To the Graduate Council:

I am submitting herewith a thesis written by Laila M. Emarah entitled "The Study of Liquid Crystalline Phases as an Experimental Procedure for Chemistry Education." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Science Education.

A. Paul Wishart

A. Paul Wishart, Major Professor

We have read this thesis and recommend its acceptance:

Alexander Van Hook

W C Murphy

Accepted for the Council:

L Evans Roth

Vice Chancellor
Graduate Studies and Research

THE STUDY OF LIQUID CRYSTALLINE PHASES AS AN EXPERIMENTAL PROCEDURE FOR CHEMISTRY EDUCATION

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Laila M. Emarah

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Special gratitude is expressed to the writer's husband, Abdel Razek, and her three children, Nermean, Margie, Ahmad, and to her mother, Neffesah, for their assistance, understanding, and cooperation throughout the study.

ABSTRACT

The present study was an attempt to introduce an advanced subject in chemistry, liquid crystals, in a simple form which could be suitable for chemistry education in college. Liquid crystals have found a variety of applications in chemistry, physics and biology yet they are rarely, if at all, included in courses taught at the undergraduate or graduate levels.

The present study was concerned with phase behavior and phase formation in mixtures of dodecyl amine ($-NH_2$/$-ND_2$)/water and/or deuterium (D_2O). After preparation the mixtures were heated until homogeneous solutions were obtained. Drops from these homogeneous solutions were placed on ordinary glass slides then covered by thin glass microscope cover slips. Slides of human nerve tissue and ovary tissue were obtained from The University of Tennessee Center for the Health Sciences. Dodecyl amine samples and tissue samples were studied using a Nikon polarizing microscope fitted with a 35mm camera. A thin hot plate fixed to the microscope stage was used to heat the samples so that the effect of temperature on the phase formation could be studied.

The dodecyl amine (Aldrich 98%) used during the course of this study was recrystallized twice from acetonitrile and then fractionally distilled two times in a rotating band column at 135°C and 15 torr. The melting point of the purified amine was found to be 28.3°C which is in good agreement with the most recent published data. The deuterated amine was prepared by mixing molten protio amine with an excess of D_2O for several hours. The melting point of the deuterated amine was found to be 29.1°C.

The results of these investigations were presented in the form of colored photomicrographs. The effect of concentration variation on phase behavior in dodecyl amine ($-NH_2$/$-ND_2$)/water and/or D_2O mixtures was studied in detail. Also the effect of temperature on the phase behavior in the previously mentioned mixtures was qualitatively studied. A comparison between the structural appearance of the nerve tissue samples, ovary samples and dodecyl amine mixtures was conducted.

The results indicated the existence of two new liquid crystal phases which had not been reported in the literature. The first was a "three-dimensional hexagonal crystal" "A" phase. This phase was anisotropic and composed of single crystals which had a layer arrangement parallel to each other. The results showed that this phase was stable at room temperature, over a period of eighteen months. The second phase was a two-dimensional octagonal "pre-M_1" or "B" phase. This phase was anisotropic and composed of octagonal micelles which possessed a core. It was found that this "B" phase was similar to "A" phase regarding its polarizing ability.

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CHAPTER I

INTRODUCTION

The study of phase relations in dodecyl amine ($-NH_2$/$-ND_2$)/water (H_2O/D_2O) system displays a number of different amphiphilic liquid crystal phases. These liquid crystal phases when studied under a polarizing microscope can be used as an experimental approach to chemistry education on the college level.

Purpose of the Study

The present experimental research represents an attempt to introduce an advanced subject in chemistry, liquid crystals, in a simple form which can be suitable for chemistry education in college. The subject to be introduced, liquid crystals, is rarely, if at all, taught on undergraduate or even graduate levels. One of the main objectives of studying liquid crystals as a subject is to enhance the learner's ability to think logically about what is going to occur and also to draw conclusions which could be generalized in other situations. In addition, some new chemical concepts can be presented to the learner at a time when he/she could visually see examples of liquid crystalline phases and their special characteristics.

Importance of the Study

Liquid crystals have found a variety of applications in chemistry, physics (scintillation detectors), medical science, biology and biochemistry (lipids and phospholipids). The properties of liquid crystals have been studied by using techniques and instrumentation which vary in complexity from a simple test tube to electron microscope and x-ray diffraction, etc. The present study is a simple experiment which could be completed in a relatively short time period and could fulfill most of the requirements for an attractive, stimulating and educative tool. It could also help in the process of building mental structures among students toward the process of intellectual development. Moreover, the ease of handling, preparation and measuring, together with the simplicity of instrumentation is expected to attract more students toward chemistry, in particular, and science, in general, which is the first step in the direction toward the production of more scientifically educated people.

Definition of Terms

The following definitions were formulated for the purpose of this study:

Phase. Phase is a name given to any homogeneous and physically distinguishable portion of a system having definite boundaries. In chemistry, the phases could be solid, liquid or gaseous or liquid crystalline.

Liquid crystal. When certain solid organic compounds or solutions are heated, they do not pass directly into the liquid state, but first adopt a state which has properties intermediate between those of a true crystal and those of a true liquid. Thus on reaching a certain temperature, the solid undergoes transformation into a turbid phase which is both birefringent and fluid, the consistency varying in different cases from that of a paste to that of a freely flowing liquid. At a higher temperature, this phase "melts" to form a clear isotropic liquid of normal type. On cooling these changes take place in the reverse order, though some supercooling may occur when the transition temperatures are reached, as in the case of ordinary crystallization (Hartshorne, 1970).

Amphiphilic compounds. These compounds have molecules possessing a polar group which tends to be soluble in water (hydrophilic) and insoluble in hydrocarbons (lipophobic), while the rest of the molecule tends to be insoluble in water (hydrophobic) and soluble in hydrocarbons (lipophilic). Because of this dual character such compounds are called amphiphiles.

Smectic phases. Smectic phases are those molecules which are arranged in layers with their long axis normal to the planes of the layers.

Nematic mesophases. The term "nematic" means threadlike and is used because of the mobile threadlike lines which are observed in nematic phases which have been prepared by rapid cooling of the melt. The properties of nematic phases indicated that the molecules are approximately parallel to one another, but that they are not in layers.

Myelin. The myelin sheath is acquired a short distance from the cell body. The proximal portion of the axon is as a rule unmyelinated. The sheath is of varying thickness and is composed of a semifluid, doubly refracting substance known as myelin. Electron microscopy studies, however, have revealed that myelin was formed primarily by a double layered infolding of the Schwann cell membrane, which became wrapped spirally around the axon in a few or many concentric layers (Truex, 1969).

Summary

This chapter discussed the purpose and importance of the study as well as the definition of some of the terms used.

CHAPTER II

REVIEW OF RELATED LITERATURE

Introduction

Science plays an important role in the nature and development of society. The need for a better understanding of science by the general public as well as students becomes important. The twentieth century is rich with many scientific and technological discoveries. However, there is recent and discouraging news about enrollment trends in science courses. Many students are turning away from science and looking for answers to their problems elsewhere. Apparently, many students are rejecting science without really knowing what it is, or appreciating its importance. Many attempts to explain and correct this phenomenon are described in science teaching literature. A few of these attempts by Anderson (1976) are reported based on his experience as a physics teacher. Anderson made the following observations in an attempt to understand the current loss of interest in science among students.

> Physics at the senior level of elementary school is characterized by an enormous amount of subject matter. In many textbooks, a new concept is being introduced at each fifth or tenth minute interval. For example, one has tried to give a sort of "civic education" in physics by studying through, in a short period, practically all areas of physics as for example, mechanics, optics, electricity ... etc. The very large amount of subject matter works against the conception of the individuals as being self-regulating beings who need time in order to grasp the new subject matter. Also, individuals should have the chance to ponder, try again, discuss, get ideas ... etc.

Concept Development in Science

Coulson (1971) indicated in his discussion about chemistry disciplines that any subject which aims to hold the attention of students must have a fun factor associated with it. The subject must also stimulate and provide intellectual pleasure. Intellectual pleasure can only be sensed by someone who has reached a certain stage of mental as well as intellectual development.

According to Piaget (1964) the building and rebuilding of what he calls "mental structures" is the idea that underlies the process of intellectual development. A central idea in his theory is the concept of mental structure. At the present time, it is not possible to indicate the physiological and chemical nature of these structures. Instead their existence in the brain is hypothesized from observable behavior. These structures represent a tightly organized mental system to guide behavior (Renner, 1973). Piaget (1964) indicated that these mental structures do not come from simply making a mental record of the world. This indication was confirmed by Van Senden (1949) who reported that blind people who gained sight after surgery were unable to identify objects without handling them. Thus the ability to develop understanding requires more than a simple photographing of the environment.

Building of mental structures starts from birth where certain very primary structures are present. The process of development of mental structures is viewed by Piaget as a dynamic interaction of the organism and the environment. It is a process of equilibrium or self-regulation. Factors such as experience, social transmission and maturation play an important role in the process of building mental structures. Those factors were well discussed in detail by Renner and Lawson (1973) and from that article the following brief discussion about those contributing factors was adapted. There are basically two types of experience: physical and logical (mathematical). Physical experience means the actual physical action on objects in the world. At some point during this type of experience the learner begins to see more in his interactions with the world in such a way that this interaction produces some kind of generalization. The authors give an example to illustrate the learner's interactions in which they indicate that individuals in this particular stage will find no difference between counting ten objects from the left or from the right. When a learner reaches this stage he/she will develop the logical (mathematical) experience which enables him/her to operate logically within his/her environment.

The idea of "social transmission" according to Renner (1973) means that a learner has to interact and share viewpoints and thoughts of other people. Social interactions can lead to conflict, debate, and shared ideas. All of these interactions will require that the learner carefully examine his/her present beliefs. Such a process has the potential to change and develop mental structures. The development of mental structures which could result from experience and social transmission would require a period of time to take place. Evidence indicates that these mental structures require varying periods of time for optimum development. The process of developing mental structures is part of the overall process of maturation.

Application to Science Education

After presenting the ways in which intellectual developments could be achieved through the building of mental structures, one has to ask if science education could be one of these ways. The answer to science educators such as Piaget, Renner and others is clearly positive. The support to this answer comes from the knowledge of the learning cycle of science according to Piaget's theory. Exploration, invention and discovery are the three phases of the learning cycle and represent a process which will lead the learner to move from physical action to abstract mental operations.

Chemistry, being an experimental discipline, is well suited to showing that the pursuit of an intellectual discipline can be a very important scientific and chemical study as well as a pleasurable exercise. The beauty of crystal forms and the symmetry of atomic and molecular arrangements provide sources of pleasure to students of all ages. All students enjoy performing or watching chemistry experiments such as the "clock reaction," the "blue bottle" experiment and the ammonium dichromate "volcano" (Coulson, 1971).

Chemistry stands in a central position among the traditional science subjects and its many possible relationships with physics and biology produce interlinking equilibria which can make a significant contribution to a liberal education. In teaching the majority of science courses the laboratory can be used to lead the students through inquiry to develop understanding of the concepts to be learned. Renner and Lawson (1973) give an example using the concept of energy conservation to show the importance of science laboratories. They indicate that a science laboratory can help very much in promoting equilibration and disequilibration among students. When this situation is well utilized, the conceptualization of the discipline can be introduced as a process that will cause equilibrium. According to Piaget's theory this results in the process of building the mental structures in the learner. The utilization of chemistry experiments can thus be used to enhance the process of intellectual development.

A study of liquid crystals is an attempt to introduce an advanced subject in chemistry in a simple form which can be suitable for chemistry education in college. Liquid crystals are rarely taught to the undergraduate or graduate levels. Liquid crystals have found a variety of applications in chemistry, physics (scintillation detectors), and biology (lipids and phospholipids). The properties of liquid crystals have been studied using techniques and instrumentations which vary in complexity from a simple test tube to electron microscopes and x-ray diffraction, magnetic fields and others.

Research Relating to Liquid Crystals

Liquid crystals consist of two, three, or more components, at least one of which possesses typical amphiphilic properties. Another may be regarded as a solvent, for example, water or an organic liquid, and it is the solvent that endows these mesophases with their lyotropic character (Ekwall, 1975).

Amphiphilic compounds are characterized by possessing in the same molecule two groups: (1) a polar group which tends to be soluble in water (hydrophilic) and insoluble in hydrocarbons (lipophobic), (2) a lipophilic group which tends to be soluble in hydrocarbons (lipophilic) and insoluble in water (hydrophobic). Because of this dual character such compounds are called amphiphiles (Hartshorne and Stuart, 1970).

Among the most interesting examples of amphiphiles (see Figure 1) are those in which the two opposing tendencies are strong and fairly equally balanced, since these compounds form mesomorphic phases when they are mixed with water in certain proportions. They include the detergents, soaps, lipids and phospholipids. Although the term "detergent" means cleansing agent and includes soap, it is now commonly used to refer to soap substitutes. Soaps are made by boiling natural fats and oils with strong bases such as sodium or potassium hydroxide.

Typical polar groups in such amphiphiles are -COONa, -COOK, $-SO_3Na$, and $-N(CH_3)_3Br$, which are ionic, and $-N^-N^+\ (CH_3)_3$, the glyceride ester group $-COO\cdot CH_2\cdot CHOH\cdot CH_2OH$, and NH_2 and its substitute $-ND_2$, which are nonionic. Typical lipophilic groups are long-chain paraffin radicals, with or without side groups, e.g., $-(CH_2)_nCH_3$ when "n" is greater than 11. In some compounds the polar group is at the end of a long lipophilic chain, while in others, as in the phospholipids, it connects two such chains.

Winsor (1968) has presented a comprehensive review of the phase relationships and other physico-chemical properties of binary and multi-component solutions of amphiphiles. In that article, emphasis is laid on the formation and structure of liquid crystalline phases.

