0.90 (0.96)
6	BS	1	3.31 (rough)
7	T	1	4.27 (4.54)
8	M	2	3.80 (3.95)
9	---	1*	1.29 (rough)

T: Triplet, Q: Quartet, M: Multiplet, BS: Broad singlet

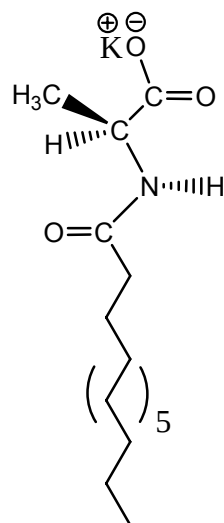
* The signal of the H-atom labeled as 4 and 9 overlap with the signals of the H-atoms 3.

** The numbers in the paranthesis are the estimated chemical shifts predicted from the computer program ChemDraw Ultra 8.0.



DL-KDDA

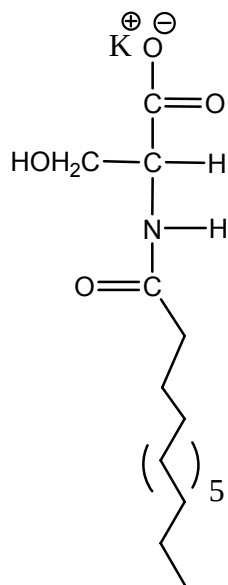
(i)



L-KDDA

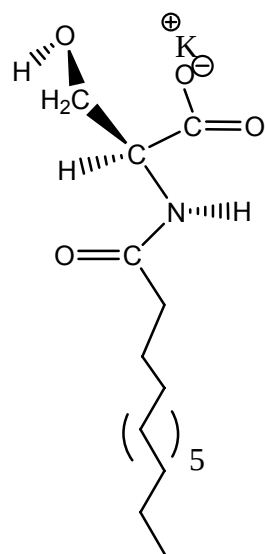
(ii)

(a)



DL-KDDS

(i)



L-KDDS

(ii)

(b)

Figure 27. The molecular structures of (a): (i) DL-KDDA, (ii) L-KDDA and (b): (i) DL-KDDS, (ii) L-KDDS.

4.3 Preparation of liquid crystal samples for microscopic, laser diffraction, mass density and SAXS measurements

The liquid crystal phases were prepared by weighing appropriate amounts of the ingredients into test tubes which were sealed off by flame as soon as possible in order to avoid water loss. Homogeneous liquid crystal phases were obtained by leaving the sealed test tubes in a water bath at about 50-60 °C and centrifuging and using a vortex occasionally.

Polarizing light microscopy

After obtaining homogeneous liquid crystal phases, a small amount of the liquid crystal sample was transferred into microslides of 0.2, 0.3 and 0.4 mm thickness for microscopic investigation. Approximately, one third of the microslides was filled with the liquid crystal sample which was placed in the centre of the microslides. Both ends of the microslides were covered with parafilm at low temperatures to prevent water loss. For high temperature investigations, the ends of microslides were sealed off by flame.

For the construction of phase diagrams, microslides of 0.2, 0.3 and 0.4 mm thickness containing the sample were placed into a set-up made from brass, Figure 28. This set-up is a completely closed-system, so that the temperature is easily controlled with an accuracy of ± 0.1 °C.

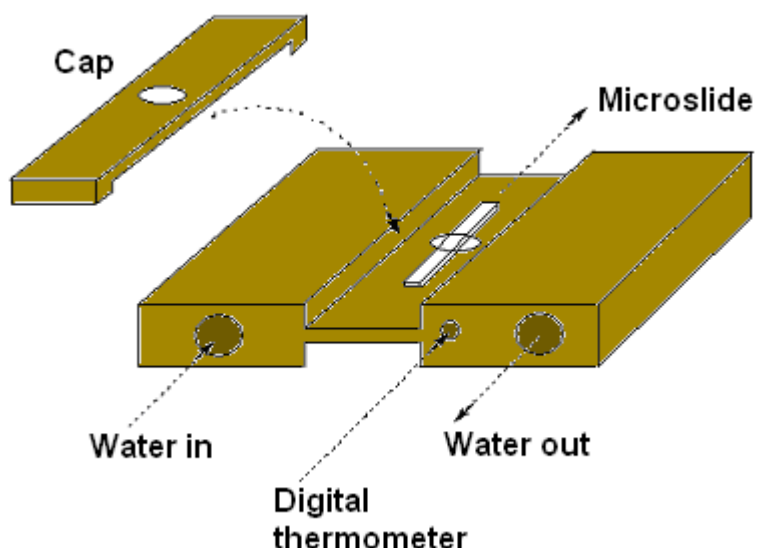


Figure 28. The experimental set-up for determination of phase transitions temperatures from microscopic investigations. This set-up was placed on the rotating stage of the polarizing light microscope. The holes, on the cap and the one below the microslide, were closed when no measurement was performed.

By setting the temperature to a desired value on the thermostat, the phase transitions and corresponding temperatures were determined.

Laser light diffraction

Laser light diffraction method was used to determine the pitch of the chiral nematic phases. It was observed that a well diffraction pattern could only be obtained when the sample thickness was increased to about 2.8 mm. So, a hole of 6.0 mm in diameter was drilled in a glass of 2.8 mm thickness which was cemented to a microslide as shown in Figure 29.

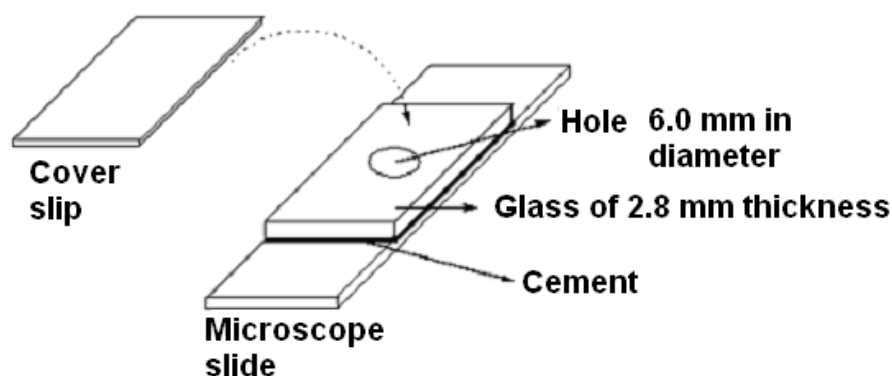


Figure 29. A schematic drawing of the measuring cell. The liquid crystal sample was covered with a cover slip.

Then, the liquid crystal sample was transferred into the measuring cell in Figure 29. After the hole was completely filled with the sample, it was covered with a cover slip, which was tightened with silicone grease in order to avoid water loss. Thus, a completely closed-system was obtained. Then, the measuring cell was placed into the set-up in Figure 30.

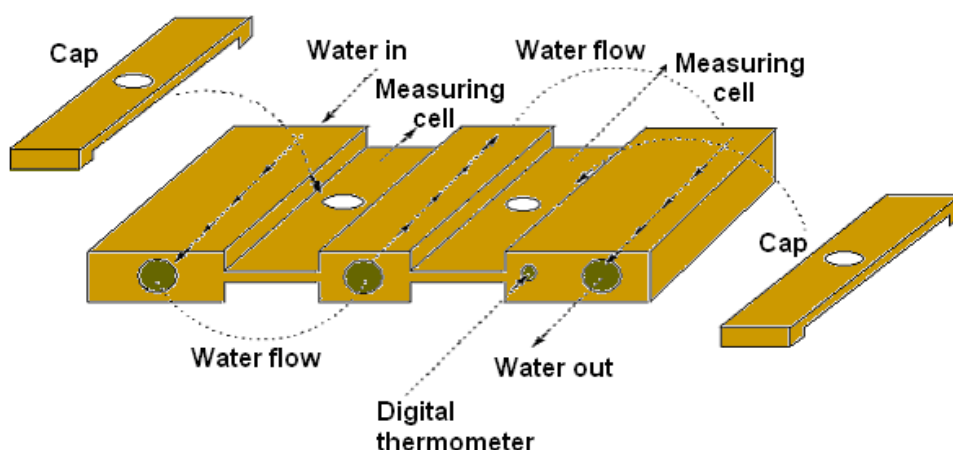


Figure 30. The measuring holder produced from brass was used to determine pitch length by laser diffraction. This set-up has two places where the measuring cell can be placed, so that laser diffraction measurements of two different liquid crystal samples can be made at the same time.

After the preparation of the set-up in Figure 30, the laser diffraction measurements were made. The temperature was increased by 2.5 and 5 °C intervals in every 15 minutes

Small angle x-ray scattering

For SAXS measurements, the liquid crystalline samples were transferred into sealed cylindrical glass capillaries, which were 0.7 mm in diameter, using a small vacuum pump and then placed into a temperature control unit (metal-block), Figure 31. A two-dimensional detector was used and its position was calibrated with characteristic reflection of silver behenate ($C_{21}H_{43}COOAg$) as reference material. The exposure times of the samples were about 2-6 hours. Prior to the x-ray experiment, the samples were kept at room temperature (~ 25 - 26 °C) at least for 24 hours. The nematic phases were not aligned in a magnetic field, however, the chiral nematic phases which gave circular like diffraction patterns were oriented in a magnetic field of 1.1 Teslas, Figure 32.

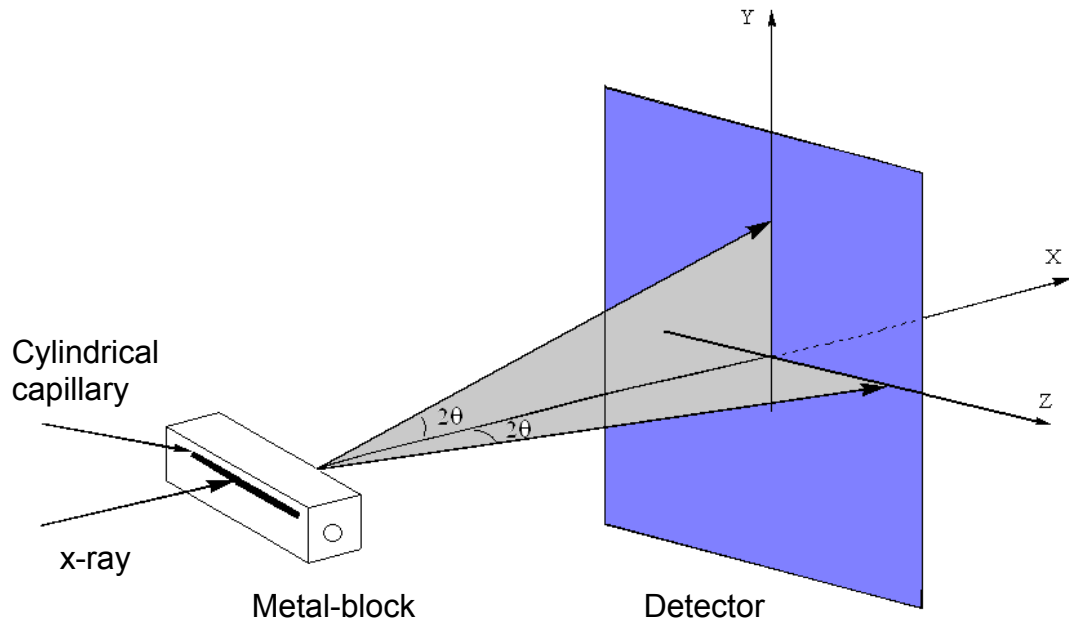


Figure 31. A schematic representation of SAXS experiment. X-ray beam coincides with the x-axis. The choice of direction of axes is arbitrary.

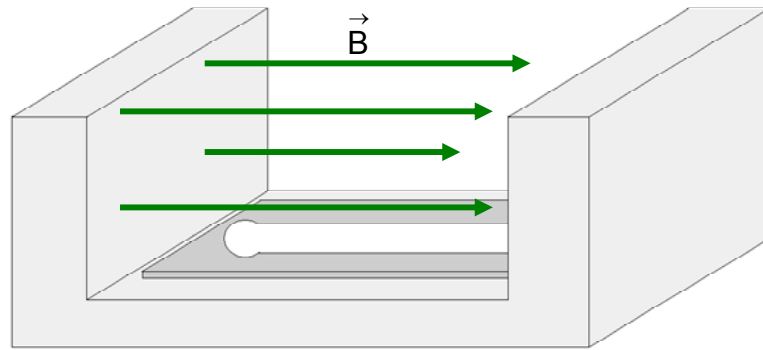


Figure 32. The position of the cylindrical capillary including the chiral nematic phase in a magnetic field of 1.1 T. By this way, the helix axis of the chiral nematic phase is aligned parallel to the magnetic field direction and long capillary axis. $\vec{B}$ represents the magnetic field direction.

4.4 Experimental procedure for isotropic micellar solutions

The aqueous solutions of each of the amphiphilic molecules having certain concentrations were prepared dissolving them in water, separately. In order to provide the complete dissolution in water, the samples were mixed on a vortex, then centrifuged and finally ultrasonicated at least for 15 minutes. Thereafter, the viscosity and mass density measurements were applied using these isotropic solutions, separately, as described in the following parts.

4.4.1 Mass density measurement

The solutions were transferred into the U-tube of the densimeter. The solutions were equilibrated at the desired temperatures for 15 minutes. The densities of the solutions were taken between 25 and 45 °C at 5 °C intervals. The densities of each solution were repeated 3 times.

4.4.2 Viscosity measurement

We used two different falling ball viscometers, Figure 33, whose positions in the water bath were calibrated according to the literature value of pure water. In order to measure the viscosity of the solution, the viscometer was filled with approximately 7 mL of the solution and the glass ball was released to fall down into the viscometer. Then, the viscometer was closed with its cap. The viscometer was put into water bath in the vertical position and equilibrated at least for 30 minutes at each temperature. The time of the descent of the ball in the solution between levels 1 and 2 was recorded.



Each concentration was repeated 3 times. The viscosities of the solutions were calculated using the following equation:

$$\eta = K(\rho_{\text{ball}} - \rho_{\text{sol}})t_{\text{desc}} \quad (16)$$

where η is the viscosity of the solution, ρ_{ball} and ρ_{sol} are the densities of the ball and the solution, respectively, t_{desc} is the time of the descent of the ball in the solution and K is viscometer constant. The ρ_{ball} and K are given as 2.53 g/cm^3 and 0.3 (for size 1) by the manufacturer, respectively. The viscosity measurements were applied to the isotropic micellar solutions in the temperature range of 25 and $45 \text{ }^\circ\text{C}$ at $5 \text{ }^\circ\text{C}$ intervals.

Figure 33. A falling ball viscometer.

4.5 Phase compositions

The most convenient liquid crystalline racemic nematic and chiral nematic phases were prepared with appropriate amphiphile, salt, Na_2SO_4 , n -decanol and water. Accordingly, the racemic nematic and chiral nematic phases of KDDA and KDDS were prepared with the following aims:

- (i) to characterize the nematic and chiral nematic phases under polarising light microscope, e.g determinations of their textures and their optical anisotropies,

- (ii) construct partial phase diagrams from polarising light microscope,
- (iii) measure the helical pitches of the chiral nematic phases and evaluate the helical twisting powers of KDDA and KDDS systems from laser light diffraction measurements,
- (iv) determine the differences in the mass densities of the racemic nematic and chiral nematic phases from mass density measurements, and
- (v) detect the differences between the sizes of achiral micelles of racemic nematic phases and that of chiral micelles of intrinsically chiral nematic phases from small-angle x-ray scattering.

For these experimental measurements, the racemic nematic and chiral nematic phases having different compositions were prepared and they are given in the following tables, 5-10.

Table 5. The compositions of the individual racemic nematic and chiral nematic phases obtained from (a) alanine and (b) serine amides in the mixtures of Na₂SO₄, n-decanol (DeOH) and water in mole percent. The transition temperatures, $T_{N\phi}$ from nematic to turbid phases, ϕ , are also given. These phase compositions were used for the characterization of the phases under polarising light microscope, mass density and SAXS measurements. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat.

Phase code	$X_{KDDA}\%$	$X_{Na_2SO_4}\%$	$X_{DeOH}\%$	$X_{H_2O}\%$	Phase Type	$T_{N\phi}/^{\circ}C$
DL-1	2.52	1.16	1.14	95.17	N	~62.5
L-1	2.52	1.16	1.14	95.17	N*	
DL-2	2.75	1.16	1.14	94.95	N	~67.0
L-2	2.75	1.16	1.14	94.95	N*	
DL-3	3.02	1.14	1.14	94.71	N	~71.5
L-3	3.02	1.14	1.14	94.71	N*	
DL-4	3.25	1.15	1.13	94.48	N	~74.0
L-4	3.25	1.15	1.13	94.48	N*	

(a)

Phase code	$X_{KDDS} \%$	$X_{Na_2SO_4} \%$	$X_{DeOH} \%$	$X_{H_2O} \%$	Phase Type	$T_{N\phi} / ^\circ\text{C}$
DL-1	2.51	1.19	1.17	95.14	N	~58.5
L-1	2.51	1.18	1.17	95.17	N*	
DL-2	2.75	1.18	1.16	94.92	N	~62.0
L-2	2.74	1.18	1.16	94.92	N*	
DL-3	3.00	1.18	1.16	94.67	N	~65.0
L-3	3.00	1.18	1.16	94.66	N*	
DL-4	3.25	1.17	1.16	94.42	N	~68.0
L-4	3.25	1.17	1.16	94.42	N*	

(b)

Table 6. The concentrations of the components in mole percent for mass density and SAXS measurements on going from the racemic nematic phase to its intrinsically chiral nematic phases for (a) KDDA and (b) KDDS.

$X_{DL-KDDA} \%$	$X_{Na_2SO_4} \%$	$X_{DeOH} \%$	$X_{H_2O} \%$	$X_{L-KDDA} \%$
2.52	1.16	1.15	95.17	—
1.90	1.16	1.14	95.17	0.62
1.26	1.16	1.14	95.17	1.26
0.67	1.16	1.14	95.17	1.85
—	1.16	1.15	95.17	2.52

(a)

$X_{DL-KDDS} \%$	$X_{Na_2SO_4} \%$	$X_{DeOH} \%$	$X_{H_2O} \%$	$X_{L-KDDS} \%$
2.51	1.19	1.17	95.14	—
1.88	1.19	1.17	95.14	0.63
1.25	1.19	1.17	95.14	1.26
0.63	1.19	1.17	95.14	1.88
—	1.18	1.17	95.14	2.51

(b)

Table 7. The compositions of the chiral nematic phases of L-KDDA in mole percent. The phase types are given at room temperature. T_{CN^*} and $T_{N^*\phi}$ represent the phase transition temperatures from crystalline phase to chiral nematic phase and from chiral nematic phase to turbid phase, respectively. These phases were used for (i) the construction of the partial phase diagram, (ii) the determination of the effect of the temperature on the pitch and (iii) also calculate the helical twisting power and its temperature dependence. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat.

Run	X_{L-KDDA} %	$X_{Na_2SO_4}$ %	X_{DeOH} %	X_{H_2O} %	Phase Type	T_{CN^*} /°C	$T_{N^*\phi}$ /°C
LA-1	1.94	1.17	1.15	95.74	N*	~3.5	~46.0
LA-2	2.17	1.16	1.14	95.53	N*	~3.5	~53.0
LA-3	2.22	1.16	1.14	95.48	N*	~3.4	~54.5
LA-4	2.35	1.16	1.14	95.35	N*	~3.3	~58.5
LA-5	2.52	1.16	1.14	95.18	N*	~3.0	~61.5
LA-6	2.61	1.16	1.14	95.09	N*	~2.8	~64.5
LA-7	2.75	1.16	1.14	94.95	N*	~2.3	~67.0
LA-8	2.86	1.16	1.14	94.84	N*	~1.9	~69.0
LA-9	2.99	1.15	1.13	94.73	N*	~1.3	~71.0
LA-10	3.17	1.15	1.13	94.55	N*	~0.4	~73.0
LA-11	3.26	1.14	1.13	94.47	N*	~-0.2	~74.5
LA-12	3.38	1.14	1.13	94.35	N*	~-1.0	~75.0

Table 8. The average pitch values of the L-KDDA systems whose compositions and phase codes were given in Table 7. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat. The standard deviations of the measured pitches were 3-5% with respect to their average values.

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	4.85	0.206
20.0	6.60	0.152
25.0	9.14	0.109
30.0	13.5	0.0741
35.0	19.7	0.0508
40.0	20.3	0.0493

LA-1

(a)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	3.22	0.311
20.0	4.26	0.235
25.0	5.50	0.182
30.0	7.25	0.138
35.0	9.38	0.107
40.0	12.3	0.0813
45.0	16.2	0.0617
50.0	20.9	0.0478

LA-2

(b)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	2.88	0.348
20.0	3.44	0.291
25.0	4.61	0.217
30.0	6.05	0.165
35.0	7.46	0.134
40.0	9.54	0.105
45.0	12.4	0.0807
50.0	15.5	0.0645

LA-3

(c)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
5.0	1.79	0.560
10.0	1.99	0.504
15.0	2.52	0.398
20.0	3.08	0.325
25.0	3.83	0.261
30.0	4.99	0.201
35.0	6.26	0.160
40.0	7.93	0.126
45.0	9.67	0.103
50.0	11.8	0.0848
55.0	14.3	0.0699

LA-4

(d)

T/°C	P/μm	P ⁻¹ /μm ⁻¹
15.0	2.20	0.454
20.0	2.58	0.389
25.0	3.35	0.298
30.0	4.23	0.236
35.0	5.03	0.199
40.0	6.66	0.150
45.0	8.06	0.124
50.0	9.58	0.104
55.0	11.0	0.0909
60.0	14.1	0.0709

LA-5

(e)

T/°C	P/μm	P ⁻¹ /μm ⁻¹
5.0	1.51	0.664
10.0	1.68	0.595
15.0	2.00	0.500
20.0	2.40	0.416
25.0	2.97	0.336
30.0	3.76	0.266
35.0	4.76	0.210
40.0	5.78	0.173
45.0	7.05	0.142
50.0	8.82	0.113
55.0	10.2	0.0980
60.0	12.1	0.0826
65.0	14.5	0.0690

LA-6

(f)

T/°C	P/μm	P ⁻¹ /μm ⁻¹
15.0	1.75	0.572
20.0	2.09	0.478
25.0	2.80	0.393
30.0	3.17	0.316
35.0	3.83	0.261
40.0	4.73	0.212
45.0	5.94	0.168
50.0	7.32	0.137
55.0	8.60	0.116
60.0	10.3	0.0971
65.0	12.4	0.0807

LA-7

(g)

T/°C	P/μm	P ⁻¹ /μm ⁻¹
10.0	1.52	0.660
15.0	1.69	0.593
20.0	1.99	0.503
25.0	2.38	0.420
30.0	3.01	0.332
35.0	3.62	0.276
40.0	4.61	0.217
45.0	5.73	0.175
50.0	7.06	0.142
55.0	8.22	0.122
60.0	9.54	0.105
65.0	11.4	0.0877
70.0	14.1	0.0709

LA-8

(h)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	1.59	0.628
20.0	2.03	0.493
25.0	2.19	0.457
30.0	2.78	0.359
35.0	3.43	0.292
40.0	3.94	0.254
45.0	5.06	0.197
50.0	5.75	0.174
55.0	7.62	0.131
60.0	8.92	0.112
65.0	10.8	0.0926
70.0	12.4	0.0806

LA-9

(i)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	1.54	0.650
20.0	1.66	0.602
25.0	1.93	0.517
30.0	2.42	0.414
35.0	2.91	0.343
40.0	3.79	0.264
45.0	4.72	0.212
50.0	6.10	0.164
55.0	6.70	0.149
60.0	8.12	0.123
65.0	9.94	0.101
70.0	11.7	0.0855

LA-10

(j)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
20.0	1.61	0.621
25.0	1.89	0.529
30.0	2.35	0.425
35.0	2.96	0.338
40.0	3.87	0.259
45.0	4.64	0.216
50.0	7.06	0.142
55.0	8.57	0.117

LA-11

(k)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	1.46	0.683
20.0	1.62	0.618
25.0	1.84	0.544
30.0	2.14	0.467
35.0	2.59	0.386
40.0	3.24	0.309
45.0	3.95	0.253
50.0	4.93	0.203
55.0	5.97	0.167

LA-12

(l)

Table 9. The compositions of the chiral nematic phases of L-KDDS in mole percent. The phase types are given at room temperature. T_{CN^*} and $T_{N^*\phi}$ represent the phase transition temperatures from crystalline phase to chiral nematic phase and from chiral nematic phase to turbid phase, respectively. These phases were used for (i) the construction of the partial phase diagram, (ii) the determination of the effect of the temperature on the pitch and (iii) also calculate the helical twisting power and its temperature dependence. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat.

Run	$X_{L-KDDS}\%$	$X_{Na_2SO_4}\%$	$X_{DeOH}\%$	$X_{H_2O}\%$	Phase Type	$T_{CN^*}/^{\circ}C$	$T_{N^*\phi}/^{\circ}C$
LS-1	1.78	1.20	1.17	95.85	N*	~15.4	~45.0
LS-2	1.96	1.19	1.17	95.68	N*	~15.1	~48.0
LS-3	2.10	1.19	1.17	95.54	N*	~14.9	~52.0
LS-4	2.27	1.19	1.16	95.38	N*	~14.8	~53.0
LS-5	2.44	1.19	1.17	95.20	N*	~14.4	~58.0
LS-6	2.51	1.18	1.16	95.15	N*	~14.2	~59.0
LS-7	2.59	1.19	1.16	95.06	N*	~14.1	~60.0
LS-8	2.74	1.18	1.16	94.92	N*	~13.9	~62.0
LS-9	2.90	1.18	1.16	94.76	N*	~13.5	~64.0
LS-10	3.09	1.18	1.16	94.57	N*	~13.2	~65.0
LS-11	3.26	1.17	1.15	94.42	N*	~12.8	~67.0
LS-12	3.41	1.17	1.15	94.27	N*	~12.1	~71.5
LS-13	3.61	1.17	1.15	94.07	N*	~11.8	~70.5
LS-14	3.75	1.17	1.15	93.93	N*	~11.2	~72.0

Table 10. The average pitch values of the L-KDDS systems whose compositions and phase codes were given in Table 9. The temperature was controlled with an accuracy of ± 0.1 °C by using a thermostat. The standard deviations of the measured pitches were 4-6% with respect to their average values.

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	25.1	0.0399
20.0	27.5	0.0364
22.5	30.7	0.0326
25.0	34.1	0.0293
27.5	38.7	0.0259
30.0	42.1	0.0238
32.5	45.7	0.0219
35.0	51.6	0.0194
37.5	56.0	0.0179
40.0	58.4	0.0171

LS-1

(a)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	15.5	0.0647
20.0	16.7	0.0599
22.5	17.7	0.0564
25.0	19.9	0.0501
27.5	21.2	0.0471
30.0	23.0	0.0436
32.5	25.2	0.0397
35.0	27.7	0.0361
37.5	33.2	0.0301
40.0	36.0	0.0278
42.5	39.4	0.0254

LS-2

(b)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	14.3	0.0698
20.0	16.1	0.0623
22.5	17.8	0.0562
25.0	19.1	0.0523
27.5	19.6	0.0511
30.0	22.2	0.0451
32.5	25.0	0.0400
35.0	25.9	0.0386
37.5	27.9	0.0359
40.0	31.2	0.0320
42.5	33.9	0.0295
45.0	35.4	0.0282

LS-3

(c)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	9.91	0.101
20.0	11.1	0.0903
22.5	11.7	0.0854
25.0	12.7	0.0790
27.5	13.6	0.0736
30.0	14.3	0.0698
32.5	16.7	0.0599
35.0	17.9	0.0558
37.5	18.9	0.0528
40.0	20.7	0.0484
42.5	20.9	0.0478
45.0	23.9	0.0418
47.5	24.6	0.0407

LS-4

(d)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	7.42	0.135
20.0	7.79	0.128
22.5	8.22	0.122
25.0	8.69	0.115
27.5	9.28	0.108
30.0	9.84	0.102
32.5	10.7	0.0933
35.0	11.6	0.0860
37.5	12.8	0.0785
40.0	14.11	0.0709
42.5	15.8	0.0633
45.0	18.1	0.0552
47.5	21.1	0.0474
50.0	25.3	0.0395
52.5	29.8	0.0335

LS-5

(e)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	7.04	0.142
20.0	7.24	0.138
22.5	7.61	0.131
25.0	7.86	0.127
27.5	8.25	0.121
30.0	8.79	0.114
32.5	9.47	0.106
35.0	10.3	0.0969
37.5	11.3	0.0887
40.0	12.4	0.0807
42.5	13.7	0.0732
45.0	15.1	0.0664
47.5	16.6	0.0602
50.0	18.3	0.0546
52.5	20.2	0.0496
55.0	22.2	0.0451

LS-6

(f)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	5.52	0.181
20.0	5.78	0.173
22.5	6.27	0.159
25.0	6.69	0.149
27.5	7.10	0.141
30.0	7.52	0.133
32.5	8.09	0.124
35.0	8.93	0.112
37.5	9.38	0.107
40.0	9.81	0.102
42.5	11.1	0.0904
45.0	11.3	0.0888
47.5	11.5	0.0872
50.0	12.8	0.0783
52.5	12.8	0.0785
55.0	15.1	0.0663

LS-7

(g)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
17.5	5.12	0.195
20.0	5.34	0.187
22.5	5.59	0.179
25.0	5.88	0.170
27.5	6.24	0.160
30.0	6.64	0.151
32.5	7.13	0.140
35.0	7.74	0.129
37.5	8.49	0.118
40.0	9.47	0.106
42.5	10.7	0.0932
45.0	12.5	0.0802
47.5	15.0	0.0667
50.0	15.6	0.0643
52.5	16.0	0.0626
55.0	17.8	0.0561

LS-8

(h)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	3.83	0.261
20.0	4.08	0.245
25.0	4.66	0.215
30.0	5.13	0.195
35.0	5.76	0.174
40.0	7.02	0.142
45.0	8.43	0.119
50.0	9.74	0.103
55.0	11.5	0.0871

LS-9

(i)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
20.0	3.94	0.254
25.0	4.48	0.223
30.0	4.91	0.204
35.0	5.73	0.175
40.0	6.55	0.153
45.0	8.70	0.115
50.0	11.9	0.0840
55.0	15.6	0.0643
60.0	21.4	0.0468

LS-10

(j)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	3.05	0.328
20.0	3.40	0.294
25.0	3.83	0.261
30.0	4.54	0.220
35.0	5.43	0.184
40.0	6.21	0.161
45.0	6.93	0.144
50.0	8.30	0.121
55.0	9.35	0.107

LS-11

(k)

T/°C	P/ μm	P ⁻¹ / μm^{-1}
15.0	3.05	0.328
20.0	3.40	0.294
25.0	3.42	0.293
30.0	3.90	0.257
35.0	4.58	0.219
40.0	5.25	0.191
45.0	5.97	0.168
50.0	6.96	0.144
55.0	9.35	0.107

LS-12

(l)

T/°C	P/μm	P ⁻¹ /μm ⁻¹
15.0	2.29	0.437
20.0	2.49	0.401
25.0	2.83	0.354
30.0	3.25	0.308
35.0	3.77	0.265
40.0	4.28	0.234
45.0	5.28	0.189
50.0	5.61	0.178
55.0	6.12	0.163
60.0	6.79	0.147
65.0	7.40	0.135

LS-13

(m)

T/°C	P/μm	P ⁻¹ /μm ⁻¹
15.0	2.28	0.440
20.0	2.44	0.410
25.0	2.60	0.385
30.0	2.93	0.341
35.0	3.47	0.289
40.0	3.99	0.251
45.0	4.88	0.205
50.0	5.23	0.191
55.0	6.88	0.146
60.0	7.14	0.140

LS-14

(n)

5. RESULTS AND DISCUSSION

5.1 Polarizing light microscopic investigations of racemic nematic and chiral nematic phases

5.1.1 The lyotropic nematic phases

The racemic nematic phases of DL-KDDA and DL-KDDS showed characteristic schlieren textures as in Figure 34.

