STUDIES OF THE STATIC DIELECTRIC CONSTANT OF SOME MONO AND MULTILAYER LANGMUIR FILMS

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CERTIFICATE

Certified that the thesis entitled "STUDIES OF THE STATIC DIELECTRIC CONSTANT OF SOME MONO AND MULTILAYER LANGMUIR FILMS" which is being submitted by Miss Usha Khanna in fulfilment for the award of Doctor of Philosophy in Physics of the University of Roorkee is a record of her own work carried out by her under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree.

This is further to certify that she has worked for a period equivalent to 24 months full time research for preparing her thesis for Ph. D. Degree at the University.

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ABSTRACT

Dielectric and optical behaviour of thin insulator films have been the subject of intensive theoretical and experimental investigations from the last many years as thin films are being currently used for the development of a variety of miniaturized solid- state devices such as 'diodes', 'triodes', capacitors and optical devices such as interference filters etc. Particularly, interesting is the dielectric as well as optical behaviour of 'built-up' Langmuir films of metallic salts of fatty acids such as barium stearate etc. which have been chosen for the present studies. Incidentally, such 'built-up' films of barium stearate have been shown to be promising for making thin film devices like, tunneling sandwich between superconductors etc. and antireflection coatings etc. These films have great advantages that their thicknesses are very accurately known and are closely controllable in a small range. The added advantages are the smoothness, reproducibility, high dielectric strength and well defined structure etc. These films have also been shown to have high structural perfection and practically free from porosity and gross defects, unlike evaporated film systems.

The quest for devices application of these thin insulating molecular films, has greatly enhanced the interest of workers towards an understanding of their dielectric and optical behaviour. Some experimental work has been done on this behaviour of films but there is no theoretical interpretation of the results. In the present work, a theory has been formulated for the first time for the calculation of static dielectric constant and refractive index of 'built-up' films of barium palmitate, margarate, stearate and behenate.

Measurements of the dielectric constant have also been carried out here and a good agreement is found between the calculated and measured values.

The conventional dielectric theory can not be applied as such in the case of 'built-up' molecular(Langmuir) films, as these constitute a crystal with long hydrocarbon chain of molecules as entities and require the calculation of inter- and intra-molecular interactions to be made. For present calculations, these interactions have been calculated in the presence of static electric field by considering the interaction between different parts of the molecules. Electron diffraction studies have shown that the hydrocarbon chains of the molecules form a hexagonal array with their axes normal to the plane of film. It is known that the molecules of Ba-salts of the fatty acids consist of two parallel hydrocarbon chains with polar group $(COO)_2$ Ba at their one extremity. However, the author has made a reasonable assumption that the molecule is equivalent to the two 'effective' molecules each consisting of one hydrocarbon chain and half of the end group. These 'effective' molecules thus form the hexagonal array with their axes normal to the supporting surface. The extent of the molecules is taken into account by regarding these hydrocarbon chains as divided into small identical groups which can be assumed to be isotropic and to behave like point dipoles.

The calculation of dielectric constant has been made on mono- and multimolecular 'built-up' films of Ba-salts of fatty acids, along the symmetry hexagonal axis (which is the direction of electric field) by calculating the local field.

The local field inside the monolayer at one molecule due to other molecules is calculated by considering the interaction between the small units of the molecules and following the assumption of local additivity. For calculating intermolecular contribution to the local field, the interaction between the hydrocarbon chains and the end groups are calculated, separately. The intramolecular contribution to the local field is calculated by the interaction between the units of the same molecule.

The local field inside the multilayer film is calculated, following Müller treatment, that the molecules are continuously distributed in all layers except the one in which the molecule is situated.

The refractive index of these 'built-up' Langmuir films is calculated along the symmetry hexagonal axis which corresponds to the semi-major axis of the index ellipsoid of positive uniaxial crystal film. The refractive index which is given by the dielectric constant at very high frequency has been calculated for mono-and multimolecular 'built-up' films essentially on the same lines as static dielectric constant (chapter IV). The calculations have been made using Maxwell's equation. The results obtained are compared with the available experimental values and an agreement is found.

The 'built-up' films have been deposited by transferring the monolayers on the aluminized glass slide by a repeated dipping and withdrawal process (chapter II) across the spread monolayer on water surface. This technique of Blodgett-Langmuir enabled the deposition of films having required number of layers and hence desired film thickness. For capacitor fabrication of the type Al-Film-Al, properly selected and cleaned smooth glass slides were used (chapter V). The capacitance of these capacitors has been measured using the universal bridge and dielectric constant is calculated from the knowledge of accurate film thickness and capacitor area. A systematic study of the thickness dependence of capacitance and hence the dielectric constant, has also been made and a definite and unmistakable thickness dependence of the dielectric constant has been found in low thickness range. The results for monolayer and thick films are in complete quantitative agreement with the calculated ones. To the author's knowledge the present work provides the first experimental evidence for the expected thickness dependence of the dielectric constant on a well controlled and structurally well defined thin film system.

The following is the subject matter of the thesis which has been arranged in six chapters.

Chapter I- The surface tension phenomena, the mechanism of monolayer spreading on water, non-occurence of polymolecular films and some fundamental information about individual molecules have been discussed in this chapter.

Chapter II- The 'building-up' process of depositing the film, particularly for Y-type of film has been described in detail. The nature of these 'built-up' films and their structure, as studied through X-ray and electron diffraction have been reported. The method of their thickness determination and refractive index measurements have also been described.

Chapter III- This chapter reviews the experimental work of other workers on electrical properties of the 'built-up' films. The various properties described are dielectric constant and the loss, dielectric breakdown, resistivity and conduction through these films.

Chapter IV- This chapter contains the conventional dielectric theory and its limitations. The theoretical formulation for the calculation of dielectric constant of mono-and multimolecular 'built-up' films of barium salts of long chain fatty acids, is described. The calculations of refractive index of these films is also discussed.

Chapter V- The advantages of 'built-up' molecular films which have stimulated the interest in their studies, have been discussed in this chapter. The experimental details regarding the sandwich fabrication, selection and cleaning of the substrate have been given in detail. The capacitance measurements of these thin film capacitors are also described.

Chapter VI- Theoretically calculated values of dielectric constant and refractive index based on the developed theory have been given for 'built-up' films of barium palmitate, margarate, stearate and behenate. The measured dielectric constant and its variation with thickness have also been provided. The results obtained have also been discussed.

CHAPTER I

MONOMOLECULAR FILMS

Thin films that form at surfaces or interfaces, reduce the abrupt change from one phase to another and warrant special attention. Thin films which reduce evaporation losses at water surfaces, are of particular interest. In these processes, the important role is played by a film just one molecular thick. Thes films are known as monomolecular films or monolayers. Monolayers at a liquid-gas interface can be controlled, manipulated and examined under far better conditions than that at other interface That is why, the monolayer at water-air interface has been extensively studied in the pioneering work of Rayleigh, Langmuir, Adam, Rideal, Harkins, Ries and others, providing much basic information. Here, a particular stress has been laid to the understanding of monolayer properties because 'built-up' films studied extensively, in the present work, have been deposited by transferring these monolayers on to solids.

This chapter provide information about the surface tension phenomena and spreading of organic substances on water. The interpretation given by Lord Rayleigh of Pockel's observations on monolayer spreading of olive oil on clean water surface and the effect of oily contamination on surface tension of water has been discussed in details. Short range forces and mechanism of monolayer spreading on water surface is discussed briefly. Some fundamental information about individual molecules like the thickness of the film or the length of molecule, obtaine through these experiments are also discussed.

1.1 SURFACE TENSION AND MONOMOLECULAR SPREADING

(a) Surface Tension of Water:

The intermolecular cohesion or attraction gives rise to the surface tension of liquid. Some amount of work has to be done for bringing the molecules from the interior of the liquid to the surface. The free energy, thus stores per unit area of this newly formed liquid surface is termed as the 'surface tension' of the liquid. The term 'surface tension' is a misnomer because, obviously, the surface of the liquid does not resemble a 'stretched skin under tension', as was supposed for a long time. However, the two definitions of surface tension that it is the force acting normal to a unit length in the liquid surface (dyne/cm) and the other stated above, i.e. the free energy per unit area of the liquid surface, can easily be seen to be equivalent.

The lowering of surface tension of water caused due to the oily contamination of the surface, is known for a long time. The amount of this lowering was first of all measured accurately by Lord Rayleigh |1|, who found that 0.81 mgm. of olive oil covering an area 555 sq. cms. of water surface, was sufficient to reduce the surface tension by about 21 dynes/cm. Rayleigh had also estimated the average thickness of thin oil film on water to be about 16Å, using area-density method, to be described in sec. 1.1(c).

A detailed and systematic experimental study of the effect of oily contamination on the surface tension of water, was later, carried out by Pockels |2|. For the experiments on the surface tension of water, she used extremely simple apparatus, consisting of a long narrow trough filled to the brim with water and two using the simple formula of the area-density method (sec. 1.1(c)).

(b) Monomolecular Spreading of Olive Oil on Water: Interpretation of Pockel's Observations:

Rayleigh |3| repeated many of Pockel's experiments to interpret her interesting observations, described above. He suggested, that when olive oil is placed on the water surface, it spreads out as a monomolecular layer on the surface and in the critical area observed by Pockels, the oil molecules are closely packed just touching each other. This ingenious suggestion of Rayleigh, thus originated the fascinating subject of monomolecular films. Rayleigh found, that the thickness of the films come out to be nearly equal to the known length of the molecules. But Rayleigh's detailed explanation of Pockel's observations, as has been given below, clearly show that the monomolecular theory rests not merely on the numerical coincidence, but is based on far firmer foundation of the idea of tangible floating molecules.

Following, Rayleigh's suggestions, all of the Pockel's observations can be interpreted as follows. The molecules of olive oil, spread out quickly as a monomolecular layer on the water surface, as the drop of the oil is added to the surface. The cause and mechanism of the spreading phenomenon is described further in sec. 1.3(a). It is obvious, that the area of available water surface for spreading can accommodate as many molecules, as can be closely packed in a completed monolayer on the area. The number n, of the molecules spread on the water surface, is clearly given by the area of the water surface divided by the cross sectional area (sec. 1.1(c)) of the molecule. If the number of molecules in the amount of olive oil placed on the area is greater than n, the

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Pockels |2| observed that the surface tension of water remain unchanged, if no excess oil in the form of small drops remain on contaminated surface, permanently, after a very small amount of olive oil is added to contaminate fairly large area of water surface. However, the surface tension of contaminated water surface, was found to remain practically constant (equal to that of a clean water surface) up to a certain critical area, below which an abrupt fall was noted, when the area of this contaminated surface was reduced by gradually drawing-in the barriers. The value of this critical area depends on the amount of the oil placed on the water surface. She also proved that the surface tension of water remains the same, if the amount of olive oil to contaminate the water surface is less than that, enough to give a critical thickness of about 10Å. Beyond this limit, as the amount of olive oil is increased, the surface tension falls rapidly. From the knowledge of contaminated area and the density of oil,. the amount of olive oil enough to give this critical thickness, can be easily estimated using the simple formula of the area-density method (sec. 1.1(c)).

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Thus, it will be clear from above explanation that in al of Pockel's experiments |2|, spread oil molecules form a manolaye in area greater than the critical area and molecules are not closely packed in the spread layer. In all stages of compression of the monolayer by the barriers, which are gradually reducing the area of the contaminated water surface, the oil molecules do not touch each other and move about on the surface due to excess space available. If the area in which the spreading of oil takes place is greater than the critical area, the molecules remain sufficiently far apart from each other and therefor the electrostatic repulsive forces between molecules do not come intc play. Thus, no work is required to be done for compressing the monolayer by barriers, to decrease the contaminated area graduall equal to that of critical area. The free energy of the underlyin water surface will, therefore, remain intact and the surface tension of water will remain unchanged upto the critical area. The molecules in the compressed monolayer get closely packed just touching each other, when the surface has attained the critical area. At this stage, the mutual electrostatic repulsion between molecules comes into play, rather abruptly and the first resistance to compression arises and the molecules in the monolayer start experiencing an outward force. This outward force exerted on the element of unit length in the monolayer is known as the 'surface pressure' of the monomolecular film (dyne/cm). At this critical stage, as the mutual repulsion just comes into play, some work will have to be done to compress the monolayer,furthermore (or to decrease the area of the contaminated surface), even slightly and the free energy of the underlying water surface gives the required energy. Therefore, when the area of the contaminated water surface is reduced, below the critical area, the surface tension of water falls suddenly and rapidly. It can be easily shown |4|, from the energy considerations that the surface pressure of the film is equal to the reduction in the surface tension. It is obvious, that the critical area value will depend on the amount of oil placed on water surface. Therefore, if the number of available molecules is greater, the critical area will also be greater having the molecules closely packed just touching each other.

In the experiments referred to above, the amount of contaminating oil was kept constant and the area of contaminated water surface was varied. Pcokels |2| in her experiments, made observations on the surface tension, keeping the area constant to compress them or to remove any undesirable surface contamination, laid the foundation of nearly all the work with films on liquids |4–6|.

Rayleigh's successful explanation of Pockel's observations made it to realise, that a detailed study of monomolecular layers may furnish the fundamental information about the individual molecules, e.g., their length, their corss-sectional area, the strength of molecular cohesion and that of the polar groups etc. The promising glimpse into the fundamental aspects of individual molecules by using extremely simple apparatus, has greatly inspired the extensive experimental investigations of monomolecular films. The theoretical study of the monomolecular films has also been very attractive, because a monomolecular film can possess the properties of two-dimensional solids, liquids or gases |4| and may even, exhibit simultaneously, the properties of both liquids and gases, unlikely for three-dimensiomal state of matter. Thus, the investigation of monomolecular film is one of the most interesting and fascinating field.

A large number of experimental methods have yielded information on the mechanical, electrical, optical and chemical properties of molecules in the oriented array, which characterizes monolayers and have contributed much information of the shape and size of molecules. All, of course, depend on the formation of a suitable film for study. A large number of organic substances, e.g. fatty acids, alcohols, esters, ketones, sterols, dyes, proteins etc. are known to spread as monolayers on liquids (usually aqueous) |4–9|. Among the substances, extensively water surface will, therefore, remain intact and the surface tension of water will remain unchanged upto the critical area. The molecules in the compressed monolayer get closely packed just touching each other, when the surface has attained the critical area. At this stage, the mutual electrostatic repulsion between molecules comes into play, rather abruptly and the first resistance to compression arises and the molecules in the monolayer start experiencing an outward force. This outward force exerted on the element of unit length in the monolayer is known as the 'surface pressure' of the monomolecular film (dyne/cm). At this critical stage, as the mutual repulsion just comes into play, some work will have to be done to compress the monolayer, furthermore (or to decrease the area of the contaminated surface), even slightly and the free energy of the underlying water surface gives the required energy. Therefore, when the area of the contaminated water surface is reduced, below the critical area, the surface tension of water falls suddenly and rapidly. It can be easily shown |4|, from the energy considerations that the surface pressure of the film is equal to the reduction in the surface tension. It is obvious, that the critical area value will depend on the amount of oil placed on water surface. Therefore, if the number of available molecules is greater, the critical area will also be greater having the molecules closely packed just touching each other.

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Thus, it will be seen that Rayleigh's monomolecular theory |3| explains experimental observations in a most remarkable way. His ideas now seem to be absolutely indispensable for interpreting the basic surface phenomena. The phenomena of monomolecular spreading is the most fundamental one in the field of physics and chemistry of surfaces |4|.

(c) Experimental Evidence for Monomolecular Spreading of Other Organic Substances.

As has been seen above, Rayleigh's monomolecular theory provided a powerful tool for interpreting the basic surface phenomena. It should also be noted, that extremely simple-apparatus was sufficient for studying the basic phenomena. In fact, Pockels application of movable barriers to confine films, to compress them or to remove any undesirable surface contamination, laid the foundation of nearly all the work with films on liquids |4-6|.

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Devaux |10| studied a number of materials with simple but elegant experimental method, noting that films behaved sometimes as solids and sometimes as fluids. Hardy |11| found that oil which do not contain polar functional group, do not spread in the same way, as the animal and vegetable oils.

The first studies on the fatty acids, were naturally to see, whether they really spread on the water surface as a monolayer. The monomolecular spreading was justified by Langmuir |12|, by estimating the thickness of spread films. This was done mostly by the simple area-density method. If a spread film occupies on area 'A' of the water surface and 't' is the average thickness of the film, Axt is, obviously, the volume occupied by the film. This volume 'V', multiplied by the density 'd' of the film, gives the mass 'm' of the acid spread. From the knowledge of A, d and m, the average thickness of the film 't' can easily be estimated. When the area 'A' is reduced down to the critical area, in which the molecules in the film become closely packed, touching each other, the corresponding value of 't' now obtained will, evidently, be equal to the length of the molecule. This is so, because the molecules stand perpendicularly on the water surface due to the close packing of the molecules. Thus, the length of the molecule in monolayer could be estimated from experimentally determined critical area and the corresponding amount of acid spread. If, the thickness of the spread film, thus estimated tallies with the experimental values of the chain length, obtained by other methods, e.g. X-ray diffraction measurement of the chain length in bulk crystal of fatty acid, the basic assumption of monomolecular spreading of the fatty acid, is correct. Thus, the measurements of thickness of fatty acid monolayer on water, by the above area-density method, are in agreement |13,14| with their corresponding chain length in bulk, studied by X-ray diffraction |15|. Thus, this experimental work supports the Rayleigh's hypothesis |3| of monomolecular spreading. It has been established, that the spreading of fatty acid on water is monomolecular in nature. Many other substances, e.g. alcohols, esters, ketones, sterols, proteins etc. have also been found to be spread monomolecularly. Thus, Rayleigh's original hypothesis, given for the case of monomolecular spreading of olive oil, now seems to be applicable in almost all the cases.

As has been stated above, the area-density method involves the density of the monomolecular film. While estimating the thickness of spread layer, the density of the layer has invariably been assumed, to be equal, to that of the substance in bulk phase and this is the point of objection in this method. However, this assumption is justified only, when the substance in bulk phase has close packed layer structure, similar to that in the monomolecular film which is, in general, not true. Therefore, the area-density method can not be expected to yield accurate value of the thickness. It seems that for studying the nature of spreading of fatty acids on water, Langmuir and Adam had great confidence in this method and conclusions drawn for the monomolecular spreading are essentially correct, because the density of the monolayer of the fatty acid happens to be very close to that of the acid, in bulk phase.

1.2 SHORT RANGE FORCES AND ADSORPTION:

Langmuir's experiments provided strong support for the ideas of molecular orientation at surfaces and short range of molecular forces, which were then being developed independently by him |16| and Harkins |17|. Langmuir |8|, through his classical experiments on adsorption of hydrogen and oxygen, in highly evacuated bulb containing heated tungsten filaments, was led to the hypothesis of short range forces, being responsible for their adsorption. He also believed that the short range forces should be responsible for nearly all types of adsorption. Thus, the adsorption propertie of a solid or a liquid surface should completely change, even if, it gets covered by a single layer of foreign atoms.

The postulate of short range forces, therefore, leads directly to the monomolecular spreading of insoluble fatty acids, having hydrophilic (affinity for water) carboxyl groups on water surface and therefore the attachment and orientation of polymolecular chain will not take place in the absence of long range surface forces. Thus, Langmuir's postulate of short range forces, being responsible for adsorption on liquid surfaces, can also be regarded as the theoretical justification for Rayleigh's hypothesis |3| of monomolecular spreading. The monolayer spreading of a number of insoluble substances on water gives strong support to Langmuir's postulate.

However, in the work on molecular orientation, Hardy |18| considered the cohesive force between molecules to be long range in nature, often acting through distance of several thousand Angstrom units and thus thought that the orientation extended through many layers of molecules. Rothen |19| observations of adsorption phenomena of large molecules provide definite evidence for the existence of long range molecular forces. Therefore, now it seems that Langmuir's postulate of short range forces being involved in adsorption phenomena may not be generally applicable and that Hardy's long range molecular forces do exist in the case of some long molecules.

1.3 FUNDAMENTAL CHARACTERISTICS OF MONOLAYERS

(a) Cause and Mechanism of Spreading of Monolayer on Liquid:

A non-volatile substance, insoluble in a liquid, spreads on its surface if the adhesion (or affinity) between the molecules of the liquid is greater than the cohesion (or affinity) between molecules of the substance itself |4|. The mechanism of the spreading on liquids is explained taking the case of olive oil on water, the spreading being caused due to the motions of the surfac water molecules. Water molecules are in constant motion along the surface and diffuse long distances. The oil molecules adhere to the water molecules and are carried outwards along the surface because of the surface diffusing motions. The surface diffusing motions of water molecules go on continuously underneath the oil drop and the oil molecules which spread first are continuously pushed out farther by the out-ward surface pressure of these, just leaving the oil drop. Obviously, the spreading of a liquid on a solid surface can not take place by the above mechanism since the (surface) atoms or molecules of solids remain practically fixed-up in their positions.

The substances like long chain fatty acids and alcohols, which have a molecular structure composed of a large nonpolar or hydrophobic portion, the hydrocarbon chain and at one extremity a polar or hydrophilic functional group (such as -COOH or -OH) are capable of forming monolayers on water surfaces. The polar groups tend to confer water solubility while the hydro-phobic part prevents it, the balance between them determines, whether a molecule will form an insoluble monolayer. Short chain fatty acids and alcohols, such as acetic acid or ethyl alcohol are, of course, completely miscible with water. As the length of the hydrocarbon chain is increased, water solubility decreases. Thus, in the case of spreading of stearic acid on water, the adhesion (or affinity) of the stearic acid molecules, containing a polar carboxyl group, to the polar water molecule is greater than the cohesion (or affinity between stearic acid molecules themselves. The stearic acid molecules thus spread out due to surface diffusing motions of water molecules with their hydrophilic (affinity for water) carboxyl group (heads) attached to the water molecules. Since the nonpolar hydrocarbon chains with hydrophobic methyl group are very weakly attracted by water molecules, it remains more or less vertically oriented. The presence of polar groups in the chain may thus result in its slight tilting. In the absence of hydrophilic grou such as polar group, no monolayer is formed on water. Long chain hydrocarbons, such as, hexadecane or liquid petrolatum merely floa as drops or lenses on a water surface, without spreading. The interaction within the monolayer forming molecules are also important. If the intermolecular (chain-chain) interactions are stron enough, it will be difficult to produce a monolayer even when a suitable polar group is present.