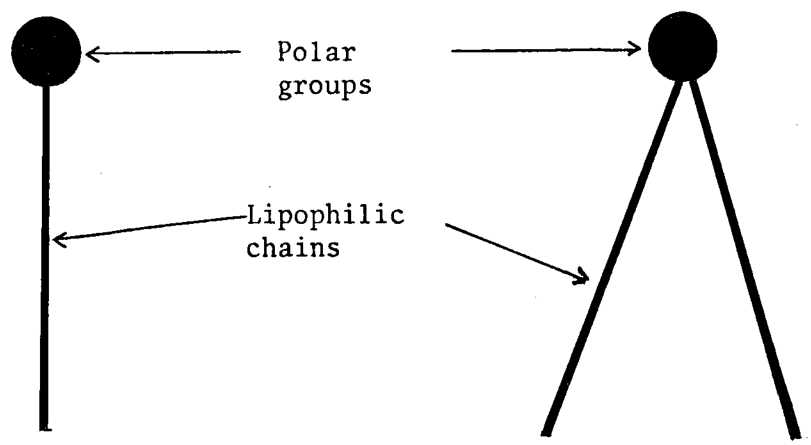


Figure 1. Types of amphiphilic molecules (schematic).

Mesophases in Binary Systems of Amphiphiles and Water

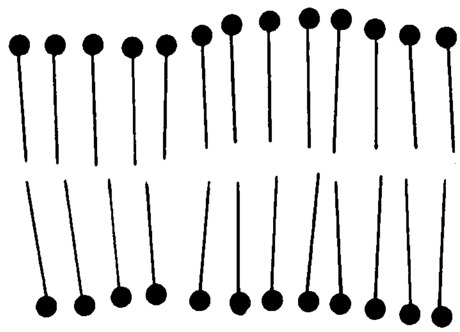
(a) The neat phase or "G" phase or "lamellar." There is general agreement that this is smectic with the amphiphile molecules forming double layers as shown in Figure 2 separated by layers of water. The polar groups are on the outside of the layers in contact with the water (Smectic Mesophases: the word "smectic" (soaplike) is used because the soaps, such as ammonium oleate, form liquid crystals of this type.

(b) The middle or "M_1" phase. This is stable at higher water concentrations than the "G" phase. The amphiphile molecules are grouped into rod-like micelles of indefinite length, which are arranged side by side in a hexagonal pattern, and has been proposed that in each rod the molecules are arranged radically around the major axis with polar groups on the outside, as shown in Figure 3.

(c) The viscous isotropic or "V_1" phase. This appears in some systems at concentrations intermediate between those within which the "G" and "M_1" phases are stable. Its structure is a matter of some doubt and is not one on which ordinary optical observations can give any information beyond showing that it is isotropic.

(d) Inverse phase "V_2" and "M_2." In some systems at concentrations of the amphiphile greater than these at which the "G" phase is stable, and the viscous isotropic phase, "V_2" occurs, the amphiphile is to be succeeded with further increase of concentration by another middle phase, "M_2." The "M_2" phase has been found by Luzzati (1967) as the "M_1" phase, but with the polar groups directed inwards and enclosing a water core as shown in Figure 4 (Hartshorne and Stuart, 1970) and many other phases (Brown, 1975).

Water



Water

Figure 2. Smectic layer in neat phase ("G").

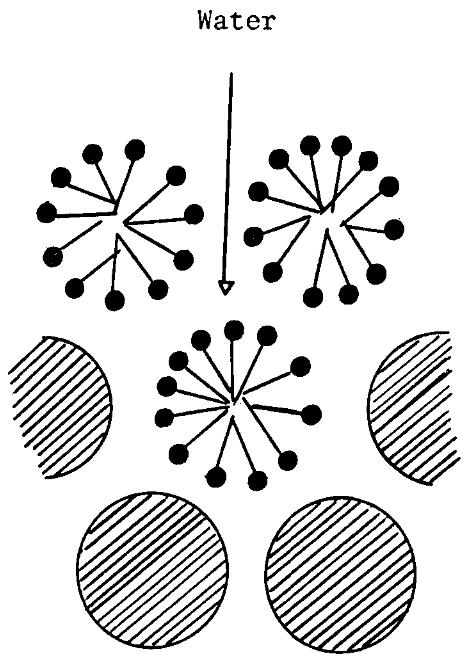


Figure 3. Spherical micelle (diametrical section) of "M_1" phase.

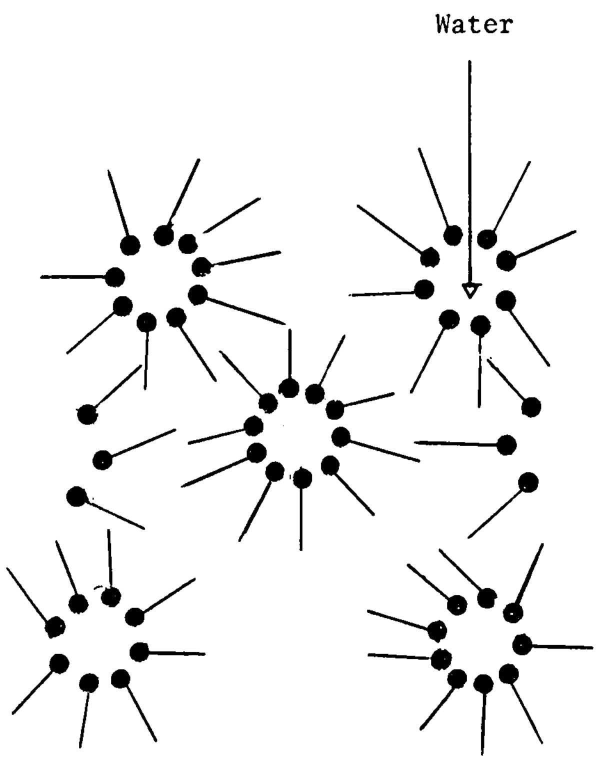


Figure 4. Inverse middle phase ("M_2") showing a cross section of micellar rods.

Importance of Amphiphiles Containing One Amine Group

Amphiphiles containing one amine group (e.g., $CH_3(CH_2)_{11}$-NH_2 and $CH_3(CH_2)_{11}$-ND_2) as the only hydrophil, are especially interesting because this compound dissolves relatively more water than other amphiphiles and forms more than one liquid crystal phase. It is interesting that these different phases have a similarity with observed phases in brain tissue and ovary tissue. The polar group NH_2 (or ND_2) is relatively small as compared to polar groups in other amphiphiles, and the observation that some crystallinity is retained when water penetrates the solid forms layers between polar groups may be connected with the molecular dimensions.

The behavior of binary systems (amphiphiles/water) associated with variations in concentration and temperature is usually studied using:

1. X-ray diffraction measurements (Luzzati, 1966).
2. Electron microscopy (Elbers, 1965 and Balmara, 1967).
3. Polarizing microscope (Ralston, 1942 and Rosevear, 1954 and Lawrence, 1958).
4. Differential scanning calorimetry (Chmielewski and Van Hook 1978).

The study of binary system (dodecylamine(-NH_2/ND_2)/water (H_2O/D_2O)) phase behavior with varying compositions and temperature with a polarizing microscope is the easiest suitable method for college students.

Summary

In the view of Coulson, chemistry is considered as an experimental discipline which is well suited to showing that the pursuit of an intellectual discipline can be a very important scientific study as well as a pleasurable experience of a lasting effect. Coulson also indicated that chemistry stands in a central position among the traditional science subjects and its many possible relationships with physics and biology produce interlinking equilibria which can make a significant contribution to a liberal education. Renner and Lawson indicated that the laboratory can be used to lead the students through inquiry to develop understanding of the concepts to be learned in chemistry.

The investigator found few publications dealing specifically with the present study even though there exists voluminous literature relating to research on liquid crystals.

CHAPTER III

MATERIALS AND METHODS

Materials

The polarizing microscope (Nikon) fitted with a 35mm camera was used. The principle of a typical polarizing microscope is reflected light by the adjustable mirror diffuser, polarizer, substage iris diaphragm, condenser, stage, objective, slot, analyzer, Bertrand lens, pinhole stop and the eyepiece.

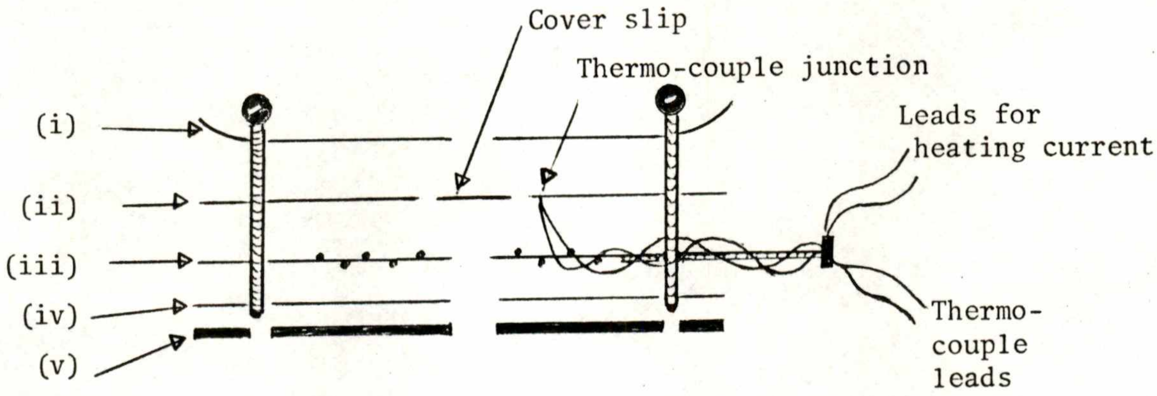
Dodecyl amine ($-NH_2$/$-ND_2$) was prepared in the Chemistry Department at The University of Tennessee, Knoxville, using Chmielewski and Van Hook's method.

Ordinary glass slides and thin glass microscope cover stops were used to cover the samples.

A thin hot stage that was employed is shown in Figure 5 (Hartshorne, 1970).

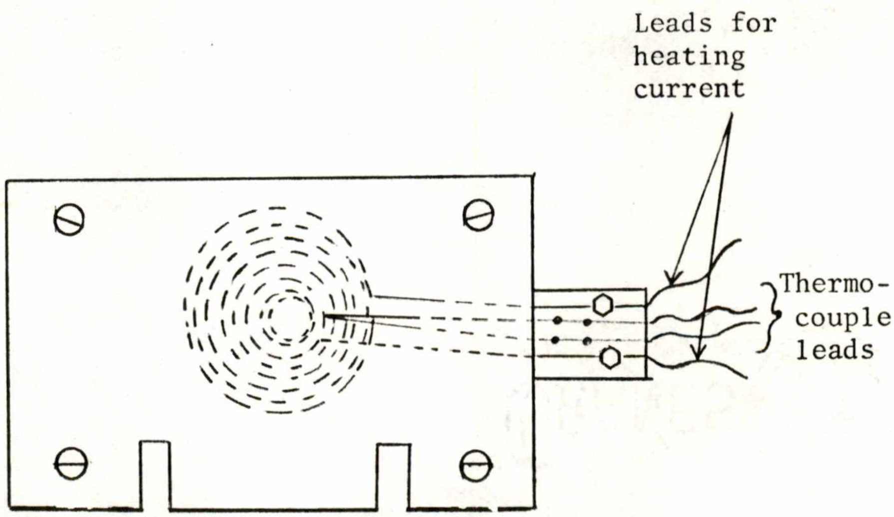
Methods

Aldrich 98% dodecyl amine was recrystallized twice from acetonitrile and then fractionally distilled two times in rotating band column at 135°, 15 torr. The melting point of the purified amine was 28.3° and is in good agreement with the most recent data. The IR spectrum of the purified sample was identical with that tabulated by Sadtler. The deuterated amine was prepared by mixing molten protio amine with an excess of D_2O for several hours. The process was repeated three times and a ratio of total D_2O to amine was 70:1 deuterium of the product



a. Section showing components separated.

(i) Copper plate
(ii) Thin sheet of mica
(iii) Sheet of mica with tongue
(iv) Thin sheet of mica with a 1/4-inch central hole
(v) Sheet of asbestos paper with a 1/4-inch central hole



b. Plan

Figure 5. Simple thin hot stage for heating the sample on the microscope stage.

amine was made by IR using a set of six standard samples of varying H/D ratio, and showed 98% deuteration. The melting point of the deuterate amine was 29.1° (Chmeilewski and Van Hook, 1978).

Three types of samples of varying composition were prepared at room temperature:

1. dodecyl amine-NH_2/H_2O (0%-100%) by weight
2. dodecyl amine-ND_2/D_2O (0%-100%) by weight
3. dodecyl amine-NH_2/half H_2O and half D_2O (0%-100%) by weight

After preparation, the mixtures were heated until homogeneous, placed on ordinary glass slides and covered with thin glass microscope cover slips. Slides containing samples of human nerve tissue were obtained from The University of Tennessee Center for Health Science through Jere Baxter, M.D. These samples were studied with a polarizing microscope (Nikon) fitted with a 35mm camera. The effect of temperature was studied by using a thin hot stage for heating the sample on the microscope stage.

CHAPTER IV

EXPERIMENTAL RESULTS

Results and/or more important observations are shown in Figures 6 through 35. Brief comments concerning the figures are included.

Three-Dimensional Hexagonal Crystal Phase or "A" Phase at Room Temperature

Figures 6-11 show the structure of the single crystal of "A" phase and the characteristics of the single crystals of "A" phase.

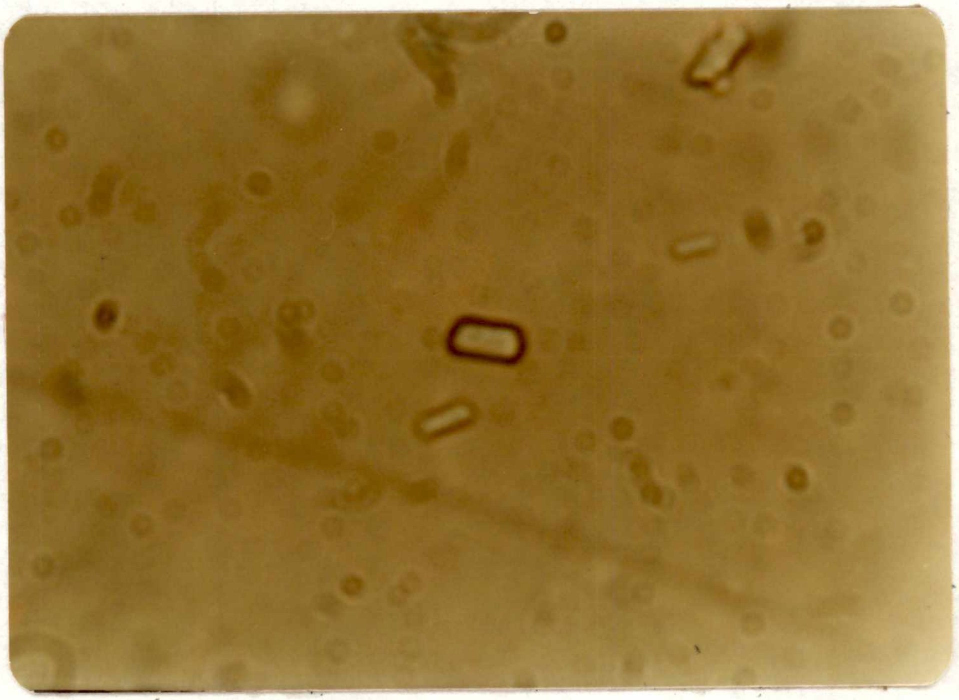


Figure 6. Three-dimensional hexagonal single crystal phase or "A" phase in dodecyl amine $-NH_2$/water system 0% weight water, showing no parallel layer structure. Crossed polars $\leftrightarrow\updownarrow$, x1000.