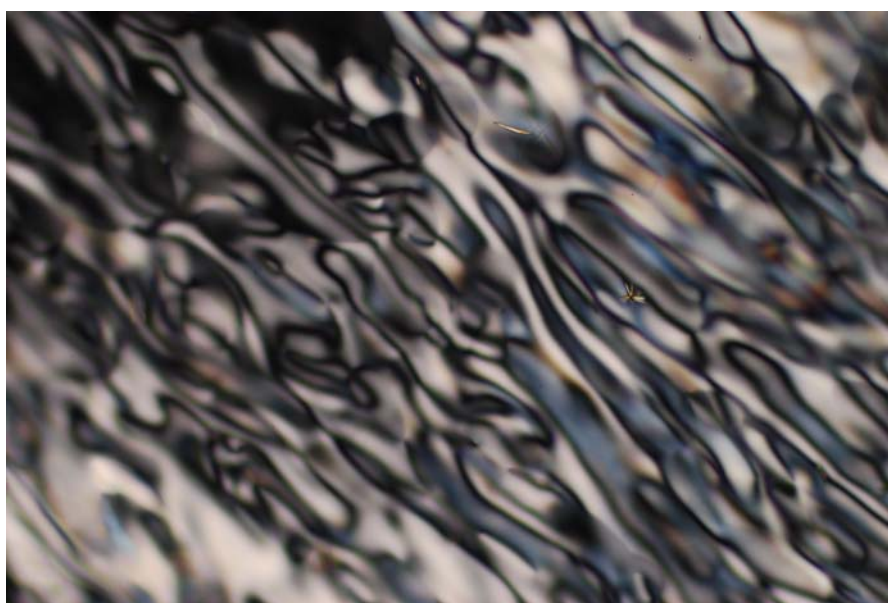


Figure 34. A characteristic schlieren texture obtained from racemic nematic phases, DL-KDDA or DL-KDDS. The thickness of microslide was 0.2 mm. The photograph was taken approximately 15 minutes after the sample was transferred into the microslide. Magnification was 50x.

They mostly aligned in a few hours to give a pseudo isotropic texture, Figure 35, i.e. their director aligned homeotropically to the glass surface of the microslides.

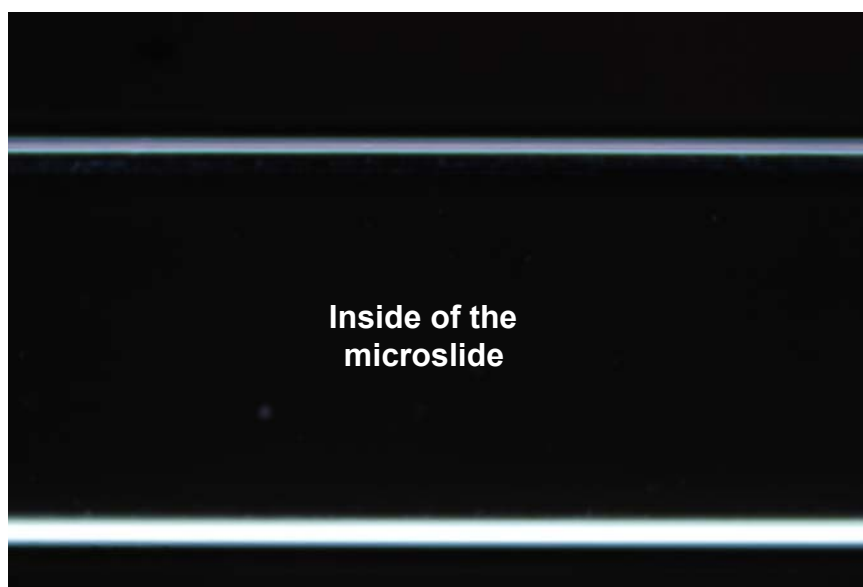


Figure 35. The pseudo-isotropic texture of DL-KDDA. The similar texture was also observed for DL-KDDS. The thickness of the microslide was 0.2 mm and the magnification was 25x.

The conosopic investigations applied to the aligned nematic phases gave cross-dark brushes as presented in Figure 36a. A separation at the center of the cross-dark brushes was not observed, i.e. the phases were uniaxial. When a $\frac{1}{4} \lambda$ retardation plate was introduced into the path way of the incident light, a characteristic colors for a phase having $\Delta n > 0$ was observed, Figure 36b. These results indicated that the racemic nematic phases of DL-KDDA and DL-KDDS were N_D^- [96].

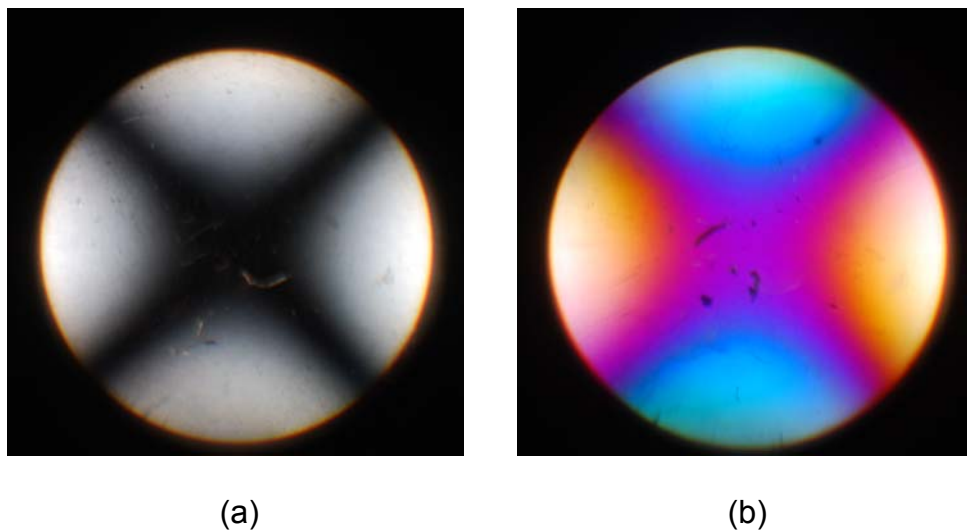


Figure 36. The conoscopic investigation of the homeotropically aligned textures of DL-KDDA and DL-KDDS.

5.1.2 The lyotropic chiral nematic phases

The textures of the chiral nematic phases of L-KDDA and L-KDDS were fingerprint textures as shown in Figure 37 and 38, respectively. The helix axes of both L-KDDA and L-KDDS phases were perpendicular to the long capillary axis.

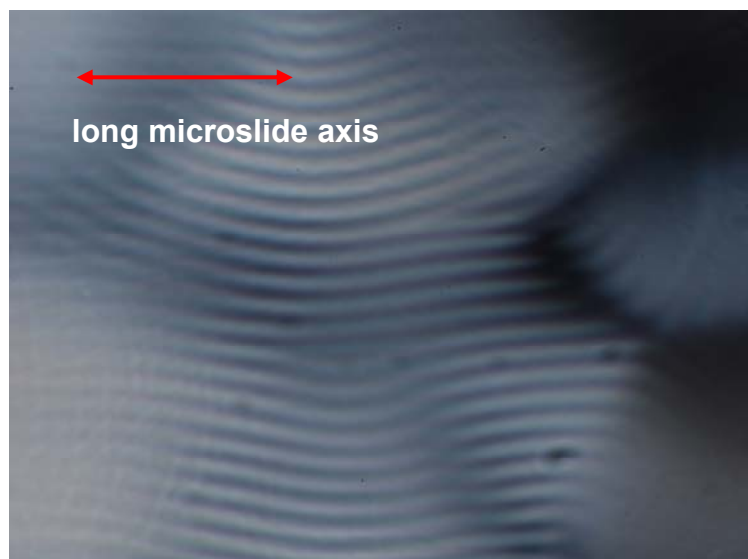


Figure 37. The fingerprint texture of the chiral nematic phase of L-KDDA. The thickness of the microslide was 0.2 mm and the magnification was 100x.

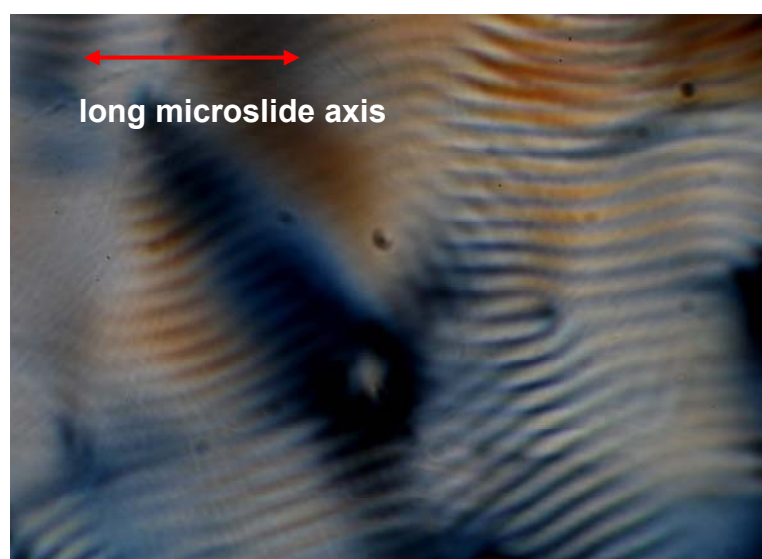


Figure 38. The fingerprint texture of the chiral nematic phase of L-KDDS. The thickness of the microslide was 0.2 mm and the magnification was 50x.

5.2 The phase diagrams of potassium N-dodecanoyl-alaninate and potassium N-dodecanoyl-serinate systems

The phase diagrams were constructed according to the phase compositions of KDDA and KDDS systems, which were given in Table 7 and 9, respectively.

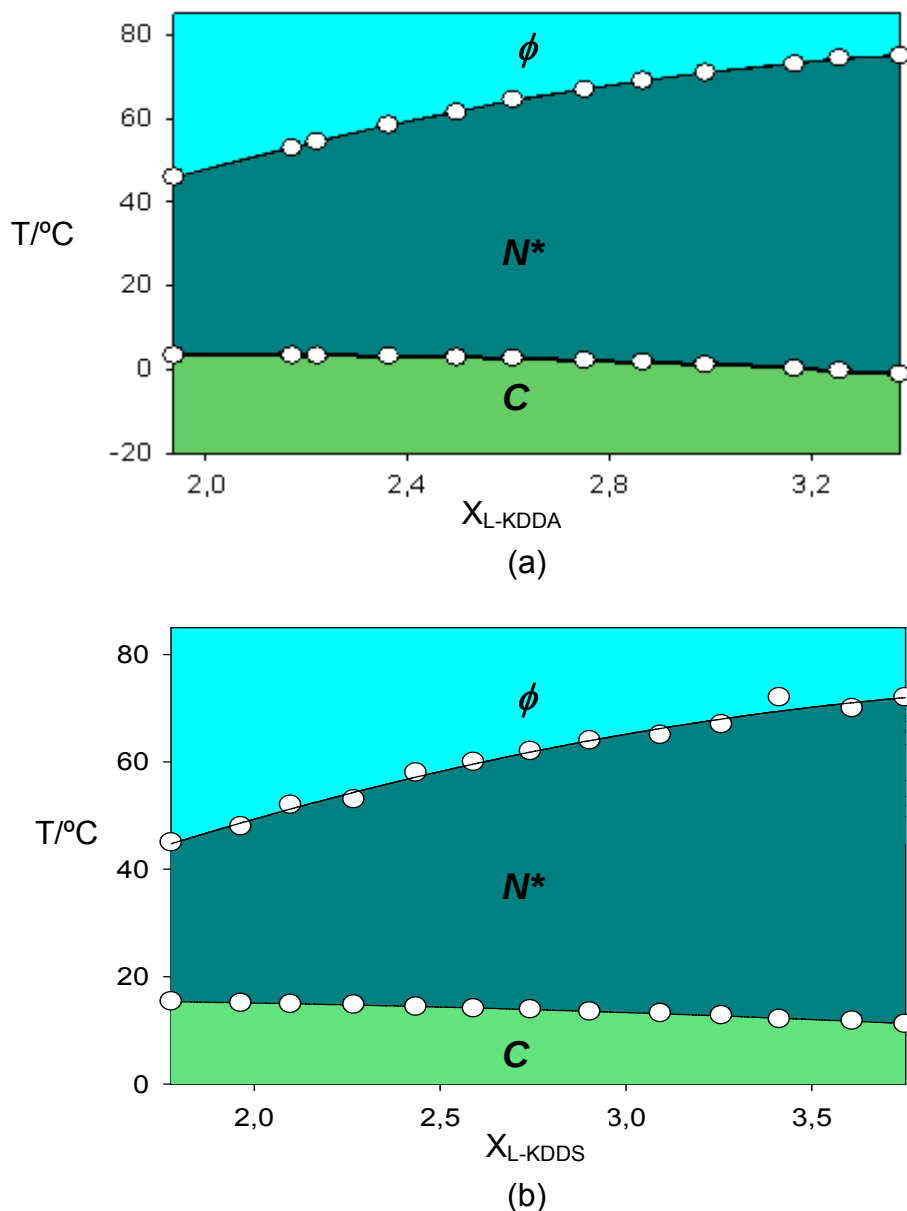


Figure 39. The partial phase diagram of (a) KDDA and (b) KDDS. C, N^* and ϕ represent solid, chiral nematic and turbid phases, respectively.

As seen from the phase diagrams, Figure 39a and b, KDDA and KDDS gave approximately similar phase diagrams, except that their phase transition temperatures were different.

When the chiral nematic phases (racemic nematic phases) in the test tube were heated, they turned into a “turbid” phase at higher temperatures. This phase corresponded to the phase separation appeared under the polarising light microscope as in Figure 40. This means that the phase separation occurred at high temperatures before the N* (and N) phases became isotropic. In general, this phase region is observed above isotropic phase, however, in KDDA and KDDS systems, it was observed above the N* phases. As the phases entered into the turbid phase region, a more concentrated isotropic phase was separated from the water phase as a result of a change of the balance between attractive and repulsive intermicellar forces [41]. This change in the intermicellar forces may originate from a marked decrease of head group hydration with increasing temperature.

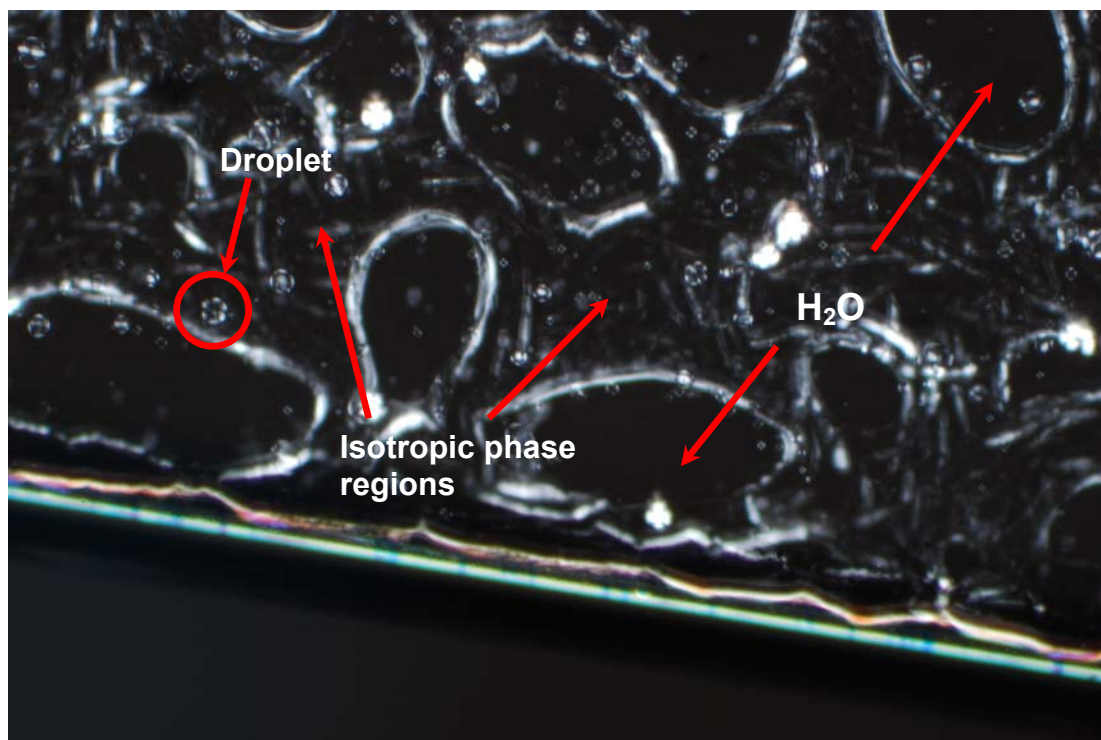


Figure 40. The phase separation of the chiral nematic phases of L-KDDS (%X=2.51). The temperature was ~60-61 °C. The completely dark areas are water phase. The isotropic phase regions include the droplets. The thickness of the microslide was 0.2 mm and the magnification was 25x.

5.3 The pitches of the chiral nematic phases and their temperature dependences

In the section 2.1.1.5, the pitch was defined as the linear distance traveled by the 2π rotation of the director. It is inversely proportional to the concentration of the chiral dopant or amphiphilic molecule, i.e. as the concentration of the chiral amphiphilic molecule is increased, the pitch is shortened or vice versa. In our systems, L-KDDA and L-KDDS, the pitches of the chiral nematic phases were shortened as given in the Figure 41.

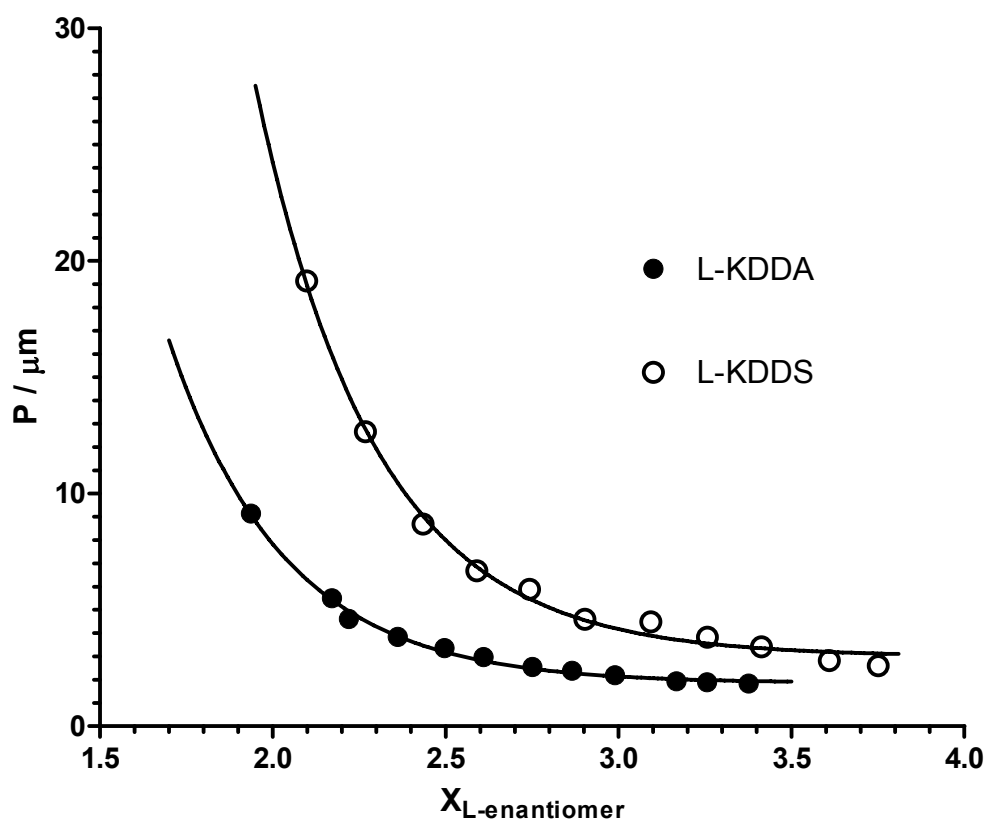


Figure 41. The change in the pitch of the chiral nematic phases of L-KDDA and L-KDDS systems with the concentrations of the L-enantiomers at 25 °C.

When the amount of the chiral amphiphiles in the chiral nematic, N^* , region is increased, the number density of the chiral amphiphiles is increased, which results in the decrease in the pitch. Accordingly, the pitches of the L-KDDA and L-KDDS were shortened by increasing their concentrations in the N^* region. However, at the N^* - L_α transition, the pitch increases to infinity because the micelle sizes become infinite. Furthermore, as seen from Figure 41, the pitches of the L-KDDA chiral nematic phases for all L-enantiomer concentrations are shorter than those of the L-KDDS. This shows that the chiral interaction forces between the micelles in the L-KDDA system are more favored than those in the L-KDDS system. This result may be interpreted by distortion mechanism of chiralized micelles. The chiral molecule causes the rotation of one surface of the micelle to the left or right with respect to the other surface of the micelle, Figure 42 [97]. Hence, an angle, so-called distortion angle ϕ , between two surfaces of the micelle arises from the rotations of the micelle surfaces, which leads to a twisted micelle, Figure 42. In L-KDDA system, this angle is larger than that in L-KDDS system, because the L-KDDS molecules make hydrogen bonds between their hydrophilic parts, which do not allow the rotation of the micelle surfaces efficiently.

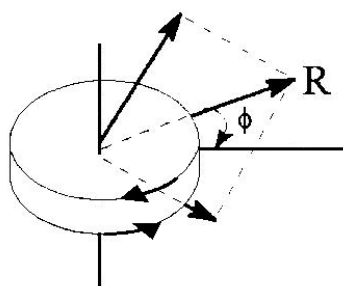


Figure 42. The occurrence of the twisted micelle, resulting through torques caused by the chiral amphiphiles at opposite surfaces.

The effect of the temperature on the pitches of the L-KDDA and L-KDDS was also investigated in this thesis. Although there are some studies related to the investigation of the temperature dependence of the pitch in the literature [20,21,24,29,35,36,97-100], the variation of the pitch with temperature is not understood clearly. According to these studies, the pitch can be lengthened, be shortened or not be changed when the temperature is increased. There are two mechanisms to explain the temperature dependence of the pitch in the thermotropic chiral nematic phases [101]. The first mechanism indicates the change in the intermolecular distance along the helix axis, the second one involves the variation of the average displacement angle, or twist angle, of the director of one chiral molecule with respect to the adjacent chiral molecule [35,36]. When the intermicellar distance increases, the pitch is increased. On the other hand, the increase in the twist angle, which is the rotation angle of one micelle with respect to the adjacent micelle along the helix axis, implies the increase in twist. This means that the first and second mechanisms have opposite effects on the twist. Furthermore, the second mechanism involves the interactions between the adjacent micelles [35].

In order to investigate the effect of the temperature on the pitches of L-KDDA and L-KDDS, we measured the pitch as a function of temperature on different samples having different compositions by laser light diffraction method. The results are summarized in the following section.

5.3.1 The system potassium N-dodecanoyl-L-alaninate

The chiral nematic phases of L-KDDA were prepared for the investigation of temperature dependence of the pitch, P , and twist, P^{-1} , Table 7. Here, we will give only the result of one sample, LA-5, whose pitch values were given in Table 8e, Figure 43. The other temperature dependence of the twist results for L-KDDA having different phase compositions were shown in Table 8.

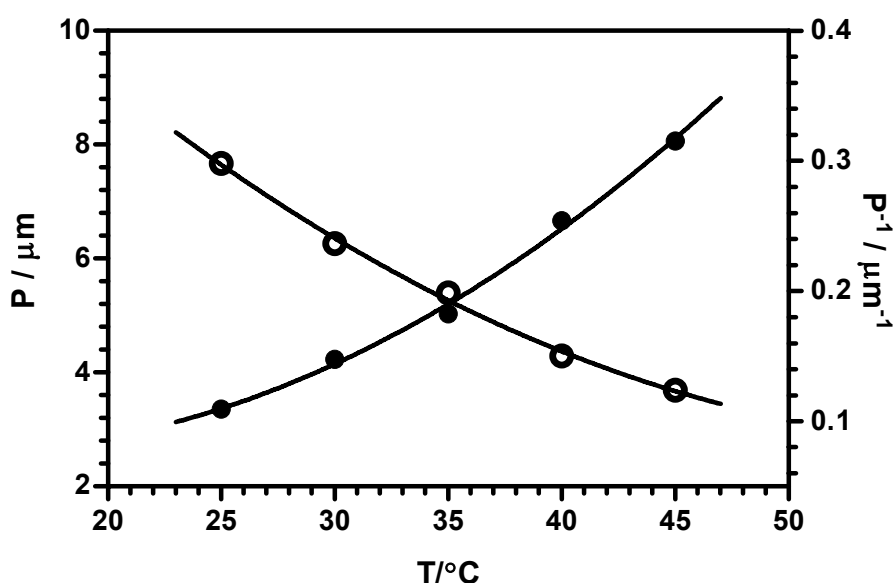


Figure 43. The temperature dependences of P (●) and P^{-1} (○) for the phase LA-5 (%X=2.52).

As seen from the Figure 43, the pitch increased as the temperature was increased, i.e. the twists decreased. For the other phase compositions, similar temperature dependence of the twist was observed. The curves of the graphs of the temperature dependences of both P and P^{-1} obeyed the second order polynomial with regressions ≥ 0.99 :

$$P = a + bT + cT^2 \quad \text{or} \quad P^{-1} = a' + b'T + c'T^2$$

where a , a' , b , b' , c and c' are the constants.

As mentioned in the previous part, 5.3, while the first mechanism is related to the change in the intermicellar distance along the helix axis, d , the second mechanism involves the variation of the average displacement angle or twist angle, θ , of one chiral micelle with respect to the adjacent chiral micelle, Figure 44.

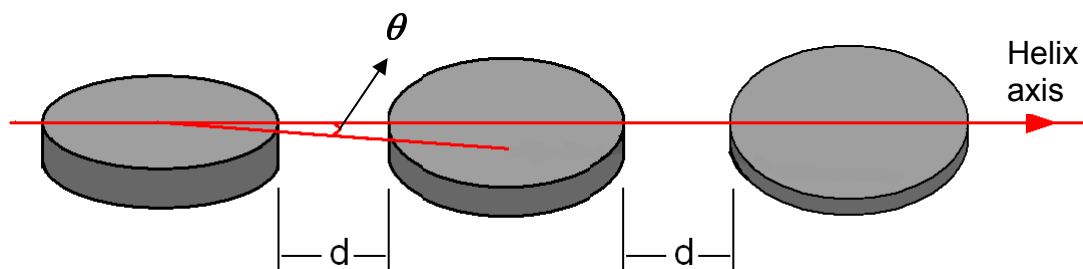


Figure 44. The schematic representation of the intermicellar distance, d , and the twist angle along the helix axis.

As reported in the literature [35], the two mechanisms related to the temperature dependence of the twist are based on the change in the molar volume of the micelles as a result of the thermal motion. When the molar volume increases, the intermicellar distance (first mechanism) or the twist angle (second mechanism) increases [36] or vice versa. If the intermicellar distance increases, the pitch is lengthened, i.e. the twist decreases. On the other hand, if the displacement or twist angle gets larger, the pitch is shortened which leads to the increase in the twist. The SAXS results, which will be discussed in details in the next part, indicate that the volume of one chiral micelle for the chiral nematic phase of L-KDDA, phase LA-5,

decreased from 108 nm^3 to 91 nm^3 in the temperature range of 25 and 45 °C. This corresponds to the decrease of 16% in the molar volume. However, the pitch increased by a factor of 2.40 at this temperature range (from $3.35 \text{ }\mu\text{m}$ to $8.06 \text{ }\mu\text{m}$). If these two parameters, the change in the molar volume and in the pitch with increasing temperature, are compared with each other, the contribution of the change in the molar volume does not correspond to the change in the pitch completely.

On the other hand, Radley reported that the increase in the pitch of the L-KDDA (and L-KDDS) was a consequence of the increase in the intermicellar distance [35], i.e. the first mechanism is dominant on the temperature dependence of the twist for L-KDDA. However, the SAXS results indicate that the intermicellar distances get shorter along the helix axis, i.e. Radley suggestion is not correct. Furthermore, according to the SAXS results, as the intermicellar distance decreased with increasing temperature, the twist angle increased. So, we may conclude that the second mechanism is more dominant than the first mechanism on the temperature dependence of the pitch or twist for L-KDDA system. It should be noted that the decrease in the twist angle, which causes the increase in the pitch, is a result of the reducing of the intermicellar chiral interactions between two adjacent chiral micelles along the helix axis. We think that the intermicellar interaction parameter, k_H , which will be determined from the viscosity measurements of the isotropic micellar solutions, may help us to support whether the second mechanism is dominant in our systems.

5.3.2 The system potassium N-dodecanoyl-L-serinate

The chiral nematic phases of L-KDDS were prepared for the investigation of temperature dependence of the pitch, P , and twist, P^{-1} , Table 9. We will give only the result of one sample here, LS-6, Figure 45. The other temperature dependence of twist results for L-KDDS having different phase compositions were shown in Table 10.

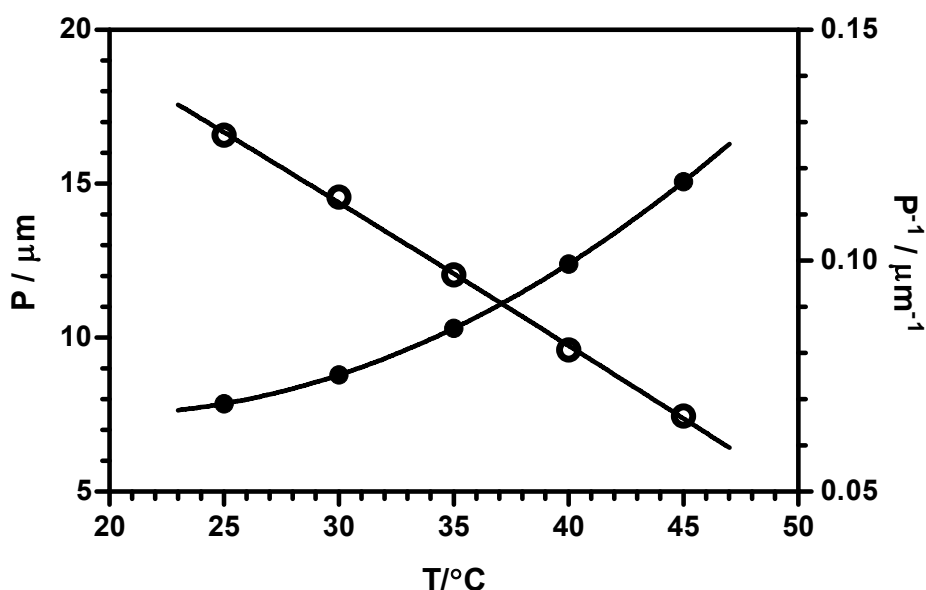


Figure 45. The temperature dependences of P (●) and P^{-1} (○) for the phase LS-6 (%X=2.51).

The temperature dependence of the twist of L-KDDS system exhibited similar behaviour as L-KDDA system. The volume of one chiral micelle of L-KDDA, phase LS-6, decreased from 221 nm³ to 194 nm³ in the temperature range of 25 and 45 °C. This corresponds to the decrease of 12% in the molar volume. However, the pitch increased by a factor of 1.92 at this temperature range (from 7.86 μm to 15.07 μm). This result is similar to the result obtained

from the L-KDDA system. Hence, as we interpreted the temperature dependence of the twist of the L-KDDA system, the change in the twist angle may be dominant effect on the temperature dependence of its twist which will be discussed in the section of the SAXS results.

5.4 The helical twisting powers (htps) of the chiral nematic phases and their temperature dependences

The htp is a measure of the chirality of the chiral dopant or L-enantiomer in the chiral nematic phases. As defined in the section 2.1.1.5, the htp is proportional to the mole fraction of the chiral dopant or amphiphilic enantiomer, x , and the twist, P^{-1} , according to the equation $P^{-1} = (\text{htp}) \cdot x \cdot r$ where r is the enantiomeric purity of the chiral dopant or the amphiphilic enantiomer [59]. The htp is quantitatively determined from the slope of the graph of the twist versus the mole fraction. The determination of the htp is important for the investigation of the chiral nematic phases. For this purpose, the htps of the chiral nematic phases of L-KDDA and L-KDDS were calculated from the slope of the graph of twist, P^{-1} , versus mole fraction of L-enantiomers, Figure 46 and 47. The twist values were given in Table 8 for L-KDDA and in Table 10 for L-KDDS.