On other liquid subphases, other kinds of interaction than the strong dipole water interaction can be effective. It appears for example, that n-octacosane, the (28 carbon) saturated hydrocarbon, will spread to form monolayer on mercury |20|. Presumabl in this case, where the liquid subphase has a very high surface tension, dispersion forces are adequate to provide attraction between the organic compounds and the surface and a film is forme in which the molecules are spread out flat on the mercury. A few partially fluorinated organic compounds can also spread to fo insoluble monolayers on organic liquids. In these cases, parts of molecules are attached to the subphase while other parts preve complete solution.

(b) <u>The Formation of Spread Monolayers</u>:

The spreading of a monolayer with the aid of volatile solve in the conventional manner can occur in two ways. With some substances, for example, fatty acids in hexane or petrolatum ether on water, the spreading solution spreads to a thin layer whose interference colours are visible and the monolayer forming molecules take up positions at water-solvent interface. The solvent then evaporates, only the monolayer remains. Alternative result in its slight tilting. In the absence of hydrophilic group, such as polar group, no monolayer is formed on water. Long chain hydrocarbons, such as hexadecane or liquid petrolatum merely float as drops or lenses on a water surface, without spreading. The interaction within the monolayer forming molecules are also important. If the intermolecular (chain-chain) interactions are strong enough, it will be difficult to produce a monolayer even when a suitable polar group is present.

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Spreading can be performed without a solvent in some cases, where a material does not spread spontaneously. For example, if a droplet of oleic acid or a small crystal of cetylalcohol, is placed on a water-surface, molecules leave the bulk phase and diffuse out over the liquid, the spreading process may be hastened by convective flow in the liquid and in some cases, by vapour phase transport.

(c) States of Monolayers:

Devaux |10| shortly after 1900, pointed out that molecules in monolayers could exist in different states, more or less analogous to three-dimensional matters; solid, liquid and gaseous. He showed that the fluidity of a monolayer could be qualitatively estimated from the mobility of talc particles dusted into the film. It is quite certain, that various monolayer states represent different degrees of molecular freedom or order, resulting from the lateral intermolecular adhesive forces and the strength of anchorage of the molecules to the surface, respectively. If the 'anchorage' or perpendicular attraction between the film molecules and the liquid is weak, the film may not be formed at all or will tend to crumple up under small lateral compression. If the attraction between film molecules and liquid is reasonably strong but the lateral adhesion is small, the film molecules move about independently on the surface, partaking in the translatory motion of the underlying liquid molecules; such a film resembles a gas or a dilute solution on the surface and is called a 'gaseous' or 'vapour' film. A strong lateral adhesion makes the molecules adhere together into large coherent islands of film and restrains their free thermal motions on the surface. The film is liquid or solid, depends on whether the molecular movement is less or more restricted, determined by the amount and small details of distribution of the intermolecular adhesive forces |4|. It is possible in some cases to change the phase of film by changing the temperature or pressure.

(d) Fundamental Information about Individual Molecules from Monolayer States:

Langmuir's film balance |4|, whose range has recently been considerably extended by the use of the electron microscope and radioactive isotropes |21|, remains the principal instrument for basic studies on monomolecular films. With this simple device, the measurement of size of molecules, the estimation of their shapes, their cohesion and strength of polar groups can all be obtained.

The film balance essentially consists of a small shallow waxed trough filled with water on which the monolayer of substance is spread. A barrier in the form of waxed rectangular brass bar is laid across the long edges of the trough behind the monolayer.

The film is made to push against a delicately suspended floating barrier, which measures the surface pressure exerted by the film, as the film is compressed to any desired area. The pressure of the film against the float is balanced by twisting the torsion wire to which the floated barrier is attached. The degree of twisting, required to keep the float stationary, is a measure of the surface pressure. As the temperature variations, accidental contamination, vibrations and dust particles may cause major errors in these experiments, greatest care has to be taken, regarding them.

A single simple plot of surface pressure against area (pressure-area curve of the monolayer) yield, among other things, the cross sectional area and length of the molecules, strength of its polar groups and also the approximate strength of the intermolecular cohesion. As the area of monolayer decreases, the surface pressure increases and the slope of π-a curve gives the compressibility of the monolayer or the strength of molecular cohesion. Near the collapse pressure, the molecules in the film get closely packed. The cross sectional area of the molecule can be determined with a prior knowledge of the number of molecules in the monolayer i.e. the number of molecules in the substance spread. The length of the molecule or the thickness of the monolayer can be found by the area-density method (sec. 1.1(c)), already described. The collapse pressure gives both the strength of anchorage of the film to the surface i.e. the strength of polar groups and the strength of cohesion.

Stearic acid, for example, has been found to have a cross sectional area of 20 sq. Angstroms, a chain length of 25Å, its monolayer having a high collapse pressure of 42 dynes/cm. (therefore the molecules having strong polar group) and low compressibility (or high molecular cohesion).

1.4 INHOMOGENEITY OF MONOLAYERS:

For a long time, investigators assumed the monolayers to be homogeneous at all stages of compression. Zocher and Stieble |22| first examined the monolayer film under a powerful dark-field illuminator mounted in the bottom of the trough and focussed on the surface of the liquid bearing monolayer. A microscope may be used above the surface to detect inhomogeneity of the film at low pressure or sometimes even in the region of collapse, consisting of molecular aggregates or islands. This technique was improved by Adam |23|, who suggested that varying the liquid level in the trough provided a simple means for accurate focussing. The ultramicroscope has also been used by Bruum |24| in an interesting study of collapsed films. The method, however, was capable of detecting only gross impressions of the size and shape of these aggregates.

Elliptically polarized light reflected from the surface covered by monolayer has been examined by Freundlich, Bouhet, Tronstad and others, for studying the structure of the films. But, because, the difficulties of the interpretation of the optical effect of the films in terms of the individual molecules, this method could not contribute much regarding the structure of monolayer. However, the Bouhet optical method |25| indicates the lack of homogeneity in the film.

The studied surface potential which varies with molecular concentration or packing in a monolayer, definitely, established the inhomogeneity of the films (except gaseous) |26|. This surface potential arises from the surface field of force due to the unbalanced forces of molecules in the surface. This method also could not resolve the detailed structure of the monolayer due to the dimensions of the electrodes used.

The electron microscope was first applied to the study of monomolecular films by Epstein |27|,who showed that it was possible to detect fatty acid monolayer films, after depositing them on glass slides and shadowing with an evaporated metal film. Recently, Ries |21| and his coworkers refined this technique to study the structure of monolayers at various stages of compression. The electron micrographs clearly show that at a low pressure the film is inhomogeneous and with increasing compression or pressure large homogeneous areas of continuous monolayer appear. Also, electron micrographs of a collapsed film suggest a mechanism for the collapse |21|. More information of the origin of single monomolecular layers has been obtained by shadowing method. Combined film balance and electron microscope technique in conjunction with radioactive tracer technique are being used |21| for studying mixed films or monolayers with two or more components, the results obtained being of biological importance. Electron microscope has also been used to determine thickness of monolayer by shadow casting technique |21|.

The next chapter describes the technique of building-up multilayer films by transferring monolayers on to solid slides.

The nature and structure of such'built-up' films have also been discussed. The deposition technique of Y-type films is given in detail. The determination of thickness, X-ray and electron diffraction studies are also discussed. The Skeletonization of the film and the optical properties of these 'built-up' films are also described.

CHAPTER II

BUILT-UP MOLECULAR FILMS AND THEIR PROPERTIES

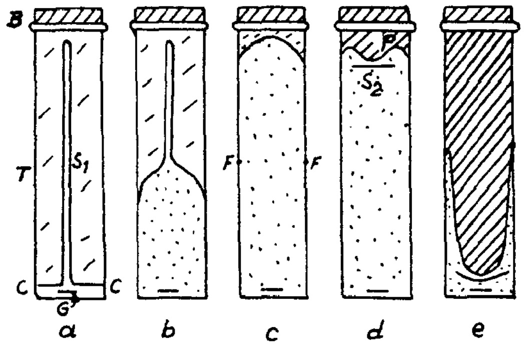
This chapter describes in detail, the experimental method of 'building-up' the multilayer films and their nature of deposition. A particular mention has been made of the 'building-up' of Y-type films which have been studied in the present work. The general properties and structure of these 'built-up' films are also discussed, as observed through X-ray and electron diffraction studies. The methods of determining their thickness and refractive index have also been described.

2.1 BUILDING-UP OF MULTILAYER FILMS:

(a) Experimental:

Mono-and multilayer films of long chain fatty acid compounds can be 'built-up' by the well-known technique of Blodgett and Langmuir |8,28-30|. The technique has been described in detail, specifically, for barium stearate and it has been followed for other substances like barium palmitate, margarate and behenate which have also been studied in the present work.

The technique for 'building-up' multilayer films consisting a very simple apparatus, is illustrated in fig. (1). The long narrow trough T waxed from inside, is first levelled and then the surface of deionized water (specific resistance $\simeq$ $6x10^5$ ohms cm.) filled to the brim of the trough, is cleaned by sweeping the barrier B over the surface to the position shown in fig. (1 a). A waxed silk thread S_1 is attached by small metal clips C to the edges of the trough and the thread is placed upon the water surface in the form shown. The thread is carefully made to touch the water surface at every point to avoid any film

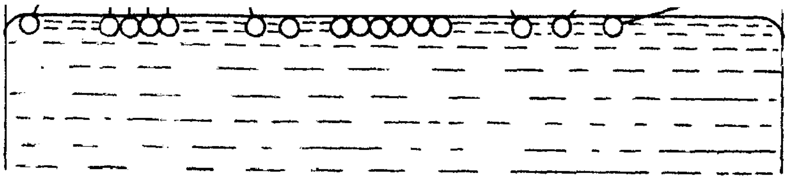


(After Langmuir, Proc. Roy. Soc. A, <u>170</u>, 1 (1939)

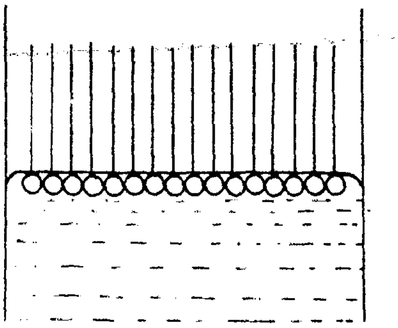
<u>FIG. 1</u> _ DIAGRAMMATIC REPRESENTATION OF THE APPARATUS FOR BUILDING-UP THE FILMS.

leakage. Stearic acid (or palmitic, margaric and behenic) dissolved in benezene (concentration commonly $3x10^{-4}$ by weight) is placed on the surface near G and the spread acid pushes the thread before it, as shown in fig.(1 b). After the spreading has completed, the thread is fastened to the edges of the trough by two small clips F, fig. (1 c).

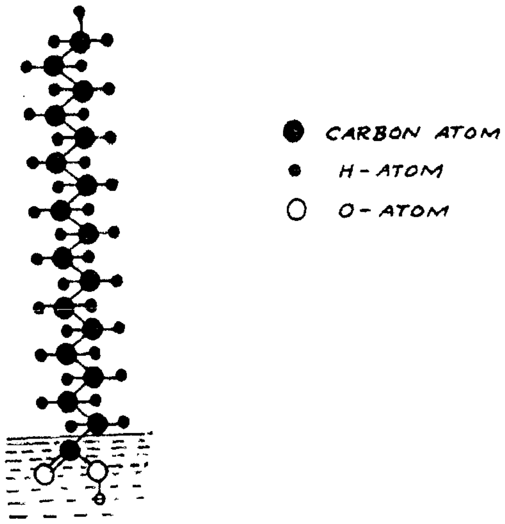
The stearic acid molecules spread monomolecularly on water surface and the state at this stage is shown in fig. (2 a). Due to relatively large space available for the molecules, some of them may tend to bendover the water surface, instead of standing upright. A small drop of the 'piston oil' oleic acid (surface pressure 29 dynes/cm.) is now placed on the surface at P to keep the stearic acid monolayer under constant compression. Under these conditions, the monolayers of oleic acid and stearic acid press against each other to give an equilibrium shape to the thread, as shown in fig. (1 d) and also the stearic acid molecules in the monolayer are now relatively close packed and stand upright, as a result of oleic acid compression. Fig. (2 b) shows that the molecules are tightly packed and approach vertical orientations at relatively high compression, where_as fig. (2 a) indicates, at low compression that the molecules are oriented at different angles or form tightly packed aggregates. Circles represent polar group of the molecules while straight lines the nonpolar hydrocarbon chains. Fig. (2 c) gives a pictorial representation of the orientation of stearic acid molecule on the water surface. It is important, that the homogeneity and density of the stearic acid monolayers would be corresponding to the compression (surface pressure 29 dynes/cm.), which is far apart



(a) Molecule bending



(b) Molecules standing closed packed



(c) Stearic acid molecule standing on water

(After Ries, Scientific American, 204, 152 (1961).)

FIG. 2 – DIAGRAMS SHOWING STEARIC ACID MOLECULES ON WATER SURFACE.

to its collapse pressure i.e. 42 dynes/cm.

The use of the thread S_2 (fig.(1 d)), for preventing accidental oleic acid contamination to stearic acid monolayer near G, was not found necessary because, it was always ensured that the thread touches the water surface at all points along it and thus, there was no chance of any leakage of oleic acid. The process of depositing successive monolayers upon the clean slide dipped into the water, in the position marked G, is then begun. Each layer, that is deposited, uses up some of the stearic acid monolayer on the water so that the thread moves forward through an area equal to the total area of the slide dipped, front and back. For easier deposition of multilayers of barium stearate from stearic acid monolayer, a low concentration (about $3x10^{-5}$ M) of barium ions should be present in the solution. The barium content of the solution is added by barium chloride and the pH of the solution is adjusted by the addition of potassium bicarbonate. The divalent barium ions in the solution undergo surface reaction with stearic acid (or palmitic, margaric, behenic acid) molecules (whose carboxyl groups touch the water surface) to form barium stearate (or palmitate, margarate etc.). The barium stearate monolayer is now transferred from the water surface to the slide, moving across it, by a continuous dipping and withdrawal process. Multilayers are more easily formed when the pH is greater than 6. The ambient temperature should be maintained at about 20-22° C.

Under these conditions, a layer is transferred on both the downward and the upward journey of the slide (rendered suitably hydrophobic) and the 'built-up' film is expected to be Y-type (sec. 2.1(b)), using the solution in the trough containing 3×10^{-5} M $BaCl_2$ and its pH adjusted equal to 7.2, by addition of 4×10^{-4} M $KHCO_3$. But, if the solution is made more strongly alkaline, pH=9, layers are deposited during the down-trips and not during the up-trips, such layers have been called X-layers (sec. 2.1(b)). The layers are preferably deposited at the rate of about 20 to 30 layers per minute. Fig.(1 e) shows the final shape of the thread after some layers have been deposited.

(b) Nature of Deposition of X,Y,Z Types of Films.

Langmuir |31| first realised the experimental possibility of transferring the monolayers from aqueous substrates to a glass or metal surface by a simple dipping and withdrawal process. Blodgett and other subsequent workers |8,28-30,32| have since carried out detailed investigation of this phenomenon, the basic points of which are now well established. Thus, it has been shown that by successive deposition, multilayer film having desired number of layers, can be 'built-up' on solid surfaces (sec. 2.1(a)).

Only condensed monolayers, which do not tend to spread indefinitely as the surface pressure is reduced to zero i.e. no compression and thus acting as two-dimensional solids or liquid rather than gases |8| are found to exhibit the above phenomenon of deposition. Initially, fatty acids were used |28,29| which condensed by means of calcium or barium ion in the substrate but subsequently many other organic compounds have been employed e.g. esters, ketones, phenols, proteins etc.

Langmuir |8| and Bikerman |32,33| pointed out that the nature of deposition of monolayers on a solid surface depends upon the contact angle between the solid and film covered water surface. During deposition, to facilitate the transference of the monolayers, the spread layer is kept under constant pressure (sec. 2.1 (a)). For example, if a slide of glass or metal is being dipped across a fatty acid monolayer on water, the curve of contact between water and the slide surface advances, relative to the slide, which gives the 'advancing' contact angle. On the contrary, while taking out the slide from water, curve of contact recedes relative to the slide and this is termed as 'receding' angle of contact. Obviously, when the slide is entering water and advancing angle is obtuse, the water surface will fold down naturally on the solid surface thus turning the upper most groups (methyl groups) of the monolayers towards the solid surface. The molecules will be deposited with their methyl groups in contact with the slide and the surface of deposited monolayer will be composed of carboxyl groups (sec. 2.1 (c)) and this orientation of the molecules is termed as 'exotropic'. As the adhesion of the methyl groups to the solid surface is relatively low, the slide should, obviously, be lowered into water at a slow speed after deposition of the monolayer. If the advancing angle is acute, the methyl groups remain turned away from the solid surface and there will be no deposition when the slide is entering the water. Thus, a monolayer can be deposited on a slide at its entry into water only, if the slide surface has been rendered fairly hydrophobic i.e., non-wettable by water, thus giving large contact angle. No deposition of the monolayer, therefore, take place on the first immersion of an ordinary glass slide which is easily wettable by water (low contact angle).

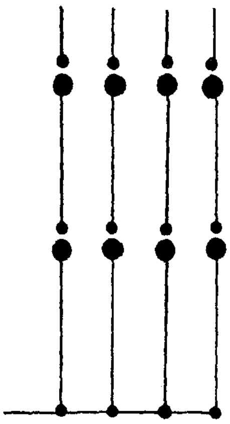
When the slide is being taken out and the receding angle is acute, the water surface folds up on to the slide thus turning the lower most group i.e. the polar carboxyl group towards the slide surface, for deposition of the molecules. The water molecules, which are sandwiched between the polar groups of the monolayer and the slide surface, are slowly squeezed out because of strong affinity between the polar groups and the solid surface. In this deposition, the polar carboxyl group is in contact with the solid surface and the deposited monolayer surface consists of methyl groups. The orientation of molecules with carboxyl groups towards the slide surface and methyl groups away from the slide, is termed 'endotropic'. Evidently, the polar groups remain turned away from the slide surface when the receding angle is obtuse and there will be no deposition when the slide is leaving the water surface. Thus, a monolayer can be deposited on a hydrophilic solid surface i.e., wettable by water and therefore, having a low contact angle like that of an ordinary glass slide, on its withdrawal across the water surface. If the speed of withdrawing the slide is high the sandwiched water molecules will not be efficiently squeezed out and therefore no deposition will occur. The squeezed out water molecules are forced to come down on the surface of water not due to gravity, but, because of their replacement by the fatty acid molecules in the monolayer whose polar carboxyl groups have strong adhesion to the solid surface.

Thus, from above it is clear that if both the advancing and receding angles are obtuse, deposition of monolayer will take place only on lowering the slide across the water surface.

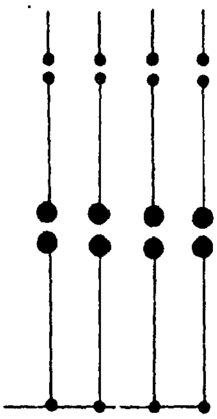
Such a deposition or film thus 'built-up' is termed X-type. Obviously, a X-type film will consist of a series of exotropic layers which are oriented in such a way that the methyl groups are towards the solid surface and carboxyl groups away from it and thus, the surface of X-film will be composed of carboxyl groups. Since, here the molecules in the adjacent layers are oriented in the same direction, the distance between two successive planes containing carboxyl groups will clearly be equal to the chain length of the molecules (assuming that the molecules are oriented perpendicularly to the slide surface) (see fig. 3.a).

When the advancing angle is obtuse and the receding angle is acute, the deposition will naturally take place on both dipping and withdrawal of the slide across the water surface. This deposition or the film thus 'built-up' is called Y-type. Obviously, a Y-type film will be made up of a series of alternating exotropic and endotropic layers. Thus, the surface of the Y-film will be composed of methyl groups and the molecules in the adjacent layers are oppositely oriented. It is clear that the distance between two successive planes containing carboxyl groups will be equal to twice the molecular chain length (see fig. 3.b).

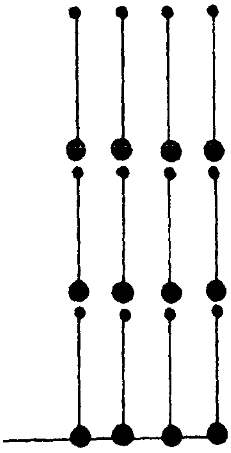
When both the advancing and receding angles are acute, the deposition will, obviously, take place on withdrawing the slide across the monolayer. Such a deposition or the film thus made up is termed Z-type (this is rather uncommon). Obviously, a Z-type film consists of a series of endotropic layers which are oriented in the same direction and the surface of these films are composed of methyl groups. Since, here the molecules in adjacent



(a) X-Type film



(b) Y-Type film



(c) Z-Type film

FIG. 3 – DIAGRAMMATIC REPRESENTATION SHOWING THE MOLECULAR ORIENTATION OF XYZ TYPE FILM.

• — METHYL GROUPS, ● – CARBOXYL GROUPS.

layers are oriented in the same direction, the distance between two successive planes containing carboxyl groups, will clearly be equal to the molecular chain length (fig. 3 c).

As the contact angle between the film covered water surface and the solid being dipped, is well known to depend on the nature of the film forming substance, the rate of dipping and withdrawal, the surface pressure of the film and the pH of solution etc.; clear cut experimental considtions have to be laid down for the deposition or 'building-up' of any given type of film i.e. X,Y or Z. Blodgett and Langmuir |29|, for example, have done for the case of Y-films of metal stearate. It should be noted that the contact angle between a liquid and a solid is considerably modified |4| by any contamination, greasy or otherwise, of the solid surface and also by its roughness. Therefore great care has to be taken regarding these factors also, while following the experimental conditions for building-up a particular type of film.

(c) Deposition Ratio of Monolayer:

Many early studies showed that when a close packed film under high surface pressure is deposited to a solid surface, the area of the film transferred is equal to the geometrical area of the solid i.e. the deposition ratio is one. The 'deposition ratio' of a monolayer is simply as the ratio of the apparent area of the slide coated with the area of the monolayer. thus removed from the water surrace. Since the surface of a slide is, in general, rough on a molecular scale, its apparent area (the one usually mesured) is less than the real area. The deposition ratio was found to be unity within experimental errors. This was, indeed, demonstrated by Bikerman |32|, who showed that stearate monolayers could even be deposited on grooved surfaces or fine wire gauges.