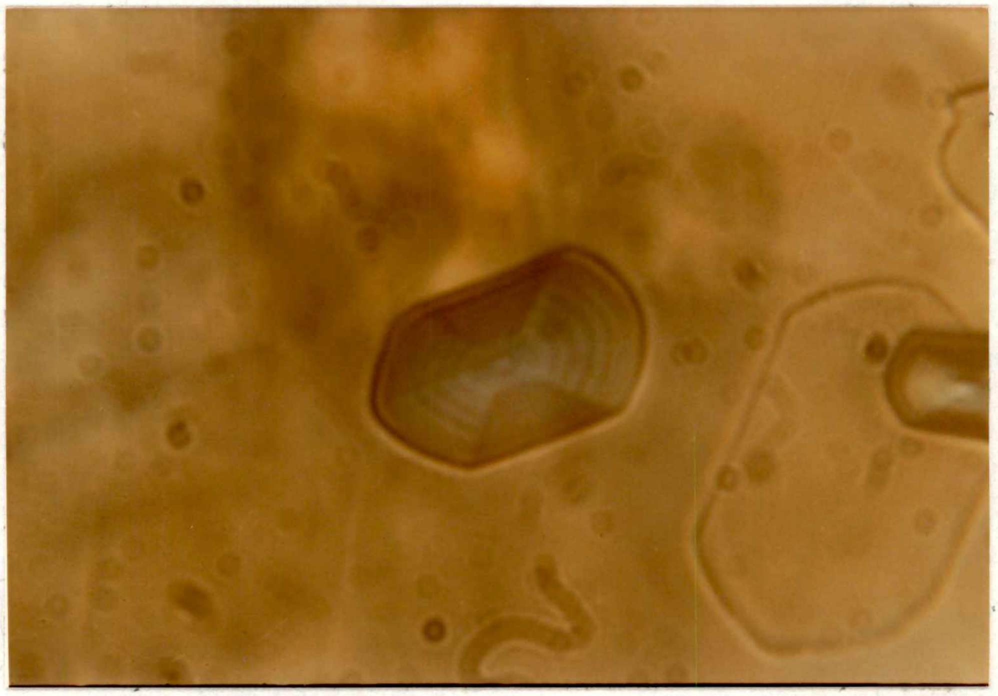


Figure 7. Three-dimensional hexagonal single crystal phase or "A" phase in dodecyl amine $-NH_2$/water system 70% weight water, showing the parallel layer structure. Crossed polars, x1000.

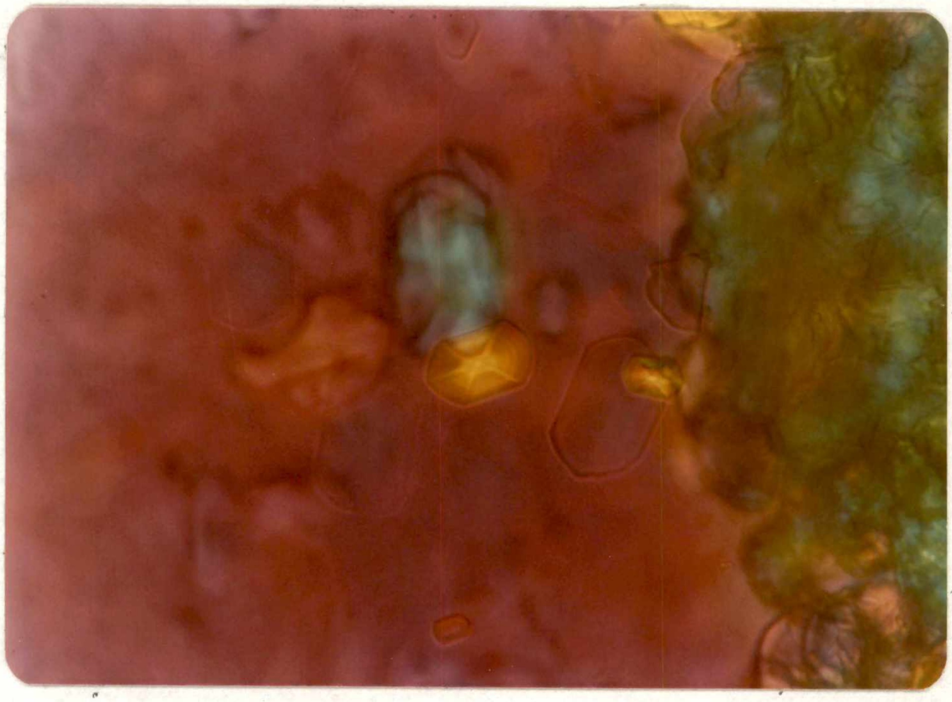


Figure 8. Three-dimensional hexagonal single crystal phase or "A" phase in dodecyl amine $-NH_2$/water system 70% weight water, showing the trigonal axes of the crystal. Crossed polars, x400.

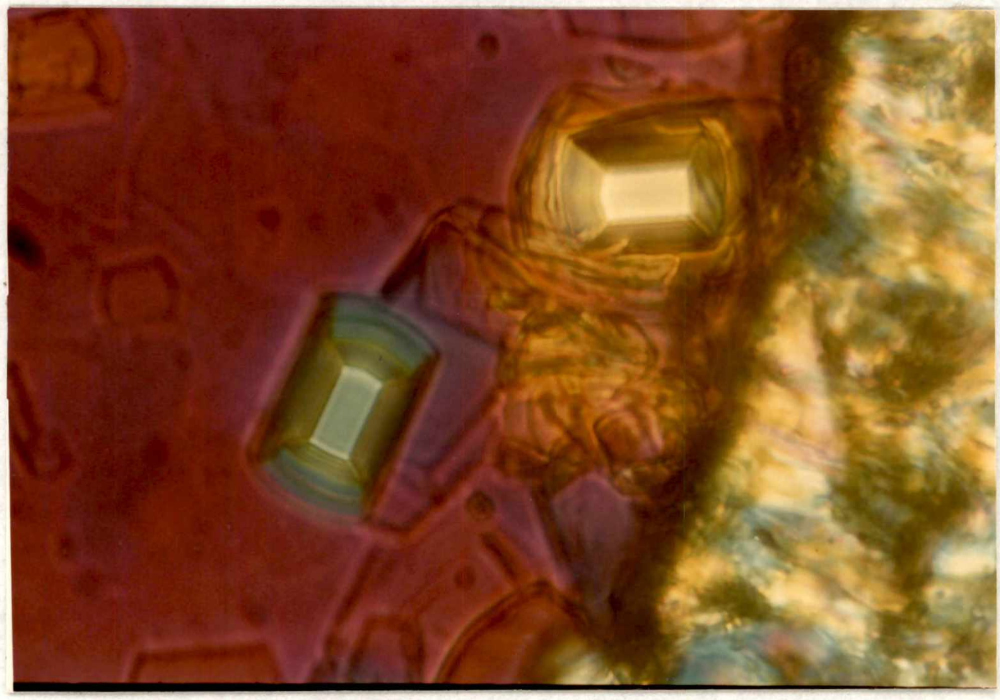


Figure 9. Three-dimensional hexagonal single crystal phase or "A" phase in dodecyl amine $-NH_2$/water 70% weight water, showing the optical activity of "A" phase and X, Y, Z space dimensions. Crossed polars, 600.

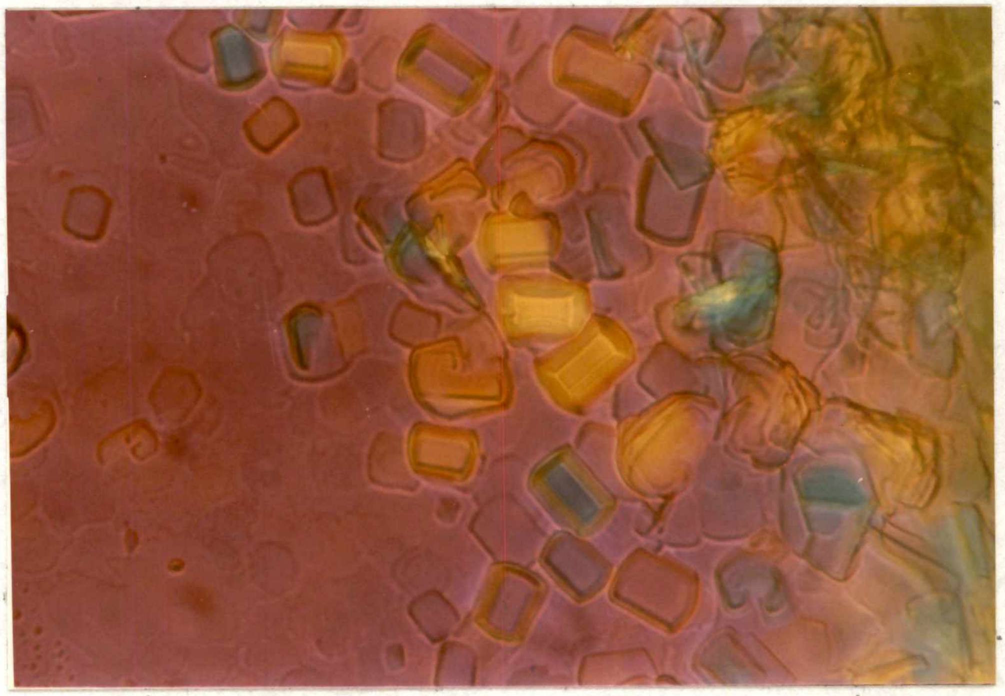


Figure 10. Aggregation of the single crystals of the "A" phase (the stable nongrowth ones) and growth of some single crystals of the "A" phase (unstable growth ones) in dodecyl amine $-NH_2$/water system 70% weight water. The picture was taken after two hours from the preparation time of the sample. Crossed polars, x600.

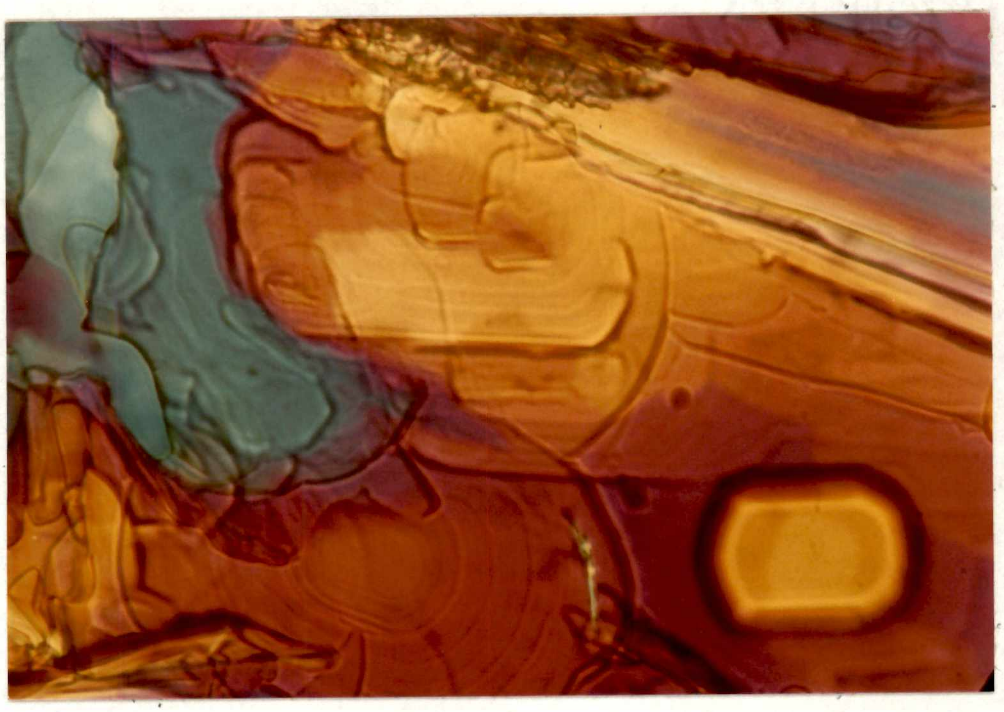


Figure 11. The growth of the single crystals of the "A" phase (unstable growth ones) and nongrowth of the single crystals of the "A" phase (stable nongrowth ones) in dodecyl amine $-NH_2$/water system 70% weight water. This picture was taken after 18 months from the preparation time of the sample. Crossed polars $\updownarrow\leftrightarrow$, x600.

Two-Dimensional Octagonal Phase or "Pre-M_1" Phase or "B" Phase at Room Temperature

Figures 12-14 show the "B" phase micelles and its structure and characteristics.