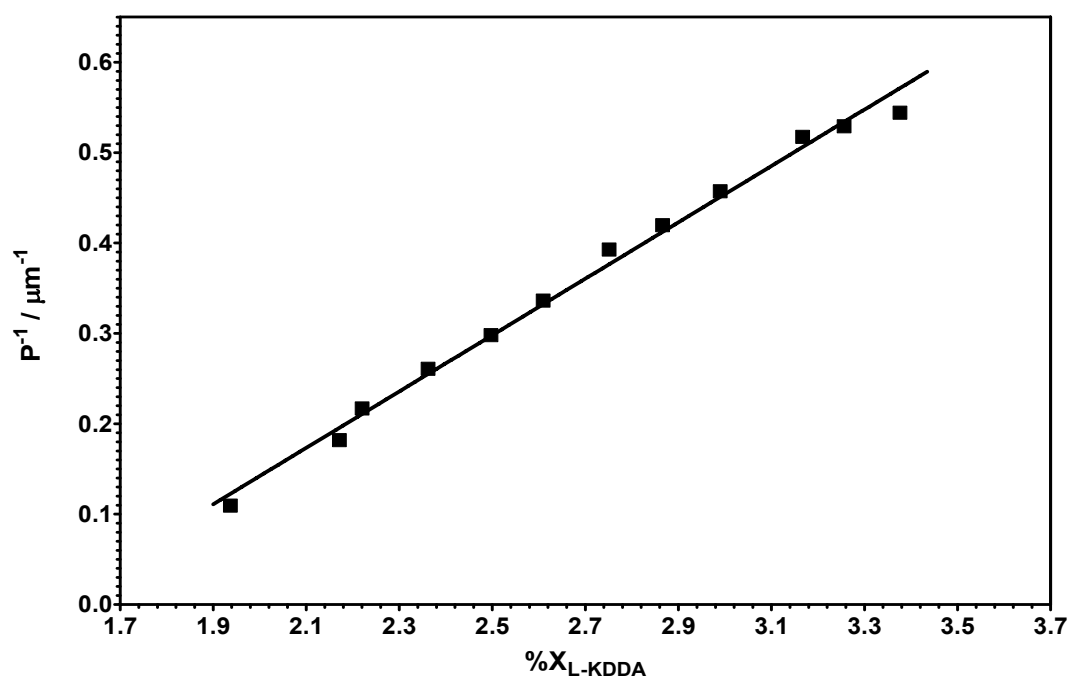


Figure 46. The temperature dependence of the twist for L-KDDA system at 25 °C.

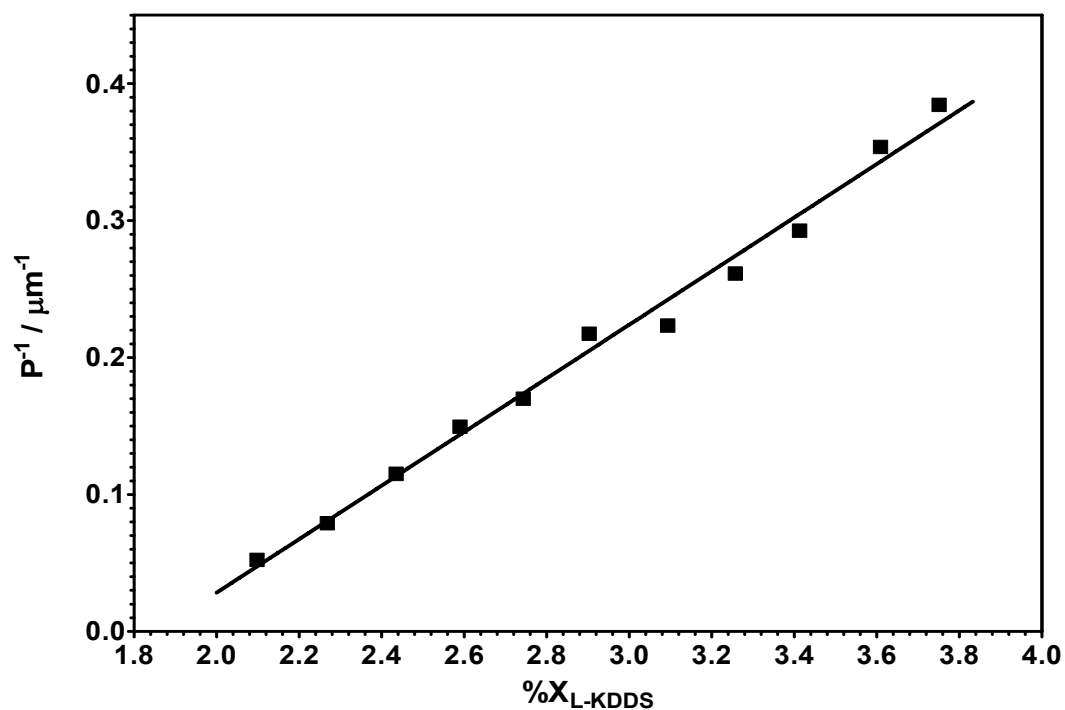


Figure 47. The temperature dependence of the twist for L-KDDS system at 25 °C.

The h_{tp} s of L-KDDA and L-KDDS were also determined at five different temperatures, Table 11.

Table 11. The temperature dependence of the h_{tp} s of L-KDDA and L-KDDS.

T/°C	$h_{tp} / \mu\text{m}^{-1}$	
	L-KDDA	L-KDDS
25.0	31.19	19.57
30.0	26.67	17.12
35.0	22.34	14.65
40.0	17.54	12.92
45.0	14.42	10.85

The temperature dependence of the h_{tp} s of both L-KDDA and L-KDDS were drawn in Figure 48 according to the data in Table 11.

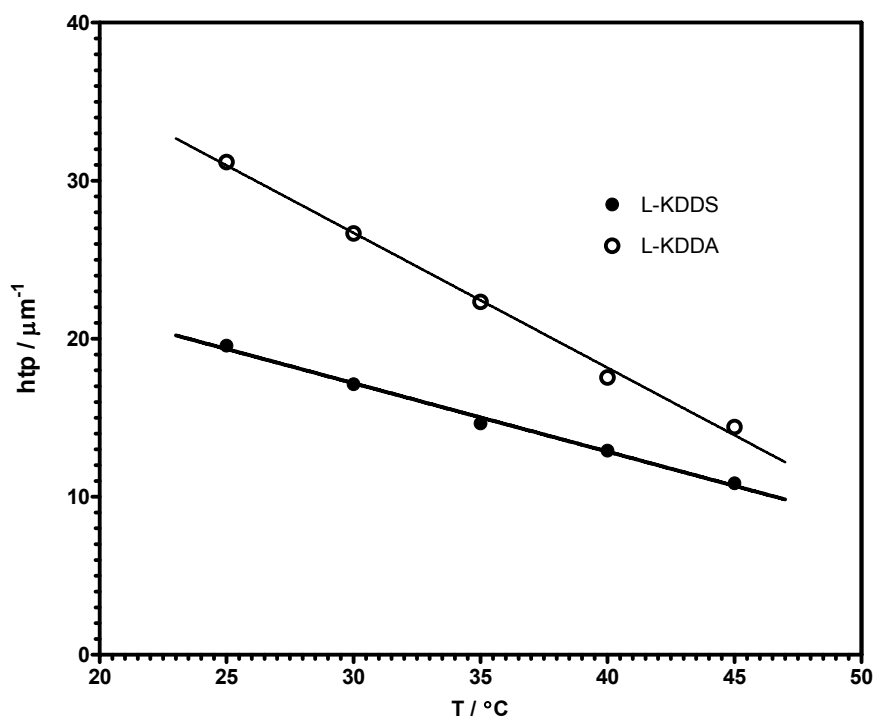


Figure 48. The temperature dependence of the h_{tp} for L-KDDA and L-KDDS.

According to the literature, the h_{tp} is dependent on the size of the head group of an amphiphilic molecule [29] and the temperature [102-105]. Those literatures stated that if an amphiphilic molecule has a bulky head group attached to the hydrophobic alkyl chain, it exhibits smaller h_{tp} and in the second case, it decreases with increasing temperature as a result of the inversion of the sign of the h_{tp} . If we compare the h_{tp} s of L-KDDA with those of L-KDDS systems, the h_{tp} s of L-KDDA are greater than those of L-KDDS at all studied temperatures. This result is different from the literature mentioned above, then the L-KDDS molecule has a comparable head group as L-KDDA, and we did not observe an inversion of the sign of the helices studied in our systems. The decrease in the h_{tp} s of L-KDDA and L-KDDS systems may be attributed to the same consequences similar to the decrease of the pitches of L-KDDA and L-KDDS systems with temperature.

5.5 Mass density measurement of lyotropic nematic and chiral nematic phases

In our previous study [17], we measured mass densities of the lyotropic nematic and chiral nematic phases composed of DL-alaninehydrochloride dodecylester (DL-ADDE) and DL-serinehydrochloride dodecylester (DL-SDDE) and their L-enantiomers, L-ADDE and L-SDDE, respectively. We observed that DL-ADDE had higher mass density values than its L-enantiomer when their phase compositions were kept equal to each other. However, the serine system showed opposite behaviour, i.e. the mass density of L-SDDE was greater than that of DL-SDDE. These results showed that the volumes of chiral micelles were larger than those of their racemic micelles in the alanine systems whereas the volumes of racemic micelles were larger than those of the chiral micelles in the serine systems. These results were interpreted as a result of the different molecular arrangement of each amphiphilic molecules in the racemic and chiral micelles, seperately.

Now, the question is: can the mass density measurements help us to determine the differences in the micelle sizes between the racemic DL-KDDA and chiral L-KDDA, and also between DL-KDDS and L-KDDS? It is anticipated that such measurements would be useful for the planned SAXS measurements, as will be discussed there. To find an answer to this question, the mass densities of lyotropic nematic and chiral nematic phases of KDDA and KDDS systems were measured in two different ways. In the first way, the mass density measurements were applied to the phases as the racemic mixtures were replaced by their L-enantiomers step by step at

constant total amphiphiles concentration. In the second way, however, the mass density of pure DL-mixture and its L-enantiomer were determined keeping their phase compositions to be equal at four different amphiphile concentrations. The results were given in the following parts.

5.5.1 The system potassium N-dodecanoyl-DL and L-alaninate

The phase compositions and mass density results of KDDA system were given in Table 12 as DL-KDDA were replaced by L-KDDA. The mass densities of KDDA on going from the racemic nematic phase to its intrinsically chiral nematic phases were also plotted in Figure 49.

Table 12. The mass density results for KDDA at 25 °C on going from the racemic nematic phase to its intrinsically chiral nematic phases whose phase compositions were given in Table 6a.

DL-KDDA%	L-KDDA%	$\rho_{25^{\circ}\text{C}}/\text{gcm}^{-3}$
100	0	$1.068594 \pm 2.5 \times 10^{-5}$
75.3	24.7	$1.068784 \pm 2.0 \times 10^{-5}$
49.9	50.1	$1.069003 \pm 3.7 \times 10^{-5}$
26.7	73.3	$1.069377 \pm 2.8 \times 10^{-5}$
0	100	$1.069586 \pm 1.6 \times 10^{-5}$

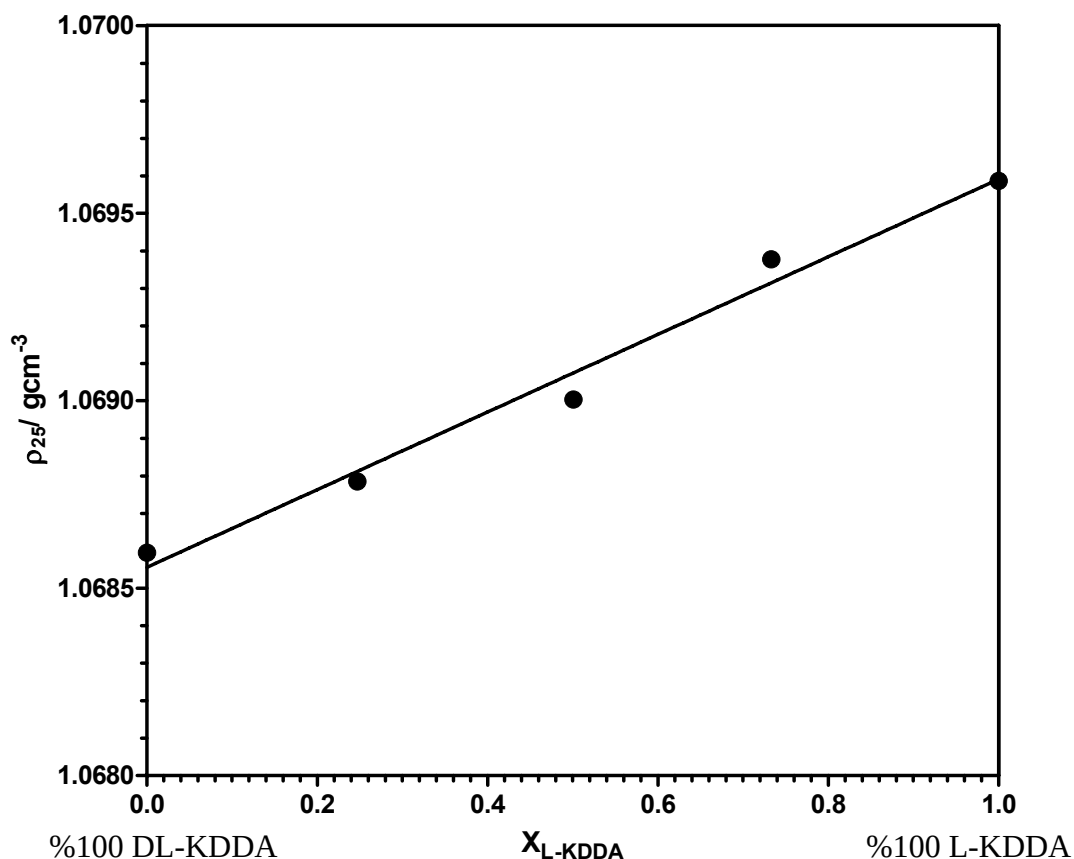
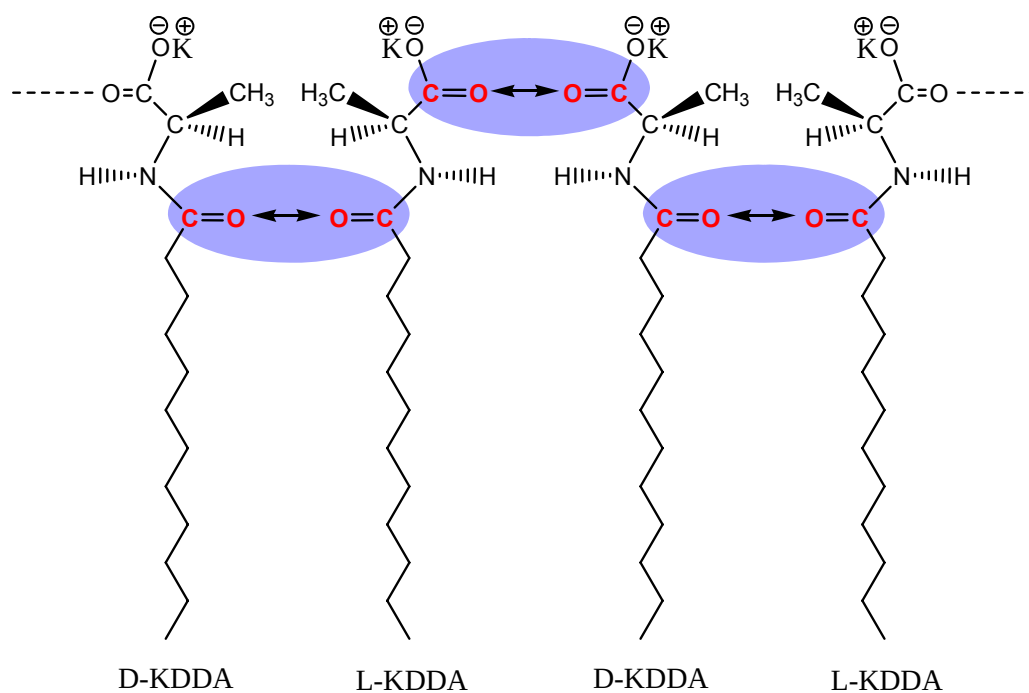
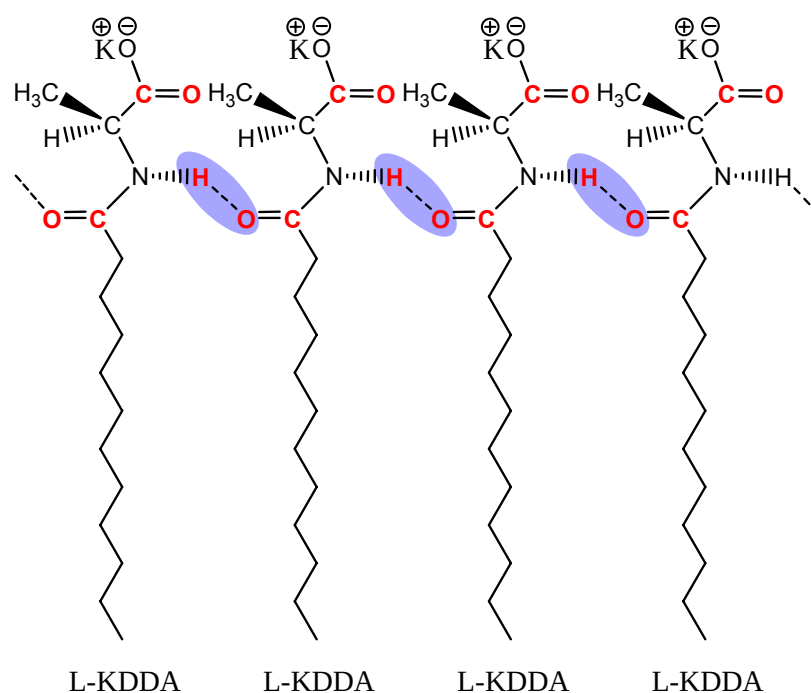


Figure 49. The change in the mass density of KDDA system on going from the racemic nematic phase to the intrinsically chiral nematic phase.

As seen from the Figure 49, the mass density of KDDA system increased as the DL-racemic mixture was replaced by its L-enantiomer. This result indicates that the chiral micelles of the intrinsically chiral nematic phase are smaller than those of the racemic nematic phases. This may be attributed to the difference in the arrangements of the amphiphilic molecules in the racemic and chiral micelles, Figure 50a and b.



(a)



(b)

Figure 50. The molecular arrangement in the micelles of (a) racemic nematic and (b) chiral nematic phases of KDDA, where the volume of the racemic micelles appear to be larger than that of the intrinsically chiral micelles. The arrangements of these molecules were derived from stick models.

In the case of racemic nematic phase, D-enantiomers and L-enantiomers repelled each other because there are repulsion forces between the amidic carbonyl groups and also the carbonyl groups of the carboxylate ion parts of the head groups. However, in the case of intrinsically chiral nematic phase, L-enantiomers make hydrogen bond between –N-H groups and –C=O groups of the amidic parts. Hence, it may be concluded that the L-enantiomers may produce more compact micelles than the DL-racemic mixtures, i.e. the chiral micelles of L-KDDA are smaller than the racemic micelles of DL-KDDA.

The mass density measurements were repeated by using different phase compositions of DL-KDDA and L-KDDA, Table 13. The same results were obtained as the L-enantiomers had greater mass densities than the DL-racemic mixtures where the phase compositions of DL-KDDA and L-KDDA to be equal to each other, Figure 51.

Table 13. The mass density results of the racemic nematic phases and their intrinsically chiral nematic phases for KDDA at 25 °C, keeping the concentrations of DL-mixtures and L-enantiomers to be equal to each other. The phase compositions were given in Table 5a.

Phase code	$\rho_{25^{\circ}\text{C}}/\text{gcm}^{-3}$	Phase code	$\rho_{25^{\circ}\text{C}}/\text{gcm}^{-3}$
DL-1	$1.068594 \pm 2.5 \times 10^{-5}$	DL-3	$1.070989 \pm 1.6 \times 10^{-5}$
L-1	$1.069586 \pm 1.6 \times 10^{-5}$	L-3	$1.071660 \pm 2.3 \times 10^{-5}$
DL-2	$1.070112 \pm 2.0 \times 10^{-5}$	DL-4	$1.072283 \pm 1.8 \times 10^{-5}$
L-2	$1.070928 \pm 1.7 \times 10^{-5}$	L-4	$1.072985 \pm 2.1 \times 10^{-5}$

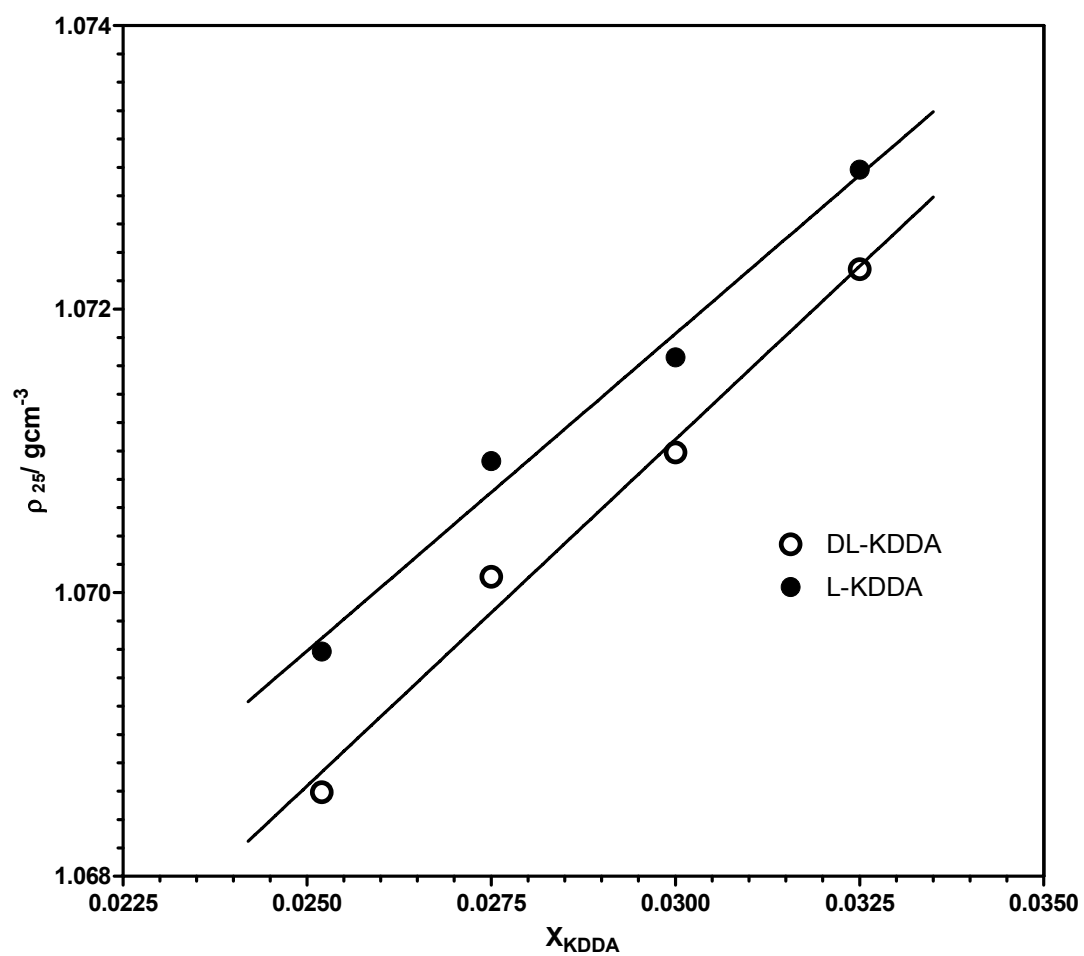


Figure 51. The concentration dependence of the mass densities of DL-KDDA and L-KDDA at 25 °C.

5.5.2 The system potassium N-dodecanoyl-DL and L-serinate

The mole percents and mass density results of DL/L-KDDS system were given in Table 14 as the DL-KDDS mixture was replaced stepwise by its enantiomer, L-KDDS. These results were also represented in Figure 52.

Table 14. The mass density results on going from the racemic nematic phase to its intrinsically chiral nematic phases for KDDS at 25 °C. The phase compositions were given in Table 6b.

DL-KDDS%	L-KDDS%	$\rho_{25^{\circ}\text{C}}/\text{gcm}^{-3}$
100	0	$1.083121 \pm 1.3 \times 10^{-5}$
74.9	25.1	$1.083244 \pm 1.8 \times 10^{-5}$
49.9	50.1	$1.083462 \pm 2.7 \times 10^{-5}$
25.0	75.0	$1.083689 \pm 2.8 \times 10^{-5}$
0	100	$1.083973 \pm 2.2 \times 10^{-5}$

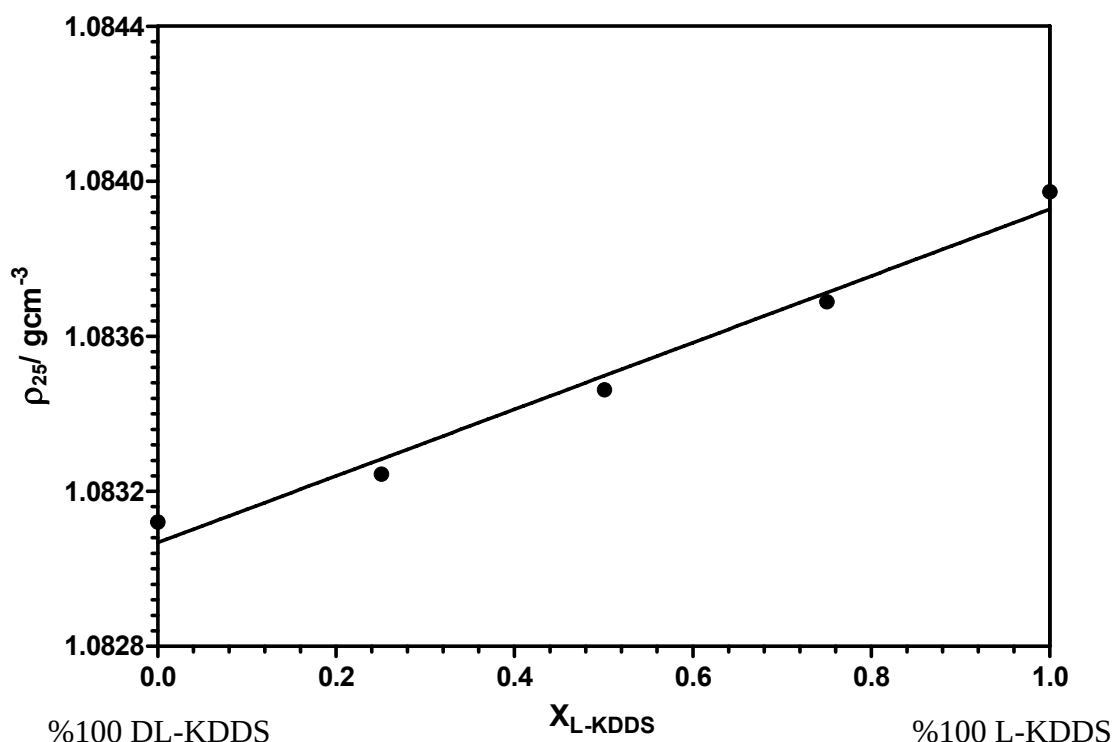
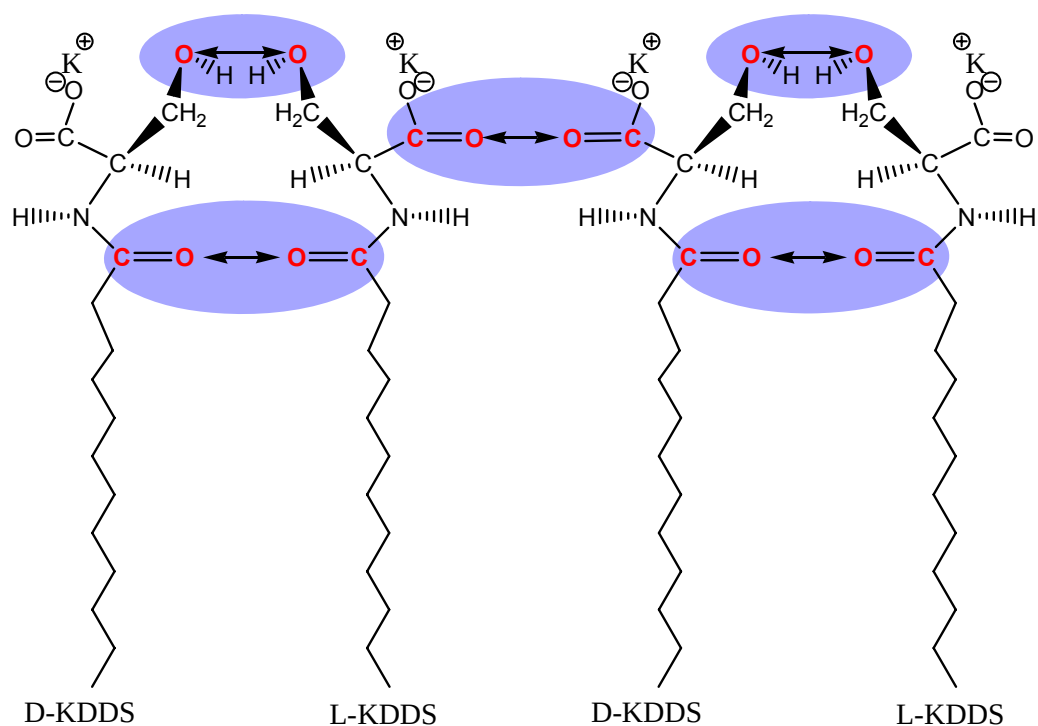


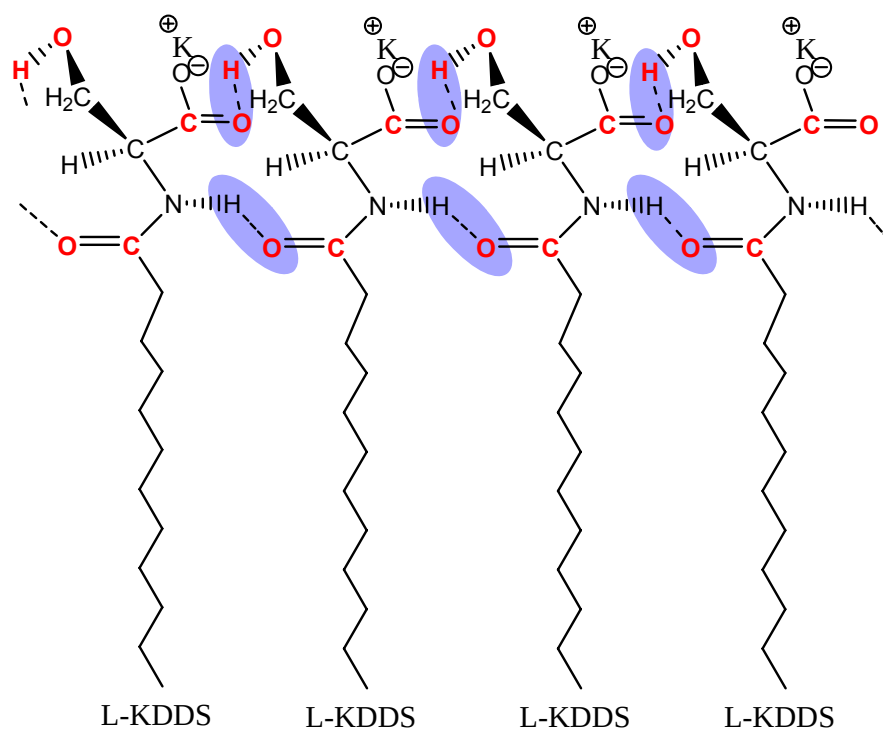
Figure 52. The change in the mass density of KDDS system on going from the racemic nematic phase to the intrinsically chiral nematic phase at 25 °C.

The mass density results of KDDS system is similar to those of KDDA, except that the density difference ($\sim 8.52 \times 10^{-4} \text{ g/cm}^3$) between L-enantiomer and DL-racemic mixture of KDDS was slightly smaller than that of KDDA ($\sim 9.92 \times 10^{-4} \text{ g/cm}^3$).

As was discussed in the section of the mass density results of KDDA system, the mass density difference between DL-KDDS and L-KDDS may be explained by the different molecular arrangement of the amphiphilic molecules in the micelles, Figure 53.



(a)



(b)

Figure 53. The molecular arrangement in the micelles of (a) racemic nematic and (b) chiral nematic phases of KDDS. The arrangements of the molecules were drawn according to stick models.

In the case of racemic nematic phase, D-enantiomers and L-enantiomers appear to repel each other because there are repulsion forces between the amidic carbonyl groups, the –OH groups and also the carbonyl groups of the carboxylate ion parts of the head groups. However, in the case of intrinsically chiral nematic phase, L-enantiomers make hydrogen bonds between –N-H groups and –C=O groups of the amidic parts, and between –OH groups and the carbonyl groups of the carboxylate ion parts. Hence, it may be expected that the L-enantiomers may produce more compact micelles than the DL-racemic mixtures, i.e. the chiral micelles of L-KDDS are smaller than the racemic micelles of DL-KDDS.

If the alanine and serine systems are compared with each other, it may be expected that the density difference between the DL-KDDS and L-KDDS should have been greater than that of DL-KDDA and L-KDDA as a result of the increased repulsion forces between the head groups in DL-KDDS. However, our systems have n-decanol which exists between the amphiphilic molecules, and this may screen out some part of repulsions between the head groups. Hence, the head groups of DL-KDDS may not repel each other effectively.