2.2. THE 'BUILDING-UP' PROCESS OF Y-FILMS:

The process of 'building-up' Y-films by depositing successive monolayer is illustrated in fig. (4). In this case, the slide has suitably been rendered hydrophobic by depositing a thin Al-layer, under vacuum by thermal evaporation (sec. 5.3) or for deposition on glass, by placing some molten ferric stearate on the surface and rubbing it vigorously with clean towel, which removes all but one layer of ferric stearate molecules. Fig.(4 a) shows the lowering of the slide across the monolayer on water surface, with polar carboxyl groups, touching the water molecules. Under these conditions, the first layer is deposited on the first downtrip (fig. 4 b). The following uptrip, (fig. 4 c) causes the deposition of the second layer; the next down journey (fig. 4,d) gives the third layer and so on. Therefore, outside water, films containing only even number of layers will exist. For getting odd numbered (having odd number of layers) films out side water, the slide is first dipped, then the monolayer of acid spread and subsequent deposition made by withdrawing the slide which gives the first deposited layer. If multilayer films of odd number is to be 'built-up' the previous procedure of dipping and withdrawal of the slide is continued. Obviously, in the deposited Y-films of even number of layers, both the upper and lower surfaces of the film are made up of hydrophobic methyl groups and in those containing odd number of layers, the upper surface consists of methyl groups while the lower one is made up of hydrophilic carboxyl group

2.3 EXPERIMENTAL DETAILS AND PRECAUTIONS

In the present investigations, extremely pure samples (Price's Bromborough Ltd.) of palmitic, margaric, stearic and behenic acids were used. Oleic acid, benzene and wax used were of E.Merck's grade and barium chloride and potassium bicarbonate being of Analar grade. Doubly distilled water was produced by redistillation of good distilled water and was deionised by passing this through the two columns of a Portable 'permutit' deioizer 'Mark 8' Fig.(5), (supplied by M/S Ion Exchange (India) Ltd). The first column contains the cation exchange material converting cations such as calcium, magnesium and sodium, into the corresponding acids and the other one containing anion exchange material, remove the acids formed by the former. The deionised water thus produced is free from dissolved solids and used for experimentation. The required concentration of the solution was achieved by weighing the substances on an extremely sensitive chemical balance. The pH of the solution was checked by the standard Beckmann pH meter. Reasonably, small temperature variations were attained by working in an air conditioned room, cooled down to the required region of temperature.

In the study of monomolecular films, the key words at all times are purity and cleanliness. Considerable care must be taken to maintain the apparatus free from all contaminations and particularly from surface active contamination. Greatest care at all stages was, however, taken against any other contamination, accidental or otherwise, by ensuring and maintaining thorough cleanliness of all parts of the apparatus. This is of

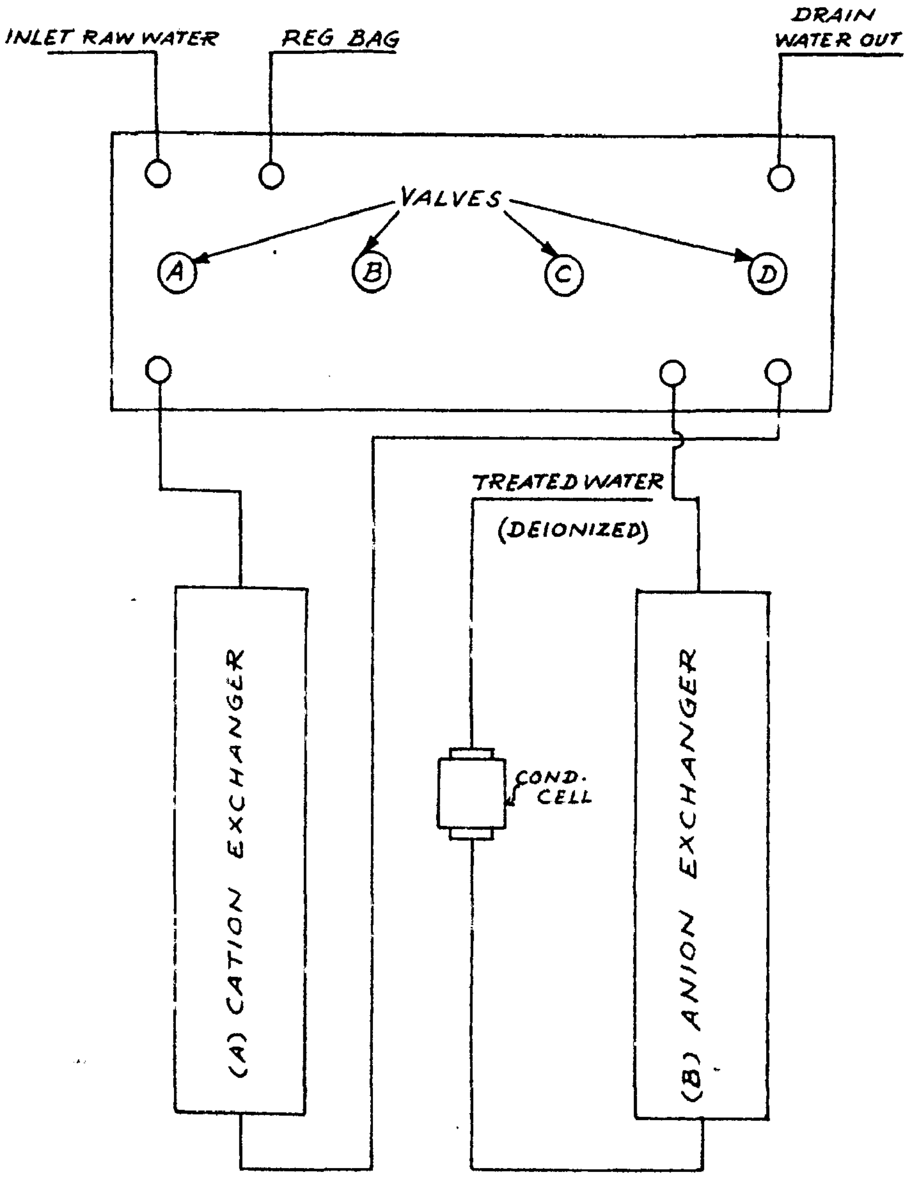
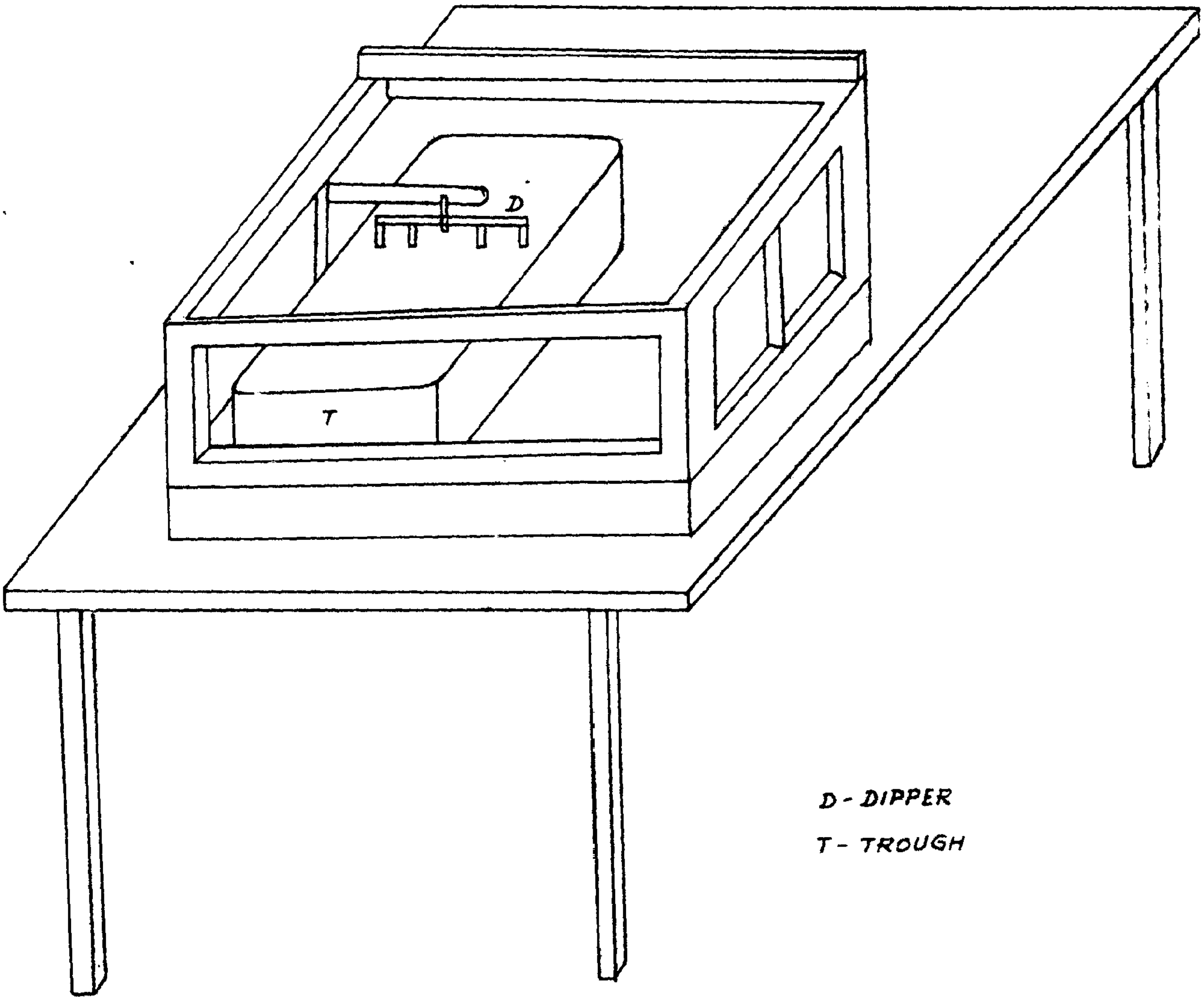


FIG.5 – BLOCK DIAGRAM OF PERMUTIT PORTABLE DE-IONISER MARK-8.



D - DIPPER
T - TROUGH

FIG.6 - APPARATUS FOR BUILDING-UP THE FILMS.

great importance as the phenomenon under study is on molecular level. Also, during the experiment much care was taken to avoid any vibrations or disturbances of the trough which, if present, would crack the spread monolayer and thus produce unevenness in the deposited film. The labelled fig. (6), shows the details of the apparatus.

2.4 PROPERTIES AND STRUCTURE OF 'BUILT-UP' MOLECULAR FILMS

(a) General Properties:

Only 'built-up' barium stearate films, deposited by Blodgett-Langmuir technique, have been studied in detail |8,28, 29,34|. The films consist of superposed sheets of oriented molecules and form positive uniaxial birefringent crystal with their optic axis perpendicular to the plane of the film. Electron diffraction studies, show that the films actually form hexagonal crystals with the symmetry axis i.e. the optic axis, perpendicular to the plane of the film. X-ray diffraction studies also prove that the films are, indeed, very thin crystals having layer by layer structure.

As already discussed, the 'built-up' film of, say, barium stearate can be of the type X, Y or Z depending on the molecular orientation in adjacent layers of the film. It has been shown theoretically that the surfaces of the Y and Z films should be composed of methyl groups while those of X films should consist of carboxyl groups. (in the case of barium stearate, divalent barium atoms substituted for hydrogen atoms of the carboxyl groups). Since the methyl groups are hydrophobic i.e. practically no affinity with water, the surfaces of Y and Z films are expected to be hydrophobic i.e. non-wettable by water having large contact angle. And since the carboxyl groups are hydrophilic, the surface of X-films should be hydrophilic (wettable by water) having very low contact angle. However, Langmuir [8] found experimentally that the surface of X and Y films have almost the same angle of contact with water. Also, X-ray diffraction studies of 'built-up' X and Y films of barium stearate [35,36] have shown that the lattice spacing normal to the film is the same in both types of films. This spacing is equal to the distance between two successive planes containing barium atoms i.e. those containing carboxyl groups. It has already been shown that for X films the distance between the barium atoms in successive planes should be half of that corresponding to Y films. The anomalies regarding X and Y films have been explained by Langmuir [37] in terms of overturning of molecules in adjacent layers of X-film, just after the deposition. According to him, this overturning of molecules results a molecular reorientation or a sort of recrystallization in the film whi arise because of the thermal vibrations. This molecular reorientation can be possible at ordinary room temperature because the molecules in the films are bound together with very weak van der Waal forces, as the films have low melting points. The reorientation of the molecules in Y films is not expected because the molecules in the first and successive double layers ar strongly anchored with their polar groups face to face (fig(3 b) which is a stable configuration, while in the case of X films, the anchoring is relatively very weak due to the methyl (inert) and polar groups being face to face; an unstable configuration. Therefore, the unstable structural configuration of X film tends to attain the stable structure of Y film by the gradual overturning of molecules in the first and successive double layers of the X films. In this way, Langmuir's theory of overturning of molecules in X films accounts for the anomalies, described above. However, there is no direct experimental evidence to support this interesting idea of Langmuir.

Porter and Wyman |38,39| measured the surface potential of X films of barium stearate and showed that each layer carries similarly oriented dipoles suggesting succession of exotropic layers i.e. the films are in the initially unstable configuration, contrary to the X-ray evidence. Later experiments showed that surface potentials depend upon the outer layer, deposited as X or Y type. The evidence, therefore, indicates that the surface potentials are due to a surface electrification produced by the recession of water from the hydrophobic surface during the withdrawal of the plate |8| while in the case of Y films there is no recession of water.

Langmuir |16| experimentally found from π-a curves that same curves are obtained for the higher saturated fatty acids and alcohols, having 14 or more carbon atoms. The monolayers of these substances are relatively incompressible and occupy areas of about 20 sq. Å/mol. Langmuir |16| confirmed experimentally that with fatty acids having from 16 to 30 carbon atoms per molecule, the cross sections remained fairly constant while the lengths of the molecules increased in proportion to the number of carbon atoms.

(b) <u>Determination of Thickness</u>:

The thickness of a monomolecular film of a long chain organic substance e.g. palmitic acid, barium stearate etc. has been determined by a number of methods divided mainly into two parts. The thickness is determined, either by the area-density method (sec. 1.1 (c)), which requires the film to remain on the water surface or the monomolecular film is first deposited onto a slide and then the thickness measured by the optical methods. The area-density method is based on the statement of Dervichian |40 that the lattice structure and tilt of the molecules in different forms are the same in two-and three-dimensions.

(i) Interferometric methods- There have been several attempts to estimate the thickness of 'built-up' molecular barium stearate films. Blodgett and Langmuir |28,29,34| used the method of interference of monochromatic polarized light, reflected by the film, for the determination of thickness. The film thickness is calculated from the knowledge of the angle of incidence for minimum reflected intensity, the wavelength used and the ordinary refractive index of the film. Jenkins and Norris |41| in their method kept the angle of incidence constant and varied the wavelength until the reflected intensity reduced down to the minimum. In another method for the determination of thickness, Holley |35| utilised a Michelson interferometer.

(ii) Polarimetric methods- Rothen and Hanson |42-44| used an apparatus called ellipsometer to measure small increments in film thickness. This polarimetric method is based on the measurements of the change in ellipticity of light reflected from the film and stearic acid or barium stearate film of known numbers are used as optical gauge for comparison purposes. In a more recent work an interference reflector of barium stearate itself, was used |45| to determine the thickness by Hartman's polarimetric method |46|

utilizing white light interference fringes.

The optical methods used for determining the thickness of the 'built-up' molecular films invariably involved the refractive index of the films or used the standard reference films. It has already been shown that the refractive index of the films can not be assumed to be equal to that of the bulk, because the density of the monolayer is not equal to the density of the substance in bulk. The refractive index of the films is necessary for evaluating the metrical thicknesses of the films by the method described above. Also, any differential phase changes upon reflections have to be eliminated to avoid spurious effects in thickness determination.

(iii) Multiple beam interfeometric methods- Multiple beam interferometric technique |47| for determining the thickness of molecular films was first applied by Courtney- Pratt |48,49|. He studied the molecular layers of fatty acids spread by the droplet retraction technique on mica cleavage surface. This method of measurement with doubly silvered mica, forming the interference system, does not directly yield the metrical thickness since it also requires the knowledge of refractive idex of the film. Moreover, the differential phase changes upon reflections at mica-silver and monolayer- silver interfaces are also involved which are not unambiguously known. Also, fairly low orders are not conveniently obtained with such an interference system.

Srivastava and Verma |50,51| carried out the direct determination of the metrical thicknesses of mono- and multimolecular films of barium stearate and other substances. In their work, the standard thin film multiple beam interferometric technique |47|

has been used to determine accurately the thickness of the films. It is well-known that this method is independent of the optical properties of the film and since the differential phase changes have been eliminated using the standard reference film of barium stearate itself, this yields the true metrical thicknesses of the films.

(c) Determination of Lattice Spacing 'C' : X-ray diffraction Studies:

X-ray diffraction studies have been carried out by number of workers |35,36,52-60| on 'built-up' films of various long chain organic compounds. The conventional seal-off X-ray sources were used in these investigations. The observations of X-ray diffraction effects show that, definitely, the 'built-up' films are crystalline in nature and is merely a mechanical growing of the crystal, layer by layer. Indeed, the building up technique can sometime be used for crystallization of some otherwise intractable substance e.g. unsaturated acids |57|.

Most of the workers studied the X-ray diffraction effect on somewhat thick 'built-up' films. However, Bisset and Iball |60| investigated X-ray diffraction from a few number of layers of barium stearate and plamitate and established the analogy with optical diffraction from ruled gratings. Clark and Lappla studied a few layers of lead stearate |61|. The lattice spacing of built-up lead stearate films was also measured by Stephens and Tuck-Lee |62| using electron microscopy.

The lattice spacing of barium stearate films perpendicular to the plane of the film was measured by Holley and Bernstein |54,55| and Frankuchen |36|. They found that the lattice spacing is the same in both X and Y types of films. According to the process of building up the film, X films should have unidirectional orientation of the molecules in the layers, therefore, its spacing, normal to the film, should be half of that in Y films in which the molecules in adjacent layers are oppositely oriented. The observed identity in spacing of X and Y films of barium stearate has, however, been explained by Langmuir |37| in terms of overturning of molecules in adjacent layers.

Since the scattering of X-rays from carbon and hydrogen atoms can be assumed to be very small as compared to that from barium atoms (large atomic number) the lattice spacing normal to the film measured by X-ray diffraction must correspond to the distance between adjacent planes containing barium i.e. unit cell height 'c'. Therefore, half of the lattice spacing 'c' in the case of Y films, must be equal to the chain length of barium stearate molecules or the metrical thickness of the monomolecular film of barium stearate.

Recently, Srivastava and Verma |51| studied the X-ray diffraction effect of 'built-up' films of different thicknesses of barium palmitate, margarate, stearate and behenate. They used a a microfocus X-ray source of the kind described by Ehrenberg and Spear |63| to over come the large exposure times and diffracted spectra were recorded on a Bragg-Müller spectrograph. They also found that the lattice spacing perpendicular to the supporting surface is double the thickness of the monolayer film.

(d) Electron Diffraction Studies of 'Built-up' Films:

The structure of mono- and multimolecular films of barium stearate and stearic acid have been studied by Germer and

Storks |64| in detail. Their electron diffraction studies show that the barium stearate films, built-up by Blodgett-Langmuir technique actually form hexagonal crystal with the symmetry axis perpendicular to the plane of the film. Upon the clean metal surface, odd number of layers have been built and investigated by the reflection method and on thin organic supporting foils by the transmission method. Germer and Storks |64| found that the hydrocarbon chain of barium stearate molecules form hexagonal arrays with their axes normal to the supporting surface and separated by distance of 4.85Å. Stearic acid molecules form crystal of monoclinic form with a=8.27 Å, b=4.96 Å, β=70°, the a and b axes lying in plane of the supporting surface. It has also been shown by them that in a 'built-up' multimolecular film of stearic acid on a metallic surface, the structure of the layer in contact with the surface is identical with structure of first layer in a 'built-up' film of barium stearate. The structure of upper layer of stearic acid film is characteristic of stearic acid itself i.e. monoclinic. This shows that the monolayer of stearic acid in contact with the metal surface undergoes chemical action to form metal stearate. Changes in structure of monomolecular layers of fatty acids, alcohols etc. with temperature have also been extensively investigated by Taneka |65|, Brumimage |66| and Menter and Tabor |67| using electron diffraction technique. Recently, electron diffraction technique have also been used by Stephen and Tuck-Lee |62| for studying the structure of lead stearate 'built-up' films and suggested a monoclinic or orthorhombic structure depending upon the space group.

(e) Skeletonization of 'Built-Up' Films:

The metallic ion content such as barium or calcium of these 'built-up' molecular films depend upon the pH of the solution, the concentration of the metallic ion content i.e. barium salts and the concentration of the other salts such as sodium or potassium which have an antagonistic action |68|. Obviously, in the case of barium stearate molecular'built-up'films, when the barium content is low, the multilayers thus formed contain stearic acid, apparently in solid solution. This stearic acid can be dissolved out of the multilayers, by dipping them for a short time in benzene to which 1 % of 90 % ethyl alcohol has been added |8|. The film remains optically clear after the removal of the stearic acid (not over about 60 %), but a striking change is observed in the interference colour reflected by the film. Optical measurements prove that this change in colour is due not to a change of thickness but to a change of refractive index. If half of the material of the multilayer is dissolved out, there is even less than 1 % change in the thickness. After the removal of free stearic acid, the neutral barium stearate film thus remains as a skeleton film containing voids, previously occupied by the stearic acid.

The stability of skeleton films, containing as much as 40 % of voids, seems to indicate an extraordinary rigidity for the hydrocarbon chain inspite of the large surface tension forces that should tend to cause a collapse of the molecules into an amorphous mass. On heating the skeleton film to 50 to 60°C there is, of course, a collapse as indicated by a decrease of thickness and by a marked scattering of light. If half the films consist of staric acid and this is removed by skeletonization, each molecule of barium stearate remains in contact with about 3 out of 6 neighbouring molecules. The free rotation around the carbon-carbon linkage take place about an axis inclined 35^{o} from the axis of the hydrocarbon chain. The presence of the neighbouring molecules can thus prevent free rotation so that the molecules are held in a rigid form and collapse is prevented. Skeleton films of cadmium arachidate obtained by spreading arachidic acid on water containing cadmium chloride, are particularly stable, however, the free fatty acid should be dissolved out with ethyl alcohol.