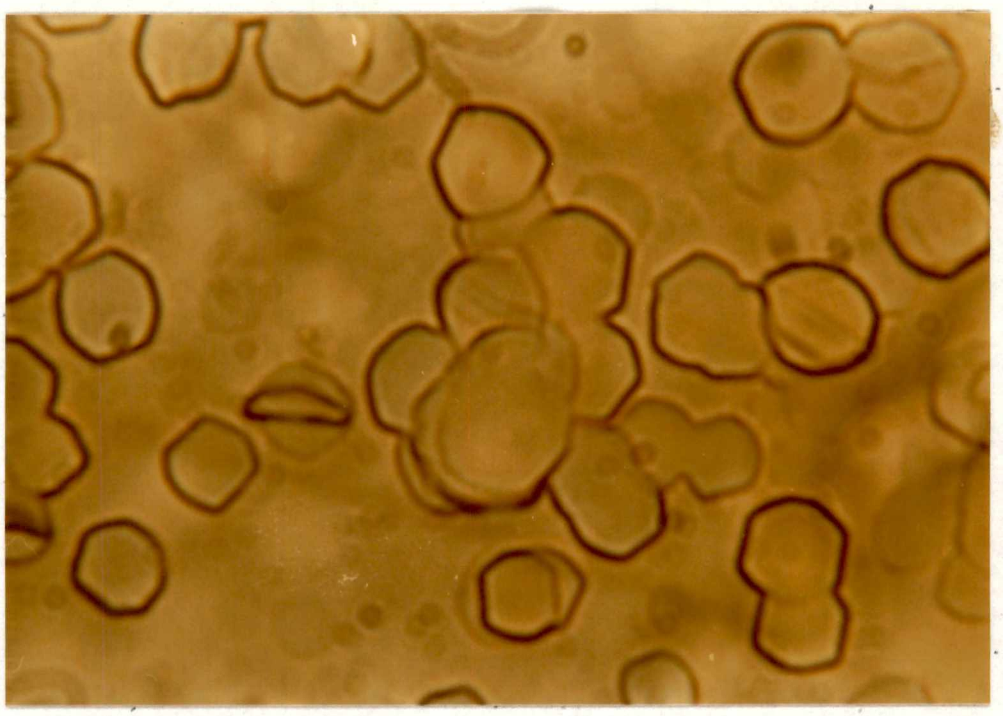
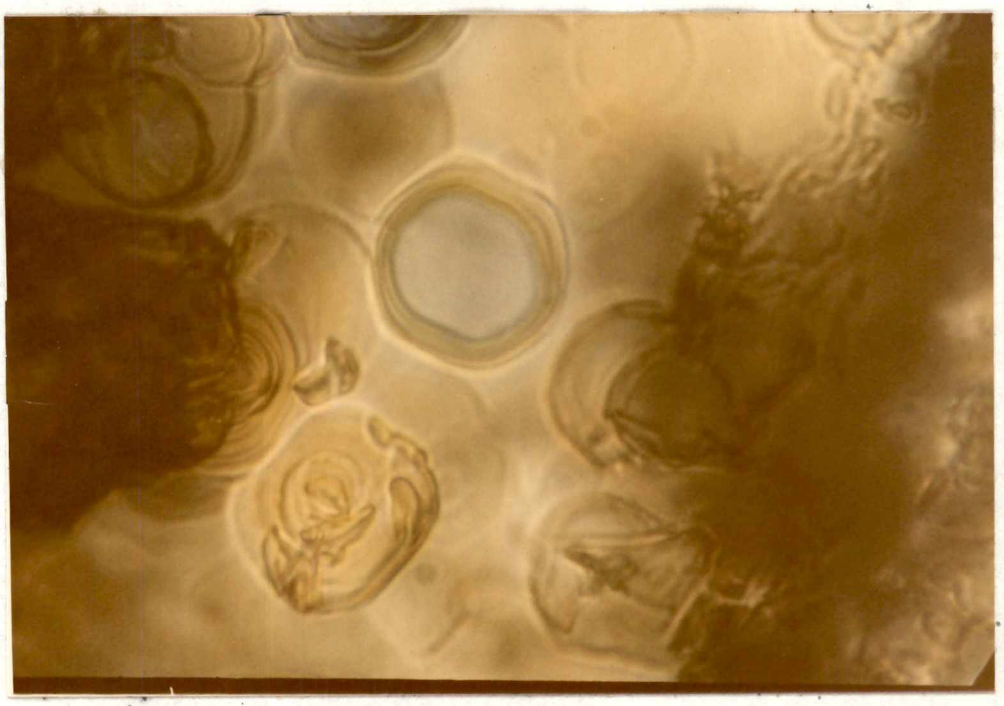
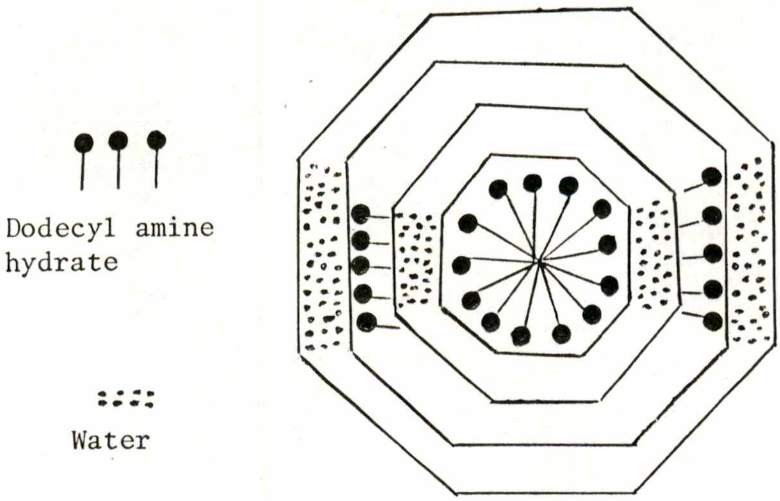


Figure 12. Two-dimensional octagonal "pre-M_1" phase or "B" phase micelles in dodecyl amine $-NH_2$/water system 0% weight water, showing no layer structure. Crossed polars, x1000.



a. Two-dimensional octagonal micelle of "pre-M_1" phase. Crossed polars, x600.



b. Two-dimensional octagonal micelle of "pre-M_1" phase or "B" phase showing its structure (schematic).

Figure 13. The micelle of "pre-M_1" phase or "B" phase in dodecyl amine $-NH_2$/water system 70% weight, showing the dodecyl amine hydrate core surrounded by alternating layers of water and dodecyl amine.

2 3

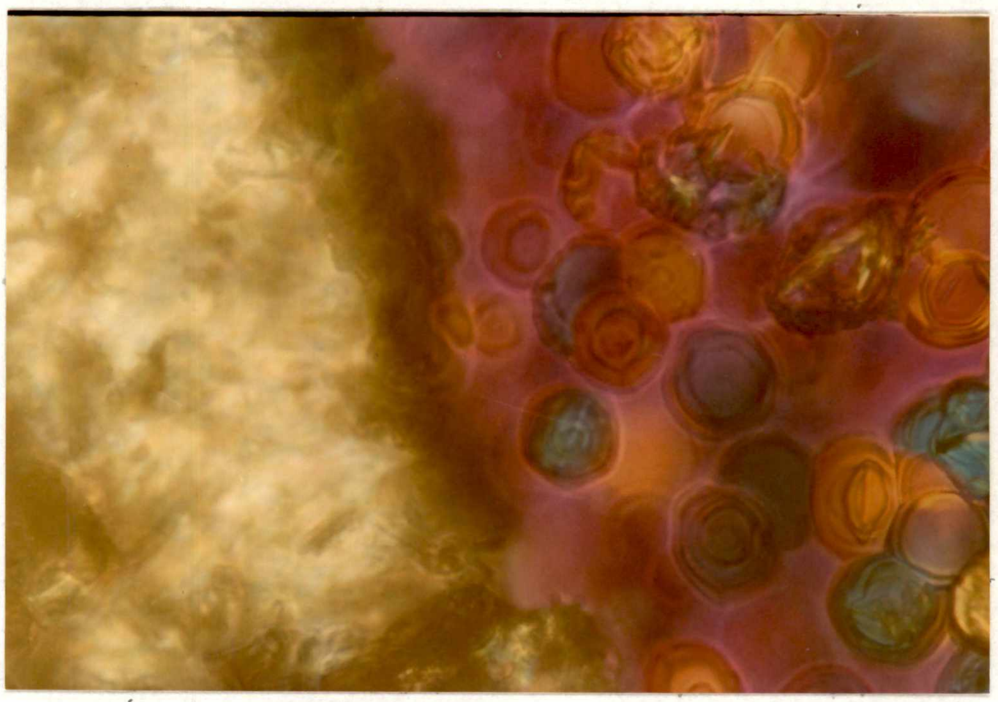


Figure 14. "Pre-M_1" phase in dodecyl amine -NH_2/H_2O system 70% weight water. Region 2. Crystal phase or "D" phase (unknown structure) with its location between "A" phase and "B" phase. Region 3. This shows the aggregation of "B" phase micelles to give the final structure for "M_1" phase. Crossed polars ⇔, x600.

Liquid Crystalline Phases in Dodecyl Amine ($-NH_2$/$-ND_2$)/Water (H_2O/D_2O) System (Figures 15-19)

1 2 3 4

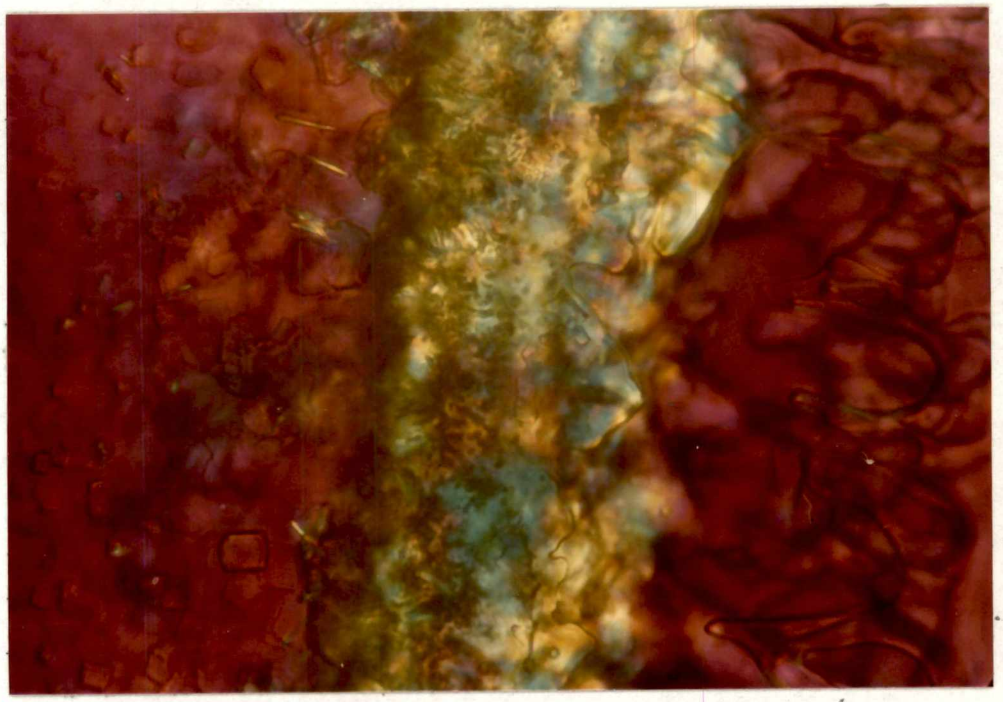


Figure 15. The mesophases in dodecyl amine $-NH_2$/water system 70% weight water. Region 1. Three-dimensional hexagonal crystal phase or "A" phase. Region 2. Crystal phase or "D" phase. Region 3. Middle phase or "M_1" phase. Region 4. Viscous isotropic phase. Crossed polars $\leftrightarrow\updownarrow$, x600.

4 5

3

2

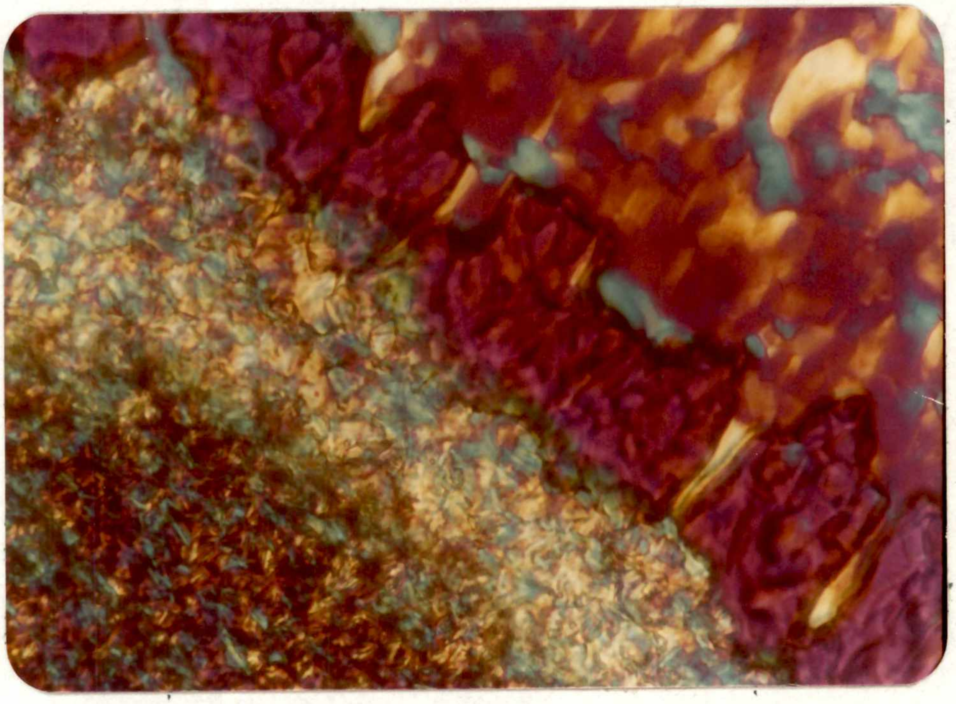


Figure 16. The mesophases in dodecyl amine $-NH_2$/water system 70% Weight Water. Region 2. Crystal Phase or "D" Phase (Unknown Structure). Region 3. Middle Phase or "M_1" Phase. Region 4. "Viscous Isotropic" Phase. Region 5. Neat Phase or "G" Phase. Crossed Polars, x600.