The mass density measurements were repeated by using different phase compositions of DL-KDDS and L-KDDS, Table 15. Similar results were obtained as the KDDA system, Figure 54.

Table 15. The mass density results of the racemic nematic phases and its intrinsically chiral nematic phases for KDDS at 25 °C, keeping the concentrations of DL-mixtures and L-enantiomers to be equal to each other. The phase compositions were given in Table 5b.

Phase code	$\rho_{25^{\circ}\text{C}}/\text{gcm}^{-3}$	Phase code	$\rho_{25^{\circ}\text{C}}/\text{gcm}^{-3}$
DL-1	$1.083121 \pm 1.3 \times 10^{-5}$	DL-3	$1.087256 \pm 1.0 \times 10^{-5}$
L-1	$1.083973 \pm 2.2 \times 10^{-5}$	L-3	$1.087623 \pm 1.2 \times 10^{-5}$
DL-2	$1.084639 \pm 1.8 \times 10^{-5}$	DL-4	$1.089276 \pm 1.7 \times 10^{-5}$
L-2	$1.085561 \pm 1.7 \times 10^{-5}$	L-4	$1.089987 \pm 2.3 \times 10^{-5}$

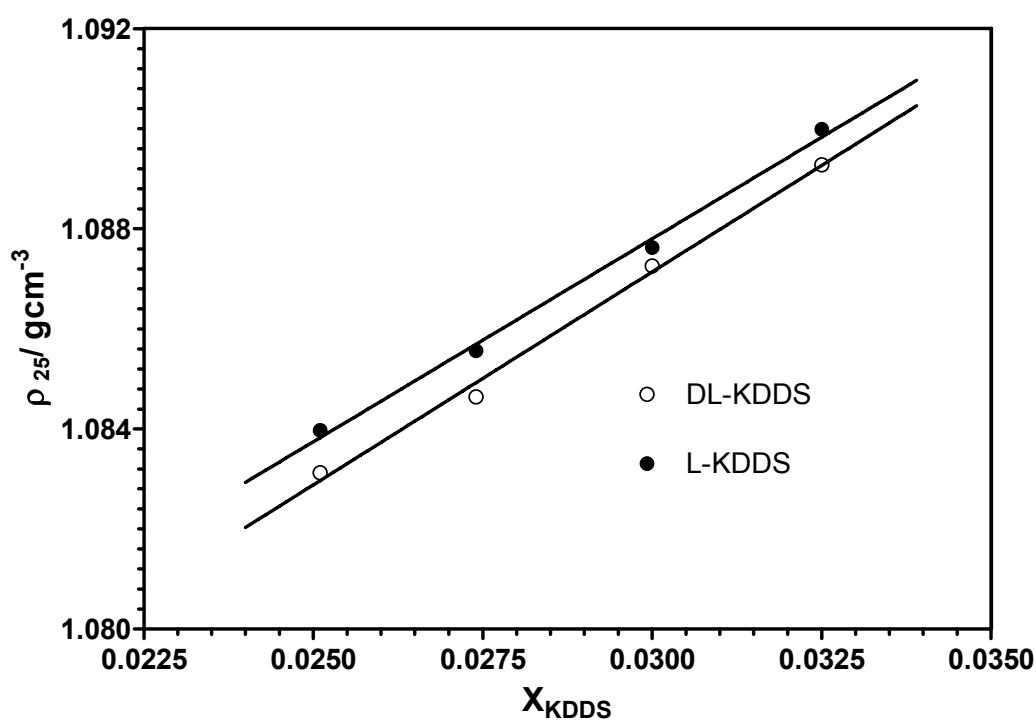


Figure 54. The change of the mass densities of DL-KDDS and L-KDDS at 25 °C, as their concentrations were increased.

5.6 Determination of micelle sizes of the racemic nematic and chiral nematic phases from small-angle x-ray scattering measurements

In order to determine the micelle sizes of the racemic nematic and chiral nematic phases, small-angle x-ray scattering measurements were performed on the racemic nematic and chiral nematic phases of KDDA and KDDS systems. The racemic nematic phases gave ellipsoid like diffraction patterns because their director aligned perpendicular to the incident x-ray beam. In this configuration, the Bragg's values, both $d_{\perp}$ and $d_{\parallel}$, were evaluated. However, the helix axes of the chiral nematic phases without the magnetic field aligned parallel to the x-ray beam, that is why, circular like diffraction patterns were obtained. Hence, the chiral nematic phases were oriented in the magnetic field, where helix axes were also perpendicular to the incident x-ray beam, in order to determine both $d_{\perp}$ and $d_{\parallel}$.

As we will discuss in the next subparts, the diffraction patterns obtained from the nematic and chiral nematic phases should be ellipsoid like in shape in order to evaluate the $d_{\perp}$ and $d_{\parallel}$ values. Otherwise, an average of the both values are obtained, hence the micelle dimensions cannot be determined. The reason of the observation of the circular like diffraction, caused from the non-aligned chiral nematic phases, was interpreted as a consequence of the isotropic distribution of the helix axis in the cylindrical capillary [63,73,106].

5.6.1 The racemic and chiral nematic phases of potassium N-dodecanoyl-DL-alaninate and L-alaninate

Lyotropic racemic nematic phases of DL-KDDA, when placed in flat microslide, aligned spontaneously by wall effect. The same phenomenon occurred in the cylindrical capillary so that a schlieren texture of DL-KDDA was obtained that relaxed into a pseudo-isotropic texture, Figure 55.

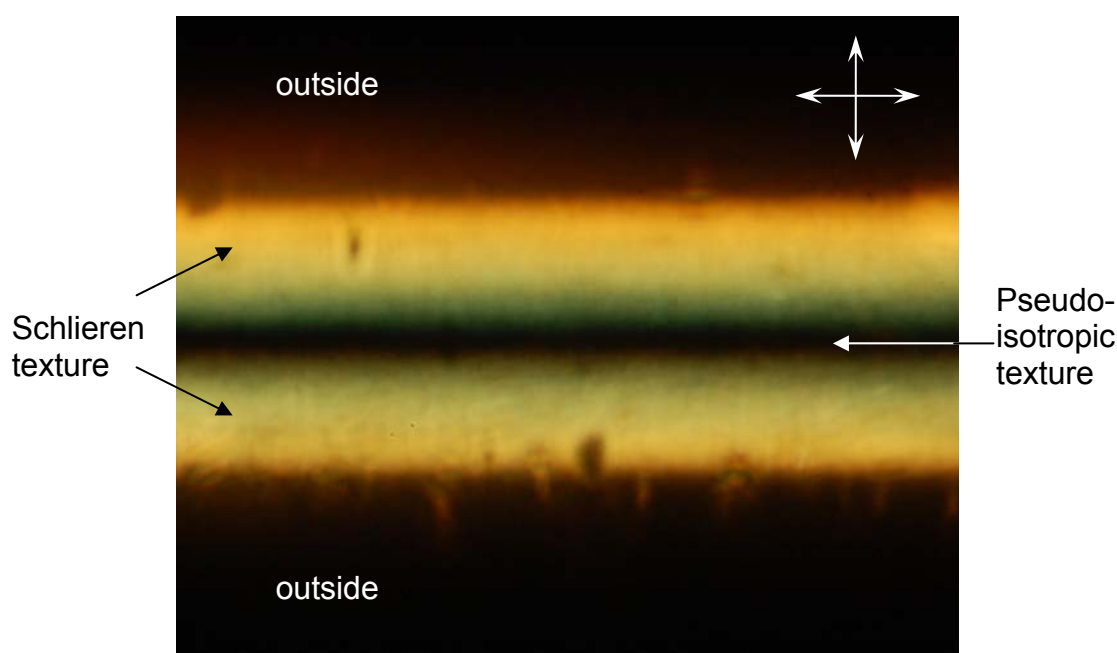


Figure 55. Observation of the schlieren texture at the edges of the capillary and the pseudo-isotropic texture at the center along the long axis of the capillary of the racemic N_D - phase of DL-KDDA. The microphotographs were taken at room temperature ($\sim 25^\circ\text{C}$). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.

In the case of N_D - phases of DL-KDDA whose phase compositions were given in Table 5a, the x-ray beam was perpendicular to the directors of the phases that gave ellipsoid like x-ray diffraction patterns with intense arcs at the long axis of the ellipsoids, Figure 56.

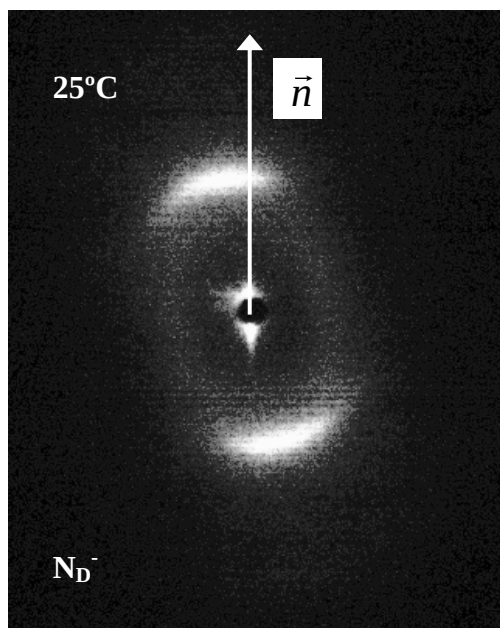


Figure 56. SAXS diffraction pattern of the racemic N_D^- phase of DL-KDDA (%X=2.52) system in a cylindrical capillary of 0.7 mm in diameter at 25 °C. The shadow in the center is the beam-stop. The arrow shows the direction of the phase director ($\vec{n}$).

When the scattering intensity of the N_D^- phases, along and perpendicular to the $\vec{n}$, is plotted versus the scattering angle 2θ , two maxima were obtained, respectively, Figure 57.

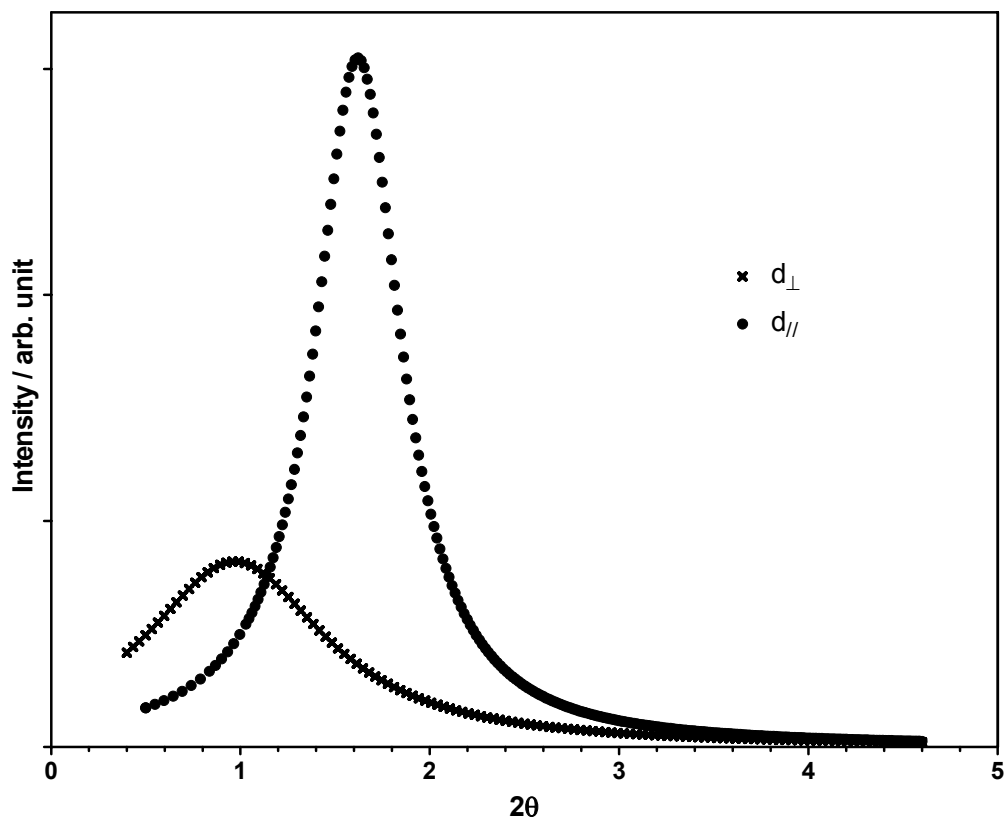


Figure 57. The intensity versus 2θ for the racemic N_D - phases of DL-KDDA ($\%X=2.52$) at 25 °C. $//$ and $\perp$ represent the scattering intensities obtained from the periodicity along and perpendicular to the phase director, $\vec{n}$, respectively. The curves were fitted to Lorentzian function and were found to be in good agreements with it.

The chiral nematic phase of L-KDDA gave fingerprint textures consisting of dark and bright lines (cholesteric stripes) and its helix axis aligned spontaneously perpendicular to the long capillary axis, Figure 58.

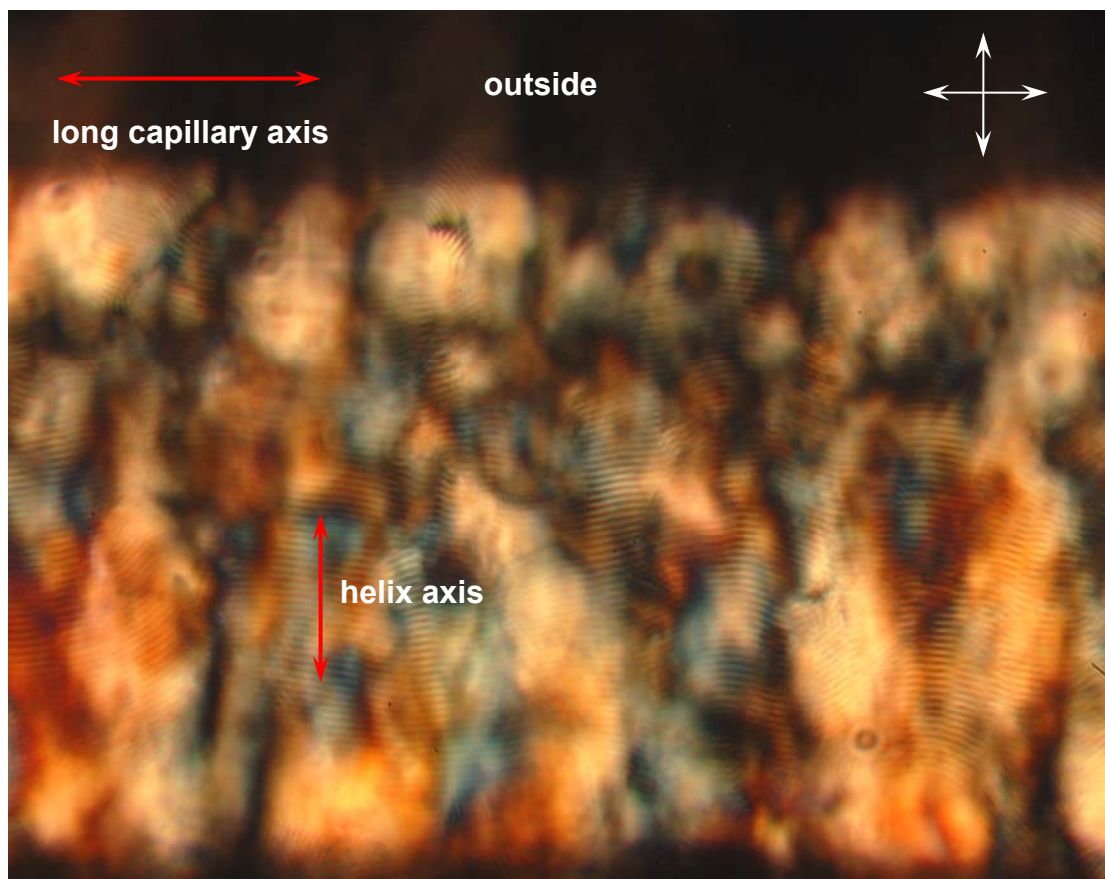


Figure 58. The fingerprint texture of the N_D^+ of L-KDDA (%X=2.52) in the cylindrical capillary. The microphotographs were taken at room temperature ($\sim 25^\circ\text{C}$). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.

The cholesteric stripes in Figure 58 except at some dislocation were aligned along the long axis of the cylindrical capillary with a certain tilt angle. This result indicates that the helix axis is perpendicular to the long axis of the capillary, but it is distributed isotropically about it, Figure 59.

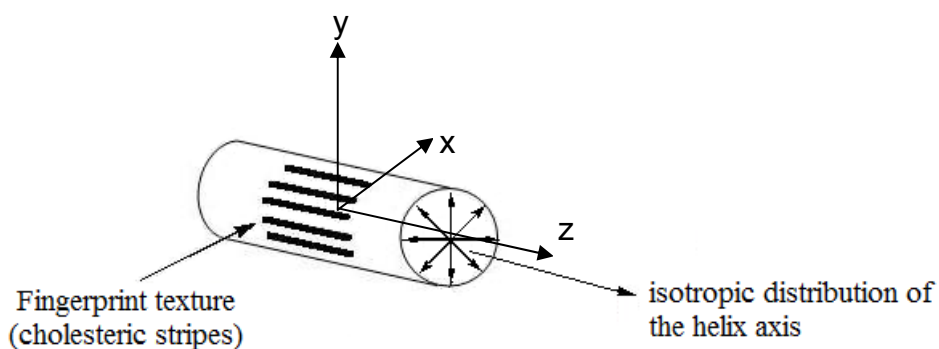


Figure 59. Schematic representations of the orientation of the cholesteric stripes and the helix axis in the intrinsically N_D^+ phase of L-KDDA in a cylindrical capillary.

When the same x-ray experiment was repeated with this intrinsically N_D^+ phase of L-KDDA, using the same mole fraction as its racemic mixture in Table 5a, without putting them in a magnetic field, a ring as a diffraction pattern was obtained with intense arcs along the z-axis at 25 °C, Figure 60.

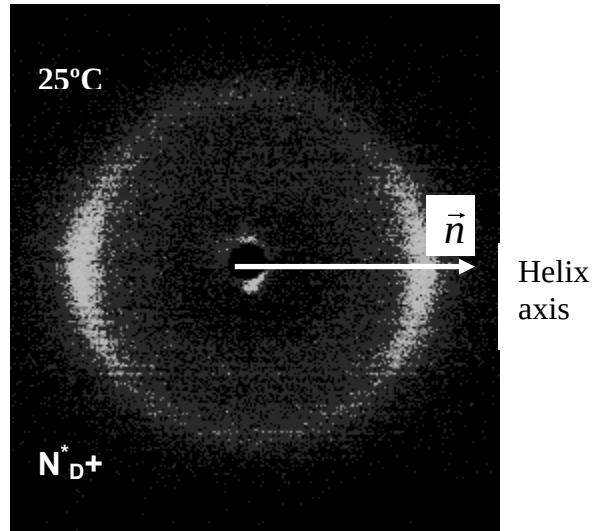


Figure 60. SAXS diffraction patterns of the intrinsically N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter without applying a magnetic field at 25 °C. The shadow in the center is the beam-stop.

When x-ray beam is sent to the non-aligned N_D^+ phase, it is scattered from the rims and the centers of the micelles at the same time, Figure 61, i.e. statistically it appears from Figure 61 that the x-ray beam strikes the micelles mainly at the rims. Consequently, the intense arcs along the z-axis may be a result of the diffraction of the x-rays arising from the edges of the micelles. This indicates that the helix axis in Figure 61 is oriented parallel and perpendicular to the x-ray beam from which the circular diffraction arises [63].

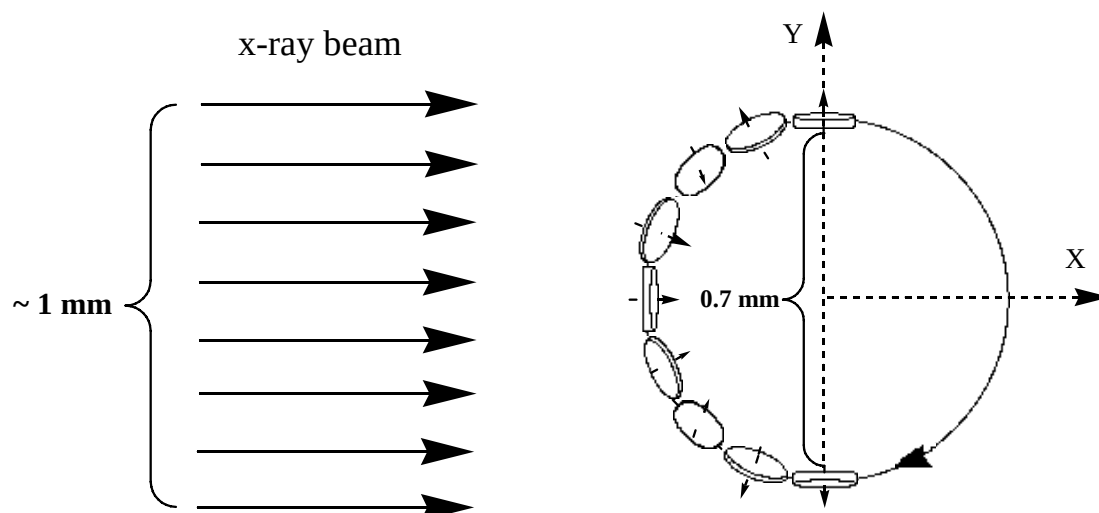


Figure 61. The diffraction of the x-ray beam from the rims and centers of the micelles. The z-axis is perpendicular to the plane of the page. The intense arcs along the z-axis, Figure 60, may correspond to the diffraction from the rims of the micelles.

When the scattering intensity of the non-aligned N_D^+ phases, along and perpendicular to the $\vec{n}$, is plotted versus the scattering angle 2θ , two maxima, which are approximately equal to each other, were obtained, respectively, Figure 62.

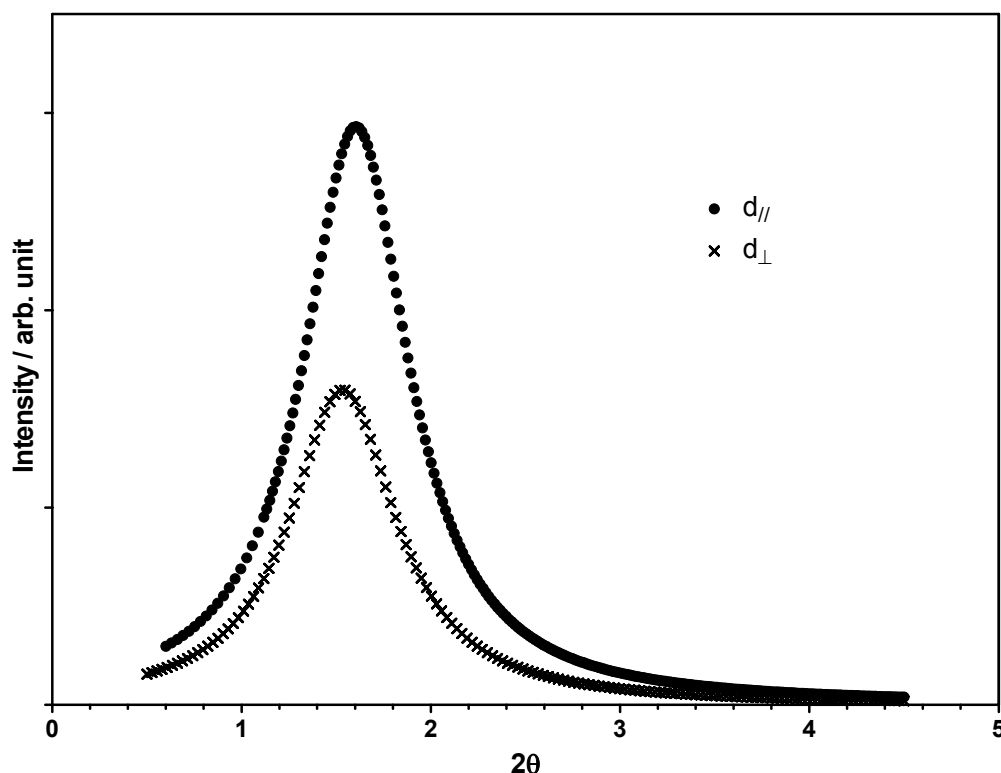


Figure 62. The intensity versus 2θ for the intrinsically non-aligned N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter without applying a magnetic field at 25 °C. The curves were fitted to Lorentzian function.

After the chiral nematic phase shown in Figure 58 was kept into a magnetic field of 1.1 T during 10-12 days, the helix axis was aligned parallel to the long capillary axis, Figure 63. In this configuration, the x-ray is perpendicular to the helix axis of the chiral nematic phase, Figure 64, which leads to the ellipsoid-like SAXS pattern as its racemic nematic phase, Figure 65.

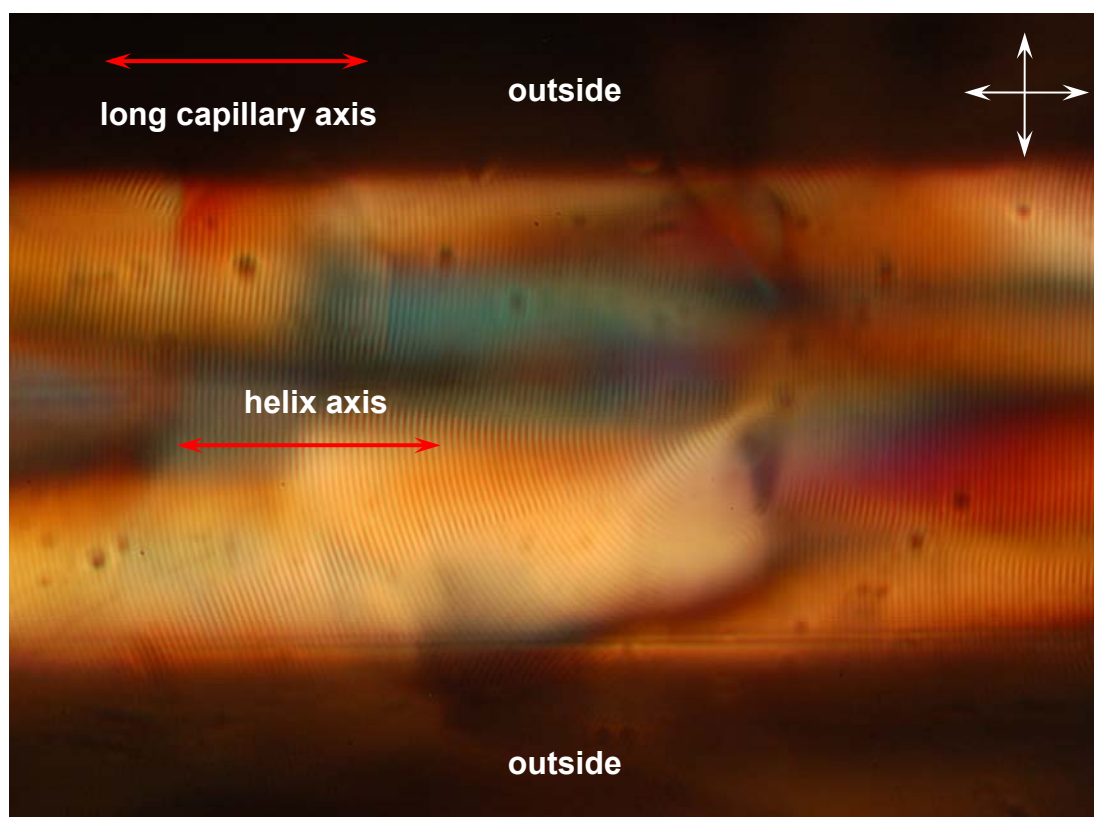


Figure 63. The fingerprint texture of the N_D^+ phase of L-KDDA (%X=2.52) in the cylindrical capillary obtained when the magnetic field direction was parallel to the long axis of the capillary. The microphotographs were taken at room temperature ($\sim 25^\circ\text{C}$). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.

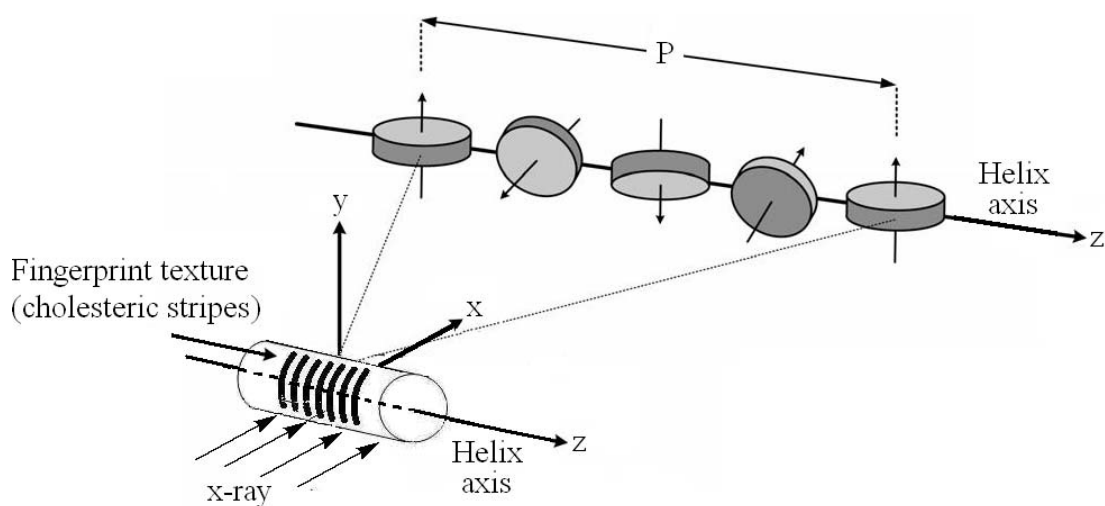


Figure 64. Schematic representation of the possible orientation of the helix axis of an N_D^+ phase when x-ray is perpendicular to the helix axis.

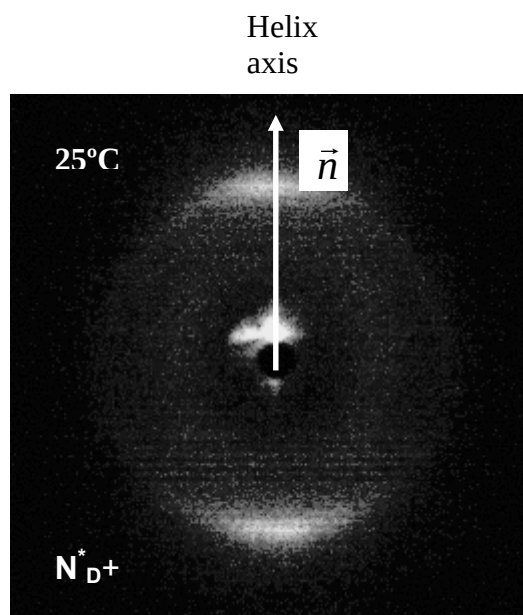


Figure 65. SAXS diffraction pattern of the intrinsically N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter with a magnetic field of 1.1 T at 25 °C. The shadow in the center is the beam-stop.

When the scattering intensity of the N_D^+ phase of L-KDDA, along and perpendicular to the $\vec{n}$, is plotted versus the scattering angle 2θ , two maxima were obtained, respectively, Figure 66.