When a drop of petrolatum or other hydrocarbon placed upon a skeleton film and the film then tilted to a vertical position, the drop moves slowly across the surface,leaving the surface apparently free from any thick film of oil. The colour of the film is restored in this way to that of the unskeletonized film. The thickness is, therefore, still the same but the refractive index increases from that of the skeleton multilayer film. It is evident that the hydrocarbon penetrates the skeleton and fills the voids originally occupied by fatty acids. These hydrocarbons can be dissolved in benzene giving again the same skeletonized film.

The stearate films are 'built-up' by changing the metallic ion content of the water and by skeletonizing the resulting monolayers, the refractive indices of these films having any desired value |8| between 1.18 and 1.51. The skeleton film, of barium stearate for which the refractive index is 1.3, had 99.2 % of the thickness of the original film, although only 63.7 % of its density |29|. Race and Reynolds |69| measured the electrical properties of the skeletonized 'built-up' films considering the free acid spaces filled with air parallel to the remaining soap film. The electrical properties are found to be in agreement with the concept of their physical structure.

(f) Optical Properties of Films: Refractive Index Measurements.

Blodgett and Langmuir |29| studied the optical properties of 'built-up' barium stearate films deposited upon microglass slides. They expected to see the interference colour when the film was built-up to a thickness of a quarter or half wavelength of light but no such interference colour occur. The failure to obtain interference effects, was due to the lack of reflection from the interference between the multilayer and the underlying glass because the refractive index of the glass and the film happened to be the same. Interference colour occured using glass of higher refractive index.

Optical studies of barium stearate films have shown that the multilayers constitute uniaxial crystals with the optic axis perpendicular to the plane of the film. The birefringence is readily demonstrated |29| by placing a 1000 layer film, built on glass, between cross Nicol prisms or crossed Polariod screens, the film being placed at azimuthal angle 45°. Navias |c.f.ref.29| has also investigated the birefringence of a 1000 layer film of barium stearate, employing a Ired gypsum plate in the usual way and found that the film behaves as a positive uniaxial crystal.

Such uniaxial crystals are characterized by two refractive indices. The refractive indices measured by Blodgett and Langmuir |29| are found to be $n_1 = 1.491$ and $n_3 = 1.535$ for barium stearate films. The equations used describe the refraction of extraordinary ray, the intersity of the ray reflected from the upper surface and from the film solid boundary, the phase change at the boundaries, Brewster's angle and other special properties of birefringent films. Lucy |70| also measured the refractive indices of barium stearate 'built-up' films, $n_1 = 1.419$ and $n_3 = 1.550$.

Recently, Tomar and Srivastava |71| have measured the refractive index of 'built-up' barium stearate films and other substances by using detector reflectrometer consisting of a simple d.c. differential bridge istead of the usual differential amplifier in the photomultiplier circuit. They have also measured the refractive indices of'built-up'films of barium margarate and barium behanate by ellipsometric method using Drude's equation |72|. Their recent measurements |73| of reflectance and transmittance on such 'built-up' films have tested the validity of Schopper's formulae and have, indeed, confirmed that these films are anisotropic.

The succeeding chapter describe the electrical measurements carried on these 'built-up' molecular films by other workers.

CHAPTER III

ELECTRICAL PROPERTIES OF 'BUILT-UP' LANGMUIR FILMS

The electrical properties of 'built-up' films have been experimentally investigated by number of workers. These 'built-up' molecular films seem to be very promising for making thin film devices like insulating sandwiched barriers between metals and superconductors and thin film capacitors etc. This chapter describes the dielectric properties of these organic films measured by other workers and conduction through organic thin films is also discussed.

3.1. DIELECTRIC CONSTANT MEASUREMENTS:

The static dielectric constant of thin insulators like 'built-up' molecular films is of potential importance for the development of thin film dielectric devices. The dielectric constant of thin insulating Langmuir films was measured by number of workers in different thickness ranges. The simplest equation for calculating the dielectric constant is the well known capacitance equation of parallel plate capacitor.

$$\frac{1}{C} = \frac{4\pi nt}{\epsilon A}$$

where A is the capacitor area, ϵ the dielectric constant, n the number of monolayers and t the thickness of a monolayer.

The earliest attempt was made by Porter and Wyman |74| to measure the capacitance of the films by placing a small drop of mercury on the film, forming the upper electrode of the capacitor. The film of organic layer was deposited on the metallic slide forming the lower electrode of the capacitor. The capacitance were measured at radio-frequencies by a radio frequency bridge. Numbers of observations were obtained using different drops of

Hg with their size varying from 1.5 to 1.8 mm in diameter and the same drop could be rolled from one place to another on a given film. They measured the dielectric constant of barium or calcium stearate films formed at pH=7 (Y layer) and pH=9 (X layer). The capacitance measurements at frequencies of 1 and .244 megacycle/sec show no significant difference between X and Y films. In both types of films, the capacity decreases with thickness and the average value of dielectric constant was found to be approximately 2.5, which is very close to the bulk phase value. The dielectric constant obtained was varying from 1.9 to 3.5 for the thickness range from about 175Å to 3525Å (7 to 141 monolayers). Their results implied that the dielectric constant was also approximately same for both type of films and approximately independent of the frequency.

Race and Reynolds |69| also studied the dielectric properties of barium stearate and cadmium arachidate films using mercury drop contact area method. The capacitance measurement was made over a frequency range from 40 to 10^6 cycles/sec by means of special guarded bridge |75|. From these measurements, the dielectric constant and dielectric loss (tanδ) of the films were calculated, from the equivalent parallel circuit |76|. They found that the dielectric constant was independent of the film thickness between 51 to 181 monolayers within the reproducibility and accuracy of their measurements. The dielectric constant measured was also independent of the frequency upto 10^6 cycles/sec. They gave additional data for films varying from 21 to 201 layers and value of dielectric constant was found to be 2.44-2.56 for barium stearate films and 2.46 for cadmium arachidate films.

Buchwald, Zahl and coworkers |77| made an attempt to measure the insulating properties of stearate films from 1 to 41 monolayers by immersing metal rods coated with the multilayers into conductive salt solution. A decrease in capacity was observed with increasing number of layers and there was at least two fold variation in apparent dielectric constant which were influenced by the choice and concentration of the electrolyte.

Handy and Scala |78| investigated the electrical properties of barium stearate films using the evaporated metal electrodes rather than mercury drop probes and the range from 1 to 10 monolayers (thickness 25-250Å) was explored. The evaporated electrode lead to a higher incidence of shorts through defects in the films but they also provide a realistic test of film uniformity and of the practical utility of Langmuir films for use as ultra-thin insulating films. They found the dielectric constant to be varying from 2.1 to 4.2 with an average value of 2.5 for stearate films containing 1 to 10 monolayers. The capacity was measured as a function of frequency and a slight change in the capacity with frequency was observed for a particular thickness. Over the range 100 c/s to 20 Kc/s, the dielectric constant drops by about 5 %. In the capacity measurements, the contribution of the oxide layer was neglected because the resistivity of the oxide layer is small compared with the resistivity of the organic layer.

Drexhage and Kuhn |79| have also studied the capacitance as a function of thickness of cadmium stearate and other films in the range from 1 to 11 monolayers. These measurements also imply constancy of the dielectric constant with thickness. Mann and Kuhn |80| calculated the dielectric constant of monolayers of cadmium salts of fatty acids of different chain length. Capacitance measurements were made with a L-C precision bridge (of Rhode and Schwarz) at a frequency of 100 c/s and at a peak to peak voltage of 10-20 mV.

Holt |81| also measured the capacitance and found the standard deviation of capacitance/unit area on each slide being commonly as small as 3 %, that is, of the order of the accuracy to which the areas of electrode can be produced and measured. No significant variation of capacitance was observed with frequency.

Horiuchi et al |82| carried out the capacitance measurements of barium and calcium stearate X-type film capacitors at 1 Kc/s. Capacitance values show that the scatter for different samples was up by the factor of 2. The capacitance was measured as a function of frequency for a constant thickness of 29 monolayers and found independent of frequency over a wide range of 1 Kc/s to 1 Mc/s. The dielectric constant was calculated from the capacitance using stearate monolayer thickness of = 24Å and was found to be 2.5 which is in good agreement with bulk phase value.

The present work has also been undertaken to investigate dielectric constant of the 'built-up' molecular films of barium salts of long chain fatty acids. The dielectric constant has been calculated theoretically (chap. IV) as well as measured experimentally (chap. V) and the results are found to be in good agreement.

3.2 Dielectric Loss Measurements:

Race and Raynolds |69| calculated the dielectric loss of the film from the equivalent parallel circuit of the special guarded bridge. This guarded bridge measured the capacitance and resistance of the films. By balancing the guard and test circuit of the bridges, the chromium plate and base plate of film holder was brought to the same potential, thus eliminating any possible losses in the mica insulation between the movable stage and base plate. At the same time, the losses caused by the glass supports from the high potential electrode were shunted to the guarded base plate and thus eliminating its effect on loss measurements of the film. The dielectric constant as well as,the dielectric loss measurements were made by Race and Reynolds |69| and it was found that these are independent properties of the films. The plot of the dielectric loss against frequency show larger deviations between measurements on the same film. However, these deviations appear to be random and show no dependence on thickness and frequency. The order of magnitude of tanδ measured was low, being less than 0.001 with standard deviations of 17 %.

The dielectric loss measurements on dry multilayer films made by Race and Reynolds |69| were of the smaller order of magnitude th than those obtained by Haskins and his coworkers |83|. Assuming equivalent parallel resistance and capacitance of the films, their data indicate a two-fold variation in dielectric constant and 15-fold variation in tanδ as a function of number of layers and the order of magnitude of tanδ was from 1000 to 10,000 times higher than the value obtained by Race and Raynold |69|. The wide difference in their values was caused by the electrolyte in which the film was immersed.

Holt | 81 | also measured the loss angle (tanδ) for the thickness range (225Å -3700Å) and found the values dropped from 0.2 at 225Å to 0.006 at 3700Å showing the standard deviation of 25 %. The variation in loss angle with frequency followed normal thin film behaviour. Handy and Scala |78| showed the variation with frequency of the imaginary part of the complex dielectric constant (proportional to C x D ; D being the dissipation factor) and noted that a slight maximum occur near 700 c/s suggesting the presence of weak polar adsorption mechanism with a charactertistic relaxation time ($\pi f_m/2$) of 0.23 msec. At higher frequencies (>10 Kc/s), the measurement uncertainity in the dissipation factor become comparable with the observed values.

3.3. DIELECTRIC BREAKDOWN CHARACTERISTICS:

Interest in the dielectric breakdown studies of thin films has been greatly stimulated because of their use in electronic devices. The breakdown charactertistic of these films have been studied because of their easy reproducibility, smoothness, high dielectric strength, uniformity and control of their thicknesses.

Porter and Wyman |74| studied the breakdown of both type of films (X and Y). X and Y films of different number of layers were covered with a drop of mercury and subjected to a variable d.c. voltage with a galvanometer in series. As the voltage increased, the readings of the galvanometer were followed. With films of higher thicknesses, there was no observable deflection in the galvanometer until a certain critical breakdown voltage was reached. But with thiner films, there were appreciable current almost from the start. They found that the breakdown voltages of X and Y films were almost the same but striking difference was obtained with films contacted with water and with mercury. The breakdown voltages of films in contact with Hg increases with thickness of the films and correspond to fields of the order of 10^6 V/cm. Apparent breakdown voltages of the films in contact with water were found to be nearly independent of the thickness and were found to depend on the direction in which the voltage is applied. The difference in result obtained for film contacted with Hg and with water may be due to the difference in the affinities of the two liquids for the surface.

D.C. breakdown measurements were also made by Race and Reynolds |69|. The voltage was varied from 0.01 V up and was obtained using a fine potentiometer and measured by a high resistance volt-meter. And for a.c. measurements the voltage was supplied by a beat frequency oscillator. The output voltage was controlled by a potentiometer on the oscillator panel and was measured with a vacuum tube voltmeter. They found that the dielectric strength measurements were very nonuniform after taking considerable care to prevent the inclusion of dust in the multilayer films. However, results obtained were disappointing. Dielectric strength were obtained as high as 2×10^6 volts/cm. They suggested that the extreme variations in dielectric strength, probably were caused by holes, cracks or dust particle in the films. In general, the films with highest dielectric strength were made from baths of highest pH.

Holt |81| measured the maximum dielectric strength and found its value varying from 1.3×10^6 volts/cm at 225Å to 2.6×10^6 volts/cm at 3700Å i.e. the increasing dielectric strength with increasing thickness.

Recently, Agarwal and Srivastava |84-86| have studied systematically the thickness dependence of dielectric breakdown of Langmuir films in the thickness range (25 to 2000Å). For the range studied, the breakdown strength was found to be a power dependent function of thickness varying as $d^{-\alpha}$, d being the thickness of the film. For the higher range of thickness (corresponding to 10-80 layers) the results were in agreement with the well known electronic breakdown theory of Forlani and Minnaja |87| which predicts the value of α to be 0.5. However, in the lower thickness range (1-10 monolayer), the value of α was found to be about 1.00 for all the films studied. These authors |88| have also studied the 'destructive' breakdown of these films and observed that at high voltages of the order of 80-90 volts, large area of the film was destroyed. V.I. characteristics in the 'nondestructive' phase have also been studied and the breakdown voltage corresponding to the initial abrupt rise of current is termed as onset breakdown voltage. Highest voltage at which the 'destruction' of the film occurs, is referred as 'maximum voltage breakdown'. A.C. breakdown studies |89| of barium stearate film have also been carried out as a function of frequency (in the region 10-200 KHz) and thickness (in the range 100-1500Å). The a.c. breakdown voltage was found to be increasing with increasing thickness and frequency. The a.c. breakdown strength varying again as $d^{-\alpha}$ with $\alpha = 0.68$ remains inexplicable. The a.c. breakdown strength is found to be somewhat smaller than the corresponding d.c. strength of the film.

Agarwal and Srivastava |90,91| have recently carried out the temperature dependent study of the dielectric strength of barium stearate films in the range (-40 to 40°C) and found that the dielectric strength decreased with increasing temperature. The results have not been explained because the actual mechanism of destruction is not yet fully understood, but their results may prove useful in device applications of the films.

3.4 RESISTIVITY MEASUREMENTS

Several workers studied the resistivity of multilayer films. The variation observed in resistivity values were generally ascribed to inhomogeneties or voids in the films. The increase in resistance was observed by Zahl and coworkers |77,83| with increasing number of monolayers. However, there was several orders of magnitude variation in resistivity which was influenced by the choiceand concentration of electrolyte. Small area probe measurements using water or mercury droplets were more successful. Porter and Wyman |74| also measured the resistance of stearate 'built-up' films and found there was no significant difference between X and Y films. They found resistance increasing with increase in thickness but values obtained at 1 Mc/s were definitely less than those at the lower frequency. It was also noted that a value of $2x10^{-4}$ ohms per layer corresponds to resistivity of about $2x10^{9}$ ohms cm. having regard to the size of the drops and the thickness of film i.e. the resistivity of both X and Y films is of the order of 10^{3} ohms cm.

The resistivity of Ba-stearate films was measured by Handy and Scala |78| at low voltage (<50mV) where the current-voltage characteristicsare linear. They plotted the resistivity against thickness and found that the points were approximately uniformly distributed over a certain limited area of the plot. For a given thickness, the upper limit of resistivity was corresponding to those layers which possess the smallest fraction of voids. The wide range of resistivity values observed for the same thickness, supported the contention that the organic films are porous. But, they found that at low thicknesses, the low voltage resistivity values were the characteristic of the oxide layer, that is, the fractional area of the oxide in direct contact with the top electrode. The resistivity of the organic layer was found to depend upon the presence of voids, in it.

3.5 CONDUCTION THROUGH THE FILM: TUNNELING PROPERTIES:

The Langmuir films in various thickness ranges were investigated by several workers using them as ultra-thin insulating barriers between evaporated metal electrodes because these films are thin, homogeneous, uniform in thickness and act as an excellent insulator. Miles and McMahan |82| first measured the tunneling current between tin-lead and tin-indium evaporated film pairs by using a monolayer of barium stearate as barriers and found it varying exponentially with barrier thickness. They reported the use of stearate monolayers as insulating barriers for electron tunneling without explaining the effect of direct contact to semi-insulating oxide layer.

Barium and calcium stearate Langmuir films from 1 to 10 monolayers in thickness range (25 to 250Å) were investigated by Handy and Scale |78| for use as ultra-thin insulating barriers between evaporated metal electrodes. These metal electrodes were oxidized in air to form metal oxide layer at the surface which

have often been employed as insulating thin films. Handy and Scala |78| observed that these metal-insulator-metal (M-I-M) sandwiches showed highly nonlinear and temperature dependent conduction characteristics. Near zero voltage, the characteristics were linear and presumably controlled by the voids present in the organic films. As the voltage increased beyond 0.1-0.2 V, the current rises very rapidly with increasing voltage and, because of current densities required, it must flow increasingly through the organic film. They also found, the voltage required for significant departure from linear conduction increased slightly with increasing layer thickness and the thicker film showed a more rapid increase in current than thinner films. At high temperature, the slope of the curve between current and temperature at constant voltage was approximately same for different number of layers which indicate that the thermal activation energy for conduction is also comparable. But at low temperatures, the slope was quite different due to the different relative contribution of tunneling and thermionic currents through the sandwiches of different number of layers. From the slope of curve and measuring voltage, the zero voltage thermal activation energy ϕ_b was determined as $.25 < \phi_b < .30$ ev for 3 layer sandwich. Their analysis presumed that conduction was dominated by tunneling at low temperatures and by thermionic emission over the insulating barrier of height ϕ_b represented by composite oxide organic layer at high temperatures. Handy and Scala |78| analyzed the I-V characteristics using theoretical expressions of Stratton |93| and Simmons |94,95| However, the reproducibility of electrical properties was poor,

apparently due to voids and inhomogeneities in the organic insulating films. It was calculated that in best samples 2 to 3 monolayers were required to eliminate voids penetrating completely through the organic films.

Horiuchi, Yamaguchi and Naito |82| also studied the electric conduction through calcium stearate films of several monolayers. They reported the detailed study of the voltage and temperature dependences of the current through monomolecular films sandwiched between aluminum and tin electrodes. Handy and Scala |78| did not explain the observed temperature dependence and the barrier height at the electrodes. The current-voltage characteristic of the junctions were observed by them with d.c. voltage at temperatures from 200 to 350°K. When a constant voltage was applied a large amount of transient current was obtained which decay approximately in proportion to 1/t. They found that the transient current was proportional to applied voltage, while the steady state current increased exponentially with increasing voltage. They also observed that when the lower tin metal electrode was negatively biased, the observed current depended upon temperature above 200°K and independent of temperature in the whole temperature range studied. It is well known that the mechanism of electron transfer through extremely thin insulators will be explained by tunneling emission or schottky emission. Pollack et al |96,97| explained the observed V-I characteristics with tunnel and schottky emissions using trapezoidal barrier models. Simmons has derived the expressions for the thermionic emission |98| and tunnel emission |95| between dissimilar electrodes including the effect of image potential.

Horiuchi et al [82] also found that trapezoidal energy model of Simmons offers an adequate explanation of the details of current-voltage-temperature characteristics. They show that tunnel emission was observed when upper Al-electrode was negatively biased and schottky emission was observed when the lower tin electrode was negatively biased. The observed barrier height at the stearate and tin interface was 0.8 ev and that at the stearate and aluminum interface was 1.3 ev, which indicates that the work function of tin is smaller than that of aluminium They tried to avoid the possible formation of aluminium oxide layer in the measurements on Al-Ca stearate-Sn sandwiches but were not successful because all the samples prepared showed ohmic characteristic with very small resistance.

Mann and Kuhn [80] studied the conductivity of the monolayers of Cd salts of fatty acids $CH_3\ (CH_2)_{n-2}\ COOH$ of different chain lengths. The sandwiches of monolayers between metal electrodes show the exponential decrease of conductivity v/s thickness predicted by the tunnel theory. The oxide layer had no influence on the d.c. conductance of fatty acid monolayers. The electron work function from metal to dielectric was obtained and had values 1.94 ev for Al and 2.28 ev for Hg. The values of vacuum work function of aluminium and mercury was found between 2.98 to 4.36 ev and between 4.50 to 4.53 ev respectively. In the multilayer systems, the current density j was found to be proportional to V (voltage) and inversely proportional to d (thickness) i.e. the plot of N_j v/s V for a given acid is a straight line. They concluded that this current must be due to impurities [99] and the current for monolayer was the sum of this impurity dependent current and the tunneling current. The good agreement between theory and experiment proved very sensitively the lack of larger imperfections in the structure of monolayer. Holes or conducting impurities in the layer would strongly influence the resistance and hence the current flowing through the film. Since the tunneling current through these holes is large compared to the residual current, it can be concluded that even the small fraction of holes can not be present. The dependence of the tunneling current on barrier distance seem to be due to this high sensitivity to imperfections.

Detailed and systematic theoretical and experimental studies of dielectric constant of 'built-up' films has been carried out in the present investigation. The next chapter describes the theoretical formulation for calculation of static dielectric constant of 'built-up' molecular films.

CHAPTER IV

THEORETICAL FORMULATION OF STATIC DIELECTRIC CONSTANT:

The experimental work of others on dielectric constant determination has been reviewed in the preceding chapter but none of them provided a theoretical interpretation to their results. As the theoretical understanding of dielectric constant is potentially important from the point of view of device applications, the present work of developing such a theory has been undertaken in the case of 'built-up' films.

This chapter describes the theoretical formulation developed by the author herself for the calculation of static dielectric constant of 'built-up' molecular films of long chain compounds for mono-and multimolecular films. Since these films constitute a crystal with long hydrocarbon chains of the molecules as entities, the conventional dielectric theory can not be applied here, as such because of large molecular dimensions. The calculation of intermolecular and intra-molecular interactions in presence of static electric field, by considering the interactions between different parts of the molecules, are therefore also discussed. This theoretical formulation derived for calculating the static dielectric constant of 'built-up' molecular films is the first one of this type.

