

Module 3: Liquid Crystals and Nanomaterials

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Module outline:

Liquid crystals

Application of liquid crystals

Concepts of nanomaterials

Applications of nanomaterials

3.1. INTRODUCTION

Liquid crystals were first accidentally discovered in 1888 by Friedrich Reinitzer, a botanical physiologist who was working in the Institute of Plant Physiology at the University of Prague. Reinitzer was conducting experiments on a cholesterol-based substance (*cholesteryl benzoate*) and trying to determine the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck by the fact that this substance seemed to have two melting points. He found a first melting point at 145.5 °C, where the solid crystal melted into a cloudy liquid. This ‘cloudy intermediate’ existed up to 178.5 °C where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. At first, Reinitzer thought that this might be a sign of impurities in the material, but further purification did not show any changes in this behaviour. He concluded that the material had two melting points, but asked his colleague Otto Lehmann, a German physicist who was an expert in crystal optics, for help in understanding this unexpected behaviour. They isolated and analysed the ‘cloudy intermediate’ and reported seeing crystallites. Lehmann then conducted a systematic study of cholesteryl benzoate and other solids that displayed the double melting behaviour. He became convinced that the cloudy liquid had a unique kind of order. It could sustain flow like a liquid but under the microscope appeared like a solid. In contrast, the transparent liquid at higher temperature had the characteristic disordered state of all common liquids. Eventually, he realised that the cloudy liquid was a new state of matter and coined the name ‘liquid crystal,’ to emphasise that it was something between a liquid and a solid, sharing important properties of both. Not just a liquid, where molecules are randomly distributed, and not just a solid, where molecules are ordered in organised structures.

A liquid crystal is a fourth state of matter: it has properties between those of a conventional liquid and those of a solid crystal. Like a liquid, it flows, and, like a crystal, it can display long-range molecular order. In terms of classifications, liquid crystals (together with polymers and colloids), are often classified as ‘soft matter’ and treated under the branch of physical chemistry of condensed matter. Liquid crystals are temperature sensitive since they turn to solid if it is too cold and to liquid if it is too hot. This phenomenon can, for example, be observed on laptop screens when it is very hot or very cold.

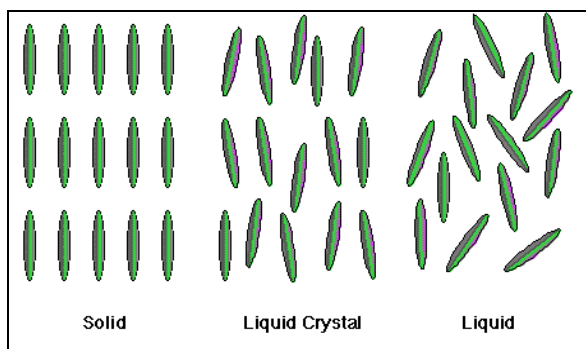


Fig.3.1. Representation of solid, liquid and liquid crystal

3.2. CLASSIFICATION OF LIQUID CRYSTALS

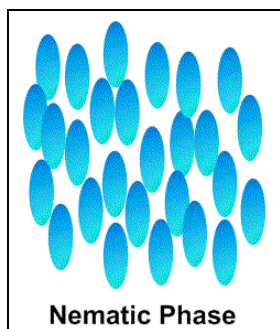
Mainly, liquid crystals are following two types

3.2.1. Thermotropic liquid crystals

Thermotropic phases are those that occur in a certain temperature range. If the temperature rise is too high, thermal motion will destroy the delicate cooperative ordering of the liquid crystal phase, pushing the material into a conventional isotropic liquid phase. At too low temperature, most liquid crystal materials will form a conventional crystal. Many thermotropic liquid crystals exhibit a variety of phases as temperature is changed. For instance, a particular type of liquid crystal molecule (called mesogen) may exhibit various smectic and nematic (and finally isotropic) phases as temperature is increased. An example of a compound displaying thermotropic liquid crystal behavior is para-azoxyanisole.