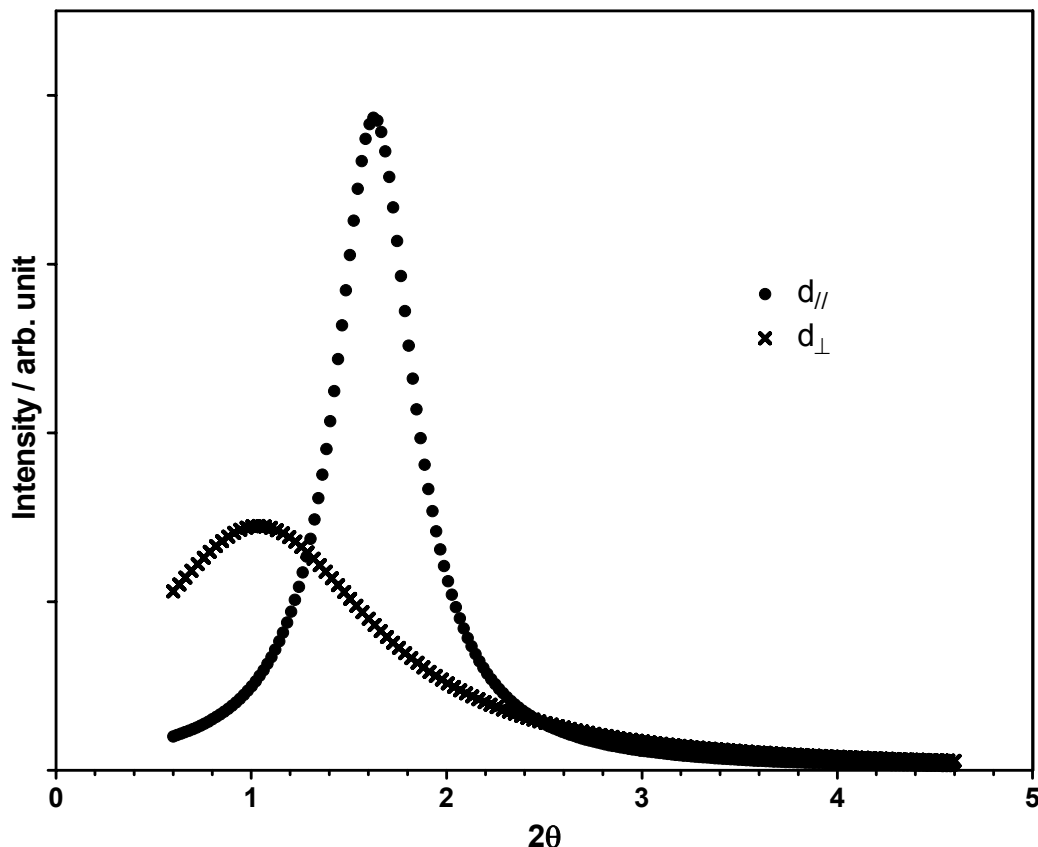
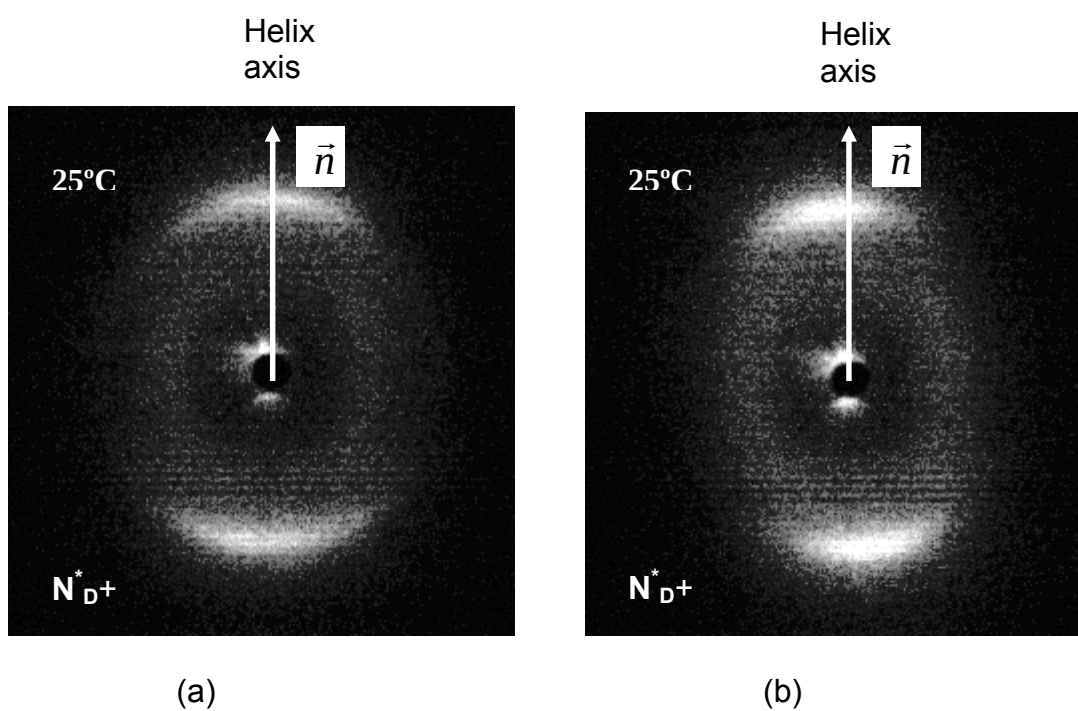
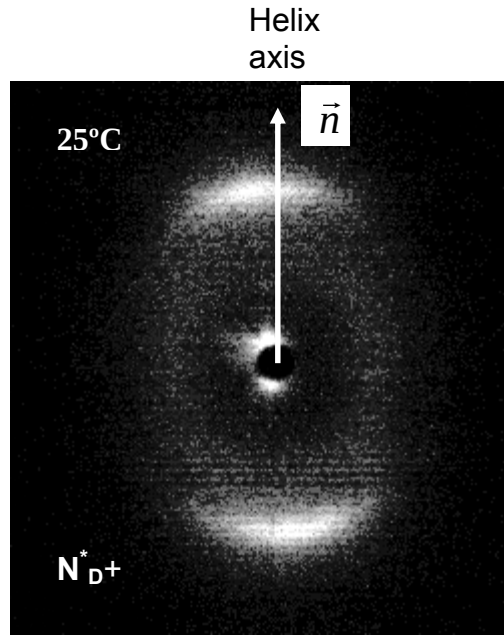


Figure 66. The intensity versus 2θ for the intrinsically N_D^+ phase of L-KDDA ($X\%=2.52$) system in a cylindrical capillary of 0.7 mm in diameter with a magnetic field of 1.1 T at 25 °C. The curves were fitted to Lorentzian function.

According to the goal of this thesis, we were interested in the question how the micelle dimensions change when the racemic N_D^- phase is transformed into N_D^+ phase by gradually replacing DL-amphiphile by its L-enantiomer. In order to understand the effect of chirality of the L-enantiomer on the micellar size clearly, the SAXS measurements were done with phases where DL-KDDA was replaced by L-KDDA step by step. The induced N_D^+

phases and intrinsic N_{D+}^* phase were aligned with the magnetic field before the SAXS measurements were carried out in order to obtain the helix axes perpendicular to the x-ray beam. The SAXS patterns of the N_D - phase of DL-KDDA and the intrinsically N_{D+}^* phase of L-KDDA phase were given in Figures 55 and 64, respectively. For other DL/L-KDDA mixtures, the SAXS patterns of the induced chiral nematic phases which were aligned in the magnetic field of 1.1 T during 10-12 days are given in Figure 67.





(c)

Figure 67. The SAXS patterns of the DL/L-KDDA mixtures: (a) 75.3% DL-KDDA; 24.7% L-KDDA, (b) 49.9% DL-KDDA; 50.1% L-KDDA and (c) 26.7% DL-KDDA; 73.3% L-KDDA.

The scattering intensities obtained from the SAXS measurements for the induced N_D^+ phase of L-KDDA, along and perpendicular to the $\vec{n}$, were plotted versus the scattering angle 2θ , as described before. Since the scattering pattern is made up of the interferences between the aggregates (micelles) in the solution, the mean distances between the centers of the micelles can be determined from the maxima of the curves by using Bragg's equation, $d = \frac{\lambda}{2\sin\theta}$, where λ and θ are the wavelength of the x-ray and scattering angle, respectively. The calculated mean distances along the direction parallel ($d_{//}$, thickness) and perpendicular ($d_{\perp}$, diameter) to the phase director of the micelles ($\vec{n}$) [4,15] are given in Table 16 for the N_D -

phase of DL-KDDA, the induced N_D^+ phases of the mixtures of DL/L-KDDA and the intrinsically chiral nematic phase N_D^+ of L-KDDA at 25°C and are drawn in Figure 68.

Table 16. The Bragg's values of KDDA system on going from racemic mixture to intrinsically chiral nematic phase at 25 °C. The phase compositions were given in Table 6a.

DL-KDDA%	L-KDDA%	$d_{\perp}/\text{\AA}$	$d_{\parallel}/\text{\AA}$
100	0	97	54
75.3	24.7	93	54
49.9	50.1	90	54
26.7	73.3	89	54
0	100	86	54

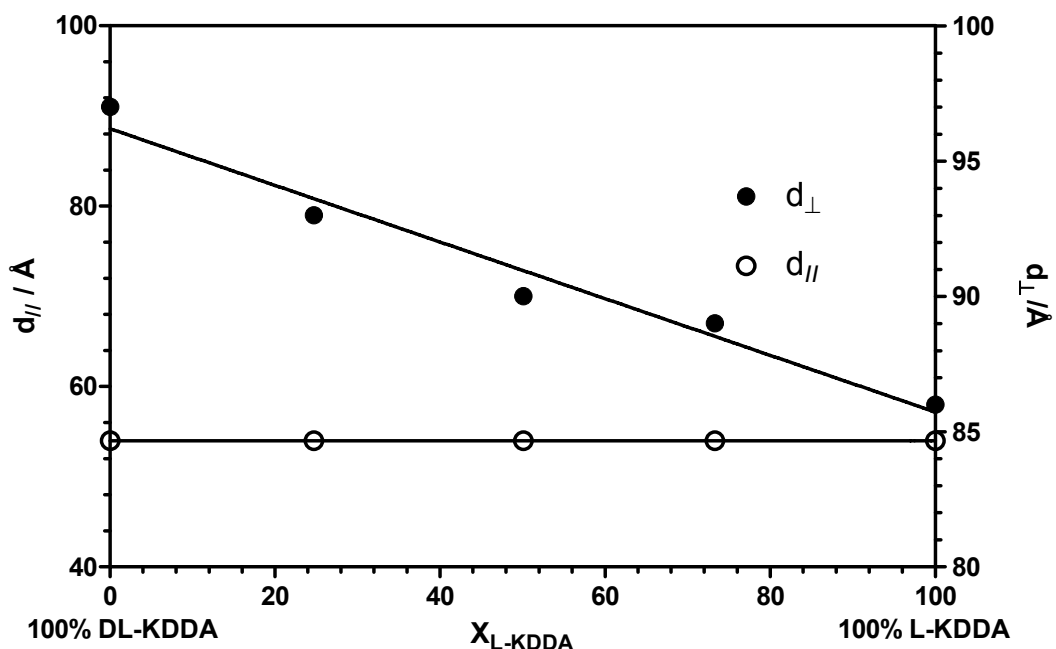


Figure 68. The Bragg's values of KDDA system on going from pure DL-KDDA to pure L-KDDA.

As the $d_{\perp}$ values decreased by increasing the concentration of L-KDDA in the mixtures, the $d_{\parallel}$ remained unchanged, $54 \pm 0.5 \text{ \AA}$, respectively.

The SAXS measurement was repeated on other DL-KDDA and L-KDDA whose compositions were equal to each other, Table 17 and Figure 69.

Table 17. The Bragg's values for different compositions of DL-KDDA and L-KDDA.

$X_{\text{DL-KDDA}}$	DL-KDDA		$X_{\text{L-KDDA}}$	L-KDDA	
	$d_{\perp}/\text{\AA}$	$d_{\parallel}/\text{\AA}$		$d_{\perp}/\text{\AA}$	$d_{\parallel}/\text{\AA}$
0.0252	97	54	0.0252	86	54
0.0275	86	52	0.0275	76	52
0.0300	72	51	0.0300	63	51
0.0325	66	49	0.0325	56	50

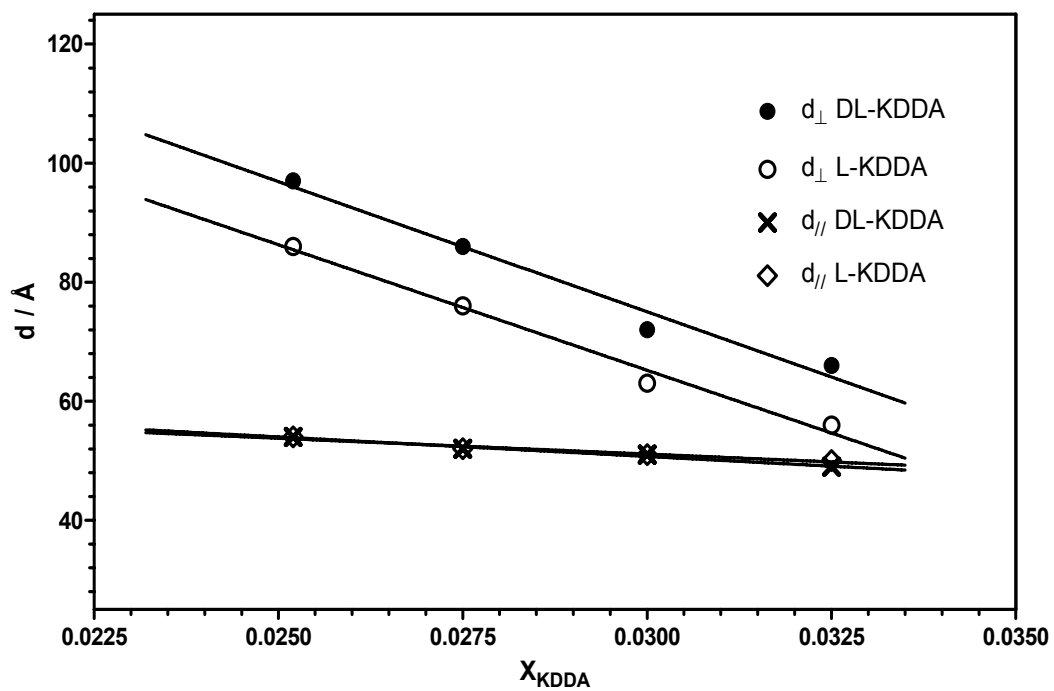


Figure 69. The concentration dependence of the Bragg's values for KDDA systems at 25 °C.

Micelle dimensions

We examined the Bragg's values and as reported in the forgoing pages, the Bragg's values, $d_{\perp}$ and $d_{\parallel}$, obtained from the x-ray diffraction patterns include water surrounding the micelle, Figure 70.

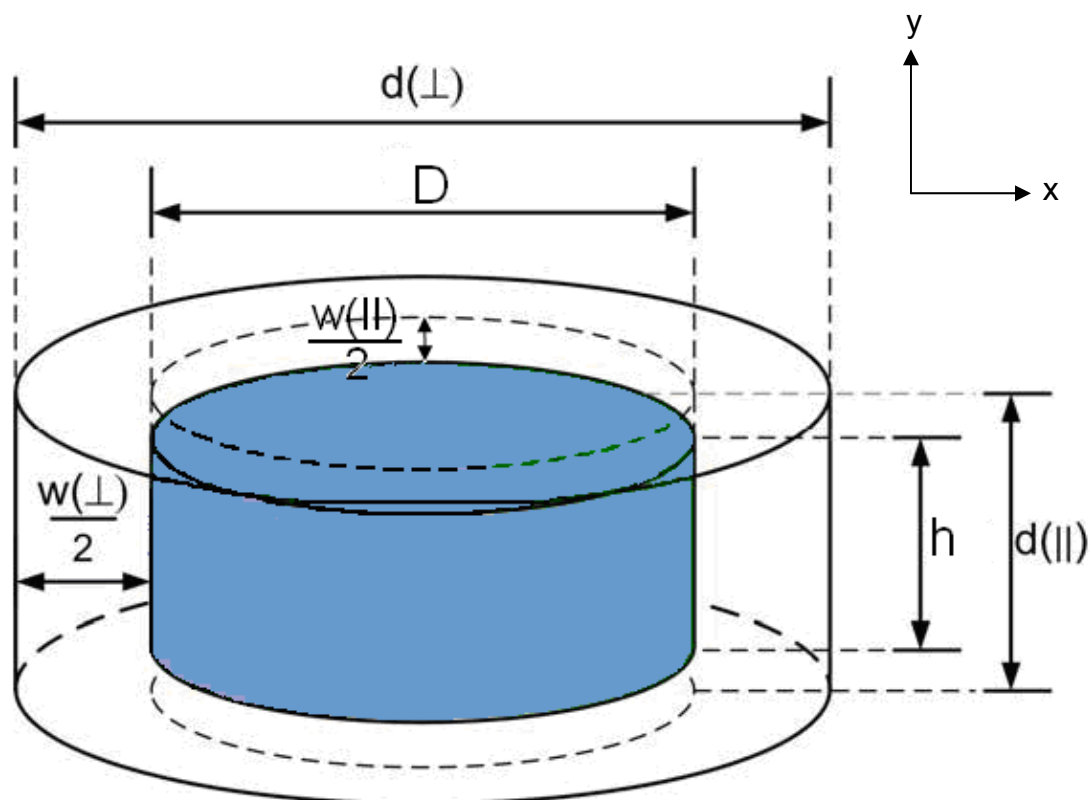


Figure 70. The schematic representation of the “naked” disc-like micelle (blue one) and surrounding water (vacancy). Here h and D represent the thickness and the diameter of the naked micelle, respectively.

In Figure 70, $d_{\perp}$ and $d_{\parallel}$ are the Bragg's values arising from the periodicities along the micelle diameter, D , and thickness, h , respectively. If we consider, the micelles are arranged in the direction y and x , $W(\perp)$ and $W(\parallel)$ represent the water layers between two adjacent micelles in the direction of the diameter and thickness, respectively. The value of the $W(\perp)$

can be calculated by subtracting the diameter, D , from the $d_{\perp}$, then multiplying by 2. The value of the $W(II)$ is calculated by the same way using h and $d_{//}$.

In order to determine the volume of one aggregate (naked micelle), V_m , first we calculated the periodic volume, V_p , available to one aggregate in the solution using the equation below [4,15]

$$V_p = \frac{\pi}{4} d_{\perp}^2 d_{//} \quad (17)$$

For the calculation of the “naked” volume of one aggregate, the following relations were used:

$$V_m = \frac{\pi}{4} d_{\perp}^2 d_{//} (1 - \phi_w) \quad (18)$$

$$V_m = \frac{\pi}{4} D^2 h \quad (19)$$

where $(1 - \phi_w)$ is equal to the volume fraction of the micelles, ϕ_{mic} . ϕ_w is the volume fraction of water in the phase. The volume fractions of the micelles was determined by using the following equation [107],

$$\phi_{mic} = \frac{W_s / \rho_s + W_{DeOH} / \rho_{DeOH}}{W_s / \rho_s + W_{DeOH} / \rho_{DeOH} + W_w / \rho_w} \quad (20)$$

where the letters s and w represent surfactant or amphiphilic molecule and water including salt Na_2SO_4 , respectively. W and ρ are the weight fractions and densities of each components in the liquid crystal samples, respectively. The density of the micelles can be evaluated by the equation 21,

$$\frac{1}{\rho} = \frac{W_s}{\rho_s} + \frac{W_{DeOH}}{\rho_{DeOH}} + \frac{W_w}{\rho_w} \quad (21)$$

where d is the density of the liquid crystalline sample [108].

In equation 19, both h and D are unknown and in order to calculate one of them an assumption is made. Our assumption was to take h of the micelle equal to the thickness of the bilayer, $\approx 31 \text{ \AA}$ (maximum length of the hydrocarbon chain, $l_{\max}=1.265n_c + 1.54$, in $\text{\AA}$) [109]. Accordingly, the parameters for disc-like micelles are determined using the equations above and the results are presented in Table 18 and 19.

Table 18. The parameters obtained from the SAXS measurements for KDDA on going from DL-KDDA to L-KDDA.

Phase code	V_p/nm^3	ϕ_{mic}	$V_{\text{mic}}/\text{nm}^3$	$D/\text{\AA}$	$W_{\perp}/2/\text{\AA}$	$W_{\parallel}/2/\text{\AA}$
100% DL	399	0.3452	138	75	10.9	12.0
24.7% L	367	0.3449	127	72	10.5	12.0
50.1% L	344	0.3449	119	70	10.1	12.0
73.3% L	336	0.3445	116	69	10.0	12.0
100% L	314	0.3446	108	67	9.7	12.0

Table 19. The parameters obtained from the SAXS measurements for DL-KDDA and L-KDDA, for different concentrations.

Phase code	X_a	V_p/nm^3	ϕ_{mic}	$V_{\text{mic}}/\text{nm}^3$	$D/\text{\AA}$	$W_{\perp}/2/\text{\AA}$	$W_{\parallel}/2/\text{\AA}$
DL-KDDA	0.0252	399	0.3452	138	75	10.9	12.0
L-KDDA	0.0252	314	0.3446	108	67	9.7	12.0
DL-KDDA	0.0275	302	0.3602	109	67	9.6	11.0
L-KDDA	0.0275	236	0.3598	85	59	8.5	11.0
DL-KDDA	0.0300	208	0.3784	79	57	7.6	10.5
L-KDDA	0.0300	159	0.3781	60	50	6.7	10.5
DL-KDDA	0.0325	168	0.3924	66	52	7.0	9.5
L-KDDA	0.0325	123	0.3921	48	45	5.7	10.0

As seen from Table 18 and 19, V_p , V_m , and D values decrease with increasing L-enantiomer concentration, and it is very interesting to observe that all these values for the L-enantiomer are remarkably smaller than those for the racemic mixture. However, according to our assumption, we cannot evaluate the real change in the thickness of the disc-like micelles because we assumed that the thickness of the micelles is equal to the thickness of the bilayer. Hence, the reason why the sizes of the chiral micelles are smaller than those of the racemic micelles may be explained on the basis of chiral interactions which lead to more compact micelles than the racemic micelles. However, this explanation is only valid when the average aggregation numbers of micelles remain unchanged.

In order to check whether the average aggregation number, N_{agg} , remains unchanged, we calculated N_{agg} according to the literature [110] taking into account n-decanol, which is also a constituent of the phases,

$$V_{mic} = N_{agg} v_a + \frac{N_{agg}}{n_a/n_{DeOH}} v_{DeOH} \quad (22)$$

where v_a and v_{DeOH} are the volumes of single amphiphilic molecule and n-decanol, respectively. n_a and n_{DeOH} are the number of moles of amphiphiles and n-decanol in the liquid crystalline samples, respectively. In the equation

22, the term $\frac{N_{agg}}{n_a/n_{DeOH}}$ represents the number of n-decanol molecule per

amphiphile molecule. The molar volume of DL-KDDA and L-KDDA molecules were determined from the density measurements of their isotropic micellar solutions below their critical micelle concentrations at 25 °C as 271.4 cm³/mol and 272.5 cm³/mol, respectively. Their v_a values are calculated dividing these molar volumes by Avagadro's number. The calculated v_a values of DL-KDDA

and L-KDDA are $450.7 \text{ \AA}^3$ and $452.5 \text{ \AA}^3$, respectively. The volume of a single n-decanol was calculated from its density and molar mass (0.826317 g/cm^3 and 158.28 g/mol , respectively) to be $318.1 \text{ \AA}^3$. The average aggregation numbers are given in Table 20 and 21 and are drawn in Figures 71 and 72.

Table 20. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , on going from DL-KDDA to the intrinsically L-KDDA where the mole fraction of the total amphiphile ($X_{\text{DL-KDDA+L-KDDA}}$) was 0.0252. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} was calculated as 2.19 according to the phase compositions in Table 6a.

Phase code	$V_{\text{mic}}/\text{nm}^3$	N_{agg}
100% DL	138	231
24.7% L	127	213
50.1% L	119	199
73.3% L	116	194
100% L	108	181

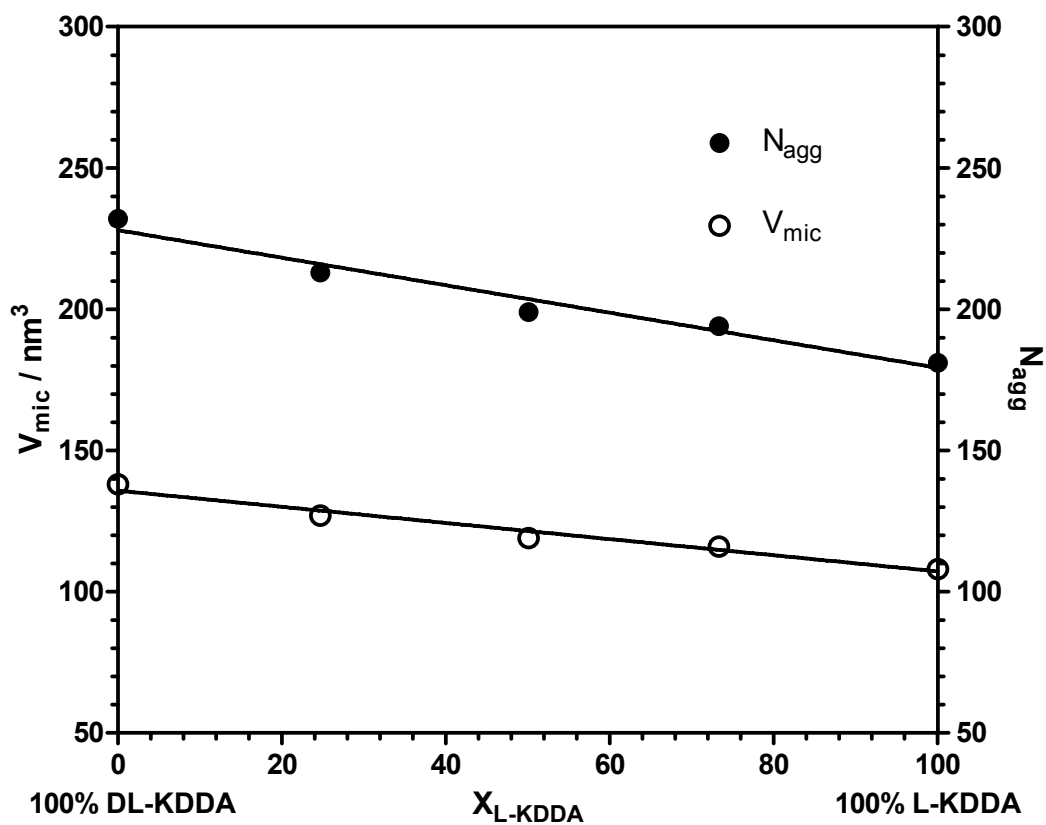


Figure 71. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of L-KDDA in the mixtures of DL/L-KDDA according to the data in Table 20.

Table 21. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , for DL-KDDA and L-KDDA phases where the mole fraction of DL-KDDA and L-KDDA were equal to each other. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} were calculated as 2.19, 2.41, 2.64 and 2.87 for the mole fractions of 0.0252, 0.0275, 0.0300 and 0.0325, respectively, according to the phase compositions in Table 5a.

Phase code	X_a	V_{mic}/nm^3	N_{agg}
DL-KDDA	0.0252	138	231
L-KDDA	0.0252	108	181
DL-KDDA	0.0275	109	187
L-KDDA	0.0275	85	145
DL-KDDA	0.0300	79	138
L-KDDA	0.0300	60	105
DL-KDDA	0.0325	66	117
L-KDDA	0.0325	48	86

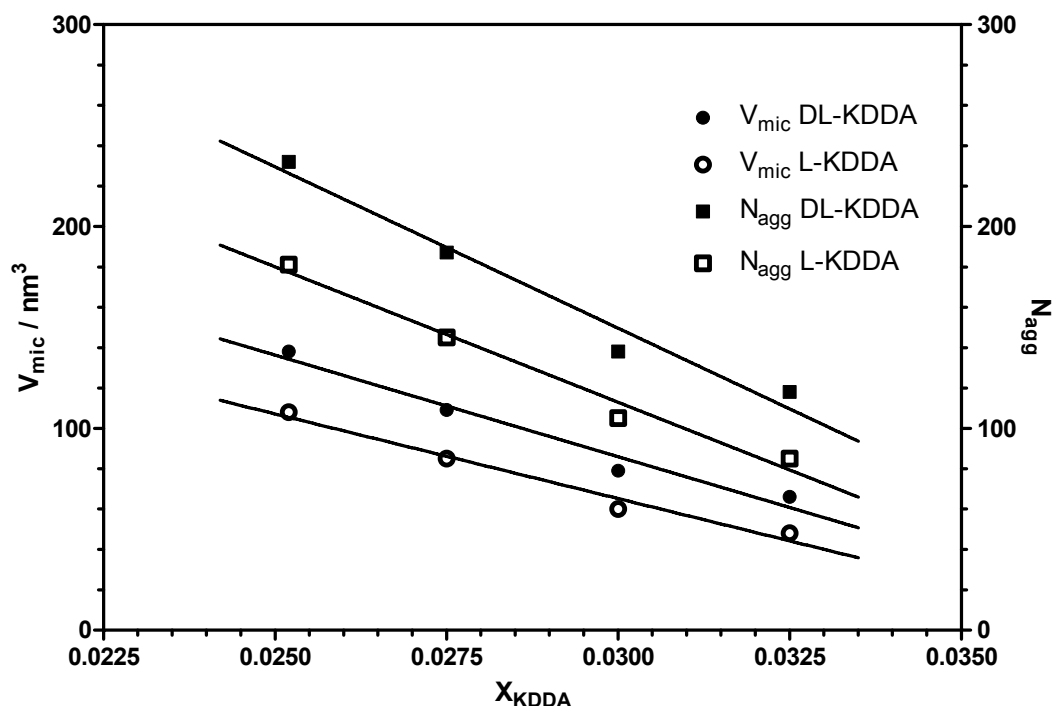


Figure 72. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of KDDA for DL-KDDA racemic nematic phases and L-KDDA chiral nematic phases according to the data in Table 21.

Gelbart et.al showed that if the repulsion forces are dominant between the micelles, these interactions enhance the micelle growth as the amphiphile concentration is increased [111], i.e. the average aggregation number increases. However, Holmes and Reynolds reported the decrease in the average aggregation number at high amphiphile concentration [112]. They explained this unexpected situation as the intermicellar interactions between charged micelles can be attractive which is mediated by the free-counterions.

Consequently, if we get back to the interpretation of why the micelle sizes of chiral micelles in L-KDDA are smaller than those in DL-KDDA, it can be said that the chiral interactions between the chiral amphiphiles within the micelle are stronger than those between the amphiphilic molecules in the

racemic micelles. In other words, as the concentration of the chiral amphiphile is increased in the intrinsically chiral nematic phases, the chiral attraction forces between chiral amphiphiles appear to get stronger that give rise to smaller micelles than the racemic nematic phases.

On the other hand, as seen from Table 18 and 19, the water layer in the periodicity of the diameter of the micelle, $W(\perp)$, decreased as the amphiphile concentration was increased, i.e. the distance between micelles became shorter. This result may be an evidence for the intermicellar attractions.

5.6.2 The racemic and chiral nematic phases of potassium N-dodecanoyl-DL-serinate and L-serinate

Lyotropic racemic nematic phases of DL-KDDS showed same behaviour as the racemic nematic phases of DL-KDDA, i.e. when they are placed in flat microslide and in the cylindrical capillary, they align spontaneously by wall effect. The following figure shows a pseudo-isotropic texture of DL-KDDS in the cylindrical capillary, Figure 73.

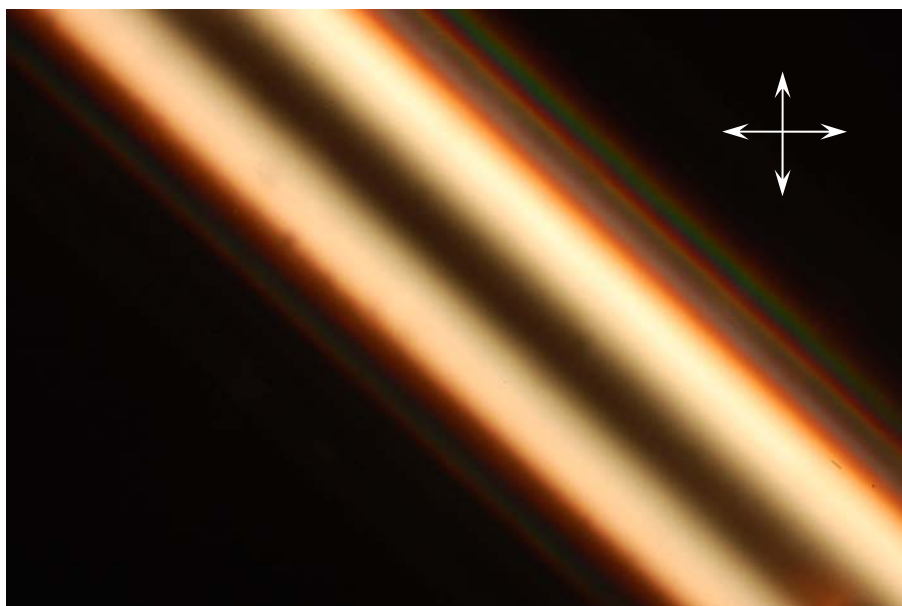


Figure 73. Observation of the schlieren texture at the edges of the capillary and the pseudo-isotropic texture at the center along the long axis of the capillary of the racemic N_D - phase of DL-KDDS. The microphotographs were taken at room temperature ($\sim 25^\circ\text{C}$). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.

The racemic N_D - phase of DL-KDDS in the cylindrical capillary whose texture was shown in Figure 73 gave an ellipsoid like diffraction same as DL-KDDA, Figure 74.