4.1 STATIC DIELECTRIC CONSTANT

The electric properties of the dielectric substances are usually described in terms of the dielectric constant. When the electric field applied is either static or alternating with a low frequency, the conductance or dielectric behaviour is the most important phenomena. At higher frequencies, the phenomena is optical but there is no sharp line of demarcation between the dielectric and optical phenomena. For most substances, the dielectric constant is independent of the strength of the electric field over a wide range but in the case of alternating field, it depends upon frequency. It also depends on parameters such as temperature which define the state of material. The so called static or the low frequency dielectric constant was investigated by number of workers, since it has proved its usefulness in investigating structure and also the understanding of the static dielectric constant is necessary for the study of high frequency dielectric constant.

The dielectric constant is familiar in the expression of force between two point charges e and e' separated by a distance r in a homogeneous unbounded dielectric, where force = $ee'/\varepsilon r^2$, in which ε is the dielectric constant, characteristic of the medium. The dielectric constant ε of a medium may be defined as the ratio of a field strength in vacuum to that in the medium for the same distribution of charge. It may also be defined and is generally measured as the ratio of the capacitance C of a condenser filled with the material to the capacitance C_0 of the condenser with vacuum, that is

$$\varepsilon = C/C_0$$

The dielectric constant thus defined is evidently dimension less.

The well known equation | 100 | of static dielectric constant is given by

$$\varepsilon_s - 1 = 4\pi \frac{P}{E} \qquad .. (1)$$

where P is the polarization which is equal to the electric moment per unit volume and E is the microscopic electric field.

Of course, in an anisotropic material the electric field will induce the polarization which is not, in general, parallel to it. And the dielectric response is described by the component of dielectric constant tensor

$$\epsilon_{ij} = 1 + 4\pi \frac{P_i}{E_j} \quad \text{.. (2)}$$

where P_i is the polarization in i-direction due to the component of the applied field E_j in the j-direction. In general, the dielectric polarization P may be considered the sum of three contributions

$$P = P_e + P_a + P_d \quad \text{.. (3)}$$

where the subscripts e, a and d refer to electronic,atómic and dipolar polarization, respectively.

4.2 CONVENTIONAL THEORY:LIMITATIONS

The static dielectric constant is calculated by calculating the electric dipolemoment induced by an external field in a dielectric from its atomic and molecular structure |101,102|. In the case of gases, one may assume that the field acting on the particles is equal to that of the external field because the mutual interaction between the particles is neglected, as in a gas of low density. But in the case of solids and liquids, however, a given molecule or atom is affected, not only by the external field but also due to the field produced by the dipoles of other molecules or atoms, as well. The problem in theory of dielectric constant of liquids and solids is therefore the calculation of the field at the position of a given atom (or molecule). This field is called the internal or local field and is different from the externally applied field E_0. The local field at an atom (or molecule) is the sum of the applied field E_0 from external sources and of the field of the dipoles within the specimen.

To calculate the local field, Lorentz |103| suggested to select a spherical region from the dielectric with the atom (or molecule) for which the local field must be calculated at the centre. The radius of the sphere is chosen large enough to consider the region outside the sphere as a continuum of dielectric constant ϵ_s. For the region inside the sphere, however, the actual structure of the substance must be taken into account.

Thus, the local field E_{loc} is given by the equation

$$E_{loc} = E_0 + E_1 + E_2 + E_3 \qquad .. (4)$$

E_0 = field produced by fixed charges external to the body.

E_1 = depolarization field; from the surface charge density on the outer surface of the specimen.

E_2 = Lorentz cavity field; the field from polarization charges on inside of a spherical cavity with the reference atom as centre.

E_3 = field of atoms inside the cavity.

The contribution $E_1 + E_2 + E_3$ to the local field at reference atom (or molecule) caused by the dipole moments of all the other atoms (or molecules) in the specimen, is given by

$$E_1 + E_2 + E_3 = \sum_i \frac{3(\vec{p}_i \cdot \vec{r}_i)\,\vec{r}_i - r_i^2\,\vec{p}_i}{r_i^5} \quad .. (5)$$

E_1, the depolarization field within the body tends to oppose the applied field E_0. This field is due to the surface charge density on the outer surface of the specimen and thus, it depends upon the shape of the specimen. In the case of thin dielectric slab between two conducting plates, the contribution of the uniform depolarization to the field is $-4\pi P$, when the field is applied normal to the thin dielectric slab |105,106|.

The field E_2 due to the polarization charges on the surface of the cavity was calculated by Lorentz |103|. If θ is the polar angle with respect to the polarization axis, the surface charge density on the surface of the cavity is $-P\cos\theta$ and the charge on the ring of radius a is $2\pi a \sin\theta . a\, d\theta \cos\theta$. The electric field at the centre of the spherical cavity of radius a is

$$E_2 = \int_0^\pi (a^{-2})\,(2\pi a \sin\theta)\,(a\, d\theta)\,(P\cos\theta)\,(\cos\theta) = 4\pi P/3 \quad .. (6)$$

The field E_3 on the atom at the centre, due to other atoms within the spherical cavity, is the only term which depends on the structure of the dielectric. It is assumed that all the atoms inside the sphere may be replaced by point dipoles parallel to each other. The i-th dipole have the dipole moment components p_{xi}, p_{yi} and p_{zi} and coordinates x_i, y_i, z_i. One may write the value of E_3 as

$$E_3 = \left(p_{xi} \frac{3x_i z_i}{r_i^5} + p_{yi} \frac{3x_i y_i}{r_i^5} + p_{zi} \frac{3z_i^2 - r_i^2}{r_i^5} \right) \quad .. \ (7)$$

For a simple cubic lattice of similar atoms, the external field direction coincides with the cube edge (z-direction). From the symmetry $p_{xi} = p_{yi} = 0$ and $p_{zi} = p$, which will be same for all atoms. Also the x,y,z directions are equivalent because of the symmetry of the lattice and of the sphere, thus

$$\sum_i \frac{z_i^2}{r_i^5} = \sum_i \frac{x_i^2}{r_i^5} = \sum_i \frac{y_i^2}{r_i^5} = \sum_i \frac{1}{3r_i^3} \quad .. \ (8)$$

so that $E_3 = 0$ for cubic lattice.

Putting these values in equation (4). The local field is given as

$$E_{loc} = E_0 - 4\pi P + 4\pi P/3 + 0$$

or $$E_{loc} = E' + 4\pi P/3 \quad .. \ (9)$$

This equation (9) is known as Lorentz relation; the field acting at an atom in a cubic site from the polarization of the other atoms in the specimen.

The values of E_3 for tetragonal and simple hexagonal lattices have been given by Müller |106,107|. The anisotropy of the Lorentz field is calculated by combining the classical cavity method with Ewald's lattice theory. He considered an infinite lattice whose elementary cell contains only one atom (or molecule) situated at the origin of the cell. If x,y,z are the axes of the optical index ellipsoid, the Lorentz field acting on any atom can be written as

$$E_x + 4\pi L_x P_x \qquad .. (10)$$

The Lorentz factors L_x, L_y, L_z can be derived from Ewald's potential and the equation $L_x + L_y + L_z = 1$. The Lorentz factors depend on the shape but not on the size of the elementary cell i.e. they depend on the ratio c/a where c is the lattice spacing in the direction of the tetragonal or hexagonal axis and a is the distance between the nearest neighbours normal to the axis. If c/a is large i.e. $c/a > 1$, $L_x = kc/a = L_y$ and $L_z = 1-2kc/a$, this result has the following interpretation that in the layer lattice the atoms are continuously distributed in all the layers except the one in which the atom is situated on which the field is calculated, thus he found k = 0.359 for tetragonal and k = 0.370 for hexagonal lattices. Similarly, for small value of c/a, $L_z = k' \, (a/c)^2$ and k' has values 0.3826 and 0.3313 for tetragonal and hexagonal lattices, respectively. These results also hold for molecular lattices.

For calculating dielectric constant, the polarizability α of the atom is taken into consideration which is defined in terms of the local electric field at the atom,

$$p = \alpha \, E_{loc} \qquad .. (11)$$

where p is the dipolemoment. The polarizability is the property of molecules where as the dielectric constant is that of the crystal structure i.e. it depends on the arrangement of atoms or molecules. The polarizability has the dimension equal to the cube of length. The total polarizability of polar molecule have three contributions viz. electronic, atomic and dipolar polarizabilities. And the polarization in a dielectric may be expressed approximately as the product of the polarizabilities of the molecules times the local field.

$$P = \sum_j n_j p_j = \sum_j n_j \alpha_j E_{loc}(j) \qquad .. (12)$$

where n_j is the concentration and α_j the polarizability, of atoms j and E_{loc} (j) is the local field at the atom site j.

If, the local field is given by Lorentz relation, then

$$P = \sum_j n_j \alpha_j (E + 4 \pi P/3) \qquad .. (13)$$

Substituting value of P in equation (1)

$$\epsilon_s - 1 = 4 \pi P/E = 4 \pi \frac{\sum_j n_j \alpha_j}{1 + \frac{4 \pi}{3} \sum_j n_j \alpha_j}$$

or

$$\frac{\epsilon_s - 1}{\epsilon_s + 2} = \frac{4 \pi}{3} \sum_j n_j \alpha_j \qquad .. (14)$$

This relation between dielectric constant and polarizability known as Clausius- Mossotti relation, holds only for crystal structures for which the Lorentz local field is obtained. Harrop and Campbell | 108 | have recently presented a review article concerning dielectric properties of thin films and suggested that the above equation is derived from the Lorentz approximation which determines the dielectric constant of a solid due to polarization.

The above relation holds only for those substances in which the linear dimensions of the atoms or molecules are very small compared with the lattice spacings. For calculating static dielectric constant of 'built-up' films of long chain fatty acid compounds, the above relation is not valid because the linear dimensions of the molecules are not comparable to the lattice distances. The structure of the film of long chain fatty acid compounds is a simple hexagonal array, the molecular chain axis of which coincide with symmetry hexagonal axis | 64 |. The theoretical formulation predicted by Müller | 107 | for hexagonal lattice was also not applicable for these films because the lattice spacing, here. is much greater than the mutual distance between the molecules and because of his assumption that the linear dimensions of the molecules are small compared with lattice distances. In the above derivation, the atoms (or molecules) are also assumed to be point dipoles but this assumption does not stand valid for these molecules because of very large chain length of the molecule.

4.3 FORMULATION OF THE FORMULA

For the calculation of dielectric constant of 'built-up' films, the local field was first calculated on one molecule due to all other molecules. The basic approach for taking into account the extent of the molecule is therefore to consider the interactions between different parts of the molecule. The local field is the sum of external applied field and the field due to all the other dipoles within the specimen. For the purpose of calculations each large molecule is thus considered to be divided into small equal parts. Both the intermolecular (the interaction between the parts of the different molecules) and intramolecular interaction (the interaction between the parts of same molecule) in the presence of static electric field have been thus calculated. The dielectric constant of the monomolecular and multimolecular 'built-up' films of barium palmitate, margarate, stearate and behenate is calculated | 109-111 | by calculating the local field inside the monolayer and multilayers for which the surface effects are not significant.

(a) Monomolecular Films:

The local field inside the monolayer arise due to the intermolecular and intramolecular contributions. The structure of 'built-up' films is known i.e. the hydrocarbon chains of the molecules form the hexagonal array with their chain axis normal to the plane of the film | 64 |. As the molecules of Ba-salts of fatty acids consist of two straight long hydrocarbon chains parallel to each other with a polar group $(COO)_2$ Ba at its one extremity. It has been considered here that the hydrocarbon chains of these molecules are divided into the small CH_2 groups each separated by 1.27Å along the chain axis. It is assumed that these CH_2 groups are spheres of isotropic polarizability and the point dipoles at its center.

In these calculations a reasonable assumption is made that a molecule of Ba-salt of fatty acid is equivalent to the two 'effective' molecules each consisting of one hydrocarbon chain and half of the end group $(COO)_2$ Ba. Therefore, these effective molecules thus form the hexagonal array with chain axes normal to the supporting surface. The intermolecular contribution to the local field is now calculated by the interaction between the small parts of different effective molecules and intramolecular by the interaction between the parts of the same effective molecule. In the calculation, the last CH_3 group has also been assumed equivalent to a CH_2 group. For calculating the intermolecular contribution E_z^1 to the local field inside the monolayer, the interaction between the hydrocarbon tails and the end groups are calculated separately. The interaction between hydrocarbon chains is calculated following the Salem's assumption | 112 |. Salem calculated the London-vander Waals dispersion attraction between long saturated chains by using the assumption of locally additive forces.

Two parallel linear chains of length L consisting of N identical units of length $(N\lambda = L)$. have been considered. The mutual distance between them is D which may be large or small relatively to L but must be large enough as compared to the length of the basic unit λ (Fig. 7). According to Salem, if the basic units, for example, are bonds of average length 1.5 $\mathring{A}$, D can be chosen as small as about 4 $\mathring{A}$ which is obviously valid in this case. Considering the basic units as point dipoles, the field at one dipole due to another i.e. the field

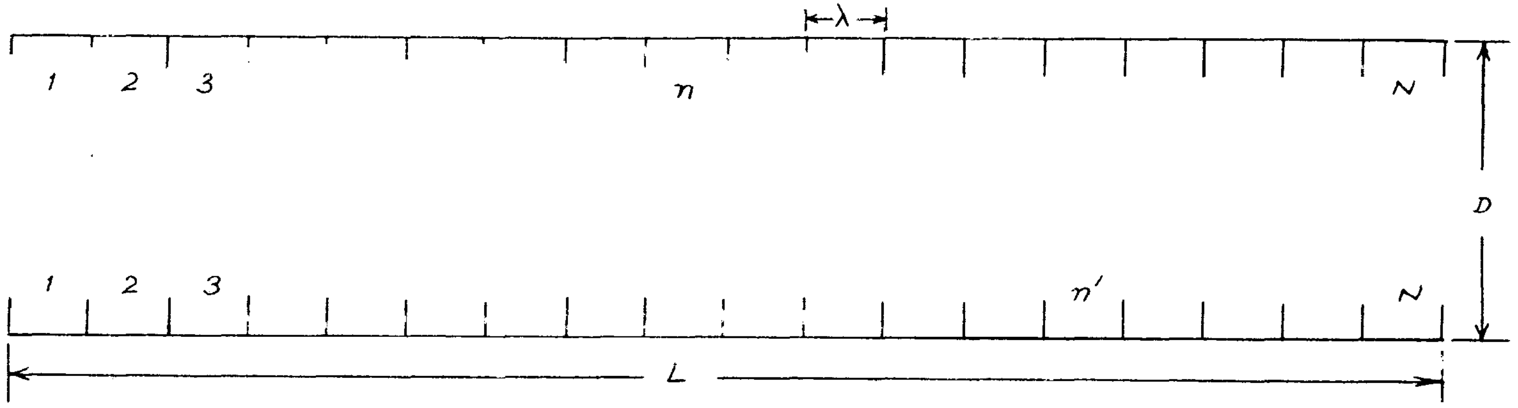


FIG.7- REPRESENTATION OF TWO IDENTIAL CHAINS.

at the centre of one unit due to other (the unit being in each chain at a distance $r \gg D$) is calculated. The field is thus given by

$$E = \frac{3\,p\,z^2 - p\,r^2}{r^5} \qquad ..\ (15)$$

where p is the electric moment of the basic unit and z is the direction of applied field. Assuming local additivity, the field at one effective molecule due to the adjacent one is calculated by taking into account the interaction of each unit of the chain with all the units of another chain. The field at one hydrocarbon chain is therefore

$$E_z^1 = \sum_i \sum_j \frac{3\,p\,z_{ij}^2 - p\,r_{ij}^2}{r_{ij}^5} \qquad ..\ (16)$$

If the units in the first chain are numbered as 1,2,3, ...,n, ..., N and those in the second chain as 1,2,3; .....,n', ...,N, the distance r between the centers of n and n' in the second chain (assuming the center of each chain unit to be at the chain axis) is given by

$$r = |D^2 + z^2|^{1/2} \qquad ..\ (17)$$

and also $z = \lambda\,(n-n')$ .. (18)

Substituting these values in equation (16)

$$E_z^1 = p \sum_{n=1}^{N} \sum_{n'=1}^{N} \frac{3\,z^2 - (D^2 + z^2)}{(D^2 + z^2)^{5/2}}$$

are considered as continuously distributed in all the layers except the one in which the molecule is situated and on which the field is calculated. The contribution of the continuous distribution to the local field is 4 π P (where P is the polarization) and that of the reference layer is the one calculated for a monolayer by the method described in the preceding section (4.3(a)).

The dipole moment and hence the polarization of the molecules is calculated from the local field.

$$P = n \alpha E_{loc} \qquad .. (24)$$

where α is the total polarizability of the molecule. n is the number of molecules per unit volume. The total polarizability is the sum of electronic atomic and orientational polarizabilities.

The static dielectric constant ϵ_s is calculated along the symmetry hexagonal axis which is one of the principal axes of the dielectric tensor, along which the external electric field is applied. For the anisotropic structure of these films, the dielectric response is given by the dielectric constant along the field direction (the symmetry hexagonal axis)

$$\epsilon_s = 1 + 4 \pi \frac{P}{E} \qquad .. (25)$$

P being the polarization along the external field direction.

4.4 REFRACTIVE INDEX CALCULATION

The refractive index 'n' of a medium is the ratio of the phase velocity c of electromagnetic radiation in vacuum ($3x10^{10}$ cm sec^{-1}) to that of the medium | 115 |. The classical equation of Maxwell | 116 | gives the relation for refract index,

$$n^2 = \epsilon\mu$$

where μ is the magnetic permeability of the medium and its value is equal to unity practically for all organic compou So that

$$\epsilon = n^2 .$$

Since both the refractive index and the dielectric constan depend upon the frequency of radiation used, the square of optical refractive index is not identical with the dielect constant at radio frequencies but the dielectric constant the centimeter wavelengths is commonly measured as the squ of the refractive index for these wavelengths.

The extent of dielectric polarization, in a cryst a given electric field of the wave, in general, depends on direction of the field. This is true because the polariza of the molecule in the crystal is caused not only by the e field of the wave but also by that of the electric dipoles produced in other molecules in its neighbourhood. It foll that the extent of polarization and therefore the refracti index depends upon the orientation of the electric field relative to the crystal axes. Incidentally, it is to be no that the refractive index of the crystal is therefore dete essentially by the direction of electric field of the elec magnetic waves and not by the direction in which the wave travelling in the crystal. Obviously, any change in the d of the crystal will also affect the extent of polarization hence the refractive index of the crystal.

CHAPTER V

EXPERIMENTAL MEASUREMENT OF THE DIELECTRIC CONSTANT

Experimental measurement of film capacitance and hence the dielectric constant have been made to justify the theoreitcal results based on the formulation described in the previous chapter. Here, the advantages of 'built-up' molecular films studied, cleaning and selection of substrate and the capacitor fabrication have been described. The measurement method of the film capacitance is also discussed.

5.1 DESIRABILITY AND ADVANTAGES OF STUDYING 'BUILT-UP' FILMS:

Interest in the dielctric behaviour studies of thin films has been greatly stimulated because of their use in passivated devices, field effect transistor, microelectronic circuitory and other devices. Particularly, interesting is the study of dielectric constant of thin 'built-up' films of barium salts of long chain fatty acids such as stearic acid etc., because of their potential applications for making thin film devices [78, 82,92,119]. Incidentally,the 'built-up' barium stearate films have recently been shown to be promising for making thin film devices such as tunneling sandwich between superconductors [92] and thin film dielectrics [81]. These films are particularly suited for such studies because they are extremely uniform in thickness which are controllable. Obviously, the uniformity and accurate value of thickness of the films are two crucial factors of present studies. The greatest advantage with these films is that their thicknesses are known accurately,as has been measured recently by Srivastava and Verma [50,51] using multiple beam interferometric technique. The uniformity of the thickness of the film which forms another crucial factor for studies, is achieved, as the degree of uniformity improves with the equation of Maxwell | 116 | gives the relation for refractive index,

$$n^2 = \epsilon \mu \qquad .. (26)$$

where μ is the magnetic permeability of the medium and its value is equal to unity practically for all organic compounds; So that

$$\epsilon = n^2 \qquad .. (27)$$

Since both the refractive index and the dielectric constant depend upon the frequency of radiation used, the square of the optical refractive index is not identical with the dielectric constant at radio frequencies but the dielectric constant at the centimeter wavelengths is commonly measured as the square of the refractive index for these wavelengths.

The extent of dielectric polarization, in a crystal for a given electric field of the wave, in general, depends on the direction of the field. This is true because the polarization of the molecule in the crystal is caused not only by the electric field of the wave but also by that of the electric dipoles produced in other molecules in its neighbourhood. It follows, that the extent of polarization and therefore the refractive index depends upon the orientation of the electric field relative to the crystal axes. Incidentally, it is to be noted that the refractive index of the crystal is therefore determined essentially by the direction of electric field of the electromagnetic waves and not by the direction in which the wave is travelling in the crystal. Obviously, any change in the density of the crystal will also affect the extent of polarization and hence the refractive index of the crystal.

Here, the dielectric constant at very high frequency ($\simeq$ optical) is calculated using only the electronic polarizability which yields the refractive index [117] from the Maxwell's relation (eq. 27). The dielectric constant from the electronic polarizability and hence the refractive index for mono-and multimolecular 'built-up' films of barium salt of fatty acids has been calculated essentially along the same lines, taking into account the interaction between the chains and along the chain to work out the intermolecular and intramolecular interactions. This yields the refractive index along the symmetry hexagonal axis which corresponds to the semi-major axis of the index ellipsoid of the positive uniaxial crystal film.

According to Rozenberg [118], the phenomenological Maxwell theory, as such, does not hold in the case of very thin films (thickness $\ll$ wavelength of light). However, he also states on the basis of his theory of two-dimensional Colloid, that the phenomenological theory can be used for unimolecular film because the exponential expression involving the thickness of the film can be neglected. When the thickness of the film is increased, the theory breaks down but it can again be used for films having thickness comparable to or greater than the wave length of light. Thus, the use of the phenomenological concepts in these calculations are justified.

The succeeding chapter discuss the advantages of 'built-up' molecular films which led to their extensive studies. Cleaning and selection of substrate, sandwich fabrication and the measurement of capacitance have also been described.