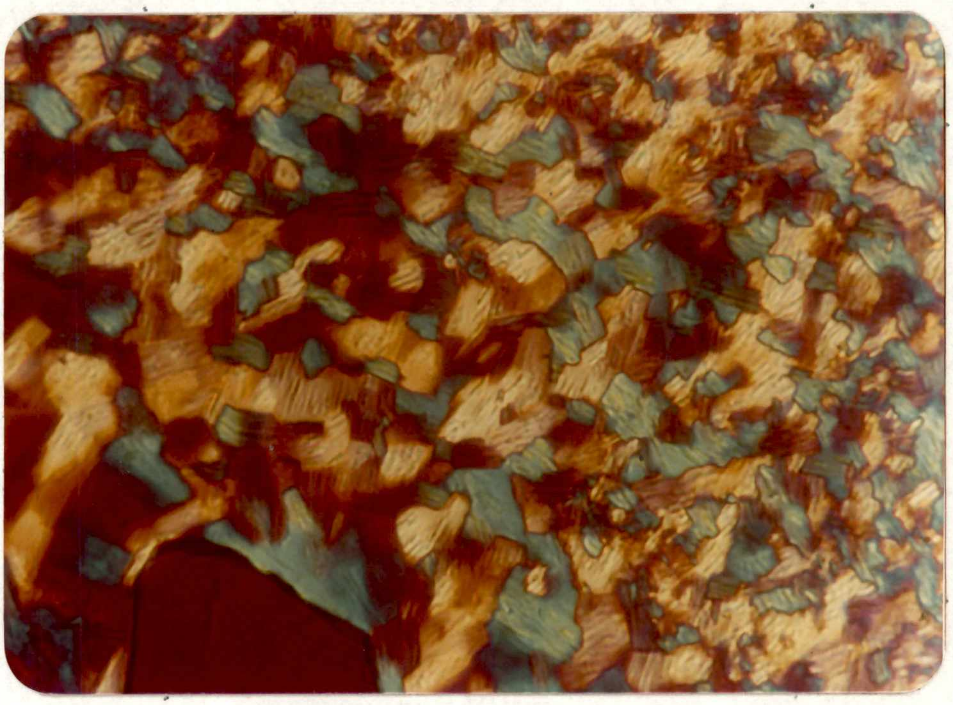


Figure 17. The middle phase or "M_1" phase in dodecyl amine $-NH_2$/ water system 70% weight water (thick sample). Crossed polars $\leftrightarrow\updownarrow$, x600.

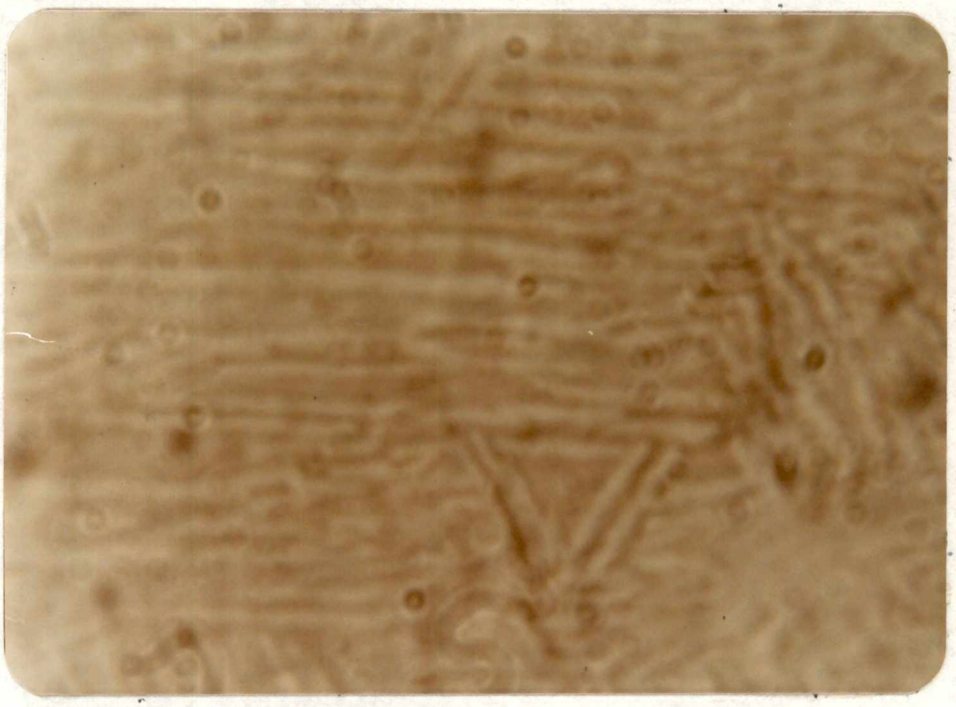
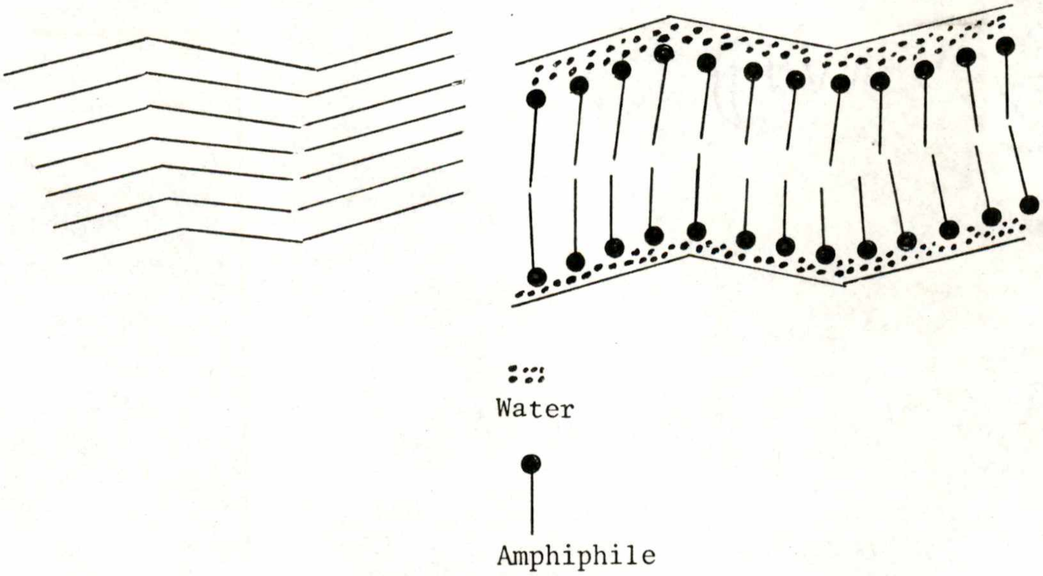


Figure 18. "M_1" phase showing the nematic structure of the middle phase (very thin sample). Crossed polars, x1500.

a. The "neat" phase structure in dodecyl amine $-NH_2$/water system 70% weight water. Crossed polars $\leftrightarrow\updownarrow$, x1500.



b. The "neat" phase structure (schematic).

Figure 19. The "neat" phase or "G" phase structure in dodecyl amine $-NH_2$/water system 70% weight water, showing the parallel double layer structure which is semactic structure phase. The light lines are water and the dark lines are amphiphile. This was a very thin sample.

The "C" Phase or "Pineapple Slice" Phase Micelle Structure and its Similarity with the Myelin Sheath of the Nerve Tissues (Figures 20-21)

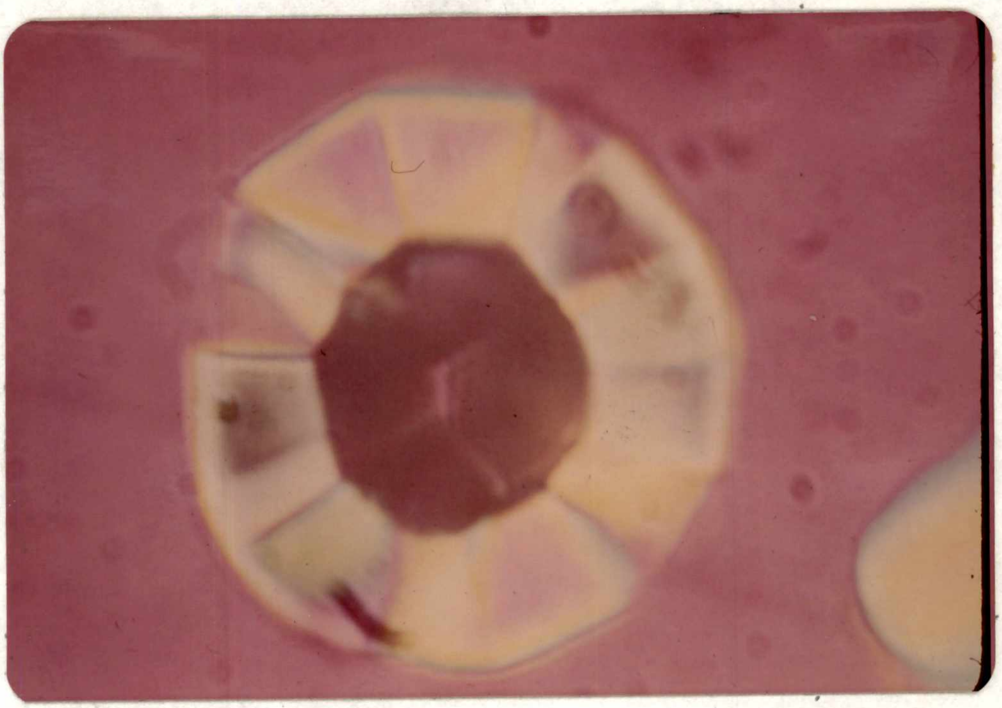


Figure 20. The "C" phase or "pineapple slice" phase or "myelinic figure" phase in dodecyl amine $-NH_2$/water system 10% weight water, showing the structure of the "C" phase micelle which consists of a core. The core is made of two layers of water on the surface and the amphiphile at the bottom. The core is surrounded by a radial section of amphiphile separated by water. These micelles of "C" phase produce colors by polarized light when the analyzer is rotated through 90°. This picture was taken after one hour from the preparation time of the sample. Crossed polars, x1000.

Figure 21. A transverse section in a myelinated nerve fiber bundle showing in the center an axon surrounded by a myelin sheath and on the outer side Schwann cells. The similarity is clear when compared with Figure 18 which shows the "C" phase in dodecyl amine/water system. Crossed polars ⟡, x1000.

The Similarity between the "G" Phase Droplets at 34° and the Ovary Tissues (Figures 22-23)

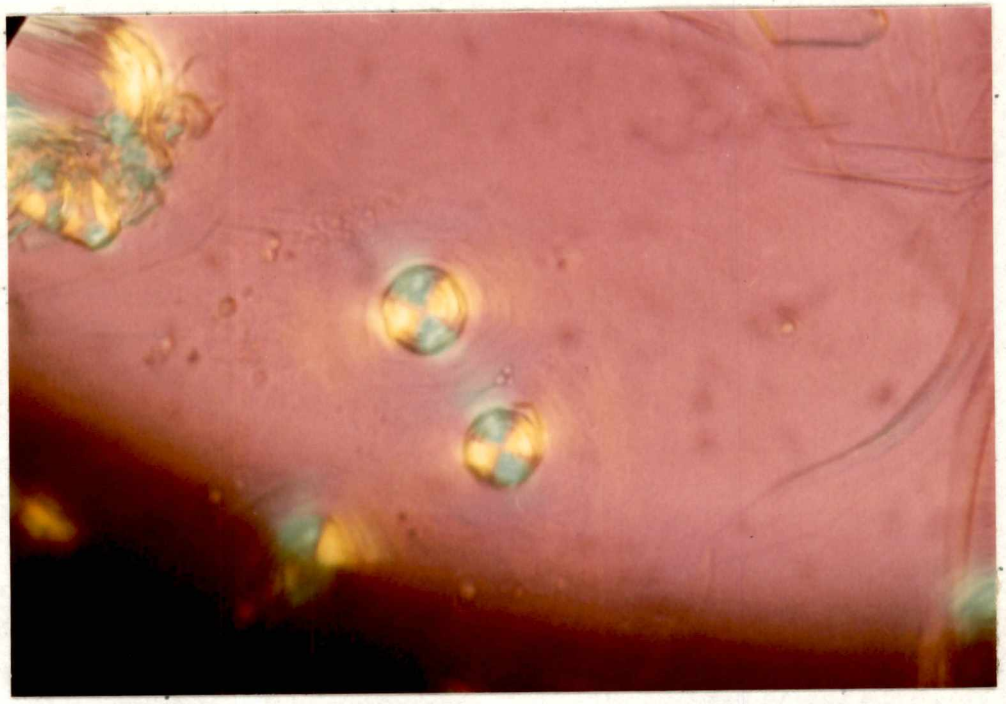


Figure 22. Droplets of "G" phase in dodecyl amine $-ND_2/D_2O$ system 55% weight D_2O at a temperature of 34°C. Crossed polars, x400.

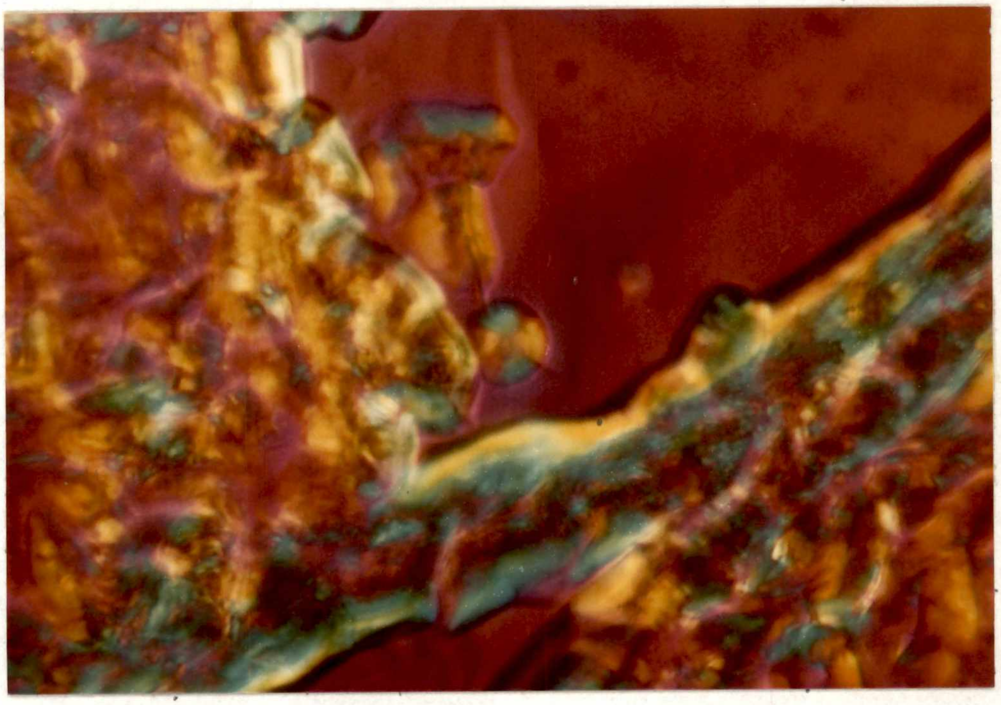


Figure 23. A transverse section of a human ovary showing the similarity of the four-section spherulite in Figures 23 and 22 in which a sample was prepared in dodecyl amine $-ND_2/D_2O$ system of 55% weight D_2O. Crossed polars, x400.