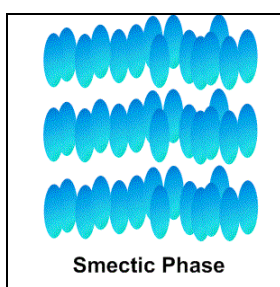
i. Nematic phase

The word nematic comes from the Greek (nema), which means "thread". Nematic liquid crystals flow as normal liquid. The nematic phase exhibits long range molecular orientation but possesses no positional ordering. In polarized light, substances in nematic phases appear to have thread like structure as shown in fig. Examples: para-azoxyanisole and para methoxy cinnamic acid.



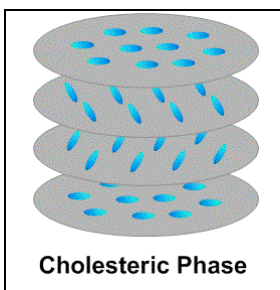
ii. Smectic phases

The word "smectic" originates from the Latin word "smecticus", meaning cleaning, or having soap like properties. The smectic liquid crystals do not flow as normal liquids, they have limited mobility. In the smectic state, the molecules are arranged in nearly parallel layers represented in fig. They flow in layers as if different planes or sheets over another. Examples: Ethyl- p- azoxy benzoate, Ethyl- p- azoxy cinnamate and n- octyl- p- azoxy cinnamate.



iii. Cholesteric phases

Cholesteric phases have properties of both nematic and smectic phases to some extent. Recently disc-shaped liquid crystal and polymer liquid crystals have also been discovered. Molecular arrangements of liquid crystals are shown in Fig.



3.2.2. Lyotropic liquid crystal

A lyotropic liquid crystal consists of two or more components that exhibit liquid-crystalline properties in certain concentration ranges. In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic liquid crystals, these lyotropics have another degree of freedom of concentration that enables them to induce a variety of different phases. A compound that has two immiscible hydrophilic and hydrophobic parts within the same molecule is called an amphiphilic molecule. Many amphiphilic molecules show lyotropic liquid-crystalline phase sequences depending on the volume balances between the hydrophilic part and hydrophobic part. These structures are formed through the

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micro-phase segregation of two incompatible components on a nanometer scale. Soap is an everyday example of a lyotropic liquid crystal.

3.3. APPLICATIONS OF LIQUID CRYSTALS

Molecules of liquid crystals are aligned in the direction of electric field applied. Liquid crystals have important role in digital system. Some of the applications are given below:

1. Liquid crystals are used to detect subcutaneous tumors; since tumor cells are at a higher temperature than normal cells, these are indicated by a colour change.
2. In electronic industry, a break in circuit is accompanied by a slight rise in temperature which is detected from the change in the colour of liquid crystal.
3. Liquid crystals are used in thermo strips and disposable thermometers to read body temperature.
4. Application of liquid crystals in optical imaging and recording is one of the promising areas of liquid crystal research.
5. Liquid crystals are also used to detect radiations and pollutants in atmosphere.
6. LCD screens are used in watches, calculators, laptop computers, television sign boards, etc.
7. Liquid crystals are used in non- destructive testing of materials under stress.
8. Low molar mass liquid crystals find use in erasable optical disks and light modulators for colour electronic imaging.

3.4. NANOMATERIALS

Richard P. Feynman (Nobel Laureate in Physics, 1965) is often credited for introducing the concept of nanotechnology. In the annual meeting of the American Physical Society at California Institute of Technology on 26 December 1959, he delivered a famous lecture entitled “There’s Plenty of Room at the Bottom”

The term nano originated from the Greek nanos which means ‘dwarf’. It is one billionth of a meter. Therefore, whenever we think about nanoscience or nanotechnology, very small objects come to the mind. Indeed, this branch of science and technology deals with materials having at least one spatial dimension in the size range of 1 to 100 nm.

$$1 \text{ nm} = 0.000000001 \text{ m} = 10^{-9} \text{ m} = \text{one billionth meter}$$

3.5. DIFFERENT TYPES OF NANOMATERIALS

Naturally Occuring	Human Origin (Incidental)	Human Origin (Engineered)
Forest fires	Cooking smoke	Metals
Sea spray	Diesel exhaust	Quantum dots
Mineral composites	Welding fumes	Buckyballs/ Nanotubes
Volcanic ash	Industrial effluents	Sunscreen pigments
Viruses	Sandblasting	Nanocapsules

The main differences between Incidental and Engineered nanomaterials are that engineered nanomaterials are intentionally designed to exploit a novel feature that accompanies the small size and are typically better controlled than randomly produced Incidental nanomaterials.