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As has already been discussed, these films are deposited using Blodgett- Langmuir tehcnique. This technique is such that the desired number of layers and hence the film of desired thickness may be deposited on to the slide, which is another advantage of these films. For example, the films of barium copper stearate could be built-up containing upto 3000 monolayers, simply by repeated dipping and withdrawal process. The 'fogged' appearance of these films when the thickness is considerably large may be checked by adding some copper salt to the solution. Similarly 'cracking' tendency of the films such as barium stearate etc. increases with increasing number of monolayers, usually commencing above 300 layers, can be minimised by the addition of some copper ions . However, these problems did not arise in the present investigation because monolayers only upto 100 layers were used for study.

These films are structurally well defined consisting of superposed sheets of oriented molecules forming positive uniaxial birefringent crystals with their optic axis perpendicular to the plane of the film | 29 |. These films are crystalline and can be regarded as almost 'two-dimensional' crystals and therefore, the 'building-up' of monomolecular layers may be regarded as a special case of a layer by layer growth of a crystal. As has already been shown, only one monolayer of 'built-up' films may be deposited and their studies are also possible. Since the building up process of films requires a high surface pressure for the monolayer transfer on to the glass slide, the molecules in the film remain, close packed.

It has been found that these layers are stable in vacuum and are also thermally stable. Handy and Scala | 78 | and Mann and Kuhn | 80 | in their recent studies on these films have demonstrated that it is possible to evaporate metals like aluminium over them without any damage to the deposited film. This has also been verified by the recent studies, carried out by the author, even on a monolayer (ch. VI). Holt | 81 | has also shown that these can be heated to in damp air over prolonged periods without damage and observed no change in their electrical properties, even if they are repeatedly and rapidly cycled from liquid nitrogen temperature to 50°C in air. Similar observations have been made by Agarwal and Srivastava | 90,91 | recently and no effect was observed due to the temperature variation.

Recently, Agarwal and Srivastava | 84-86 | found that these built-up films have the breakdown voltage of the order of several volts leading to their high dielectric strength of the order of MV/cm. They have also revealed through microscopic studies of their breakdown phenomena that these films are apparently free from imperfections. It is obvious, from their high dielectric strength that these films are highly insulating in behaviour. These organic films have also been reported to have high structural perfection |120|.

It, therefore, seems desirable that under carefully controlled conditions (sec. 2.1 (a)), the 'built-up' films are ideally suited for dielectric studies, as have been carried out by the author in the present work.

5.2 SELECTION OF SUBSTRATE AND CLEANING PROCEDURE:

Selection of the substrate for film deposition is of major importance because the desirable high degree of uniformity of 'built-up' films studied, is also governed by the surface structure of the substrate. In the present work, therefore much attention has been paid to the selection of proper substrates with smooth surfaces. The highly smooth 'Gold Seal' microglass slide having no scratches were carefully selected and used after cleaning them as described below. The planeness and smoothness of slide surfaces was studied by the standard method of matching the cleaned slide surface with a master optical flat | 47 |. On proper illumination the formation of reasonably straight, equidistant, parallel and smooth fringes show that the slide surfaces have not much curvature and are almost plane | 121 |. The smoothness of such selected microglass slides can be of a much higher degree than that of the usual optical flat. This is, for example, revealed by the absence of 'wriggle' in the fringes of equal chromatic order |FECO| taken by Srivastava and Verma | 50, 51 | on a 4-layer barium stearate film (thickness about 100Å). In such extensive measurements of small film thicknesses, it was found that the 'Gold Seal' microglass slides, in general, do not have sharp projections and waviness.

The selected microglass slides are thoroughly cleaned first with soap water, subsequently rubbed and rinsed with carbon tetrachloride to remove any dust and visible finger prints. After the wash with C.T.C., these slides are now cleaned with nitric acid and again washed with water. After cleaning with nitric acid, these are stored in sulphur chromic acid (35 c.c. $K_2 Cr_2 O_7$ sat. and 1000 c.c. H_2SO_4 conc.) for about an hour, which is most effective cleaning agent. The acid is then removed by rinsing the slide with freshly prepared deionized water and by boiling it in water for 10 minutes. After washing with deionized water and soaking in freshly laundered old linen,it is rubbed vigorously with clean dry cotton wool until no 'breath-figures' are obtained by lightly breathing on it. These cleaned surfaces are now ready for sandwich fabrication as described in the succeeding section. Conc. HNO_3 is used to dissolve out deposited layers of aluminium electrodes and then the slide is cleaned following the above procedure.

5.3 FABRICATION OF CAPACITOR:

The cleaned and carefully selected microglass slides as discussed in the preceding section are used as base for fabricating the thin film capacitor of the type Al-film-Al. For making the capacitor of this type, about two-third part of the slide was first aluminized by thermal evaporation in vacuum ($\simeq 10^{-6}$ Torr), using Edward's 'SPEEDIVAC' model 6E2 coating unit (fig. 8) which provides safe and easy-to-use evaporation and sputtering facilities in a compact unit. This unit is equipped for evaporation, sputtering and ionic bombardment. Tungeston baskets of the type H 140/121 (shown in fig. 9) have been used for evaporating Al which were supplied by M/S Edwards High Vacuum Ltd., England. After proper mounting of the filament and the slide holder in the work chamber, it is sealed and evacuated by operating three stages ; silicone oil diffusion pump backed by a high speed rotary oil pump. The backing vacuum and the final vacuum can be read directly on a meter. The high tension bombardment current is switched on to clean the work chamber interior and work surface (the slide). After the evacuation process is completed, the pressure guage indicates a pressure of about 10^{-6} Torr , the

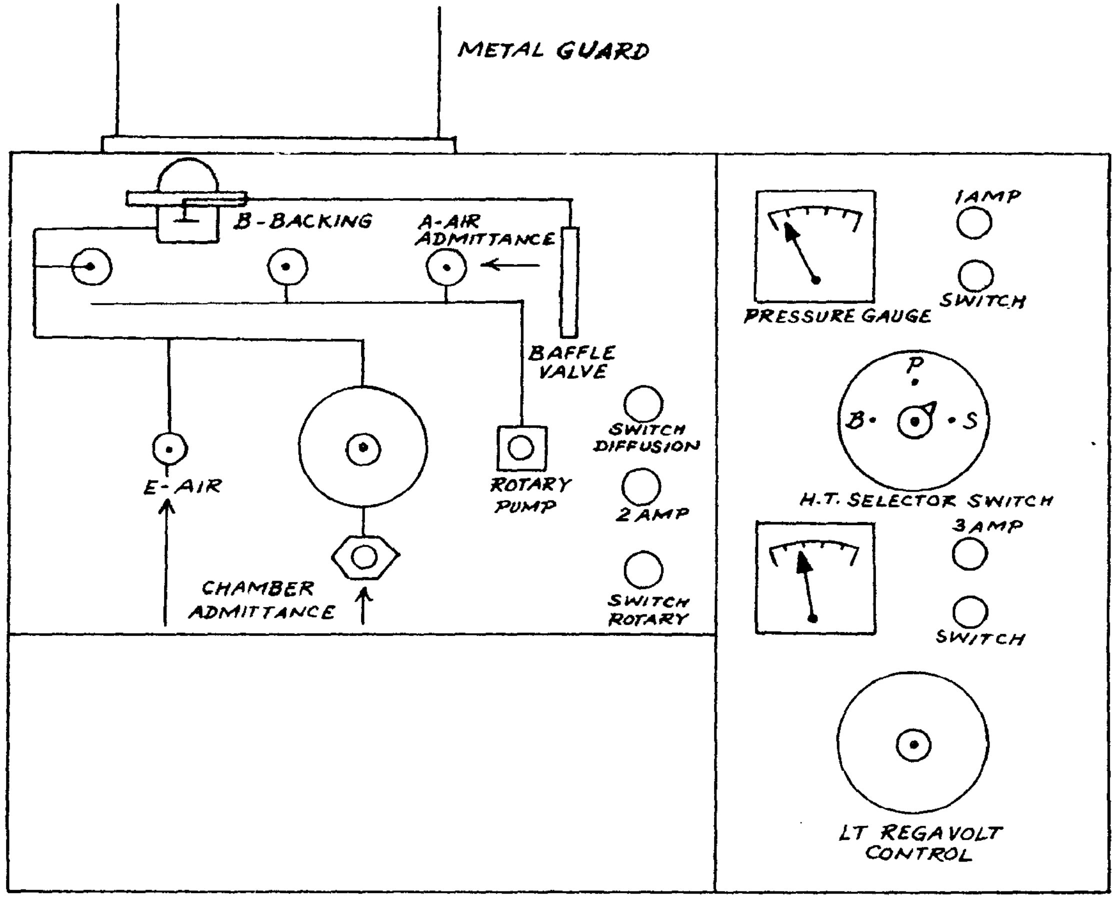


FIG.8. BLOCK DIAGRAM OF SPEEDIVAC MODEL 6E2
VACCUM COATING UNIT.

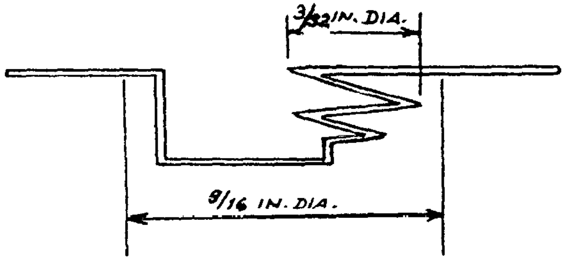


FIG.9 – TUNGSTEN BASKET.

low tension current to the evaporated source is switched on and increased by means of the 'Regavolt' control unit very slowly till the Al-piece placed does not melt and gets evaporated. The Al-wire used was of the quality Johnson and Mathey which is 99.0 % pure. The thickness of the evaporated Al-electrode was held roughly constant keeping the same distance between the filament and the slide every time and placing the same amount of Al, evaporated by passing fixed amount of current for fixed time. By controlling all these factors, thin Al-electrodes of about several hundred Angstroms were evaporated every time.

The 'built-up' films of long chain fatty acid compounds like palmitate, stearate etc. are then deposited on these aluminized slides having desired number of layer by using Blodgett-Langmuir technique described in sec. 2.1 (a). For deposition, the aluminized portion of the slide is kept upward. The upper Al-electrode is then evaporated on the film by thermal evaporation in vacuum, repeating the above discussed procedure in such a way that a sandwich structure of the type Al-film-Al (fig. 10) is obtained. For the evaporation of upper electrode on the slide containing these 'built-up' films cannot be cleaned by the ionic bombardment because the local heating produced by this may be sufficient to melt the organic film having molecules bound together by weak vander Waal forces i.e. low melting point. It has already been established | 81 | that thermal evaporation in vacuum does not cause any damage to the deposited molecular films. Thus the film sandwiches of Al-film-Al structure of areas ranging from 0.4 to 0.6 cm^2 are obtained, ready to be used for capacitance measurements. The area of the capacitor was measured accurately by using a travelling microscope.

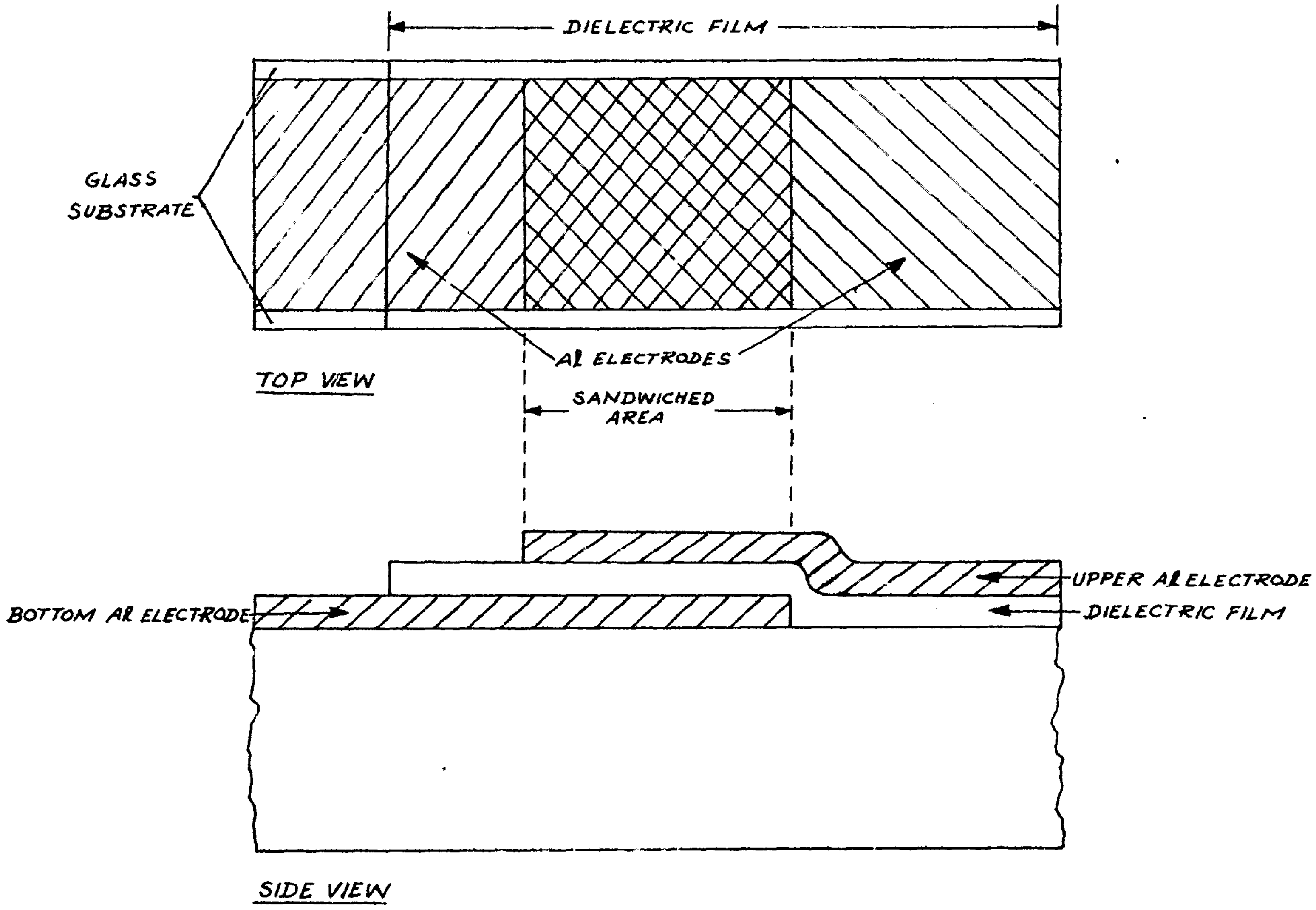


FIG.10. SKETCH OF FILM SANDWICH SYSTEM (Al-FILM-Al).

5.4 CAPACITANCE MEASUREMENTS:

The capacitance of the Al-film-Al sandwich is measured by using MARCONI TF 2700 universal bridge at 1 K c/s. The capacitance values of 0.5 pF to 1100 μF may be measured by this bridg at 1 K c/s from the internal oscillator or at frequencies of 20 c/s to 20 K c/s from external source where an alternative frequency is more appropriate. The fig. 11 shows the basic brid configuration used for the measurements. The circuit used for resistance measurement is simply a Wheatstone circuit while capacitance and industance are measured by comparison with a standard capacitor in R-C ratio arms circuits.

The detector has been made unselective to enable external a.f. source to be used for energizing the bridge. An emitter follower input stage provides the high input resistance necessar to maintain sensitivity on the high impedence ranges, being a silicon transistor in order to minimize noice. The out put of emitter follower drives a three stage amplifier via a logarithmi potentiometer, which forms the part of sensitivity. The meter always deflects to one side of zero for all a.c. measurements, as the amplifier output rectified by shunt diode is fed to the meter. Two germanium diodes connected across the meter protect it against severe overloads and the detector sensitivity is adjustable by means of variable resistor. The main balance contr comprises a step switch and a continuously variable intermediate control.

For measurements of capacitance, the Al-film-Al sandwiches were connected to the test terminals making use of Hg droplets to contact the film at both of its ends. Direct contact of

Al-electrodes by a solid probe was avoided due to the possibility of disrupting the Al-film at the place of contact. The sensitivity of the universal bridge for capacitance measurement is 0.1 p.F.

The next chapter entails the description of the values of static dielectric constant calculated theoretically and measured experimentally for 'built-up' films of barium palmitate, margarate, stearate and behenate. The results obtained theoretically and experimentally have also been discussed in detail.

CHAPTER VI

RESULTS AND DISCUSSION

This chapter describes the values of static dielectric constant calculated theoretically and measured experimentally. The theoretical values are calculated on the basis of theoretical formulation developed in sec. 4.3 for mono- and multi-molecular films. The experimentally measured values are calculated from the capacitance measured using the equation of parallel plate capacitor. The results obtained have also been discussed.

6.1 RESULTS:

(a) Static Dielectric Constant: Theoretically Calculated Values

The static dielectric constant of mono-and multimolecular films is calculated from the theoretical formulation described earlier (sec. 4.3). The theoretical formulation derived for calculating static dielectric constant of the 'built-up' films is the first one. The dielectric constant is calculated for mono- and multimolecular (thick) films only, because the explicit thickness dependence of the dielectric constant could not be derived in terms of present models. The entire calculation is based on the structure of these 'built-up' films, reported by Germer and Storks | 64 | for barium stearate films i.e. the hydrocarbon chains of the molecules form the hexagonal array with their axes normal to the supporting surface.

The dielectric constant calculations for mono- and multimolecular 'built-up' films of barium palmitate, margarate, stearate and behenate have been made along the symmetry hexagonal axis along which experimental measurement could be made. The acids corresponding to the first three substances i.e. palmitic, margaric and stearic acid are consecutive members of the same homologous series with the number of carbon atoms ranging from 16 to 18, respectively. Behenic acid is relatively farther removed in series (22 carbon atom). The layered structure of 'built-up' molecular films are simple hexagonal having the molecules oriented with their chains normal to the plane of the film and the lateral distance between the chains of hexagonal array is 4.85Å |64|. Static dielectric constant of 'built-up' films of all the four substance are calculated by calculating the intramolecular and intermolecular contribution to the local field. The values |50,51| of the length of the molecules or the thickness of the monolayer used are 23.25Å, 24.05Å, 25.75Å and 30.05Å for barium plamitate, margarate, stearate and behenate, respectively. The values of the number of chains i.e. the effective molecules per unit volume 'n' for these substances have been calculated from the knowledge of the lattice dimensions i.e. the volume of the unit cell and the value of 'n' are given in the table 1.

For calculating the local field, the assumption that these molecular hydrocarbon chains are divided into small $-CH_2$ identical units, is made. The electronic polarizability of the $-CH_2$ group is taken to be equal to 1.84×10^{-24} c.c |113| and distance between two successive $-CH_2$ groups along the chain axis is 1.27Å. The electronic polarizability of the and effective group is 3.025×10^{-24} c.c. and the distance from its nearest CH_2 group along the chain axis is 2.4Å. The distance from its i-th CH_2 group along the chain axis is calculated as $(2.4 + (i-1)\lambda)$Å. The orientational polarizability of the end group is calculated at room temperature (300°K) from the dipolemoment of COOH group (1.8 debye) |114|, assuming that -OH group rotate freely which comes out equal to 24.4×10^{-24} c.c. The values of N, the number of CH_2 groups in one hydrocarbon chain along the axis of these 'built-up' films are 15,16,17 and 21 for palmitate, margarate, stearate and behenate, respectively. The calculation is carried up to 7th nearest neighbours and distances from the reference chain are 4.85Å, 8.412Å, 9.7Å, 13.045Å, 14.55Å, 16.8024Å and 17.487Å for 1st, 2nd.... and 7th nearest neighbours, respectively. These distances are calculated from the knowledge of structure of these films and the distance of first nearest neighbour. The number of the nearest neighbours are estimated according to the simple hexagonal array. The values of dielectric constant calculated for mono- and multimolecular films are given in the table II. Initially, the capacitance and hence the dielectric constant for 8 and 110 monolayers were measured [111] and compared with those calculated theoretically for mono-and multimolecular films. Later on, the capacitance for a monolayer of each substance have been measured. As shown in the table II the results a re in good agreement.

(b) Thickness Dependence of Static Dielectric Constant:

The systematic and detailed study of thickness dependence of dielectric constant has also been carried out from 1 to 80 monolayers for barium palmitate, margarate, stearate and behenate films, respectively. Figures (12-15) are the plots between the reciprocal of the capacitance per unit area and the number of layers which are showing the variation of capacitance with thickness for these four substances. The variation of dielectric constant with thickness in the thickness range studied is shown in the figures (16-19) for barium palmitate,

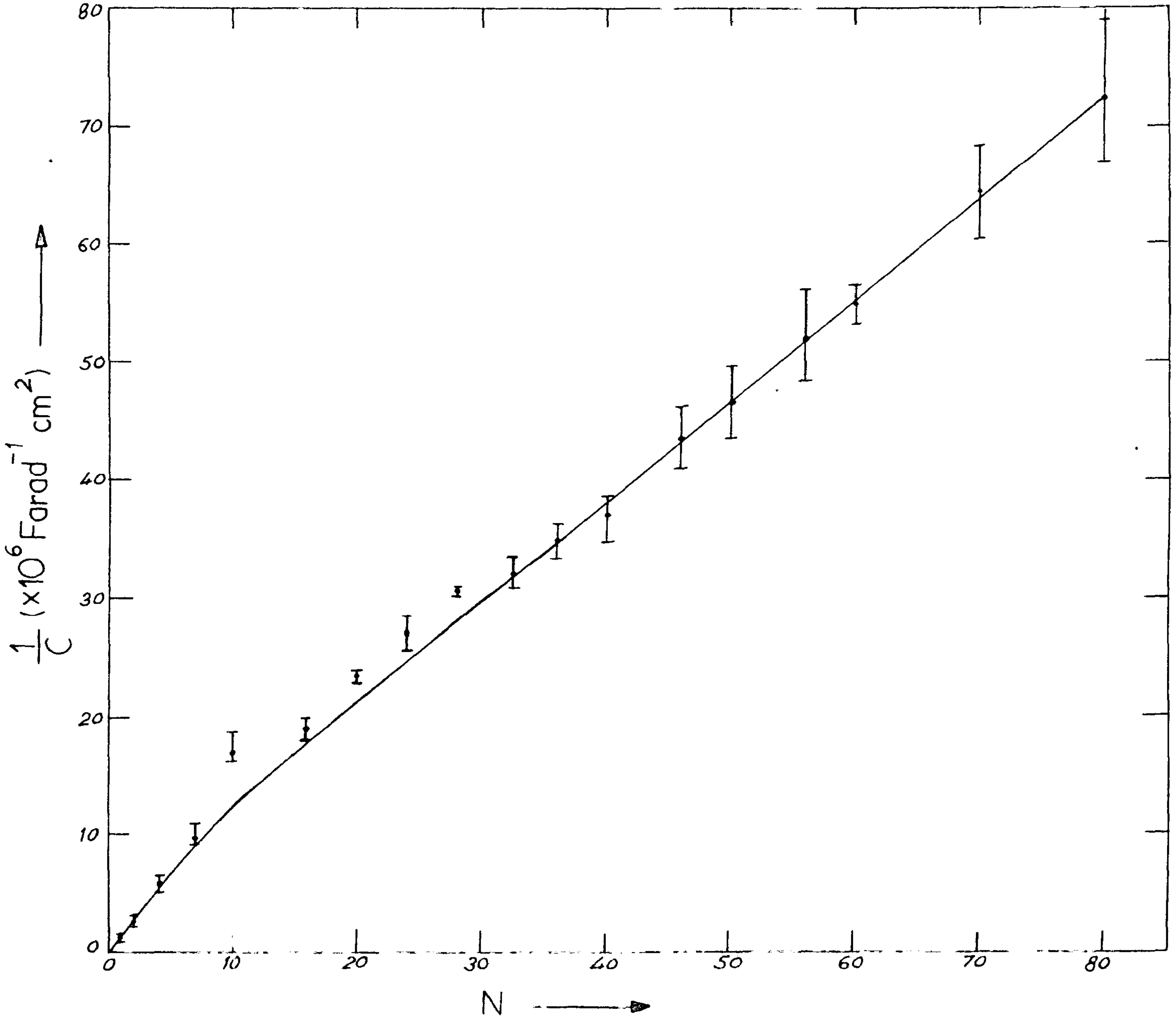


FIG.12. PLOT BETWEEN RECIPROCAL CAPACITY V/S NUMBER OF LAYERS OF BARIUM PALMITATE FILMS.