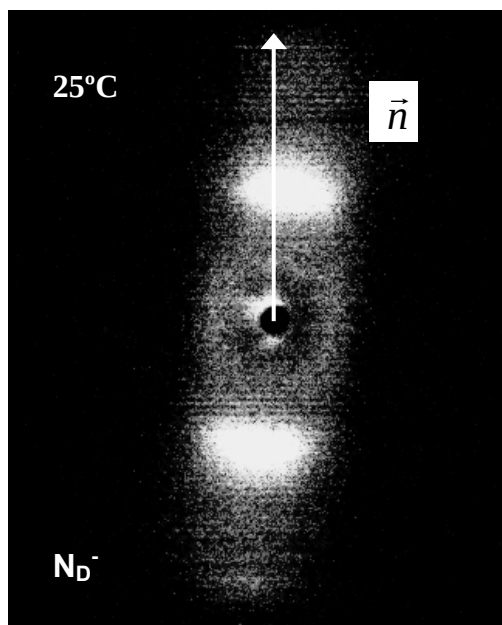


Figure 74. SAXS diffraction pattern of the racemic N_D - phase of DL-KDDS system in a cylindrical capillary of 0.7 mm in diameter at 25 °C. The shadow in the center is the beam-stop. The arrow shows the direction of the phase director ($\vec{n}$).

The scattering intensity of the N_D - phase of DL-KDDS versus the scattering angle 2θ graph exhibited two maxima, along and perpendicular to the $\vec{n}$, respectively, with intense arcs at the long axis of the ellipsoids, Figure 75.

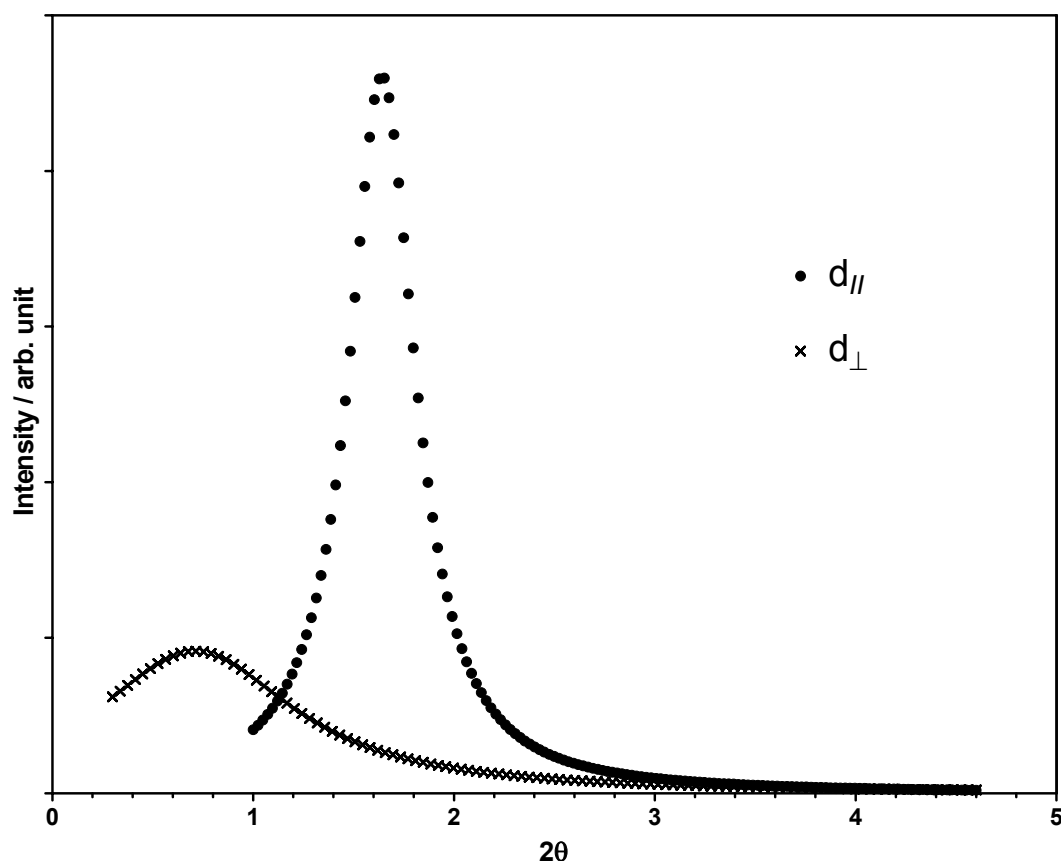


Figure 75. The intensity versus 2θ for the racemic N_D^- phase of DL-KDDS ($\%X=2.51$) at 25°C . $//$ and $\perp$ represent the scattering intensities obtained from the periodicity along and perpendicular to the phase director, $\vec{n}$, respectively. The curves were fitted to Lorentzian function.

The chiral nematic phase of L-KDDS gave fingerprint texture, Figure 76. As seen from this figure, the cholesteric stripes are parallel to the long capillary axis and this indicates that its helix axis aligned spontaneously perpendicular to the long capillary axis. As was mentioned before, this alignment of the helix axis caused to obtain circular like diffraction pattern with intense arcs along the z-axis for this intrinsically N_{D+}^* phase of L-KDDS (without placing it in a magnetic field), Figure 77.

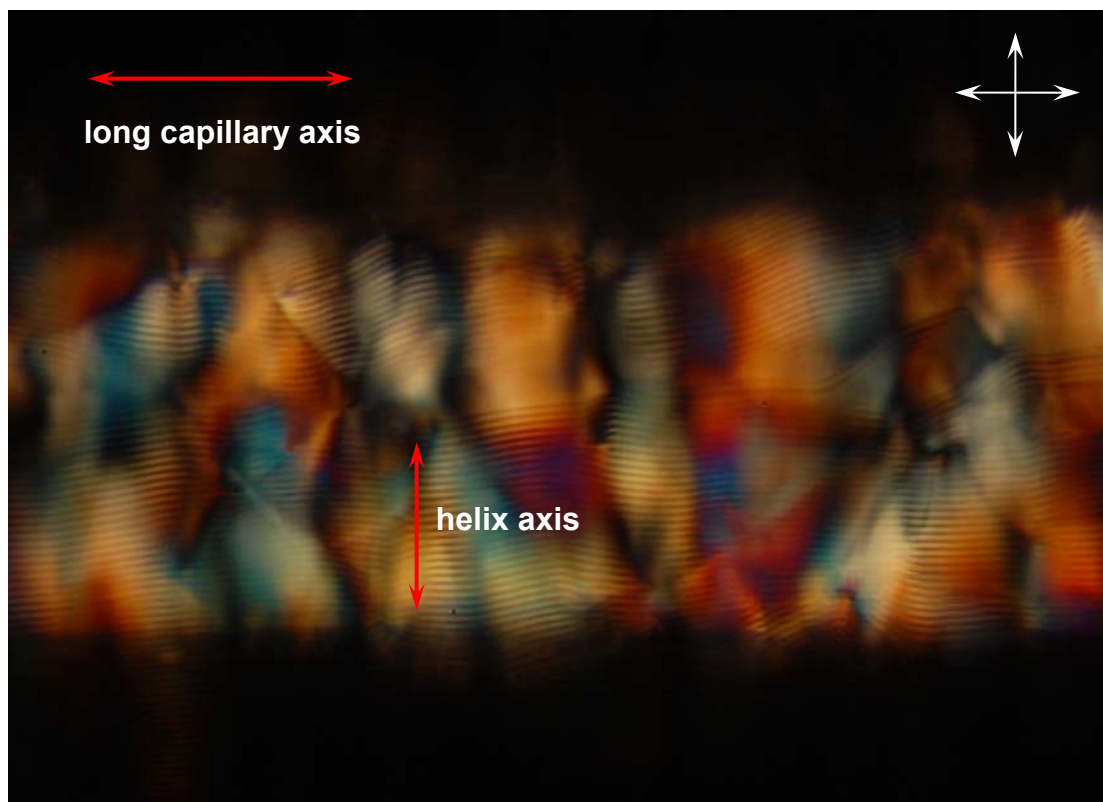


Figure 76. The fingerprint texture of the L-KDDS (%X=2.51) in the cylindrical capillary. The microphotographs were taken at room temperature ($\sim 25\text{ }^{\circ}\text{C}$). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.

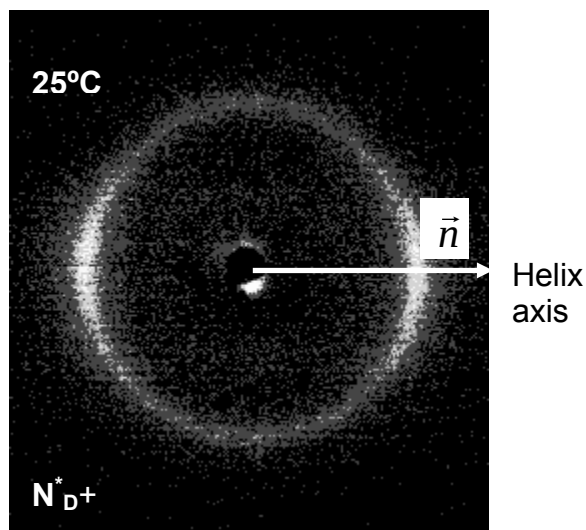


Figure 77. SAXS diffraction pattern of the intrinsically N_{D+}^* phase of L-KDDS ($X\%=2.51$) system in a cylindrical capillary of 0.7 mm in diameter without a magnetic field at 25 °C. The shadow in the center is the beam-stop.

The scattering intensities obtained from the periodicity along and perpendicular to the helix axis for non-aligned intrinsically N_{D+}^* phase of L-KDDS in Figure 77 were integrated over 2θ , two approximately equal maxima were obtained, Figure 78.

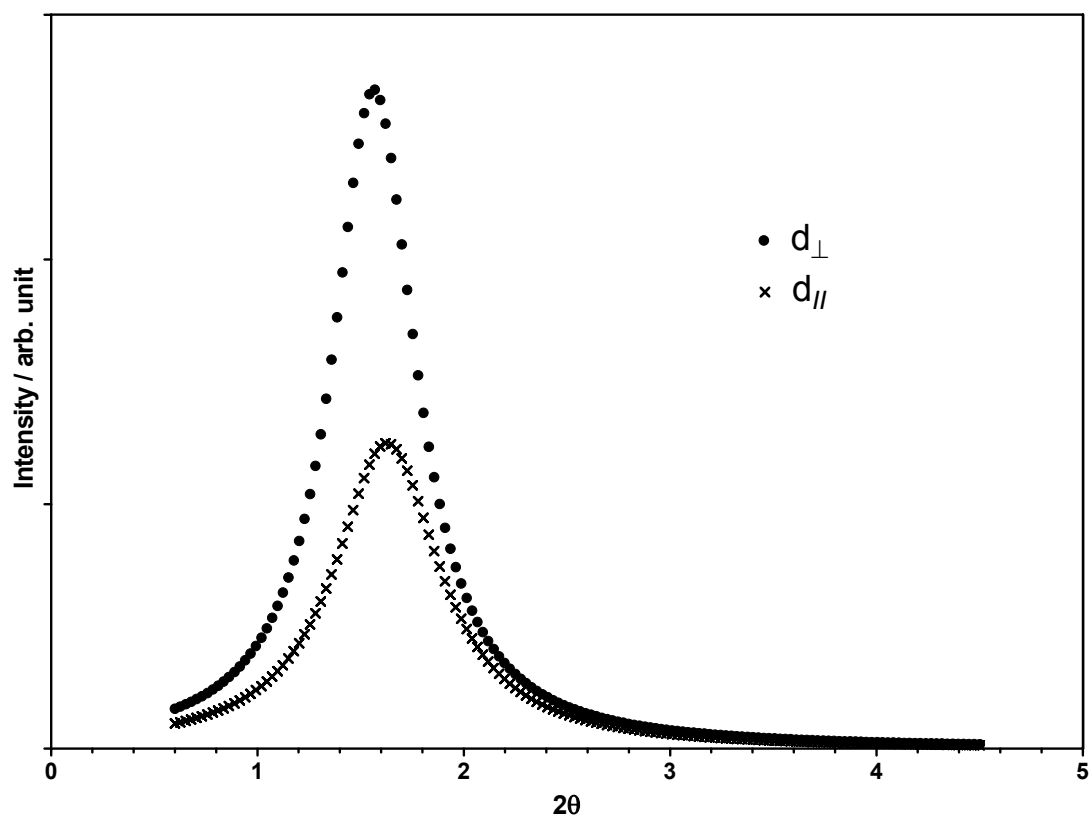


Figure 78. The intensity versus 2θ for the intrinsically N_{D+}^* phase of L-KDDS (X%=2.51) system in a cylindrical capillary of 0.7 mm in diameter without applying a magnetic field at 25 °C. The curves were fitted to Lorentzian function.

When the SAXS measurement was repeated by putting the chiral nematic phase shown in Figure 76 into a magnetic field of 1.1 T during 10-12 days, its helix axis was aligned parallel to the long capillary axis, Figure 79.

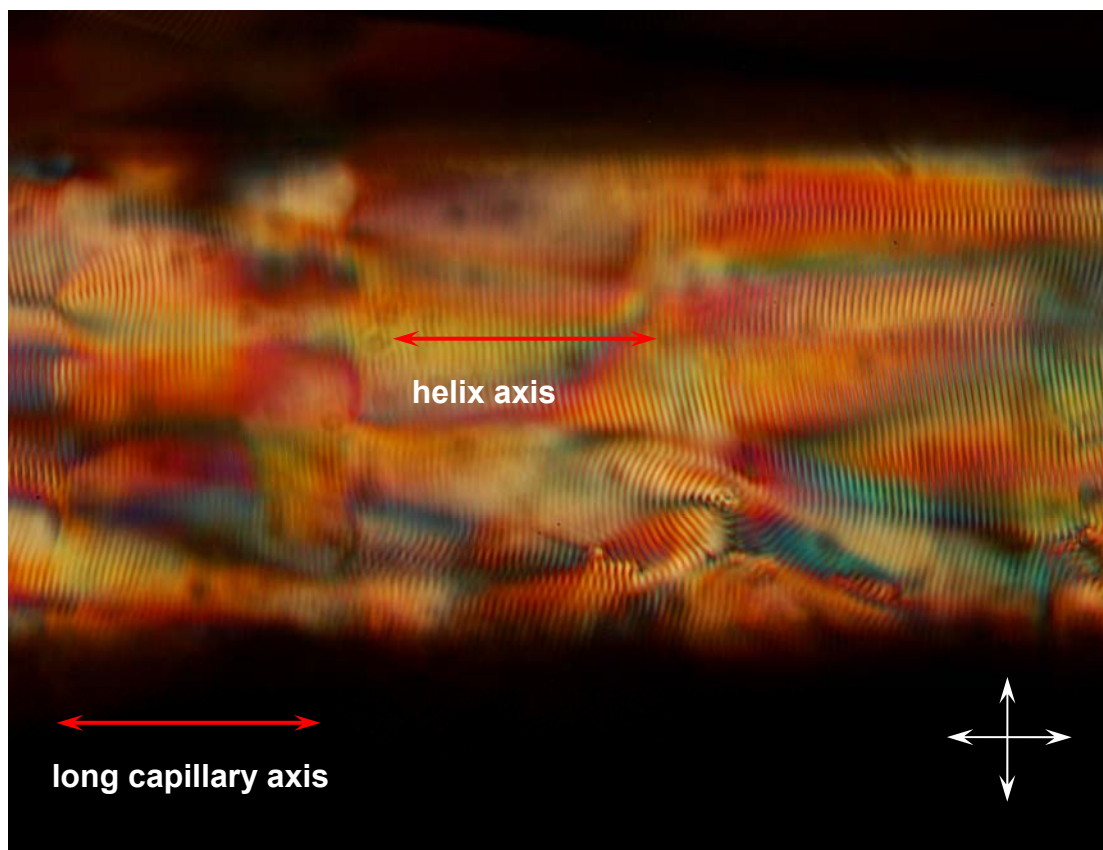


Figure 79. The fingerprint texture of the phase of L-KDDS (%X=2.51) in the cylindrical capillary. The microphotographs were taken at room temperature (~ 25 °C). The white arrows indicate the analyzer and polarizer transmission axes. Magnification: 20x.

The SAXS pattern of this aligned chiral nematic phase was ellipsoid like as its racemic nematic phase, Figure 80.

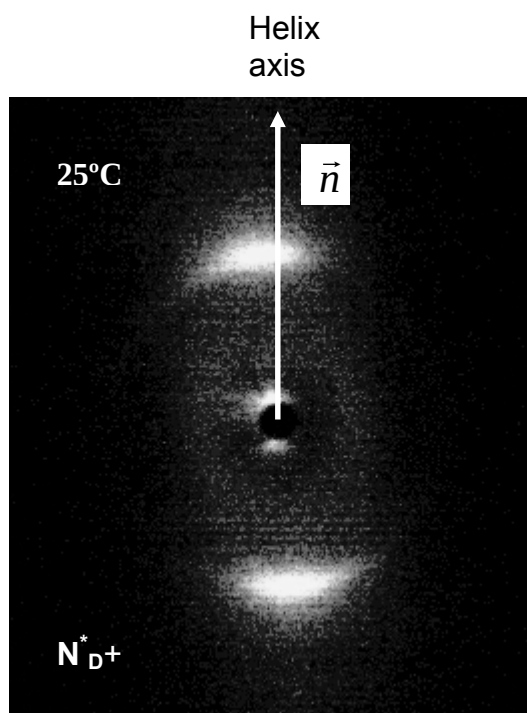


Figure 80. SAXS diffraction pattern of the intrinsically N_{D+}^* phase of L-KDDS ($X\%=2.51$) system in a cylindrical capillary of 0.7 mm in diameter with applying a magnetic field of 1.1 T at 25 °C.

When the scattering intensity of the aligned N_{D+}^* phase of L-KDDS, along and perpendicular to the $\vec{n}$, is plotted versus the scattering angle 2θ , two maxima were obtained, respectively, Figure 81.

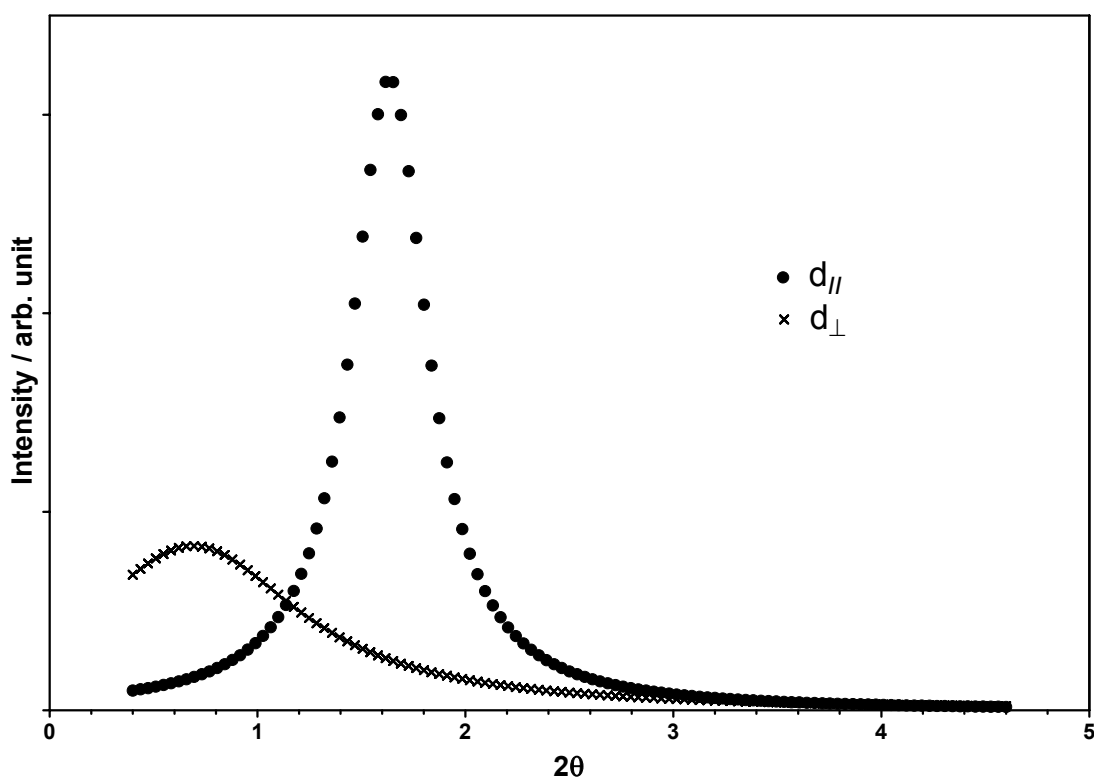


Figure 81. The intensity versus 2θ for the intrinsically N_{D+}^* phase of L-KDDS (X%=2.51) system in a cylindrical capillary of 0.7 mm in diameter with applying a magnetic field of 1.1 T at 25 °C. The curves were fitted to Lorentzian function.

The experimental results of the SAXS measurements of KDDS system were evaluated according to the calculations as described for KDDA system in the previous section. The obtained results were similar as the KDDA system. The results were summarized in the following tables and figures.

Table 22. The Bragg's values of KDDS system on going from racemic mixture to intrinsically chiral nematic phase at 25 °C. The phase compositions were given in Table 6b.

DL-KDDS %	L-KDDS %	$d_{\perp}/\text{\AA}$	$d_{\parallel}/\text{\AA}$
100	0	129	56
74.9	25.1	127	55
49.9	50.1	125	55
25.0	75.0	123	55
0	100	122	55

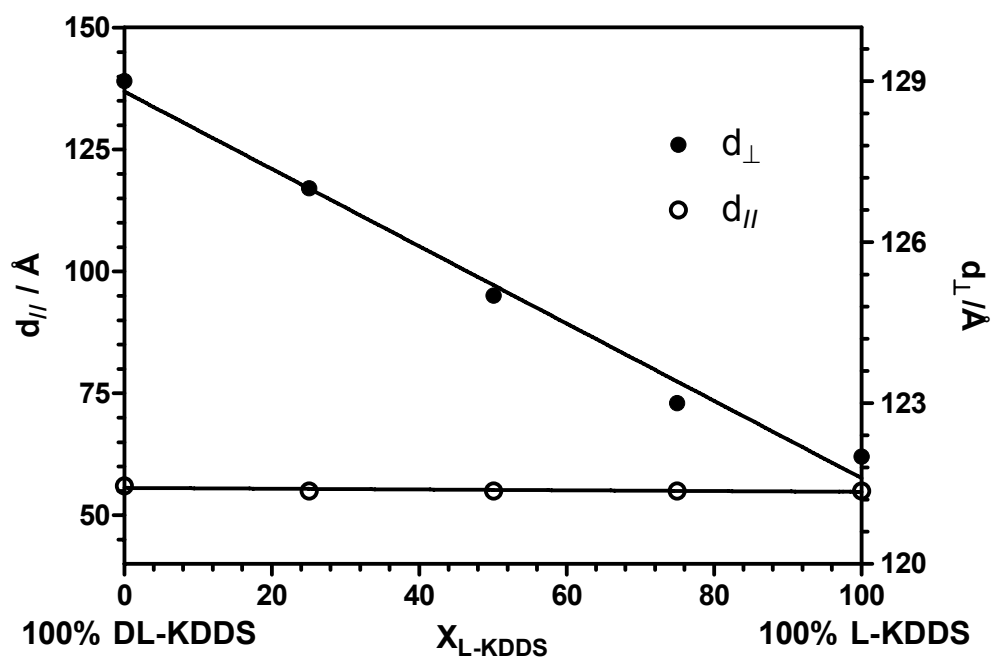


Figure 82. The Bragg's values of KDDS system on going from pure DL-KDDS to pure L-KDDS.

Table 23. The Bragg's values for different compositions of DL-KDDS and L-KDDS. The phase compositions were given in Table 5b.

$X_{\text{DL-KDDS}}$	DL-KDDS		$X_{\text{L-KDDS}}$	L-KDDS	
	$d_{\perp}/\text{\AA}$	$d_{\parallel}/\text{\AA}$		$d_{\perp}/\text{\AA}$	$d_{\parallel}/\text{\AA}$
0.0251	129	56	0.0251	122	55
0.0275	112	53	0.0275	105	53
0.0300	98	51	0.0300	93	51
0.0325	87	50	0.0325	82	49

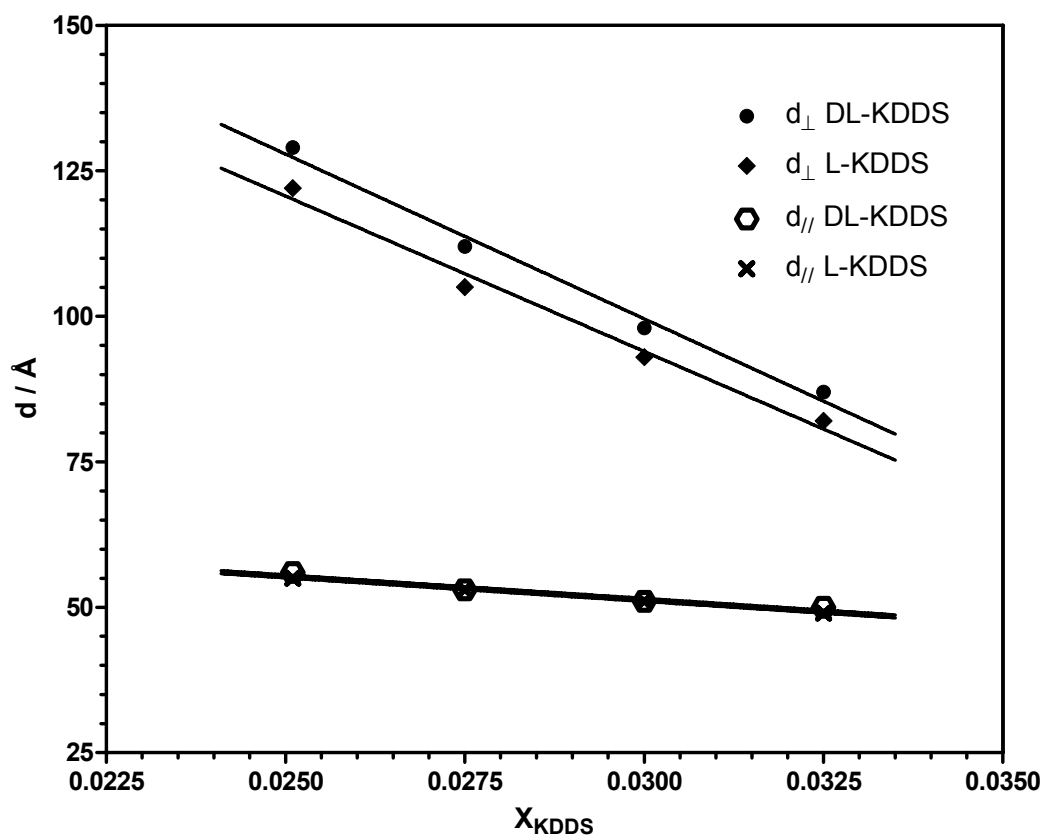


Figure 83. The concentration dependence of the Bragg's values for KDDS system at 25 °C.

Table 24. The parameters obtained from the SAXS measurements for KDDS on going from DL-KDDS to L-KDDS.

Phase code	V_p/nm^3	ϕ_{mic}	$V_{\text{mic}}/\text{nm}^3$	$D/\text{\AA}$	$W_{\perp}/2/\text{\AA}$	$W_{\parallel}/2/\text{\AA}$
100% DL	719	0.3447	248	101	14.1	12.5
25.1% L	697	0.3443	240	99	13.9	12.5
50.1% L	675	0.3442	232	98	13.7	12.5
75.0% L	654	0.3441	225	96	13.4	12.5
100% L	643	0.3442	221	95	13.3	12.5

Table 25. The parameters obtained from the SAXS measurements for DL-KDDS and L-KDDS, for different concentrations.

Phase code	X_a	V_p/nm^3	ϕ_{mic}	$V_{\text{mic}}/\text{nm}^3$	$D/\text{\AA}$	$W_{\perp}/2/\text{\AA}$	$W_{\parallel}/2/\text{\AA}$
DL-KDDS	0.0251	719	0.3447	248	101	14.1	12.5
L-KDDS	0.0251	643	0.3442	221	95	13.3	12.5
DL-KDDS	0.0275	522	0.3611	189	88	12.0	11.5
L-KDDS	0.0275	459	0.3607	166	82	11.3	11.5
DL-KDDS	0.0300	385	0.3774	145	77	10.4	10.5
L-KDDS	0.0300	346	0.3771	131	73	9.9	10.5
DL-KDDS	0.0325	297	0.3936	117	69	8.8	10.0
L-KDDS	0.0325	259	0.3932	102	65	8.7	9.5

Table 26. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , on going from DL-KDDS to the intrinsically L-KDDS where the mole fraction of the total amphiphile ($X_{DL-KDDS+L-KDDS}$) was 0.0251. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} was calculated as 2.15 according to the phase compositions in Table 6b. The molar volumes and volumes of a single KDDS molecule were determined from the mass density measurements as described for KDDA system: DL-KDDS=277.4 cm³/mol=460.6 Å³, L-KDDS=284.9 cm³/mol=473.1 Å³, 24.7%L=463.7 Å³, 50.1% L=466.9 Å³, 73.3%L=469.7 Å³.

Phase code	V_{mic}/nm^3	N_{agg}
100% DL	248	407
25.1% L	240	392
50.1% L	232	378
75.0% L	225	364
100% L	221	356

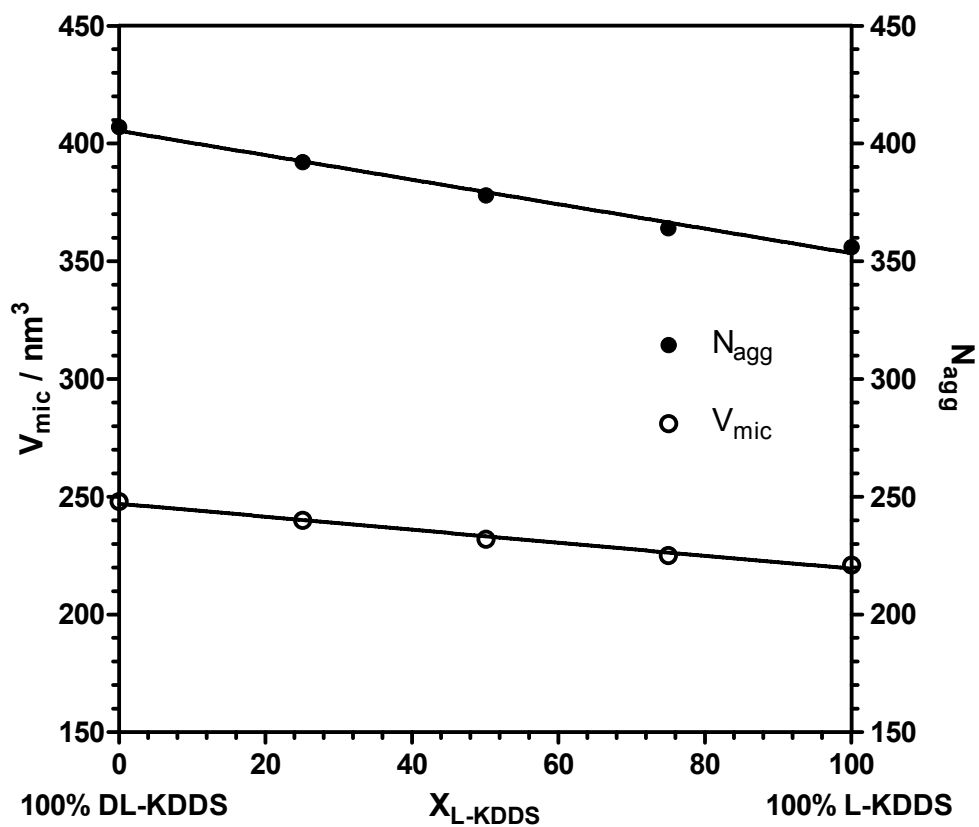


Figure 84. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of L-KDDS in the mixtures of DL/L-KDDS according to the data in Table 26.

Table 27. The comparison of the micelle volume, V_{mic} , with the aggregation number, N_{agg} , for DL-KDDS and L-KDDS phases where the mole fraction of DL-KDDS and L-KDDS were equal to each other. In these racemic nematic and chiral nematic phases, n_a/n_{DeOH} were calculated as 2.15, 2.36, 2.59 and 2.81 for the mole fractions of 0.0251, 0.0275, 0.0300 and 0.0325, respectively, according to the phase compositions in Table 5b.