3.6. PHYSICAL AND CHEMICAL PROPERTIES OF NANOMATERIALS

Physical and chemical properties that can change at the nanoscale, color, Melting temperature, crystal structure, chemical reactivity, electrical conductivity, magnetism, mechanical strength. This is a partial list of some of the physical and chemical properties that can change for a given nanomaterial. Not all of these changes will be relevant for every nanoparticle; each will have its own set of variable properties.

3.7. MAJOR CLASSES OF NANOMATERIALS AND THEIR BENEFITS

One way to categorize nanomaterials is by their chemical composition. Many of the most commercially important nanomaterials can be categorized into one of the five classes listed here.

Category	Chemical composition	Product Example
Fullerenes, Nanotubes, Nanowires	Carbon, Boron Nitride	Anti-static fabrics
Metals	Silver, Gold, Iron, Copper	Anti-microbial wound dressings
Ceramics (metal oxides)	Titanium dioxide, Zinc oxide, Ceramic oxide	Sunscreen filters, self-cleaning glass
Semiconductors (Quantum dots)	Cadmium selenide, Cadmium telluride	Medical imaging agents
Polymeric	Hydrocarbon polymers	Drug delivery devices

Nanomaterials are expected to have a wide range of applications in various fields such as electronics, optical communications and biological systems. These applications are based on factors such as their physical properties, huge surface area and small size which offers possibilities for manipulation and room for accommodating multiple functionalities.

In recent years, major progress has been achieved in molecular electronics. As the physical limits of the conventional silicon chips are being approached, researchers are seeking the next small thing in electronics through chemistry. By making devices from small groups of molecules, researchers may be able to pack computer chips with billions of transistors, more than 10 times as many as the current technology can achieve.

A very promising and rapidly-growing field of application of nanotechnology is in medicine. One interesting application involves the use of nano-scale devices which may serve as vehicles for delivery of therapeutic agents and act as detectors or guardians against early disease. They would possibly repair the metabolic and genetic defects. They would seek out a target within the body such as a cancer cell and perform some functions to fix it. The fixing can be achieved by releasing a drug in the localized area. The potential side effects of general drug therapy can be reduced significantly in this manner. As nanotechnology becomes more sophisticated, gene replacement, tissue regeneration or nanosurgeries are the promising future developments

ABOUT THE AUTHORS



Praveen P. Singh is working as Assistant Professor in the Department of Chemistry at the United College of Engineering and Research, Prayagraj, India. He obtained his B.Sc., M.Sc. in Organic Chemistry from T. D. P. G. College (V. B. S Purvanchal University) Jaunpur and D.Phil. from Department of Chemistry, University of Allahabad, India. His current research interests include the development of synthetic receptors for the recognition of biological target structures and the application of visible light chemical photocatalysis towards organic synthesis.



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EXERCISE

1. The density of NaCl is 2.163 g/cc. Calculate the edge of its cubic cell. Assuming that four molecules of NaCl are associated per unit cell.
2. Derive Bragg's equation. When an electron in an excited molybdenum atom falls from the L to the K shell, an x-rays is emitted. These X-rays are diffracted at angle of 7.75° by planes with a separation of 2.64 Å. What are the difference in energy between the K shell and L shell in molybdenum, assuming a first order diffraction? (Given that $h = 6.62 \times 10^{-34}$).
3. With the help of neat diagram describe the structure of graphite. Discuss its electrical and lubricant properties.
4. Describe the preparation, structure and applications of fullerenes.
5. Derive Bragg's equation for diffraction of X – rays by crystals.
6. Calculate the number of atoms per unit cells in SC, BCC and FCC.
7. Derive the expression for the density (d) of a cubic crystal.
8. Discuss the properties and applications of fullerenes.
9. What is a Schottky defect?
10. What are F-centres?