Heats of Fusion and Transition

The following seven figures (24-30) show the effect of temperature on the mesophases of the dodecyl amine $-ND_2/D_2O$ system. The molarity of the D_2O was 95.74%. The phase transition lytropic liquid crystals gives isotropic liquid phase at 52.9°.

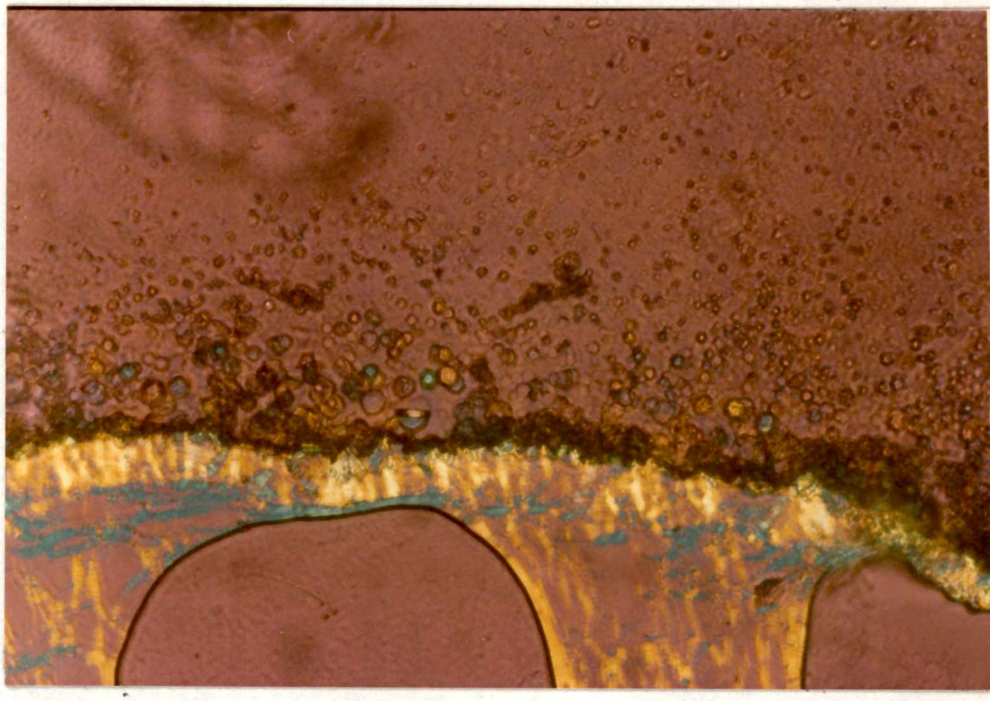


Figure 24. The effect of heat on the crystal phase "D" (unknown structure) starts to melt first. Crossed polars $\leftrightarrow\updownarrow$, x200.

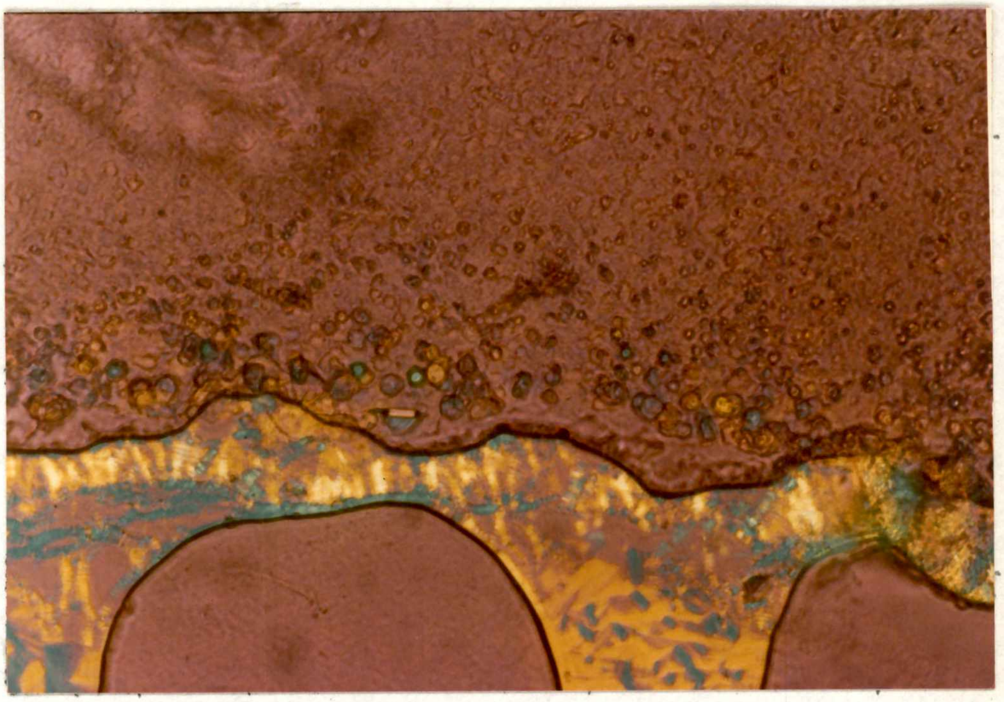


Figure 25. The crystal phase "D" gives the lyotropic phase. Crossed polars, x200.

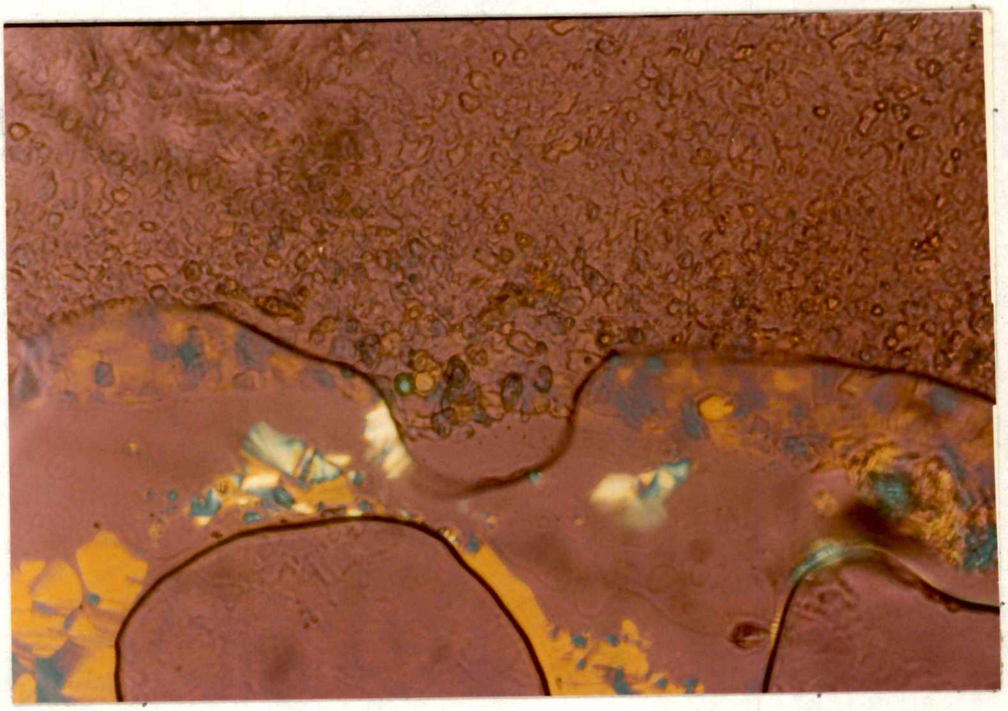


Figure 26. Crystal phase "D" and "M_1" phase melt and give the isotropic phase. Crossed polars ↔↕, x200.

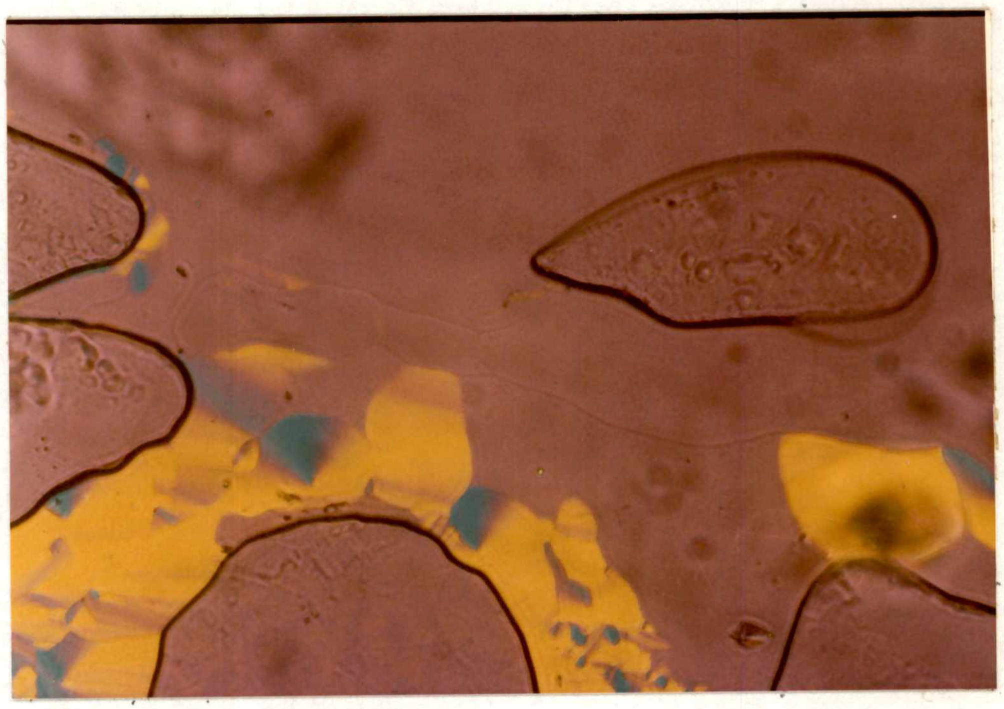


Figure 27. The "A" phase and "G" phase melt (not completely) and start to give the isotropic phase. Crossed polars $\leftrightarrow\updownarrow$, x200.

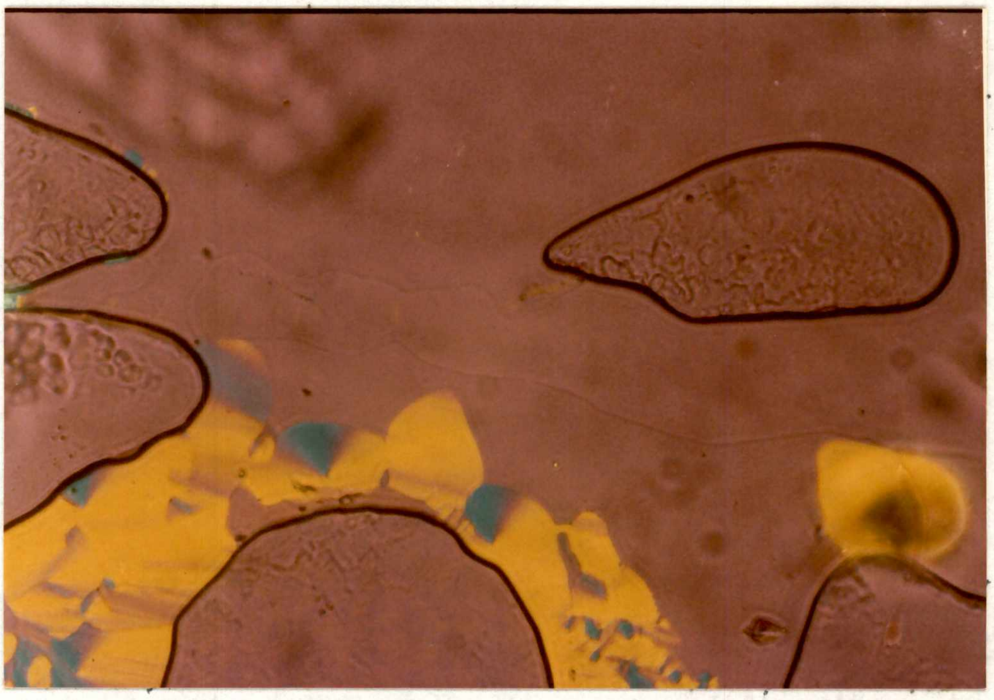


Figure 28. The increase of melting of "A" phase and "G" phase. Crossed polars, x200.

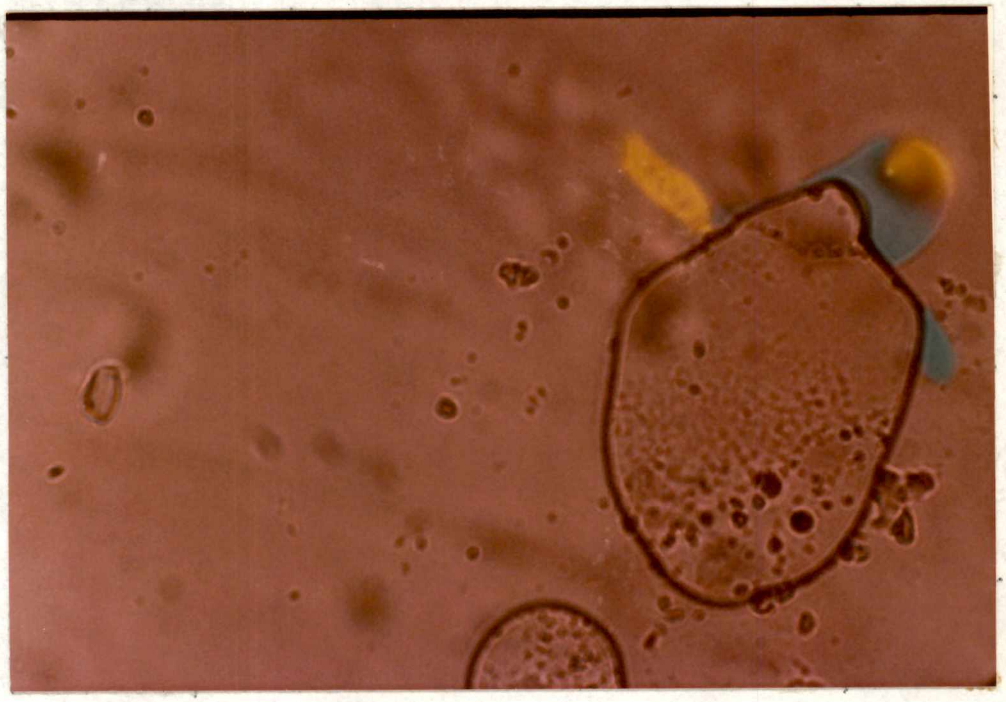


Figure 29. The "D" phase, "M_1" phase, "viscous isotropic," "G" phase and "A" phase in dodecyl amine $-ND_2/D_2O$ system disappear. Crossed polars $\updownarrow\leftrightarrow$, x200.