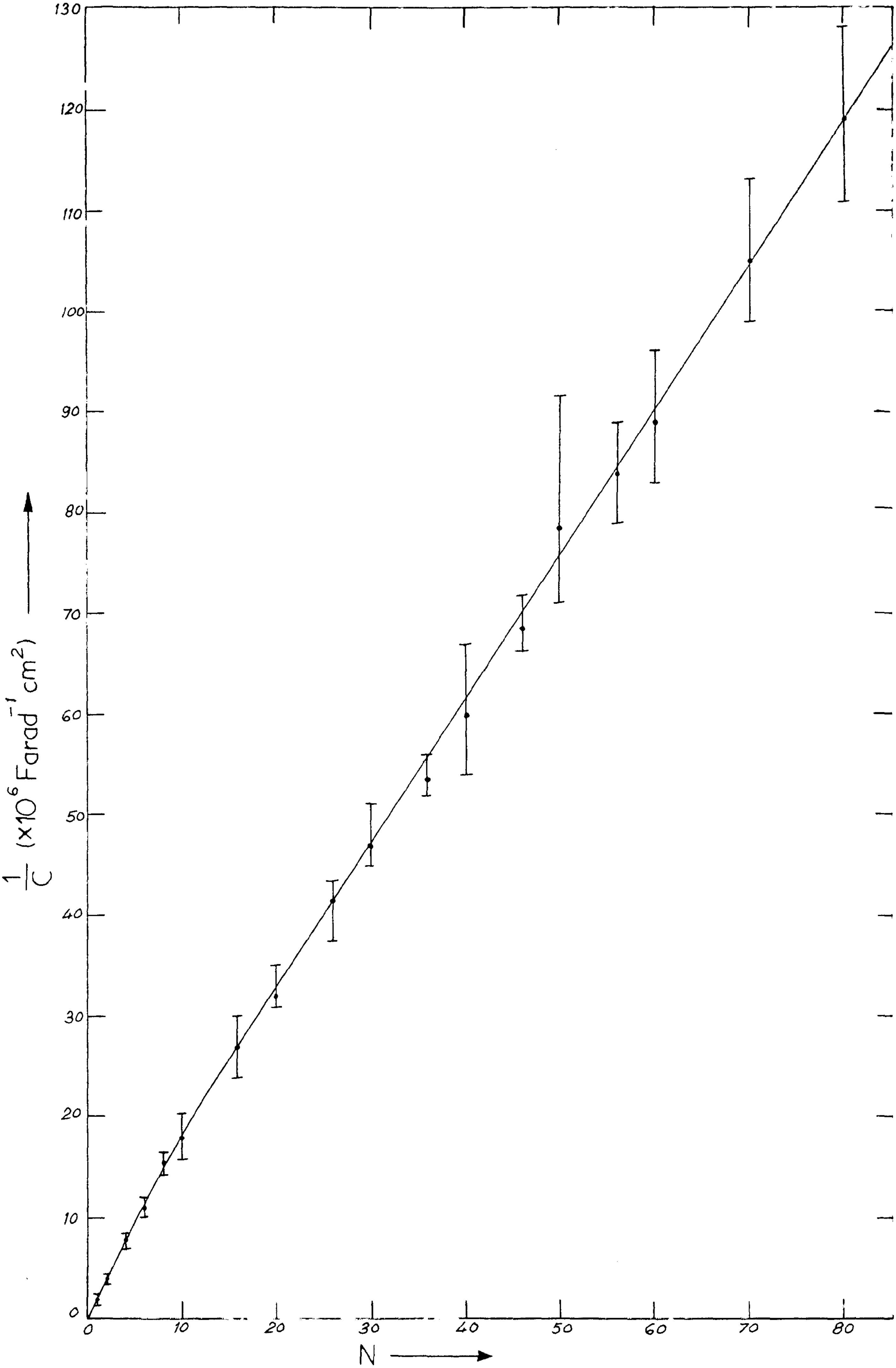
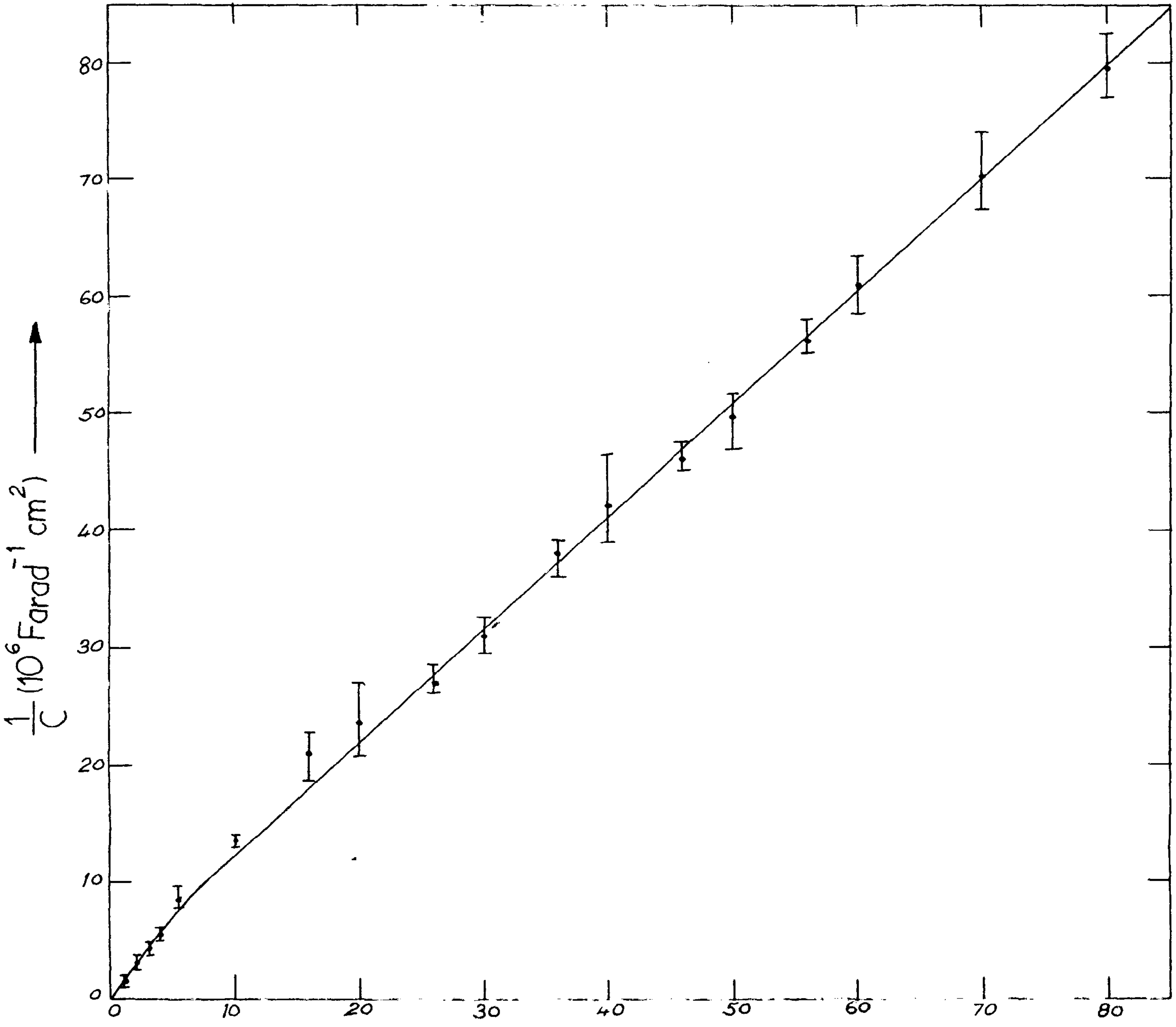


FIG.15- PLOT BETWEEN RECIPROCAL CAPACITY V/S NUMBER OF LAYERS OF BARIUM


$\frac{1}{C}$ (10^6 Farad^{-1} cm^2)
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10
20
30
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50
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70
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10
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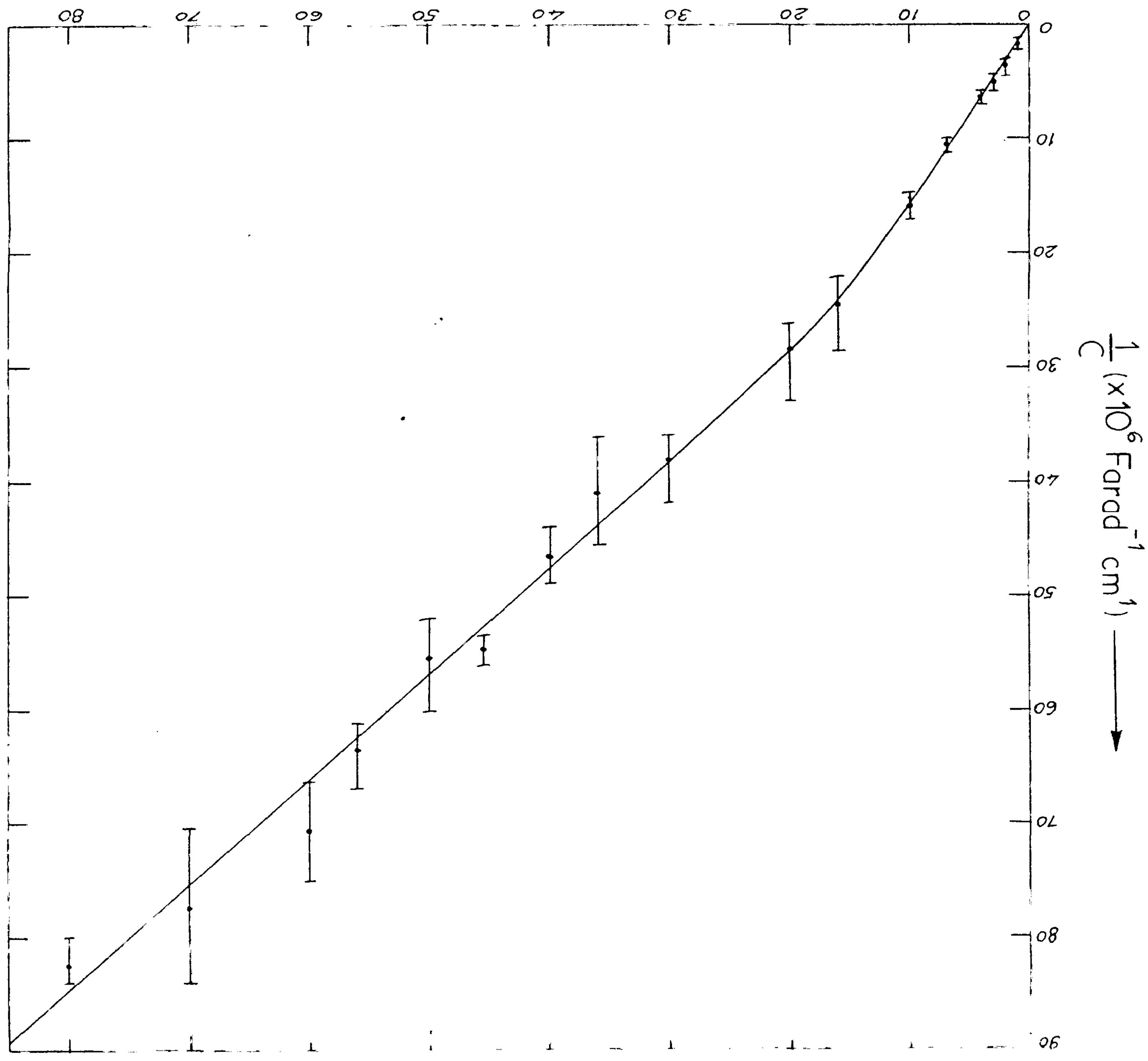
80


$\frac{1}{C}$ (x10^6 Farad^{-1} cm^1)
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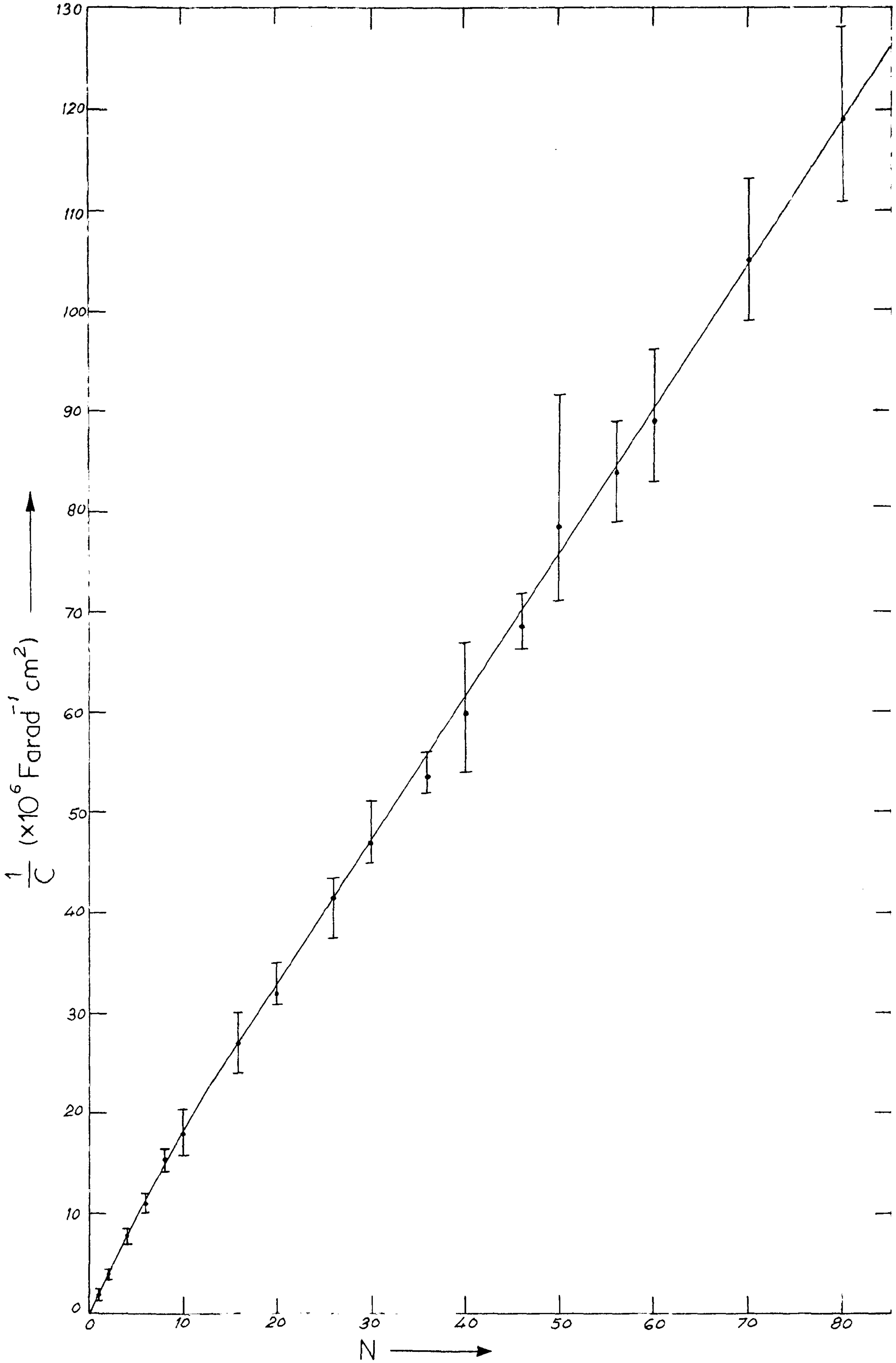

FIG.15- PLOT BETWEEN RECIPROCAL CAPACITY V/S NUMBER OF LAYERS OF BARIUM

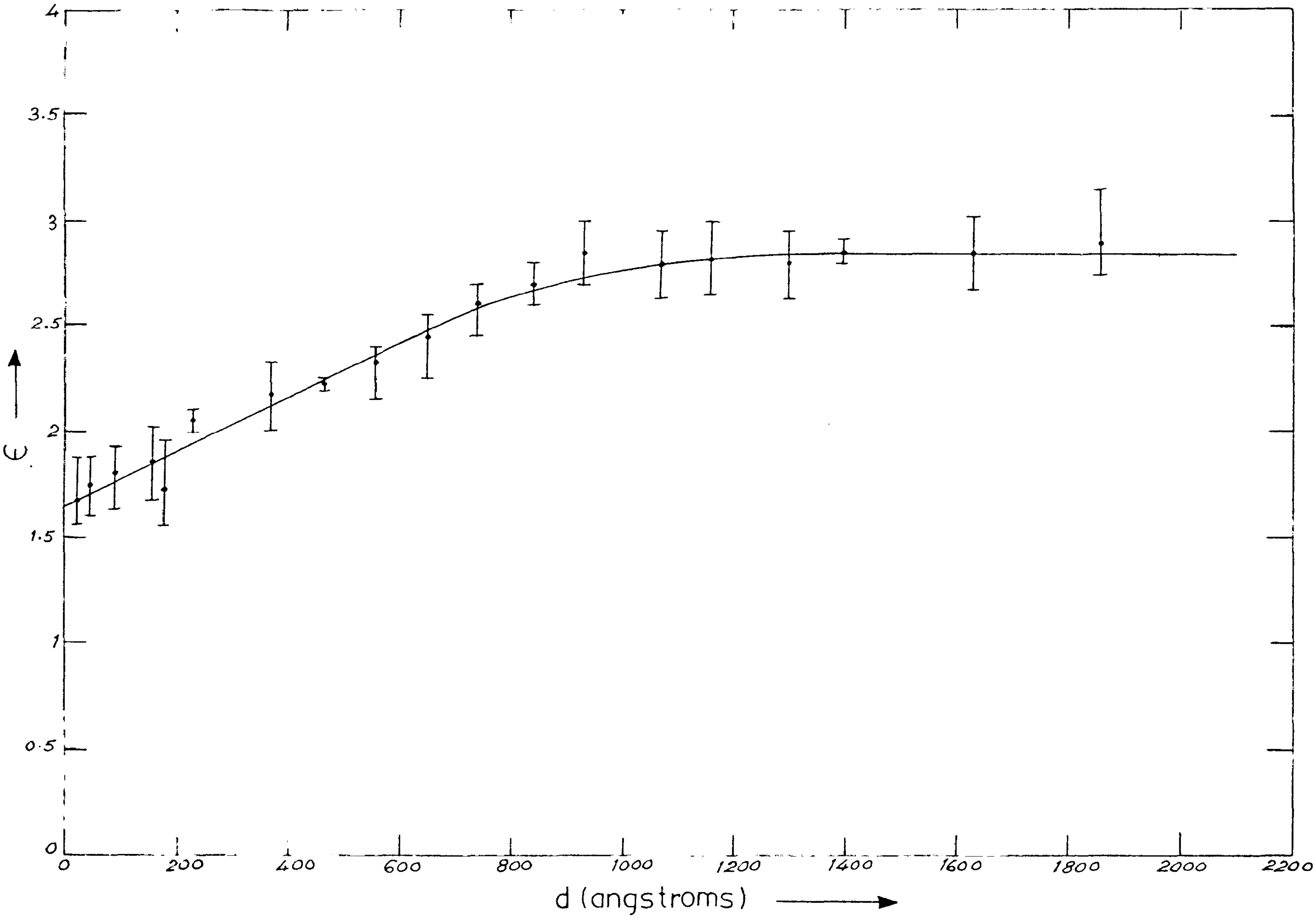

FIG.16 - PLOT OF DIELECTRIC CONSTANT VS FILM TH [illegible]

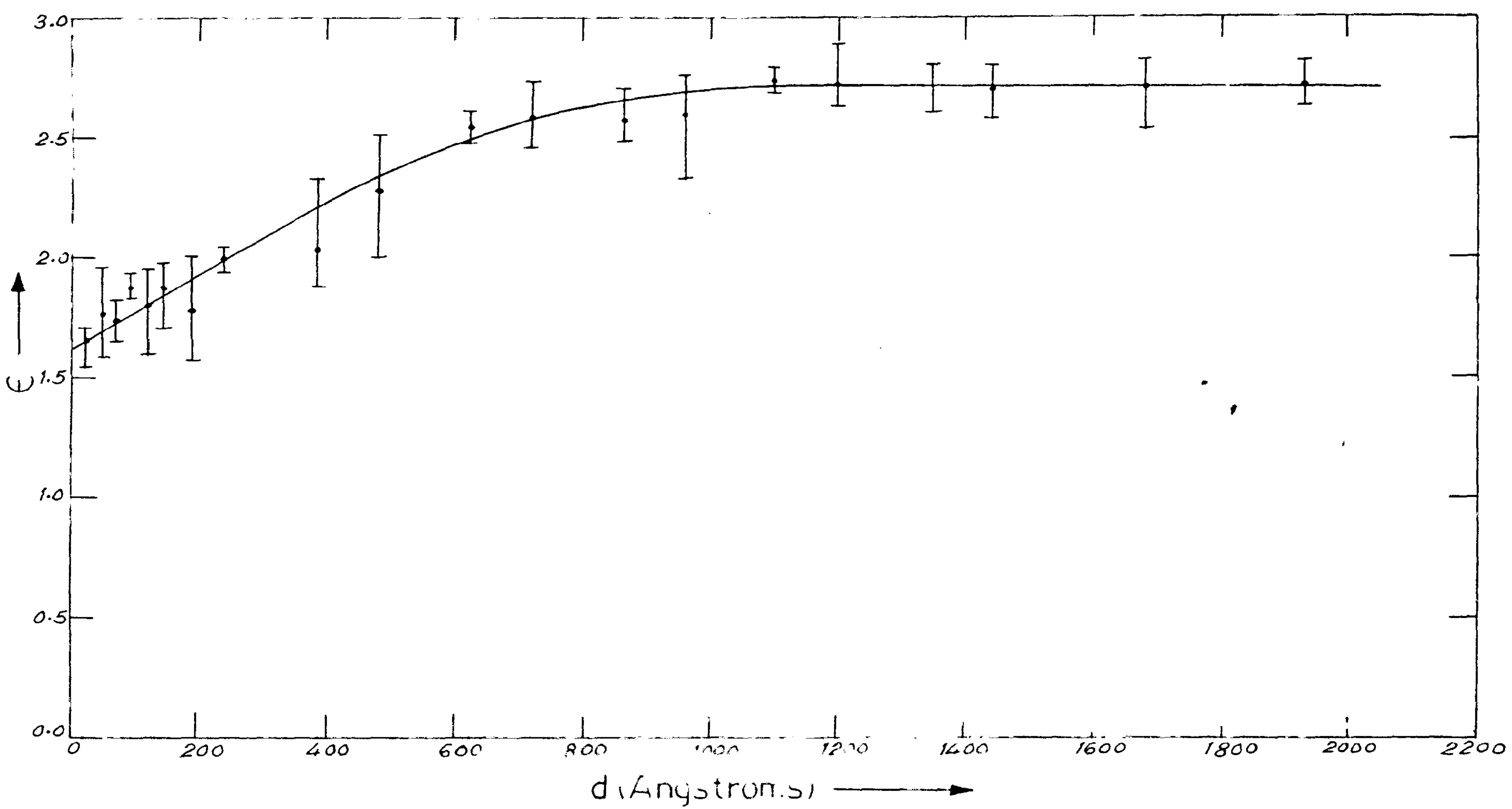

FIG.17- PLOT OF DIELECTRIC CONSTANT V/S FILM THICKNESS OF BARIUM MARGARATE FILMS.