Phase code	X_a	V_{mic}/nm^3	N_{agg}
DL-KDDS	0.0251	248	407
L-KDDS	0.0251	221	356
DL-KDDS	0.0275	189	317
L-KDDS	0.0275	166	272
DL-KDDS	0.0300	145	249
L-KDDS	0.0300	131	219
DL-KDDS	0.0325	117	204
L-KDDS	0.0325	102	174

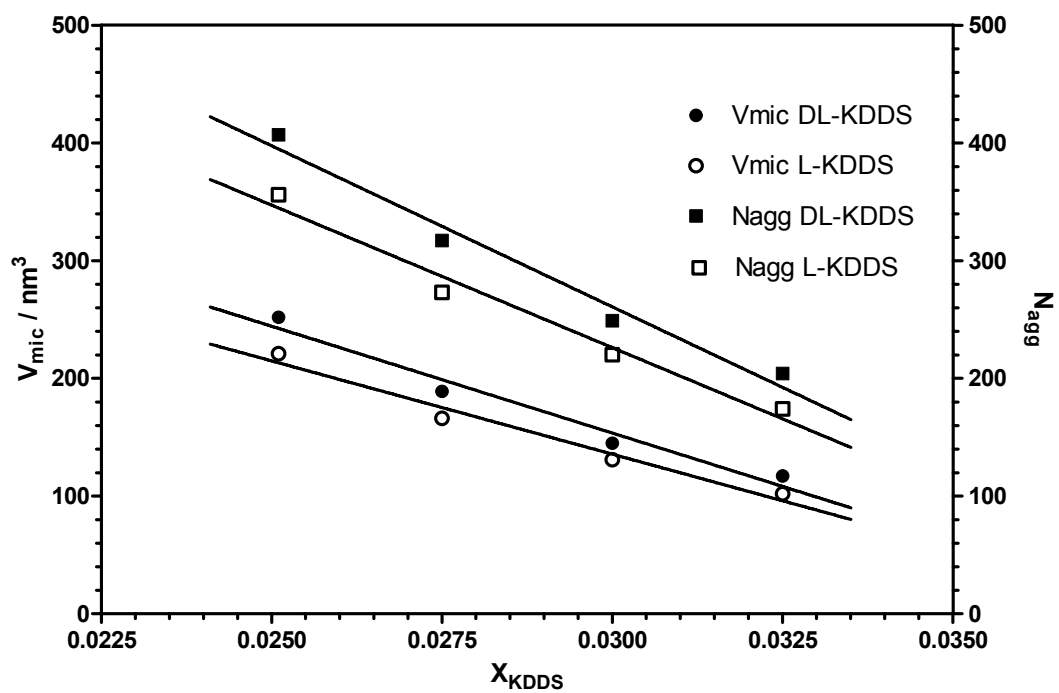


Figure 85. The variations of the micelle volumes and aggregation numbers as a function of the mole fraction of KDDS for DL-KDDS racemic nematic phases and L-KDDS chiral nematic phases according to the data in Table 27.

5.7 Comparison of the effect of the temperature on the twist angle and the helical twisting powers of the chiral nematic phases

As we discussed in the section 5.3, the pitches of the chiral nematic phases increased with increasing temperature, i.e. the twists and the h_{tp} s decreased. Radley reported this type of temperature dependence of the pitch for L-KDDA and L-KDDS systems was a result of the increase in the intermicellar distance. However, according to the SAXS measurements, the intermicellar distance, which corresponds to the water layer between two naked micelles of L-KDDA or L-KDDS along the helix axis, $W_{\perp}$, decreased as the temperature was increased, Table 28. Now, a question should be asked: although the intermicellar distances decrease, why does the pitch is lengthened with increasing temperature? In order to clarify this point, we applied the SAXS measurements on the intrinsic chiral nematic phases of L-KDDS and L-KDDA which were aligned in the magnetic field before the SAXS measurements.

According to the definition of the pitch, the full torque of the helix is completed when the micelles turn around the screw axis (helix axis) to complete 360° , Figure 86. Hence, n number of the micelles, n_{mic} , are needed to complete the rotation of the micelles. Because we know the distance between two hydrated micelles, $d_{\perp}$, and the pitch, n_{mic} can be calculated dividing the pitch by $d_{\perp}$ as described in Figure 86. After obtaining the n_{mic} values, the screw angle (twist angle), θ , were calculated using the following equation;

$$\theta = \frac{360^{\circ}}{n_{mic}} \quad (23)$$

The $d_{\perp}$, $W_{\perp}$, pitch, n_{mic} , θ and htp values for L-KDDA and L-KDDS phases are given at five different temperatures in Table 28.

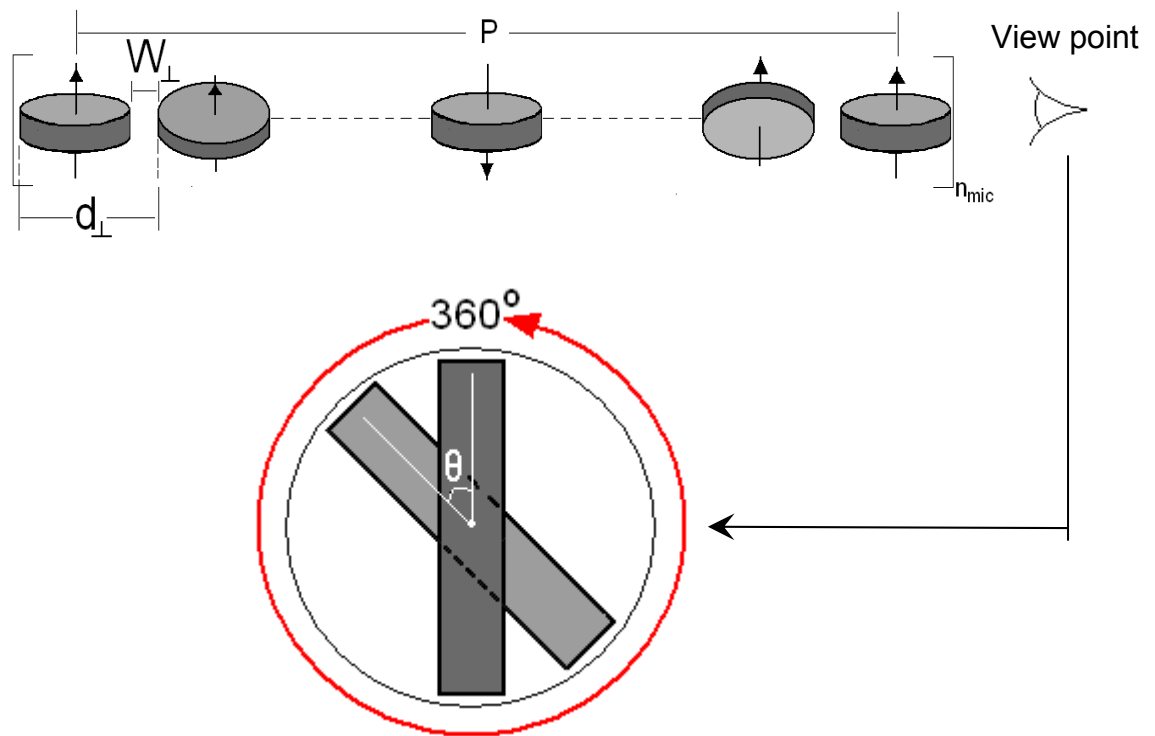


Figure 86. The figure shows the illustration of the screw angle.

Table 28. The comparison of the $d_{\perp}$, $W_{\perp}$, pitch, n_{mic} , θ and htp values for (a) L-KDDA (%X=2.52) and (b) L-KDDS (%X=2.51) phases at 25-45 °C. The temperature was controlled with an accuracy of ± 0.1 °C using a thermostat.

T/°C	$V_{\text{mic}}/\text{nm}^3$	$W_{\perp}/\text{\AA}$	$d_{\perp}/\text{\AA}$	P/\AA	n_{mic}	$\theta / ^{\circ}$	htp / μm^{-1}
25.0	108	19.4	86	33500	390	0.92	31.19
30.0	101	18.5	83	42300	510	0.71	26.67
35.0	97	17.9	81	50300	621	0.58	22.34
40.0	95	17.5	80	66600	833	0.43	17.54
45.0	91	16.9	78	80600	1033	0.35	14.42

(a)

T/K	$V_{\text{mic}}/\text{nm}^3$	$W_{\perp}/\text{\AA}$	$d_{\perp}/\text{\AA}$	P/\AA	n_{mic}	$\theta / ^{\circ}$	htp / μm^{-1}
25.0	221	26.6	122	78600	644	0.56	19.57
30.0	218	26.4	121	87500	723	0.50	17.12
35.0	211	25.9	119	102800	864	0.42	14.65
40.0	201	25.1	116	122500	1056	0.34	12.92
45.0	194	24.6	114	146900	1289	0.28	10.85

(b)

As seen from the results in Table 28, at the studied temperature range, the decrease in the screw angles are %62.0 and %50.0 for L-KDDA and L-KDDS, respectively. In addition, the decrease in the intermicellar distances are %12.9 and %7.5 for L-KDDA and L-KDDS, respectively. These results indicate that the contribution of the change in the screw angle to the twist and also helical twisting power is much larger than that in the intermicellar distance for both L-KDDA and L-KDDS systems. This means that the Radley's suggestion is not quite correct for the temperature dependence of the L-KDDA and L-KDDS chiral nematic phases [35]. Another effect, that might cause a decrease in the screw angle, may arise from weakening of the intermicellar chiral interactions as the temperature was increased. This will be discussed in section 5.9 where the intermicellar interaction parameter, k_H , is examined.

5.8 The effect of the concentration of the L-enantiomers on the twist angle and the helical twisting powers of the chiral nematic phases

In the previous section, 5.7, we suggested a model for the calculation of the screw angle and the number of the micelles along the screw axis in order to complete a 2π rotation, Figure 86, by using equation 23. Then, we applied this model to the chiral nematic phases where the concentrations of the L-enantiomers were increased. The obtained values are given in Table 29.

Table 29. The comparison of the $d_{\perp}$, $W_{\perp}$, pitch, n_{mic} , θ values for (a) L-KDDA and (b) L-KDDS phases at 25 °C as a function of the increase in the L-enantiomers.

X_{L-KDDA}	$W_{\perp}/\text{\AA}$	$P/\text{\AA}$	$d_{\perp}/\text{\AA}$	n_{mic}	$\theta / ^{\circ}$
0.0252	19.4	33500	86	390	0.92
0.0275	17.0	28000	76	368	0.98
0.0300	13.3	21900	63	348	1.03
0.0325	11.5	18900	56	338	1.07

(a)

X_{L-KDDS}	$W_{\perp}/\text{\AA}$	$P/\text{\AA}$	$d_{\perp}/\text{\AA}$	n_{mic}	$\theta / ^{\circ}$
0.0251	26.6	78600	122	644	0.56
0.0275	22.5	58800	105	560	0.64
0.0300	19.7	46600	93	501	0.72
0.0325	17.4	38300	82	467	0.77

(b)

As seen from the results, as the concentrations of the L-enantiomers are increased, the intermicellar distances, $W_{\perp}$, decrease, and the screw angles became larger. Furthermore, if the L-KDDA system is compared with the L-KDDS system, the screw angle of the L-KDDA chiral nematic phase is larger than that of the L-KDDS, and this explains why the L-KDDA system has a higher helical twisting power than the L-KDDS system. Herein, we should mention about the distortion angle ϕ again, Figure 42 in the section 5.3, which is directly proportional to the screw angle. In the other words, the higher distortion angle leads to a higher screw angle. In that section, we inferred that L-KDDS system has smaller distortion angle than L-KDDA because L-KDDS molecule includes a hydroxyl group in its head group which makes a hydrogen bond between L-KDDS molecules. The hydrogen bonds do not allow the rotation of the micelle surfaces efficiently with respect to each other, thus the distortion angle is small in L-KDDS compared to L-KDDA.

In addition, the intermicellar distance or water layer between the chiral micelles is smaller in L-KDDA than in L-KDDS. This result indicates that the chiral attractive interactions between the micelles of L-KDDA are stronger than those of L-KDDS system.

5.9 The viscosities of the studied systems in isotropic micellar solutions

The viscosities of the isotropic micellar solutions of our systems, which are the precursors of the nematic phases, were measured in order to determine the Huggins's constant k_H , which is interpreted in the literature as the intermicellar interaction parameter [90-93]. For this purpose, we measured the viscosities of each amphiphiles in the concentration range of 0.15 mol/kg and 0.35 mol/kg. The viscosities were used to evaluate the specific viscosities, η_{sp} , which were required to determine the k_H values according to the Huggins's equation, $\frac{\eta_{sp}}{C} = [\eta] + k_H[\eta]^2 C$.

The k_H values of KDDA and KDDS systems at 25-45 °C were calculated from the slope of the η_{sp}/C versus C graph where C is the concentration of the amphiphile. The following figure shows the concentration dependences of η_{sp}/C for each amphiphiles at 25 °C, Figure 87 and 88. For other temperatures, the η_{sp}/C versus C graphs were similar.

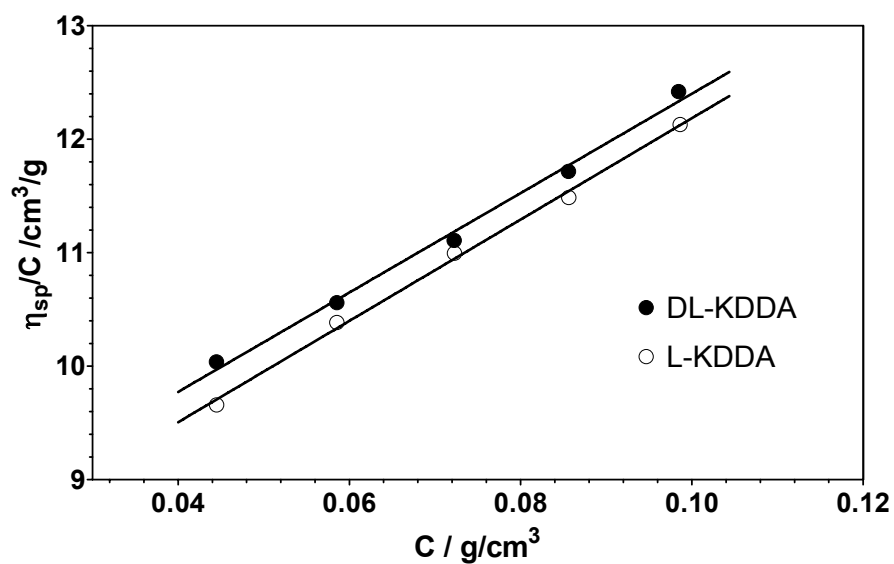


Figure 87. The concentration dependences of η_{sp}/C for DL-KDDA and L-KDDA system at 25 °C.

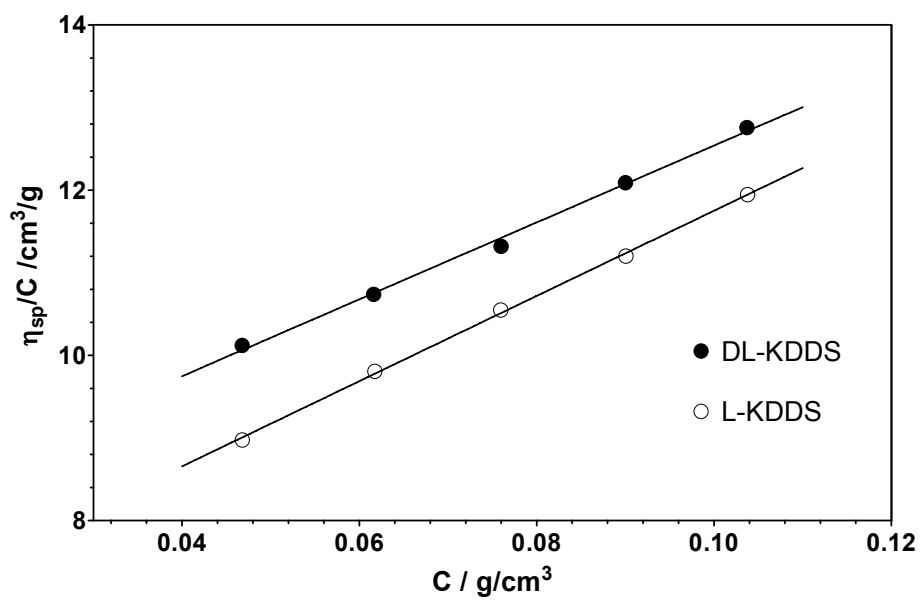


Figure 88. The concentration dependences of η_{sp}/C for DL-KDDS and L-KDDS system at 25 °C.

The calculated k_H values and their temperature dependences for the racemates and L-enantiomers were given in Table 30.

Table 30. The evaluated k_H values according to the Huggins's equation in the temperature range of 25 and 45 °C. The temperature was controlled with an accuracy of ± 0.1 °C using a thermostat.

T/°C	k_H			
	DL-KDDA	L-KDDA	DL-KDDS	L-KDDS
25.0	0.68	0.75	0.85	1.19
30.0	0.59	0.68	0.78	1.06
35.0	0.53	0.58	0.69	0.84
40.0	0.48	0.50	0.61	0.73
45.0	0.42	0.43	0.57	0.62

As seen from the Figures 87 and 88 and the values in Table 30, the intermicellar interaction parameter k_H of the L-enantiomers, L-KDDA and L-KDDS, are greater than those of their corresponding racemic mixtures, DL-KDDA and DL-KDDS at all temperatures. Furthermore, for all amphiphiles, the k_H values became smaller as the temperature was increased. These results indicate that the intermicellar interactions between the racemic micelles of DL-KDDA and DL-KDDS are weaker than those between the chiral micelles of L-KDDA and L-KDDS, respectively. Furthermore, the k_H values for the L-KDDS are larger than that of the L-KDDA. The k_H , besides the chiral interactions, appears to be also dependent on the structure of the head group, then since L-KDDS contains a hydroxyl group in the head group,

its k_H is larger than that of L-KDDA. This head group was shown to give rise to a small distortion angle in L-KDDS system as discussed in the section 5.3.

In the parts related to the SAXS results, we have calculated the distance between the racemic micelles and between the chiral micelles of KDDA and KDDS. The results were given in Table 19 for KDDA system and in Table 25 for KDDS system. According to these values, the distance between racemic micelles were larger than the distance between chiral micelles in both KDDA and KDDS systems. This result is consistent with the k_H values, i.e. a larger distance between micelles should imply a smaller k_H value and vice versa.

On the other hand, if the temperature dependences of k_H values are compared with the temperature dependences of the pitches of L-KDDA, Table 8, and L-KDDS, Table 10, the decrease in the k_H explains why the pitches of both L-enantiomers increase with the increase in the temperature. This means that as the temperature increased the interactions between chiral micelles got weaker which causes an increase in the pitches in these studied systems.

5.10 A new model for the chiral induction mechanism

In the literature, as was mentioned before, two models, a chiral dispersion interaction model and a chiral sterical interaction model, were proposed for the understanding of the chiral induction mechanism in the lyotropic liquid crystals. The first mechanism is based on a direct pairwise interaction between one chiral dopant existing in a micelle and a dopant in another micelle, Figure 89.

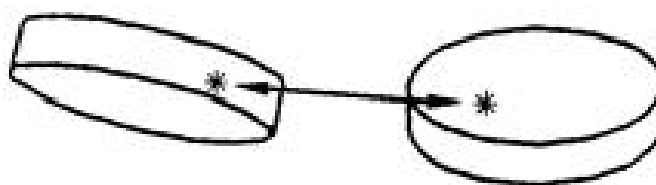


Figure 89. The schematic representation of a pairwise interaction between two chiral dopants in adjacent micelles [27].

In this model, the chiral dopant should prefer to be near the micelle surface in order to interact with the dopant in the adjacent micelle [27,29,55]. The second model indicates a distortion of the achiral micelles of the nematic phase, which is caused by the effect of the added chiral dopant, Figure 90.

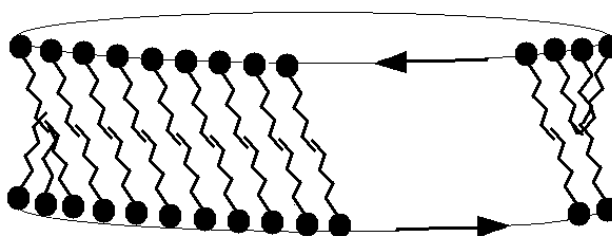


Figure 90. The schematic representation of the distortion of a micelle by the influence of an added chiral dopant.

The added chiral dopants cause the induction of a twist in the micelle shape as a result of the preferred orientation of its neighbouring achiral molecules within the micelle. Then, the long axes of the amphiphilic molecules are tilted towards the rim of the disc-like micelle [14]. Hence, one micelle surface rotates to the left or right with respect to the other micelle surface [97]. In other words, a distortion in micelle shape occurs to give a chiral micelle as seen from the Figure 90. Due to the thermal motion of the micelles in the phase, they frequently collide with each other, thus the chiral information is transferred from one micelle to its nearest neighbouring micelles by steric interaction within the phase [14,29].

Consequently, in the first model, a macroscopic twist arises from the intermicellar interactions, however, in the second model, it arises as a result of the intramicellar twist [14]. Then, the chiral information is transferred from one micelle to the adjacent micelle along the helix axis, if the intermicellar interactions are sensitive. The macroscopic twist gives rise to the formation of the fingerprint texture of the chiral nematic phases and it can be easily characterized by a polarizing light microscope, Figure 91.

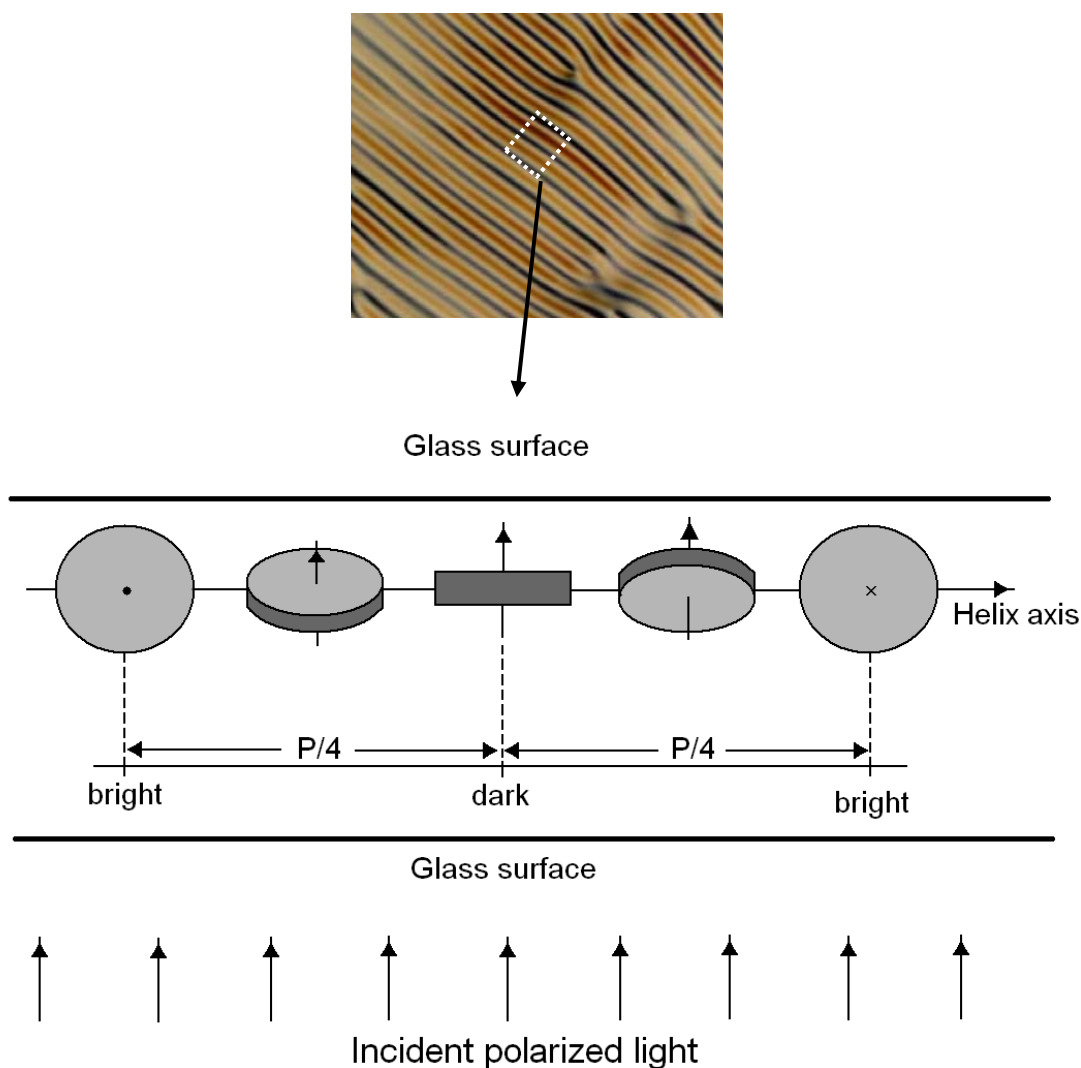


Figure 91. Top: The stripes of the fingerprint texture of the chiral nematic phase. Bottom: The arrangement of the micelles along the helix axis and the interaction of the incident polarized light with the micelles. The helix axis is parallel to the glass surface.

On the other hand, some NMR experiments using a system consisted of deuterated amphiphiles, supported that the the second model is more possible than the first model [113]. Subsequently, it was found that the apparent correlation between NMR quadrupole splitting and the bulk chirality

is superficial [114]. Thus, up to the present, there are still many aspects on the chiral induction in amphiphilic systems which are not well understood.

When these chiral induction models were proposed, they inferred from some experimental results [27]. Furthermore, Hiltrop et. al. proposed a model based on the intramicellar interactions to support the second model [14,29]. Another experimental results were published by Gottarelli et. al for thermotropic liquid crystals [61,115,116] and also for lyotropics [117] where the latter supported the distortion mechanism. Their chiral induction mechanism derived for thermotropics was based on the solute-solvent interactions, i.e. the chirality is transferred from the chiral molecule to a near solvent molecule and from this to the next near. However, then, some theoretical models were proposed for the chiral induction mechanism. For instance, Ferrarini research group was reported some mathematically calculation studies about how chiral induction occurs [57,118-125]. However, these studies, in general, are based on the configuration of the chiral dopants, in other words, the relation between the twisting power of the chiral dopant and its shape. In 1998, Berardi et.al. reported a theoretical computer simulation study on the chiral induction mechanism in nematics [126]. They calculated the most favorable twisted side-by-side interaction energy between a chiral surface molecule and a fluid particle. Then, they concluded that a twist is induced by the short-range chiral interactions and it has maximum value when the surfaces are nearest to each other. In other words, they proposed that there should be an optimum distance between the chiral micelle and the solvent molecule in order to transfer the chirality to the whole phase. In addition, in 2001, Yoneya and Yokoyama investigated the

monolayer structures of a chiral mesogen adsorbed on graphite [127]. Then, according to molecular dynamics simulations, they proposed a molecular model which was based on coupling between up-down symmetry breaking and the molecular tilt direction symmetry breaking of the monolayer.

After these introductory informations on experimental and theoretical studies, we will discuss our experimental results along these findings in the literature. As discussed before our findings consist of experimental evidences, such as small-angle x-ray scattering results, helical twisting powers, htp , screw angle, θ , intermicellar distances, $W_{\perp}$, the micelle diameters, D , and intermicellar interaction parameters, k_H , in order to discuss the chiral induction mechanism in details. If we consider all of the experimental results, we may summarize the important parameters at 25 °C in the following table.

Table 31. The important experimentally determined parameters for KDDA and KDDS systems.

	X%*	DL-KDDA	L-KDDA	DL-KDDS	L-KDDS
D/Å	2.50	75	67	101	95
	2.75	67	59	88	82
	3.00	57	50	77	73
	3.25	52	45	69	65
W _⊥ /Å	2.50	21.8	19.4	28.2	26.6
	2.75	19.2	17.0	24.0	22.6
	3.00	15.2	13.4	20.8	19.8
	3.25	14.0	11.4	17.6	17.4
N _{agg}	2.50	231	181	407	356
	2.75	187	145	317	272
	3.00	138	105	249	219
	3.25	117	86	204	174
htp / μm ⁻¹		-----	31.19	-----	19.57
θ / °		-----	0.92	-----	0.56
k _H		0.68	0.75	0.85	1.19

* X% represents the percent mole fraction of the amphiphiles in the liquid crystalline phases.

As seen from the table, the k_H of the L-KDDA system is greater than that of the L-KDDS system. This indicates that the screw angle of the L-KDDA is larger than that of the L-KDDS, which was supported by screw angles obtained from the SAXS measurements. Furthermore, the intermicellar distances in the L-KDDA system are shorter than those in the L-KDDS system. This means that the high intermicellar chiral interactions between the micelles of L-KDDA give rise to a short intermicellar distance, compared to the L-KDDS system. Similar results were found in the literature for the dopants, cholesterol and prednisolone, in the N_D phase of hexadecyl-dimethylethylammoniumbromide system [15,128,129].

As can be seen from the table, the k_H value of L-KDDA is smaller than that of L-KDDS because the L-KDDS amphiphile contains a hydroxyl group in its head group which makes hydrogen bond. Hence, the effect of this hydrogen bond should be taken into account in the comparison of the k_H of the L-KDDA with the k_H value of the L-KDDS. Furthermore, if the k_H values and the intermicellar distances of the L-enantiomers are compared with those of their racemic mixtures, the weaker intermicellar interactions (smaller k_H values) gives rise to the larger intermicellar distances, i.e. the chiral interactions in the L-enantiomer systems are stronger than the achiral interactions in the DL-racemic systems.

Another interesting result can be seen from the diameter of the micelles. For all amphiphiles concentrations, the diameters of the chiral micelles of L-KDDA and L-KDDS are smaller than those of their racemic micelles, DL-KDDA and DL-KDDS, respectively. Furthermore, as the number densities of both chiral and racemic amphiphiles are increased, the micelles

become more compact and the intermicellar distances get shorter along the periodicity of the micelle diameter.

Our results, the micelle diameters, D , the intermicellar distances, $W_{\perp}$, and the helical twisting power values, htp , of the intrinsic chiral nematic phases, and the results on the induced chiral nematic phases in the literature indicate that there must be (i) a crucial distance and (ii) a critical micelle size in order to obtain chiral induction. Consequently, the chiral interactions between the micelles must be anisotropic so that the chiral information is transferred along the helix axis via distorted micelles. The strength of the chiral interactions depend on the $htps$ of the individual intrinsically chiral amphiphiles or dopants.

Accordingly, the chiral induction does not take place completely as was suggested by pairwise interaction or sterical interaction models, but through anisotropic chiral interactions via distorted micelles for which a crucial distance between the micelles and a critical micelle size are required.

6. CONCLUSIONS

Two pairs of amphiphiles, L-enantiomer/racemic systems, L- and DL-KDDA and L- and DL-KDDS, were studied by polarizing light microscopy, laser light diffraction, mass density, small-angle x-ray scattering and viscosity methods.

The polarizing light microscopic investigations confirmed the structures given in the literature for these racemic and intrinsically chiral nematic phases (Figure 34, p. 66, and Figures 37 and 38, p. 69). Consequently, the racemic nematic phases consisted of disc-like micelles whose directors aligned perpendicular to the magnetic field direction whereas the helix axes of the intrinsically chiral nematic phases aligned parallel to the direction of the magnetic field (pp. 67-69).

The pitches of the intrinsically chiral nematic phases of the L-enantiomers, L-KDDA and L-KDDS, were determined in dependence of the concentration and temperature by laser light diffraction. It was found that the pitches became shorter with increasing concentration of the L-enantiomers as, generally, described in the literature, but they were lengthened as the temperature was raised (Figure 41, 43 and 45, pp. 73, 76 and 79, respectively). The pitches of the L-KDDA enantiomer were shorter than those of the L-KDDS enantiomer. The helical twisting powers (htps), the strength of twisting the phases of the L-enantiomers, were determined from the reciprocal pitch versus concentration at room temperature. It was found that

the τ of the L-KDDA enantiomer was higher than that of the L-KDDS enantiomer (Table 11, p. 82). This phenomenon was interpreted in terms of the hydrogen bonding existing in the L-KDDS enantiomer which prevents the rotation of the micelle surfaces with respect to each other (Figure 42, p. 74). The τ s of the L-enantiomers were decreased with increasing temperature, which were interpreted as the decrease of the screw angles along the helix axes.

The mass density measurements showed that the mass densities of the intrinsically chiral nematic phases of the L-enantiomers were considerably greater than those of the racemic nematic phases at the same mole fractions. This phenomenon was shown to arise from the certain packing of the L-enantiomers in the micelles (Figures 50 and 53, pp. 87 and 92, respectively) and indicated that the micelles of the L-enantiomers were more compact, i.e. they had smaller volumes than those of the racemic micelles.