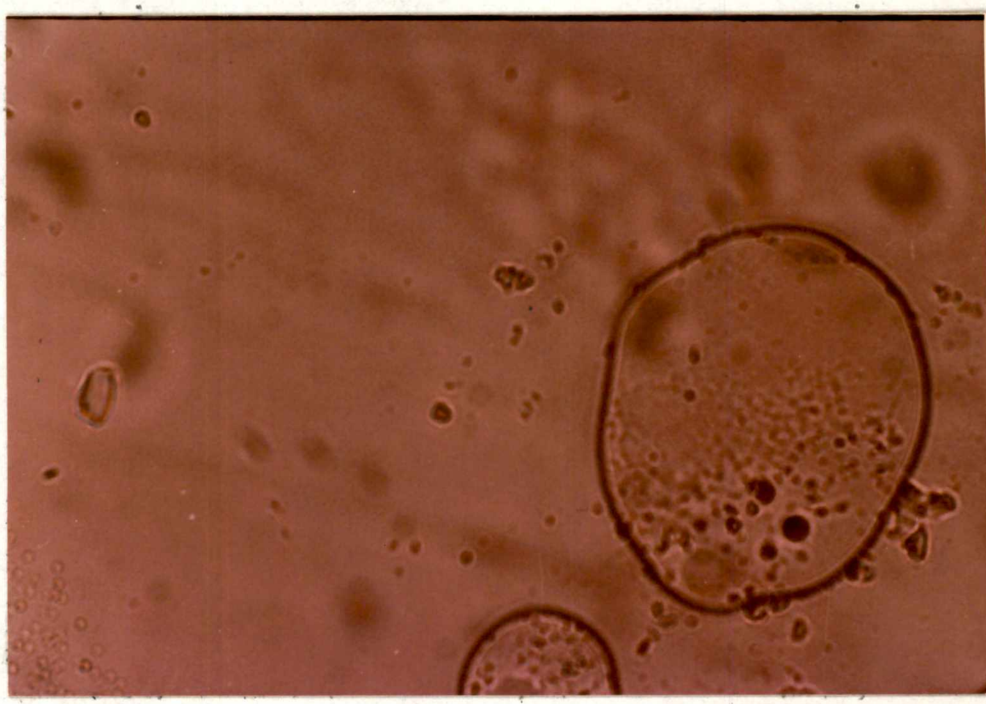


Figure 30. The lyotropic mesophases in dodecyl amine $-ND_2/D_2O$ system give the isotropic phases at 52.9°C. These are composed of amine droplets and D_2O droplets. Crossed polars $\leftrightarrow\updownarrow$, x200.

The Mesophase Formation in Dodecyl Amine/Water System at Room Temperature

The following five figures (31-35) show lyotropic phase formation. This includes the dissolution of water into the amphiphile to give the lyotropic phase or possibly the "G" phase. The central reaction takes five seconds exposure taken at one second intervals. The samples were prepared in dodecyl amine $-NH_2/(H_2O/D_2O)$ system of 5% weight H_2O plus 5% weight D_2O.

Figure 31. Step 1. The viscous isotropic spherulite which has water and amphiphile. The water is concentrated in these parts containing the polar groups of the amphiphile. Crossed polars, x1000.

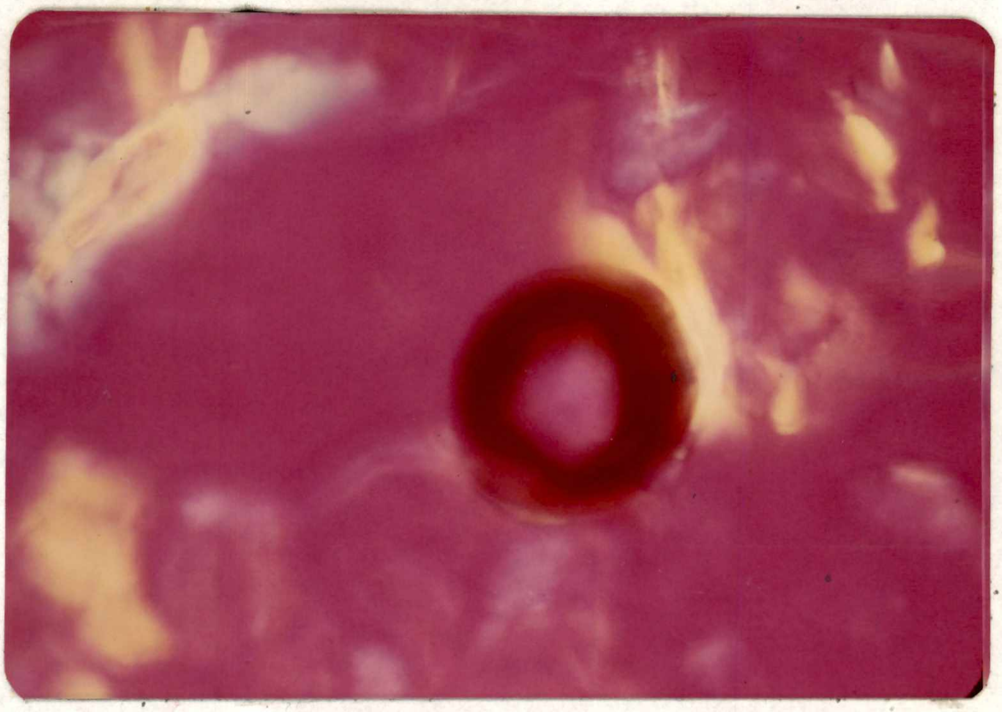


Figure 32. Step 2. Crossed polars, x1000.

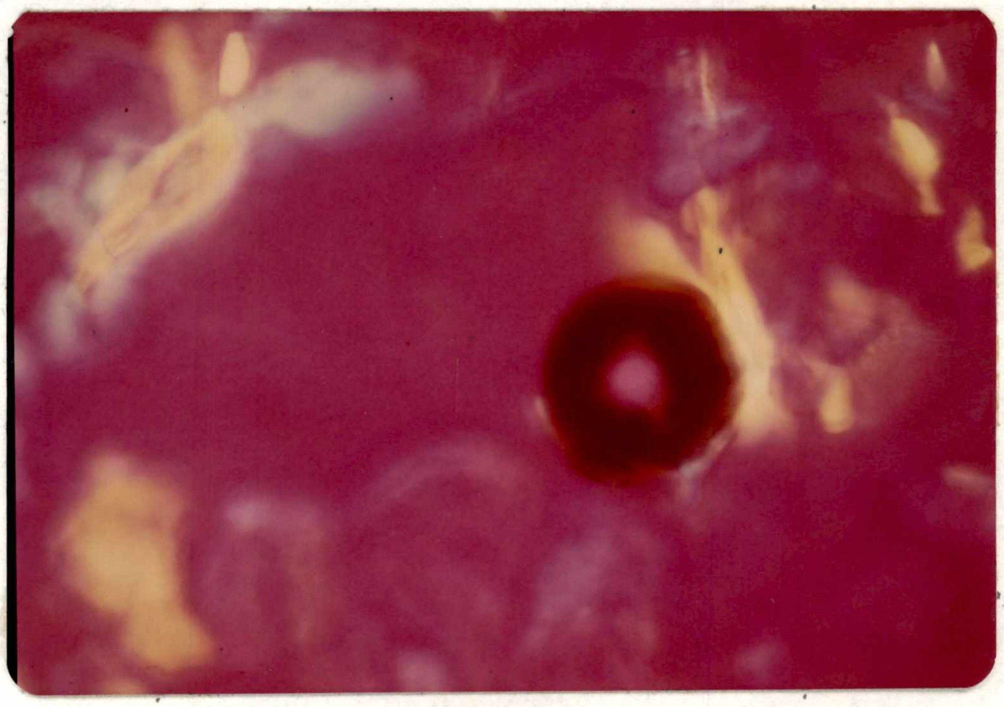


Figure 33. Step 3. Crossed polars, x1000.

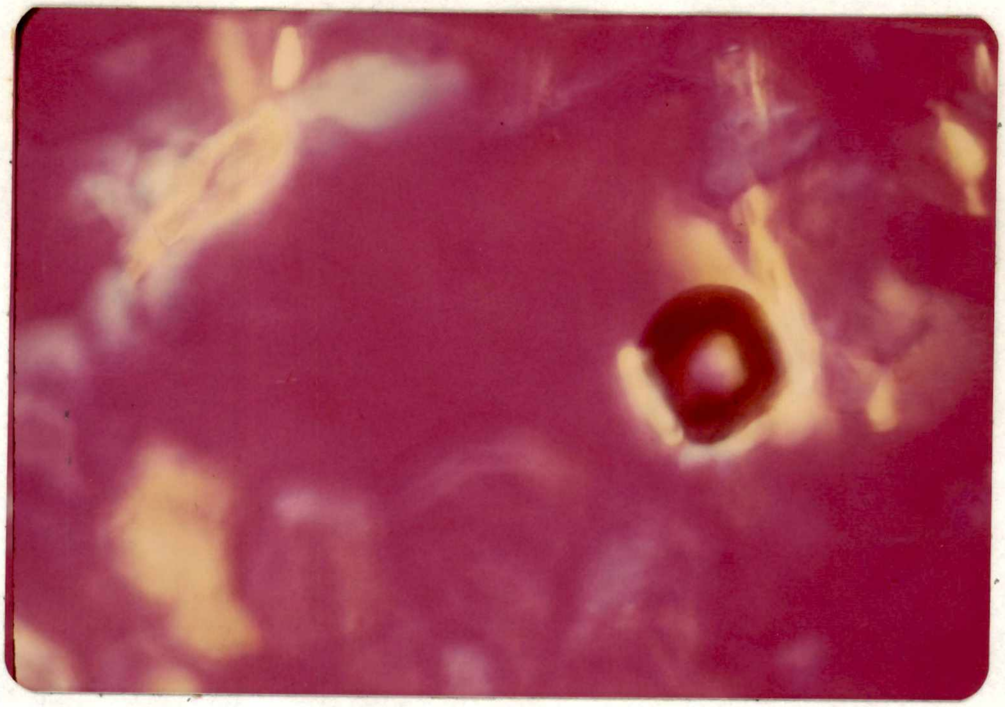


Figure 34. Step 4. Crossed polars, x1000.

Figure 35. Steps 5. These last two steps show the increase in the rate of dissolution of water in the parts of amphiphile which contain the polar groups. Crossed polars, x1000.

CHAPTER V

ANALYSIS OF EXPERIMENTAL RESULTS

Introduction

Samples of dodecylamine ($-NH_2$/$-ND_2$)/water (H_2O/D_2O) mixtures under consideration were investigated under a polarizing microscope at various magnifications. The results of these investigations are presented in the form of photomicrographs. The use of a polarizing microscope in identifying various phase structures, while in a few cases considerable experience and judgment are required, is ordinarily simple and offers a combination of directness and general applicability not found in other techniques. The microscopic method is also rapid and applicable to both phase mixtures and isolated structures. Rosevear (1954), using a polarizing microscope, found it was possible to identify five lyotropic mesophases in dodecylamine ($-NH_2$/$-ND_2$)/water (H_2O/D_2O) system at room temperature. The two crystal phases "A" phase and "D" phase extend from 0% wt to 96% wt water (H_2O/D_2O); the other three lyotropic phases extend from 10% wt to 96% wt water (H_2O/D_2O). Abrif description of each phase is given below (bulk composition entire sample).

Three-Dimensional Hexagonal Crystal Phase or "A" Phase

Figure 15 (p. 30) shows a cross section of a sample of dodecylamine $-NH_2$/H_2O system 70% wt H_2O where "A" phase is located in Region 1. The characteristics of this phase are shown in Figures 6-11 (pp. 21-26). The "A" phase is composed of single crystals which have a layer arrangement parallel to each other as can be seen in Figures 7 and 9 (pp. 22, 24). (The layer's structure is not related to the optical stress analysis phenomenon.)

In the mesophases the water can be regarded as held together by its own high internal pressure and the liquid crystalline nature which is caused by the terminal polar groups being in local solution in the water. Crystallization in three dimensions requires them to crystallize from the water (Lawrence, 1958). At the same time it can be seen from Figures 9 and 10 (pp. 24-25) that the single crystals of "A" phase are optically anisotropic and covers a three-dimensional space. It was observed that the crystal "A" phase coexists with another crystal "D" phase which has unknown structure as shown in Figures 9 and 15 (pp. 24, 30).

It was observed that in dodecylamine/water system the crystal "D" phase (unknown structure) melts before the "three-dimensional hexagonal crystal" phase or "A" phase and "G" phase as seen in Figures 24-30 (pp. 39-45). The high temperatures of the transition from <u>smectic</u> to <u>isotropic</u> solution does not require large specific forces in the planes of the polar heads because increase of temperature does not increase the solubility of hydrocarbons tails (Lawrence, 1958). This means the "three-dimensional hexagonal crystal" phase or "A" phase and "G" phase or "neat" phase in dodecylamine ($-NH_2/-ND_2$)/water (H_2O/D_2O) system are smectic phases related to the effect of heat and their structures (Figures 7, 9, 19, pp. 22, 24, 34). The "pre-M_1" phase, "M_1" phase and the crystal "D" phase in the same system are nemactic phases; however, it was difficult to identify the "viscous isotropic" phase structure by the effect of heat on it, as can be seen in Figures 24-30, pp. 39-45.