Small-angle x-ray scattering (SAXS) experiments were carried out to determine the volumes of micelles (V_{mic}), micelle diameters (D) and thicknesses (h), intermicellar distances ($W_{\perp}$), aggregation numbers of the micelles (N_{agg}) and number of micelles per helix length (n_{mic}). It turned out, in order to determine these quantities, that the x-ray beam has to strike the optical axes of the racemic nematic phases and the helix axes of the intrinsically chiral nematic phases perpendicularly (Figures 56, 74, 65 and 80, pp. 97, 122, 105 and 128, respectively). From SAXS measurements the following results were obtained:

- (i) The micelle volume, V_{mic} , the micelle diameter, D , and thicknesses, h , intermicellar distances, $W_{\perp}$, the aggregation number of the micelle, N_{agg} , and number of micelles per helix length, n_{mic} , were determined.
- (ii) The micelle volume, the micelle diameter, (Tables 18 and 24, pp. 114 and 132, respectively) and the aggregation number of the micelle, (Tables 20 and 26, pp. 116 and 133, respectively) decreased significantly as the racemic mixture was replaced gradually by its L-enantiomer.
- (iii) The quantities, V_{mic} , D and N_{agg} , were also decreased when the concentration of the racemic mixture or the L-enantiomer was increased (Tables 19, 21, 25 and 27, pp. 114, 118, 132 and 135, respectively).
- (iv) The quantities, V_{mic} , D and N_{agg} of the KDDA system were remarkably smaller than those of the KDDS system (Table 31, p. 152).
- (v) The intermicellar distance, $W_{\perp}$, and the number of micelles, n_{mic} , became smaller for both, L-KDDA and L-KDDS systems as the concentration was increased, where the quantities of the L-KDDA enantiomer were importantly smaller than those of the L-KDDS enantiomer. Moreover, the screw angles of the L-KDDA enantiomer became larger than those of the L-KDDS as their concentrations were increased (Table 29, p. 141). This result is new and may have a significant impact on the chiral induction.

These results are observed at first time for L-enantiomers/racemic mixtures and show the clear utility of the L-enantiomers/DL-mixtures compared to the induced chiral phases.

The viscosity measurements were done in order to determine the intermicellar interaction parameter, k_H , in the isotropic micellar solutions. It was found that (i) the k_H values of the L-enantiomers were considerably larger than their racemic mixtures and (ii) the k_H values of the KDDS were remarkably larger than those of the L-KDDA system (Table 30, p. 145). The latter result was interpreted to arise from the strong hydrogen bonding in the KDDS. Nevertheless, the k_H values from the L-enantiomer/racemic mixtures allow us to infer that they give some hints on the chiral interactions.

From our results, the theoretical and experimental results in the literature, we have concluded that for an optimal chirality transfer between micelles, a crucial intermicellar distance and a certain micelle sizes are required, which are recognized at first time.

REFERENCES

- [1] Pershan, P.S., 1982, Lyotropic liquid crystals, *Phys. Today*, 34-39.
- [2] Boden, N., Jackson, P.H., McMullen, K. and Holmes, M.C., 1979, Are "nematic" amphiphilic liquid crystalline mesophases thermodynamically stable?, *Chem. Phys. Lett.*, 65, 476-479.
- [3] Brown, G.H., 1983, Liquid crystals-The chameleon chemicals, *J. Chem. Edu.*, 60, 900-905.
- [4] Hendrikx, Y., Charvolin, J., Rawiso, M., Liebert, L. and Holmes, M.C., 1983, Anisotropic aggregates of amphiphilic molecules in lyotropic nematic phases, *J. Phys. Chem.*, 87, 3991-3999.
- [5] Forrest, B.J. and Reeves, L.W., 1981, New lyotropic liquid crystals composed of finite nonspherical micelles, *Chem. Rev.*, 81, 2-14.
- [6] Fisch, M.R., Kumar, S. and Litster, J.D., 1986, Pressure dependence of the nematic-to-isotropic transition in the lyotropic liquid crystal cesium perfluoro-octanoate, *Phys. Rev. Lett.*, 57, 2830-2833.
- [7] Forrest, B.J. and Reeves, L.W., 1980, Micelle motion in lyotropic nematic phases, *Mol. Cryst. Liq. Cryst.*, 58, 233-243.
- [8] Boden, N. and Holmes, M.C., 1984, Lamellar nematic tricritical behavior in lyotropic liquid crystals, *Chem. Rev. Lett.*, 109, 76-80.
- [9] Lawson, K.D. and Flautt, T.J., 1967, Magnetically oriented lyotropic liquid crystalline phases, *J. Am. Chem. Soc.*, 89, 5489-5491.
- [10] Rosevear, F.B., 1968, Liquid crystals- Mesomorphic phases of surfactant compositions, *J. Soc. Cosmet. Chem.*, 19, 581-594.
- [11] Acimis, M. and Reeves, L.W., 1980, A type-II aqueous cholesteric lyomesophase, *Can. J. Chem.*, 58, 1533-1541.
- [12] Radley, K., Reeves, L.W. and Tracey A.S, 1976, Effect of counterion substitution on type and nature of nematic lyotropic phases from nuclear magnetic resonance studies, *J. Phys. Chem.*, 80, 174-182.

- [13] Lee, H. and Labes, M.M., 1984, Helical twisting power of amino-acids in a nematic lyophase, *Mol. Cryst. Liq. Cryst.* 108, 125-132.
- [14] Partyka, J. and Hiltrop, K., 1996, On chirality induction in lyotropic nematic liquid crystals, *Liq. Cryst.* 20, 611-618.
- [15] Dörfler, H.-D., 2002, Chirality, twist and structures of micellar lyotropic cholesteric liquid crystals in comparison to the properties of chiralic thermotropic phases, *Adv. Colloid Interface Sci.*, 98, 285-340.
- [16] Melnik, G. and Saupe, A., 1987, Microscopic textures of micellar cholesteric liquid-crystals, *Mol. Cryst. Liq. Cryst.*, 145, 95-110.
- [17] Acimis, M. and Akpınar, E., 2003, Mass density measurements as a tool to distinguish between micelle size and shape in nematic and chiral nematic phases, *Phys. Chem. Chem. Phys.*, 5, 4197-4203.
- [18] Forrest, B.J., Reeves, L.W. and Vist, M.R., 1981, A type-I aqueous cholesteric lyomesophase, *J. Am. Chem. Soc.*, 103, 690-691.
- [19] Covello, P.S., Forrest, B.J., Marcondes Helene, M.E., Reeves, L.W. and M. Vist, 1983, Type-II DM lyotropic nematics and their derived cholesteric forms, *J. Phys. Chem.*, 87, 176-181.
- [20] Radley, K. and Cattey, H., 1992, Amphiphilic cholesteric liquid crystals prepared from the quaternary ammonium surfactant S-(-)-1-hexadecyl-1-methyl-2-pyrrolidinemethanol bromide, *Liq. Cryst.*, 12, 875-878.
- [21] Lasic, D.D., Helene, M.E.M. and Reeves, L.W., 1983, Cholesteric Type-II micellar mesophases prepared from 2 different single center chiral amphiphiles, *Can. J. Chem.*, 61, 1921-1923.
- [22] Galerne, Y., Neto Figueiredo, A.M. and Liebert, L., 1987, Microscopical structure of the uniaxial and biaxial lyotropic nematics, *J. Phys. Chem.*, 87, 1851-1855.
- [23] Neto Figueiredo A.M., Levelut A.M., Liebert L. and Galerne Y., 1985, Biaxial nNematic lLyomesophase studied by x-ray diffraction, *Mol. Cryst. Liq. Cryst.*, 129, 191-198.
- [24] Helene Marcondes, M.E. and Neto Figueiredo, A.M., 1988, Topology of a surface of the phase diagram of the cholesteric lyotropic mesophase: potassium laurate/1-decanol/water/l-N-lauroyl potassium alaninate, *Mol. Cryst. Liq. Cryst.*, 162B, 127-138.
- [25] Neto Figueiredo, A.M. and Helene Marcondes, M.E., 1987, Phase diagram of the cholesteric lyotropic mesophase potassium laurate-n-decanol-water-d2-brucine sulfate ferrofluid, *J. Phys. Chem.*, 91, 1466-1469.

- [26] Lopes Valente, M.C. and Neto Figueiredo, A.M., 1988, Influence of the microscopic shape anisotropy of the micelles on the pitch in a cholesteric lyotropic liquid crystal, *Phys. Rev. A.*, 38, 1101-1104.
- [27] Radley, K. and Saupe, A., 1978, Cholesteric states of micellar solutions, *Mol. Phys.*, 35, 1405-1412.
- [28] Goossens, W.J.A., 1970, A molecular theory of the cholesteric phase, *Phys. Lett.*, 31A, 413-414.
- [29] Pape, M. and Hiltrop, K., 1997, Influence of lyotropic nematic host phases on the twisting power of chiral dopants, *Mol. Cryst. Liq. Cryst.*, 307, 155-173.
- [30] Radley, K. and Lilly, G. J., 1993, Potassium salts of acylated amino acids as chiral dopants and hosts in the formation of amphiphilic cholesteric liquid crystals, *Liq. Cryst.*, 231, 183-190.
- [31] Radley, K., McLay, N. and Lilly, G. J., 1996, Trans-cis diastereorotamerization in amphiphilic cholesteric liquid crystals, *J. Phys. Chem.*, 100, 12414-12417.
- [32] Tracey, A.S. and Radley, K., 1985, Cholesteric behaviour in lyotropic liquid crystals, *Mol. Cryst. Liq. Cryst.*, 122, 77-87.
- [33] Radley, K. and Tracey, A.S., 1985, A laser diffraction and nuclear magnetic-resonance investigation of the cholesteric potassium N-dodecanoylalaninate mesophase system, *Can. J. Chem.*, 63, 95-99.
- [34] Mizuno, Y., Miyagawa, Y., Lida, M., Tada, Y. and Yokoyama, H., 1998, Effects of tripositive cobalt(III)-complex ions on the structure of a cholesteric mesophase composed of potassium N-dodecanoyl-L-alaninate, *Langmuir*, 14, 7058-7064.
- [35] Radley, K., 1992, A laser diffraction study of amphiphilic cholesteric liquid crystals prepared from potassium dodecanoyl L-serinate, *Liq. Cryst.*, 11, 753-760.
- [36] Tracey Alan S. and Zhang X., 1992, Investigation into the mechanism for generation of the helical axis in cholesteric lyotropic liquid crystals, *J. Phys. Chem.*, 96, 3889-3894.
- [37] Chandresakkar, S., 1992, Liquid Crystals, 2nd Ed., *Cambridge University Press*, Ch. 1, p.1.
- [38] de Jeu, W. H. 1980, Physical Properties of Liquid Crystalline Materials, *Gordon and Breach Science Publishers Ltd.*, Ch. 1, p.1.
- [39] Reinitzer, F., 1888, Beiträge zur Kenntniss des Cholesterins, *Monatsch. Chem.*, 9, 421.

- [40] Lehmann, O., 1889, Über fließende Krystalle, *Z. Physikal. Chem.* 4, 462.
- [41] Hiltrop, K., 1994, Topics in Physical Chemistry, Editor: H. Stegemeyer, Germany, Ch. 4, p. 143.
- [42] Chistyakov, I.G., 1975, Advances in Liquid Crystals ed. G. H. Brown, *Academic*, N.Y.
- [43] de Gennes, P. G., 1975, The Physics of Liquid Crystals, *Clarendon Press*, Oxford.
- [44] Knisely, W. N. and Keyes, P. H., 1986, High-pressure study of a reentrant isotropic phase, *Phys. Rev. A*, 34, 717-718.
- [45] Neto Figueiredo, A.M., 1992, The physics of lyotropic nematic liquid crystals, *Braz. J. Phys.*, 22, 85-91.
- [46] Khetrapal, C. et. al., 1975, NMR Studies in Lyotropic Liquid Crystals, *Springer-Verlag Berlin*, Ch. 1, pp. 3.
- [47] Luzzati, V., Tardieu, A., Gulik-Krzywicki, T., Rivas, E. and Reiss-Husson, F., 1968, Structure of cubic phases of lipid-water systems, *Nature*, 220, 485-488.
- [48] Luzzati, V., Mustacchi, H., Skoulios, A.E., Husson, F., 1960, La structure des colloïdes d'association. I. Les phases liquide-cristallines des systèmes amphiphile-eau., *Acta Cryst.* 13, 660-667.
- [49] Acımiş, M., 1989, Formation of micellar nematic phases from surfactants and aqueous ortho-phosphoric acid, *Liq. Cryst.*, 4, 697-706.
- [50] Boden, N., Radley, K. and Holmes, M.C., 1981, On the relationship between the micellar structure and the diamagnetic anisotropy of amphiphilic nematic mesophases, *Mol. Phys.*, 42, 493-496.
- [51] Yu, L.J. and Saupe, A., 1980, Observation of a biaxial nematic phase in potassium laurate-1-decanol-water mixtures, *Phys. Rev. Lett.*, 45, 1000-1004.
- [52] Hendrikx Y. and Charvolin J., 1981, Structural relations between lyotropic phases in the vicinity of the nematic phases, *J. Physique*, 42, 1427-1440.
- [53] Amaral, L.Q., Helene, M.E.M., Bittencourt, D.R. and Itri, R., 1987, New nematic lyomesophase of sodium dodecyl sulfate, *J. Phys. Chem.*, 91, 5949-5953.

- [54] Oliveira, E.A., Liebert, L. and Neto Figueiredo, A.M., 1989, A new soap/detergent/water lyotropic liquid crystal with a biaxial nematic phase, *Liq. Cryst.*, 5, 1669-1675.
- [55] Osipov, M.A., 1988, Theory for cholesteric ordering in lyotropic liquid crystals, *Il Nuovo Cimento D*, 10, 1249-1262.
- [56] Ferrarini, A, Gottarelli, E., Nordio, P.L. and Spada, G.P., 1999, Determination of absolute configuration of helicenes and related biaryls from calculation of helical twisting powers by the surface chirality model, *J. Chem. Soc. Perkin Trans. 2*, 3, 411-417.
- [57] Kuball, H.-G. and Türk, O., 1999, Helical twisting power and circular dichroism as chirality observations - Development of a sector rule for the intermolecular chirality transfer in a liquid crystal phase, *Polish. J. Chem.*, 73, 209-228.
- [58] Alcantara, M. R. and Vanin, J. A., 1984, Optical sign determinations on cholesteric lyotropic mesophases, *Mol. Cryst. Liq. Cryst.*, 107, 333-340.
- [59] de Genes, P.G. and Prost, J., 1993, in *The Physics of Liquid Crystals*, 2nd Ed., Oxford University Press, Oxford, Ch. 6.
- [60] Solladie, G. and Zimmermann, R. G., 1984, Liquid crystals: A tool for studies on chirality, *Angew. Chem. Int. Ed. Eng.*, 23, 348-362.
- [61] Gottarelli, G. and Spada, G. P., 1985, Induced cholesteric mesophases-origin and application, *Mol. Cryst. Liq. Cryst.*, 123, 377-388.
- [62] Hiltrop, K., 2001, Chirality in Liquid Crystals (Partially ordered systems), H.-S. Kitzerow and C. Bahr (Eds.), *Springer-Verlag*, New York, 2001, Ch. 14, p. 447.
- [63] Neto Figueiredo, A.M., Liebert, L. and Levelut, A.M., 1984, Study of ferrocholesteric discotic and calamitic lyotropics by optical microscopy and x-ray diffraction, *J. Physique*, 45, 1505-1512.
- [64] de Jeu, W. H., 1980, Physical Properties of Liquid Crystalline Materials, *Gordon and Breach Science Publishers Ltd.*, Ch. 4, pp.34.
- [65] Demus, D., Goodby, J., Gray, G.W., Spiess, H.-W. and Vill, V., 1998, "Handbook of Liquid Crystals", vol. 1, Fundamentals, *Wiley-VCH*, Germany, p. 217.
- [66] Davidson, P., Bourgaux, C., Sergot, P. and Livage, J., 1997, A small-angle x-ray scattering study of the lyotropic nematic phase of vanadium pentoxide gels, *J. Appl. Cryst.*, 30, 727-732.

- [67] Iampietro, D.J., Brasher, L.B. and Kaler, E.W., 1998, Direct analysis of SANS and SAXS measurements of catanionic surfactant mixtures by fourier transformation, *J. Phys. Chem. B*, 102, 3105-3113.
- [68] Bernhard, H., Pilz, I., Meisenberger, O., Witters, R. and Lontie, R., 1983, A small-angle x-ray scattering study of the quaternary structure of the 24-s component of the hemocyanins of homarus vulgaris and cancer, *Biochim. Biophys. Acta*, 748, 28-33.
- [69] Freiburger, N. and Glatter, O., 2006, Small-angle scattering from hexagonal liquid crystals, *J. Phys. Chem. B*, 110, 14719-14727.
- [70] Glassel, S., 2009, Diplomarbeit, Röntgenkleinwinkelstreuung an induzierten cholesterischen Phasen lyotroper Flüssigkristalle.
- [71] Bragg, W.L., 1913, The structure of some crystals as indicated by their diffraction of x-rays, *Proceedings of the Royal Soc. of London Series A*, 89, 248-277.
- [72] Giesselmann, F., Germer, R. and Saipa, A., 2005, Orientational order in smectic liquid-crystalline phases of amphiphilic diols, *J. Chem. Phys.*, 123, Article number: 34906, 1-6.
- [73] Charvolin, J., Levelut, A.M., Samulski, E.T., 1979, Lyotropic nematics: molecular aggregation and susceptibilities, *J. Physique*, 40, 587-592.
- [74] Tohyama, K., 1974, The pitch-independent critical field in cholesteric liquid crystalline poly- γ -ethyl-L-glutamate, *J. Phys. C: Solid State Phys.*, 7, 270-273.
- [75] Haiyang, Y., Pingping, Z., Feng, R., Yuanyuan, W. and Tiao, Z., 2000, Viscometric investigations on the intermolecular interactions between poly(methyl methacrylate) and poly(vinyl acetate) in various solvents, *Eur. Poly. J.*, 36, 21-26.
- [76] Duan, M., Ren, D. and Hu, X., 2005, Study of the interactions between hydrophobically modified polyacrylamide and poly(N-isopropylacrylamide) in water by polymer solvent method, *Poly. Bull.*, 54, 101-107.
- [77] Jukic, A., Rogosic, M. and Janovic, Z., 2006, Miscibility and interactions of polystyrene/polyolefine and polystyrene/poly(n-alkyl methacrylate) mixtures in dilute xylene solutions, 2006, *Eur. Poly. J.*, 42, 1105-1112.
- [78] Abe, F., Einaga, Y. and Yamakawa, H., 1991, Intrinsic viscosity of oligo- and polyisobutylenes. Treatments of negative intrinsic viscosities, *Macromolecules*, 24, 4423-4428.

- [79] Abdel-Azim, A., Atta, A.M., Farahat, M.S. and Boutros, W.Y., 1998, Determination of intrinsic viscosity of polymeric compounds through a single specific viscosity measurement, *Polymer*, 39, 6827-6833.
- [80] Pingping, Z., Haiyang, Y. and Yiming, Z., 1999, Viscosity behavior of incompatible poly(vinyl chloride) (PVC)/polystyrene (PS) blends in various solvents, *Eur. Poly. J.*, 35, 915-921.
- [81] Mehrotra, K.N., Mehta, V.P. and Nagar, T.N., 1970, Determination of critical micelle concentration of copper soaps in non-aqueous solvents, *J. Prakt. Chem.*, 312, 545-553.
- [82] Borse, M.S. and Devi, S., 2004, Dependence of aggregation behavior and physicochemical properties of bis-cationic surfactants on the polarity of surfactant head group, *Colloid and Surf. A.*, 245, 1-8.
- [83] Lopez-Fontan, J.L., Sarmiento, F. and Schulz, P.C., 2005, The aggregation of sodium perfluorooctanoate in water, *Colloid Polym. Sci.*, 283, 862-871.
- [84] Messina, P., Morini, M.A. and Schulz, P.C., 2003, The hydration of sodium dehydrocholate micelles, *Colloid Polym. Sci.*, 281, 695-698.
- [85] Borse, M., Sharma, V., Aswal, V.K., Goyal, P.S. and Devi, S., 2005, Effect of head group polarity and spacer chain length on the aggregation properties of Gemini surfactants in an aquatic environment, *J. Colloid Interface Sci.*, 284, 282-288.
- [86] Mata, J., Varade, D. and Bahadur, P., 2005, Aggregation behavior of quaternary salt based cationic surfactants, *Thermochim. Acta*, 428, 147-155.
- [87] Ono, Y., Kawasaki, H., Annaka, M. and Maeda, H., 2005, Effects of micelle-to-vesicle transitions on the degree of counterion binding, *J. Colloid and Interface Sci.*, 287, 685-693.
- [88] Gracia, C.A., Gomez-Barreiro, S., Gonzalez-Perez, A., Nimo, J. and Rodriguez, J.R., 2004, Static and dynamic light-scattering studies on micellar solutions of alkyldimethylbenzylammonium chlorides, *J. Colloid and Interface Sci.*, 276, 408-413.
- [89] Varade, D., Joshi, T., Aswal, V.K., Goyal, P.S., Hassan, P.A. and Bahadur, P., 2005, Effect of salt on the micelles of cetyl pyridinium chloride, *Colloid and Surf. A.*, 259, 95-101.
- [90] Huggins, M.L., 1942, The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration, *Chem. Soc.*, 64, 2716-2718.

- [91] Aveyard, R., Binks, B.P. and Fletcher, P.D.I., 1989, Interfacial tensions and aggregate structure in C₁₂E₅/oil/water microemulsion systems, *Langmuir*, 5, 1210-1217.
- [92] Kawai-Hirai, R., Matsumoto, Y., Hakoda, M. and Oya, M., 1997, Interparticle interaction in aerosol-OT microemulsion system studied by dynamic light scattering and viscosity, *Progr. Colloid Polym. Sci.*, 106, 79-82.
- [93] Ma, X. and Pawlik, M., 2007, Intrinsic viscosities and Huggins constants of guar gum in alkali metal chloride solutions, *Carbohydr. Polym.*, 70, 15-24.
- [94] Jungermann, E., Gerecht, J.F. and Krems, I.J., 1956, The preparation of long chain N-acylamino acids, *J. Am. Chem. Soc.*, 78, 172-174.
- [95] Silverstein, R.M., F. X. Webster and D. J. Kiemle, 2005, Spectroscopic Identification of Organic Compounds, 7th Ed., Ch. 2, p. 72.
- [96] Neto Figueiredo, A.M. and Salinas, S.R.A., 2005, The physics of lyotropic liquid crystals: phase transitions and structural properties, *Oxford University Press*, Great Clarendon Street, Greta Britain, pp. 29-30.
- [97] Acimis, M., Agar, A. and Gok, A., 1998, Comparison of the pitch induced from lamellar and nematic regions in some lyotropic liquid crystal systems, *Liq. Cryst.*, 24, 369-373.
- [98] Goozner, R.E. and Labes, M.M., 1985, Lyotropic Liquid Crystals of D-(2)-Octylammonium Chloride, *Mol. Cryst. Liq. Cryst.*, 116, 309-317.
- [99] Acimis, M., Dorr, E. and Kuball, H.-G., 1994, Chiral induction of micellar cholesterics from lamellar phases, *Liq. Cryst.*, 17, 299-302.
- [100] Radley, K. and Lilly, G.J., 1997, A D-2-NMR investigation of deuterated chiral dopants in amphiphilic cholesteric liquid crystals, *Langmuir*, 13, 3575-3578.
- [101] Gibson, H.W, 1979, In liquid crystals-The fourth state of matter; Saeva, F.D., Ed., *Dekker*; New York, p. 113.
- [102] Kuball, H.-G., Brüning, H., Müller, Th., Türk, O. and Schönhofer, A., 1995, Helical twisting power of chiral mono- and bis-aminoanthraquinones, *J. Mater. Chem.*, 5, 2167-2174.
- [103] Kuball H.-G., Brüning, H., Müller, Th. and Schönhofer, A., 1995, Chiral induction by optically active aminoanthraquinones in nematic phases, *Mol. Cryst. Liq. Cryst.*, 261, 205-216.

- [104] Kuball H.-G., Müller, Th. and Weyland, H.-G., 1992, Induced cholesteric phases of chiral aminoanthraquinones, *Mol. Cryst. Liq. Cryst.*, 215, 271-278.
- [105] Kuball, H.-G. and Brüning, H., 1997, Helical twisting power and circular dichroism as chirality observations: The intramolecular and intermolecular chirality transfer, *Chirality*, 9, 407-423.
- [106] Holmes, M.C., Leaver, M.S. and Smith A.M., 1995, Nematic and disrupted lamellar phases in cesium pentadecafluorooctanoate/²H₂O: A small angle scattering study, *Langmuir*, 11, 356-365.
- [107] Rodriguez, C., Sakai, T., Fujiyama, R. and Kunieda, H., 2004, Phase diagrams and microstructure of aggregates in mixed ionic surfactant/foam booster systems, *J. Colloid Interface Sci.*, 270, 483-489.
- [108] Photinos, P. and Saupe, A., 1989, Measurements of density and expansion coefficient for the nematic, lamellar smectic and isotropic phase of micellar systems, *J. Phys. Chem.*, 90, 5011-5015.
- [109] Tanford, C., 1972, Micelle shape and size, 76, 3020-3024.
- [110] Leaver, M.S. Holmes, and M.C., 1993, A small angle neutron scattering study of the lamellar and nematic phases of caesium pentadecafluoro-octanoate (CsPFO)/²H₂O and CsPFO/CsCl/²H₂O, *J. Phys. II*, France, 3, 105-120.
- [111] Gelbart, W.M., Ben-Shaul, A., McMullen, W.E. and Masters, A., 1984, Micellar growth due to interaggregate interactions, *J. Phys. Chem.*, 88, 861-866.
- [112] Holmes, M.C. and Reynolds, D.J., 1987, On the nature of interaggregate interactions in lyotropic liquid crystalline phases, *Mol. Cryst. Liq. Cryst.*, 146, 377-384.
- [113] Tracey, A.S. and Radley, K., 1984, Effects of composition on cholesteric behavior in the lyotropic mesophase system of potassium N-dodecanoyl-L-alaninate, *J. Phys. Chem.*, 88, 6044-6048.
- [114] Yarovoy, Y.K. and Labes, M.M., 1997, Effect of chiral polymers on lyotropic liquid crystals, *J. Am. Chem. Soc.*, 119, 12109-12113.
- [115] Gottarelli, G., Mariani, P., Spada, G.P., Samori, B., Forni, A., Solladie, G. and Hibert, M., 1983, Induction of cholesteric mesophases in nematic liquid crystals, and correlation of absolute configurations of some chiral oxiranes and thiiranes, *Tetrahedron*, 39, 1337-1344.

- [116] Gottarelli, G., Hibert, M., Samori, B., Solladie, G., Spada, G.P. and Zimmermann, R., 1983, Induction of the cholesteric mesophase in nematic liquid crystals: mechanism and application to the determination of bridged biaryl configurations, *J. Am. Chem. Soc.*, 105, 7318-7321.
- [117] Spada, G.P., Gottarelli, G., Samori, B., Bustamante, C.J. and Wells, K.S., 1988, A study of some lyotropic cholesteric mesophases by circular and linear dichroism and by circular intensity differential scattering, *Liq. Cryst.*, 3, 101-113.
- [118] Ferrarini, A. and Nordio, P.L., 1992, Diffusion models for the dynamics of flexible molecules, *J. Chem. Soc. Faraday Trans.*, 88, 1733-1746.
- [119] Ferrarini, A., Moro, G.J., Nordio, P.L. and Luckhurst, G.R., 1992, A shape model for molecular ordering in nematics, *Mol. Phys.*, 77, 1-15.
- [120] Ferrarini, A., Luckhurst, G.J., Nordio, P.L. and Roskilly, S.J., 1994, Prediction of the translational properties of liquid crystal dimers. A molecular field calculation based on the surface tensor parametrization, *J. Chem. Phys.*, 100, 1460-1469.
- [121] Ferrarini, A., Moro, G.J. and Nordio, P.L., 1995, A shape model for the twisting power of chiral solutes in nematics, *Liq. Cryst.*, 19, 397-399.
- [122] Ferrarini, A., Moro, G.J. and Nordio, P.L., 1996, Shape model for ordering properties of molecular dopants inducing chiral mesophases, *Mol. Phys.*, 87, 485-499.
- [123] Ferrarini, A., Moro, G.J. and Nordio, P.L., 1996, Simple molecular model for induced cholesteric phases, *Phys. Rev. E.*, 53, 681-688.
- [124] Ferrarini, A. and Nordio, P.L., 1998, On the assessment of molecular chirality, *J. Chem. Soc. Perkin Trans.*, 2, 455-460.
- [125] Pieraccini, S., Ferrarini, A. and Spada, G.P., 2008, Review article: Chiral doping of nematic phases and its application to the determination of absolute configuration, *Chirality*, 20, 749-759.
- [126] Berardi, R., Kuball, H.-G., Memmer, R. and Zannoni, C., 1998, Chiral induction in nematics: A computer simulation study, *J. Chem. Soc. Faraday Trans.*, 94, 1229-1234.
- [127] Yoneya, M. and Yokoyama, H., 2001, Chirality induction from chiral molecules to adsorbed monolayers, *J. Chem. Phys.*, 114, 9532-9538.
- [128] Dörfler, H.-D. and Göpfert, A., 2000, Comparison of structures and properties of lyotropic cholesteric phases induced by center and axial chiral compounds, *Colloid Polym. Sci.*, 278-1085-1096.

- [129] Dörfler, H.-D. and Görgens, C., 2000, X-ray structural studies of lyotropic cholesteric phases induced by adding cholesterol in the quaternary system hexadecyl dimethyl ammonium bromide/water/n-decanol/cholesterol, *Tenside Surf. Det.*, 37, 310-317.

CURRICULUM VITAE

Erol AKPINAR

Abant İzzet Baysal University
Department of Chemistry Golkoy Campus
14280 Bolu-TURKEY
Tel:+90 374 254 10 00 – 1256
akpinar_e@ibu.edu.tr

Personal Information

Place of Date and Birth: 09.02.1977, Susehri/SİVAS

Marital Status : Married

Foreign Languages : English- Writing, Speaking, Reading-Good

Nationality : TR

Computer : MS Office Applications, MS Operating Systems,
Chem - Office Ultra, SigmaPlot and GraphPad
Prism

Education

2003-2010 Abant İzzet Baysal University Faculty of Sciences
Department of Chemistry-PhD (English)

1999-2003 Abant İzzet Baysal University Faculty of Sciences Department
of Chemistry-MSc Degree (English).

1995-1999 Abant İzzet Baysal University Faculty of Sciences Department of Chemistry-BSc Degree.

1991-1995 İstanbul Çapa Anatolian Teacher High School

Experience

- Visiting Researcher – Institute of Physical Chemistry, University of Stuttgart, July-October, 2009.
- Visiting Researcher as an ERASMUS Student – Institute of Physical Chemistry, University of Stuttgart, February-September, 2008.
- Researcher-Department of Chemistry-AIBU-Bolu-Turkey -1999-...

Research interests

- Lyotropic liquid crystals
- Phase chirality in lyotropic liquid crystals
- Determination of the structural differences between nematic and chiral nematic phases
- Isotropic micellar solutions

Communications to scientific meetings

- 23rd International Liquid Crystal Conference, Jagiellonian University, Krakow, Poland, 11th-16th July **2010**.
- 24th National Chemistry Congress, Karaelmas University, Zonguldak, TURKEY, 29th June-2nd July **2010**.
- 23rd Conference of the European Colloid and Interface Society, Yeditepe University, Antalya, TURKEY, 06th-11th September **2009**.
- 21st National Chemistry Congress, İnönü University, Malatya, TURKEY, 23rd-27th August **2007**.
- 18th National Chemistry Congress, Kafkas University, Kars, TURKEY, 05th-09th July **2004**.
- 1st Aegean Physical Chemistry Days, Aegean University, Faculty of Science, Izmir, TURKEY, 05th-07th June **2002**.

- Chemical Physics IV, Osmangazi University, Eskisehir, TURKEY, 28th-29th September **2000**.

Publications

- M. Acımiş and **E. Akpınar**, 2003, “Mass density measurements as a tool to distinguish between micelle size and shape in nematic and chiral nematic phases”, Phys.Chem.Chem.Phys., 5, 4197-4203.
- **E. Akpınar**, M. Acımiş and Ç.Ocak, 2001, “Strange mass density behaviour of a micellar chiral nematic phase composed of an amphiphilic racemic mixture and its L-enantiomer”, Phys.Chem.Chem.Phys., 3, 645-646.
- Ç. Ocak, M. Acımiş, **E.Akpınar** and A. Gök, 2000, “Effects of salts and structure of chiral dopants on the induced pitch from micellar nematic phases” Phys.Chem.Chem.Phys., 2, 5703-5707.