The "three-dimensional hexagonal" phase or "A" phase is stable at room temperature over a period of 18 months, but some of "A" phase single crystals are grown through this period of time as can be seen in Figure 11, p. 26.

It should be pointed out that another mesophase, namely the "three-dimensional hexagonal" crystal phase or "A" phase in dodecylamine ($-NH_2$/$-ND_2$)/water (H_2O/D_2O) system, was not reported before and its characteristics are explained above.

Two-Dimensional Octagonal "Pre-M_1" Phase or "B" Phase

This phase is composed of octagonal two-dimensional micelles which possesses a core as can be seen in Figure 13, p. 28. Under the microscope it was difficult to identify the core material as dedocylamine and its hydrates or water; however, the core material is expected to be dedocylamine/dedocylamine hydrates, because the dodecylamine and its hydrates are amphiphiles and the amphiphile's polarizing ability is more than water (Elbers, 1959).

It was observed that this core is surrounded by parallel layers of dodecylamine and water (the layer's structure in "B" phase is not related to the optical stress analysis for the unaxial crystal, since the "two-dimensional octagonal pre-M_1" phase micelle is not crystal).

The "B" phase was found to be "pre-phase" which its micelles aggregate with deformation of its original structure which is

Figure 13a, p. 28, then after an unspecified length of time the "M_1" phase will appear as can be seen in Figures 14-16, pp. 29-31, the "M_1" phase and its nematic structure in Figures 17 and 18, pp. 32, 33. All these steps were done at room temperature. The "pre-M_1" phase coexists with the crystal "D" phase (unknown structure) over a wide range of dodecylamine/water concentration as seen in Figure 13.

The "M_1" phase over time will replace the "pre-M_1" phase location which in between "D" phase and "viscous isotropic" phase, as shown in Figures 15 and 16. It should be pointed out that another mesophase, namely "pre-M_1" phase or "B" phase, exists in dodecylamine ($-NH_2/-ND_2$)/ water (H_2O/D_2O) system.

The "C" Phase or "Pineapple Slices" Phase or "Myelinic Figure" Phase

Investigation of "C" phase clearly indicates the existence of two types of micelles (according to their optical activity, one type produces colors by polarized light when the analyzer is rotated through 90° as shown in Figure 20, p. 35. The other type does not have this phenomenon. The general appearance of this phase carries a close similarity of that of a thin slice of pineapple. According to the polarizing ability of dedocylamine and the water, the core of the single micelle of "C" phase (Figure 20) is expected to be two layers, the upper layer is water (on the surface) and the lower layer is dedecylamine, while the radial sections are made of dodecylamine separated with water as seen in Figure 20.

The analysis of the results showed that the micelles which are optically active or birefringent get attached together after 24 hours from the preparation time of the sample. After an unspecified length of time the "M_2" phase will appear in dodecylamine ($-NH_2$/$-ND_2$)/water (H_2O/D_2O) system 10% weight water, while the other nonoptically active micelles (stable ones) do not exhibit this aggregation phenomenon.

An interesting result was obtained by comparing the general characteristics of "C" phase to that of a transverse section in a myelinated nerve fiber bundle (human) specially myeline sheath. It can be seen from Figures 20 and 21, pp. 35, 36, that there is a great structural similarity between the myeline sheath in nerve tissue samples and the "C" phase micelles in dodecylamine/water system 10% weight water, according to Stewart (1965).

> A definite claim that liquid crystals entered into the structure of living cells and tissues was made in 1959 when it was shown that complex lipids present in adrenal cortex, ovaries, myelin and also in atheromatous arteries existed at body temperature in a characteristic mesophase.

In dodecylamine $-ND_2/D_2O$ system 55% weight D_2O at a temperature of 34°. The droplets of "G" phase have a similarity with a transverse section in an ovary human tissue as seen in Figures 22 and 23, pp. 37 and 38.

According to Lawrence (1958)

> Myelinic figures when cholesterol is dissolved in soap solutions, many rings, usually short fat sausage shapes are seen. The ring is sharply defined, strongly birefringent and contains an anisotropic solution. This form of the liquid crystalline phase is rarely seen with alphatic solutes where the penetration of the soap leads to liquid crystalline ternary phase at Tp. This is accomplished by formation of a membrane around the solid and then by bulging into hemispherical anisotropic forms and finally sometimes to spherulites (with the ternary systems, it

would appear that the solid which forms myelines in water must contain two components—soap and a long chain amphiphile).

However, the "C" phase micelle or "myelinic figure" phase micelle exists in dodecyl amine ($-NH_2/-ND_2$) which is an aliphatic solute/water (H_2O/D_2O) system which is a binary system. Note, the "C" phase micelle is not a Bâtonnet of "M_1" since the writer has "M_1" phase in the other concentration of water. The "M_1" phase has a different structure as seen in Figures 17 and 18, pp. 33, 34.

The "myelinic figure" phase or "C" phase was not reported in any other aliphatic solutes or other binary systems. The similarity between the "C" phase micelle and the myelin sheath, the droplets of "G" phase at 34° and the ovary tissue could be of significant importance because it provides a possible way for comparison between human tissues and a synthesized organic compound of aliphatic solutes (dodecyl amine).

"Crystal" Phase or "D" Phase (Unknown Structure)

A crystal phase "D" was observed under the microscope as seen in Figures 15 and 16 (region 2), pp. 30, 31, and Figures 9 and 14, pp. 24, 29, where it is located between the "A" phase and "pre-M_1" phase or "B" phase. The formation of "D" phase can be attributed to a partial growth and deformation of single crystals of "A" phase (unstable ones) at room temperature immediately after the preparation time of sample. It was difficult to identify the direct cause of the growth and deformation of the single crystals of "A" phase under the polarizing microscope.

The "G" Phase

The "G" phase is anisotropic and consists of a double layer of amphiphilic molecules with the polar groups interfaces with intervening layers of water molecules as can be seen in Figure 19, p. 34.

The Effect of Temperature on the Liquid Crystalline Mesophases in Dodecylamine $-ND_2/D_2O$ System (Figures 24-30, pp. 39-45)

Our experiments show that the order of melting of the various phases is as follows.

"D" phase → "M_1" phase → "viscous isotropic" phase → "G" and "A" Phase → isotropic phase of amine and water.

Summary

The dodecylamine ($-NH_2/-ND_2$)/water (H_2O/D_2O) system has six mesophases at room temperature, one of them a "pre-phase," which will disappear after a while.

The six phases which we observed are as follows:

1. "Three-dimensional hexagonal" crystal phase or "A" phase.
2. Crystal "D" phase (unknown structure).
3. "Two-dimensional octogonal" "pre-M_1" phase or "B" phase.
4. The middle phase "M_1" and inverse middle phase "M_2" phase.
5. "Viscous isotropic" phase.
6. The "neat" or "G" phase.

Factors which affect the mesophases' behavior in dodecylamine ($-NH_2/-ND_2$)/water (H_2O/D_2O) system include:

1. Concentration (not all phases appear in all concentrations).

2. Temperature (all phases appear at room temperature).

3. Time (which is very important to "M_1" and "M_2" phase formation).

CHAPTER VI

SUMMARY, CONCLUSIONS, AND IMPLICATIONS

Summary

Through this presentation some new scientific terms have been introduced to the students. The significance of introducing such terms could be better understood after discussing the basic processes through which mental structures could be built. According to Piaget's theory (Runner, 1973), there exists certain basic mental structures which are born with a child which enable him to interact with his surroundings. As long as that interaction is successful these basic structures continue to grow and guide his behavior. However, during his life the child will meet some contradictions, i.e., things which do not fit his present mental structures. These contradictions produce a disruption (disequilibrium) in the child's mental structures. The child, through guidance and continued investigation, alters his mental structures to assimilate the new situations. Once these new structures are tested and the child's efforts are rewarded, these structures are reinforced and the child adapts to the new situations. It can thus be seen from this discussion that the disruption of the existing mental structure produces a state of disequilibrium which naturally tends to return to equilibrium conditions.

Among the new terms presented in this study is liquid crystals. One is used to thinking of crystals as being solid, well-defined shapes which possess a certain number of faces. After presenting and visually studying the liquid crystal structures the learner has to readjust his or herself to the new meaning of crystal. In other words, the learner's pre-existing mental structure has been disrupted and development of new structures becomes necessary.

Another term which has been used frequently during these studies is phase. Phase is a name given to any homogeneous and physically distinguishable portion of a system having definite boundaries. In chemistry, the phases could be solid, liquid or gaseous. In the present study the result of phase behavior due to temperature changes (Figures 14-25, pp. 29-40) is of significant importance because it is expected that the learner after watching a few of these phase transformations will start to think whether or not this process will continue. It is expected that the learner will draw some kind of conclusion in which he/she could immediately understand the answer to their conclusions. Thus the learner's ability to think about new subject matter (inquiry) without being afraid and also the ability to speculate about the results has been established through a short series of visual-mental observations. According to Piaget's theory the process outlined above is simply the process of intellectual development.

As mentioned earlier (Coulson, 1970), any subject that aims to hold the attention of students must have a "fun" factor associated with it. This has been demonstrated through the use of the microscope where the bright colors of samples will tend to attract the attention of the learners. At the same time the pleasure of watching the appearance and disappearance of the light fringes could have a lasting effect and impression on the student. Moreover, the striking similarity between liquid crystals mesophases in dodecylamine/water system and ovary tissue and nerve tissue samples would be able to elicit some pleasure from students as well as showing the close relation between chemistry and the human body. This type of experimental activity shows the importance of chemistry in the student's daily life and thus it will diminish any possible isolation of chemistry for his/her life.

Conclusions

The results of these investigations showed the existence of two new phases, namely "A" phase and "pre-M_1" phase or "B" phase; however, further studies using more sophisticated techniques such as electron microscopy or x-ray diffraction are required to fully determine the structural properties of these phases. On the other hand, the structural similarity exhibited by the dedocylamine mixture and human tissues could be of significant importance for medical and for biological purposes.

Implications

It is expected that such an experiment conducted by the investigator could fulfill most of the requirements for an attractive, intellectually stimulating and educational laboratory teaching method. It could help the process of building mental structures among students toward the process of intellectual development. Moreover, the ease of handling, preparing and measuring, together with the simplicity of instrumentation is expected to attract more students toward the study of chemistry in particular and science in general. This could be an important step in the production of more scientifically educated people. It is important to indicate that the success of this experiment depends to some extent on the ability of instructors to present the general format of the experiment and to introduce the new subject matter at the proper time.

REFERENCES

REFERENCES

Andersson, Bjorn (1976); Science teaching and the development of thinking. Acta Univerfitatif Gothoburgenfif, Goteborg, Sweden.

Balmbra, R. B., Clunie, J. S. and Goodman, J. F. (1967); The structure of neat mesomorphic phase. Molecular Crystals, Vol. 3, pp. 281-291.

Brown, Glenn H. (ed.) (1975); Advances in liquid crystals. Academic Press, New York, San Francisco, London.

Chmielewski, Andrzij and Van Hook, A. W. (1978); Isotope effects in liquid crystal systems, Mol. Cryst. Liq. Cryst., Vol. 48, pp. 27-36.

Coulson, Ernest (1971); in Discipline of the curriculum (R. C. Whitfield, ed.). McGraw-Hill Book Co., Maidenhead, Berkshire, England.

Ekwall, Per (1975); in Advances in liquid crystals (Glen H. Brown, ed.). Academic Press, New York, San Francisco, London.

Elbers, P. F. and Ververgaert, P. H. J. T. (1965); Electron microscope and x-ray diffraction studies on a homologous series of saturated phosphatipylcholines, J. of Cell Biol., Vol. 25, pp. 375-384.

Hartshorne, N. H. and Stuart, A. (1970); Crystals and the polarizing microscope (4th ed.). Edward Arnold Publishers, London.

Lawrence, A. S. C. (1958); Solubility in soap solutions, Discuss. Faraday Soc., Vol. 25, pp. 51-58.

Luzzati, Vittorio and Preiss-Husson, R. (1966); Structure of the cubic phase of lipid-water systems, Nature, Vol. 210, pp. 1351-1352.

Piaget, Jean (1964); Cognitive development in children, Journal of Research in Science Teaching, Vol. 2, pp. 176-186.

Ralston, A. W., Hoerr, Charles W., and Hoffman, Everett, J. (1942); Studies on high molecular weight aliphatic amines and their salts VII. The systems octylamine-dedecylamine and octadecylamine-water, J. Amer. Chem. Soc., Vol. 64, pp. 1516-1522.

Renner, John W. and Lawson, Anton E. (1973); Pigetian theory and instruction in physics, The Physics Teacher, Vol. 11, pp. 165-169.

Renner, John W. and Lawson, Anton E. (1973); Promoting intellectual development through science teaching. The Physics Teacher, Vol. 11, pp. 273-276.

Rosevear, F. B. (1954); The microscopy of the liquid crystalline neat and middle phases of soaps and synthetic detergents. J. of the Amer. Oil Chemists' Soc., Vol. 34, pp. 628-637.

Senden, Van (1949); Piagetian theory and instruction in physics (John W. Renner and Anton E. Lawson, 1973), Physics Teacher, Vol. 11, pp. 165-169.

Stewart, Gordon T. (1966); Liquid crystals in biological systems, Mol. Crys., Vol. 1, pp. 563-580.

Truex, C. Raymond and Malcolm B. Carpenter (1969); Human neuroanatomy, 6th ed. The Williams & Wilkins Company, Baltimore.

Winsor, P. A. (1968); Binary and multi-component solutions of amphiphilic compounds. Solubilization and the formation, structure and theoretical significance of liquid crystalline solutions. Chem. Rev., Vol. 68, No. 1, pp. 1-37.

VITA

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She worked as a high school chemistry teacher in Egypt for three years during which time she got married, and came to the United States with her husband so that he could attend The University of Tennessee Graduate School. In the summer of 1977, she began work on her Master of Science degree in Education with a major in Science Education. She worked as a research assistant in the Chemistry Department during the time she was enrolled in the Graduate School. The Master's degree program was completed at The University of Tennessee in March, 1980.

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