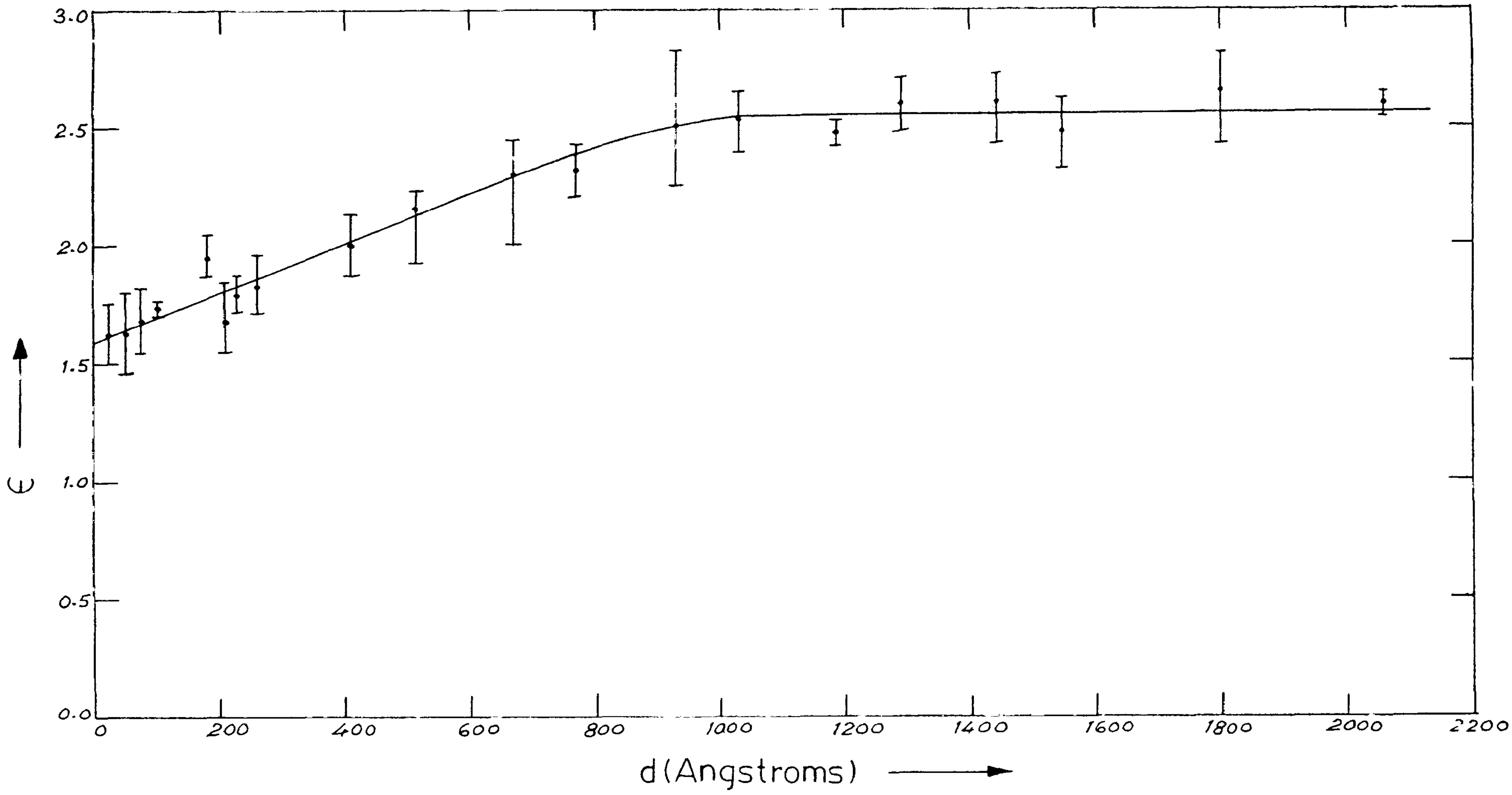

FIG.18- PLOT OF DIELECTRIC CONSTANT V/S FILM THICKNESS OF BARIUM STEARATE FILMS.

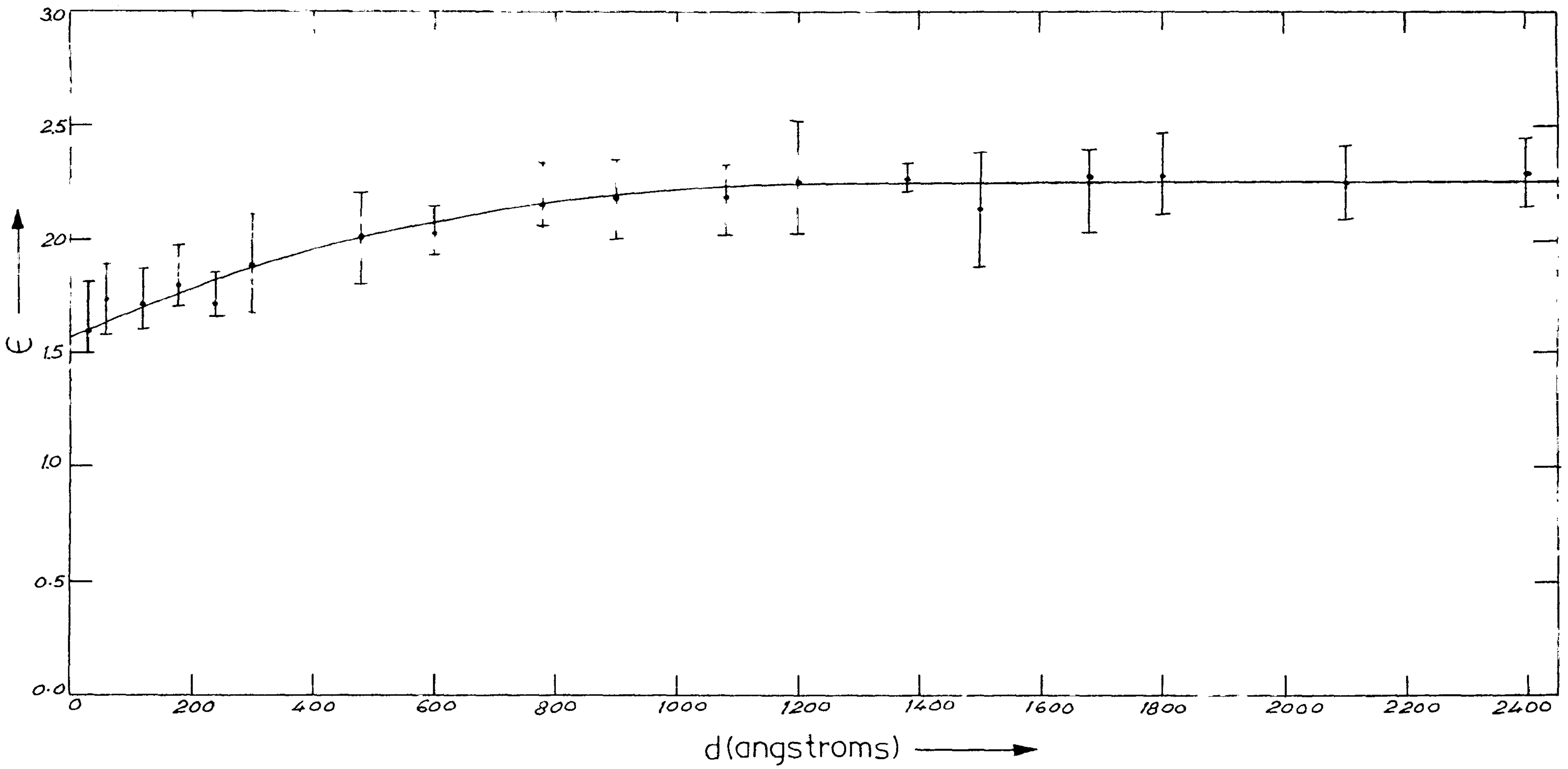

FIG.19- PLOT OF DIELECTRIC CONSTANT V/s FILM THICKNESS OF BARIUM BEHENATE FILMS.

margarate, stearate and behenate, respectively. As expected theoretically, the dielectric constant increases slowly with thickness and attains the saturation value almost at the same thickness for all these substance as is obvious from the figures (16 - 19). The experimental measured values of mono- and multimolecular (thick) films i.e. the saturation value for these 'built-up' films are in good agreement with calculated ones, as shown in the table III.

(c) Refractive Index Values:

The refractive index along the symmetry axis is calculated | 117 | for mono-and multimolecular 'built-up' films of barium palmitate, margarate, stearate and behenate. The symmetry hexagonal axis of the 'built-up' films corresponds to the semi-major axis of the index ellipsoid of the positive uniaxial crystal film. The refractive index has been obtained from the Maxwell's equation $\epsilon = n^2$, where ϵ is the dielectric constant at very high ($\simeq$ optical) frequency i.e. where only the electronic polarizabilities are effective. The refractive index is calculated for 'built-up' films as described in chapter IV. The calculated values of the indices have been compared with the corresponding values measured by Tomar and Srivastava | 73 | for these films except barium stearate films for which Blodgett-Langmuir had measured. As shown in the table IV, the calculated and measured values are in agreement.

6.2 DISCUSSION

(a) Static Dielectric Constant:

The theoretical formulation is based on the definite structure of the barium stearate films as reported by Germer and Storks | 64 |. The hydrocarbon chains of the molecules form hexagonal array with their chain axis normal to the supporting surface and separated by a distance 4.85Å. The structure of barium palmitate, margarate and behenate films have been assumed to be hexagonal, in view of the structure reported by Germer and Storks | 64 | for barium stearate films. As all the acids corresponding to these substances are very close to each other belonging to the same homologous series and the cross sectional area of them (20.4Å^2) is the same, the lateral distance between the chains of the film should be 4.85Å. As the value of unit cell for barium stearate is $4.85 \times 4.85 \sqrt{3}/2 = 20.4$Å^2, the unit cell contains only one hydrocarbon chain. Langmuir | 16 | has confirmed through experiments that the cross sectional area of fatty acids having from 16 to 30 carbon atom per molecule remained fairly constant while the length of the molecule increased in proportion to the number of carbon atoms.

Optical birefringence | 29 |, electron | 64 | and x-ray diffraction | 51 | studies show that these films are crystalline and can be regarded as almost 'two-dimensional' crystals. The building-up of multimolecular layers may thus be regarded as a special case of a layer by layer growth of the crystal.

Since the symmetry hexagonal axis, normal to the film, is obviously one of the principal axes of the dielectric tensor, the calculations give the value of ε_s perpendicular to the plane of the film.

As discussed before, a reasonable assumption is made in the present calculations that the molecule of barium stearate (or palmitate, margarate or behenate) is equivalent to the two effective molecules, each consisting of one hydrocarbon chain and half of the end group $(COO)_2$ Ba. The molecules of barium stearate (palmitate, margarate or behenate) consist of two parallel hydrocarbon chains and the end polar group $(COO)_2$ Ba. The effective molecules thus form a hexagonal array with their chain axes normal to the supporting surface. It is also considered that the hydrocarbon chains are divided into small idential CH_2 groups which are spheres of isotropic polarizability. The negligible effect of H atom at one extremity of the hydrocarbon chain is not considered in the calculation.

The main assumption of this calculation is that the small CH_2 groups and the end group are regarded as point dipoles which are parallel to each other. The dipole approximation has been used and the calculated values are found to be in good agreement with the experimentally measured ones, presumably, because the experimentally measured values of the parameters, have been used in the calculation.

In the calculation on 'built-up' monolayer film, the surface effects, which are important, have been already considered, since the interaction of the surface dipoles have been also included. Calculation on multimolecular films, of course, assumed that the film is so thick that the surface effects are not significant; Lattice sums in the calculations have been carried up to seven nearest neighbours, beyond which the terms become negligibly small. In the calculation, short range interactions and atomic polarizabilities, being small, are neglected.

As already described, a detailed and systematic study of thickness dependence of the dielectric constant has been carried out for 'built-up' films of barium palmitate, margarate, stearate and behenate also. Good quantitative agreement is found between the calculated and measured values of the static dielectric constant of mono-and thick films. The experimental study of the static dielectric constant of 'built-up' Y-films of barium palmitate etc. are carried out from 1 to 80 monolayers and found the thickness dependence in the low thickness range. The static dielectric constant of an insulator is usually regarded a constant quantity characteristic of the bulk. However, it is theoretically expected that the dielectric constant should depend upon thickness in the small thickness range, probably, because of the relatively long range electrostatic interaction between dipoles. The theoretical formulation | 109-111 | (discussed in sec. 4.3) shows that the dielectric constant distinctly depends on thickness.

Although, number of other workers have measured experimentally the dielectric constant of 'built-up' molecular films in different thickness ranges and found its average value equal to be that of the substance in bulk. Porter and Wyman | 74 | measured the dielectric constant of 'built-up' barium stearate films from 7 to 141 monolayers and found values ranging from 1.9 to 3.5 with the average value of 2.5 (bulk phase value). Race and Reynolds | 69 | carried out measurements on somewhat thicker films and found value 2.5 for cadium arachidate and 2.44-2.56 for barium stearate. Recently, the dielectric constant of 'built-up' films containing 1 to 10 monolayers, was measured by Handy and Scala | 78 | and found values ranging from 2.1 to 4.2 with an average value of 2.5 i.e. the dielectric constant independent of thickness. Similar, constancy of dielectric constant with thickness in the range from 1 to 11 monolayers was found by Drexhage and Kuhn |79| for 'built-up' films of cadmium salts of fatty acids. However, this constancy of the dielectric constant with thickness has no theoretical explanation.

In the present study, the thickness dependence in the low thickness range, of the dielectric constant (figures 16 - 19) comes out to be very definite and unmistakable. The results for monolayer and thick films are in complete quantitative agreement with the calculated ones based on the theoretical formulation (sec. 4.3). The nature of the dependence curves obtained can be fully understood qualitatively. This work provides the first experimental evidence for the expected thickness dependence of the dielectric constant of well controlled and structurally well defined thin film system. On evaporated films, for example, Chopra |122| has studied the variation of dielectric constant as a function of thickness for ZnS film using, various electrodes and substrates at different temperatures. The variation of dielectric constant with thickness has however been interpreted here in terms of structure defects like porosity of the films.

As can be seen from the curves, the dielectric constant increases slowly with increasing thickness and attains the saturation value at a thickness of about 1000Å which is about the same for all the substances studied. This may therefore be taken as a rough estimate of the range of electrostatic interaction. Quantitative interpretation of the detailed nature of the curves has not been possible because in theoretical formulation of the explicit thickness dependence of the dielectric constant could not be derived in terms of the present models.

As described earlier, Al-electrodes were deposited on microglass slides by thermal evaporation in vacuum which naturally get exposed to the atomsphere during the study. This Al electrode oxidizes to form the Al_2O_3 thin layer at its upper surface so that the organic monolayer was actually being deposited on the surface oxide, rather than directly on the metal surface. One can expect that the thickness of the surface oxide is significant compared to a monolayer thickness. The contribution of the surface oxide has been neglected in the capacitance measurements. This is reasonable, to the first approximation, since the resitivity of the oxide film is small to the resitivity of the organic layers | 78 |.

The measurements of dielectric constant of all these substances have been done on Y-type films because only the Y-films have the stable configuration and are easily deposited.

(b) Refractive Index:

The values of refractive index calculated for barium palmitate, margarate, stearate and behenate, obviously, correspond to the semi-major axis of the index ellipsoid of the crystal film. The calculated values of refractive index for mono- and multimolecular 'built-up' films of these substances have been compared with the experimentally measured values for thick films. Although the experimental value of the refractive index for monomolecular films of Ba- palmitate, margarate, stearate and behenate, has not yet been reported, it is obviously,unlikely that it will be much different from that of the thick films. The deviation of the calculated values from the measured ones is, presumably,because of the approximations made in the calculations.

As discussed before, according to Rozenberg's theory |118|, Maxwell's equation used for the refractive index calculation can be used for unimolecular film because the exponential expression containing the thickness of the film can be neglected. When the thickness of the film is increased, the theory breakdown but it can again be used for films having thickness comparable to or greater than the wavelength of light. Thus, the use of the phenomenological concept in the present calculation is justified.

TABLE I

PARAMETERS OF THE MOLECULES

Substance	Molecular Formula	No. of carbon atoms in one chain	Value of monolayer thickness [51] Å	Value of n $\times 10^{20}$	Electronic polarizabilities of the molecule $\times 10^{-24}$ c.c.
Ba- palmitate	$(C_{15} H_{31} COO)_2 Ba$	15	23.25	20.88	107.68
Ba- margarate	$(C_{16} H_{33} COO)_2 Ba$	16	24.05	20.41	111.36
Ba- stearate	$(C_{17} H_{35} COO)_2 Ba$	17	25.75	19.05	115.04
Ba- behenate	$(C_{21} H_{43} COO)_2 Ba$	21	30.05	16.34	129.76

TABLE II

CALCULATED AND MEASURED VALUES OF DIELECTRIC CONSTANT

Substance	Thickness of		Calculated value of dielectric constant		Capacitance per unit area $\mu F/cm^2$		Measured value of dielectric constant	
	monolayer Å	110 layers Å	for mono-layer	for multi-layer	of mono-layer	of multi-layer	for mono-layer	for 110 layers
Ba- palmitate	23.25	2557	1.7	2.9	0.636	0.00988	1.67±0.12	2.85±0.20
Ba- margarate	24.05	2645	1.6	2.7	0.582	0.00866	1.65±0.07	2.59±0.02
Ba- stearate	25.75	2830	1.7	3.1	0.554	0.00842	1.62±0.08	2.72±0.07
Ba- behenate	30.05	3305	1.5	2.0	0.470	0.00604	1.60±0.10	2.25±0.02

TABLE III

MEASURED VALUES OF DIELECTRIC CONSTANT FROM THE GRAPHS

Substance	Calculated value of dielectric constant		Measured value of dielectric constant for monolayer	Saturation value of dielectric constant from the graph.
	for monolayer	for multilayer		
Ba- palmitate	1.65	2.9	1.67	2.84
Ba- margarate	1.63	2.7	1.65	2.72
Ba- stearate	1.67	3.1	1.62	2.56
Ba- behenate	1.50	2.0	1.60	2.24

TABLE IV

CALCULATED AND MEASURED VALUES OF REFRACTIVE INDEX

Substance	Thickness of monolayer Å	Calculated values of refractive index		Measured values of refractive index for thick films |73|
		for monolayer	for multilayer	
Ba- palmitate	23.25	1.15	1.21	1.58
Ba- margarate	24.05	1.14	1.20	1.62
Ba- stearate	25.75	1.09	1.13	1.53*
Ba- behenate	30.05	1.11	1.15	1.54

* reference |29|.

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APPENDIX

LIST OF PUBLICATIONS

1. 'Static dielectric constant of 'built-up' molecular films of Barium Stearate' with V.K.Srivastava and V.K.Agarwal, Thin Film, Vol. 2 no. 1, 83 (May '1971).

2. 'Corrected calculation of static dielectric constant of Barium Stearate Films' with V.K.Srivastava, Thin Film (In Press).

3. 'Refractive index of 'built-up' barium stearate films' with V.K.Srivastava, Thin Films (In Press).

4. 'Studies of dielectric constant of some ''built-up' molecular films' with V.K.Srivastava, Thin Solid Films, Vol. 12 no. 1 (1972).

5. 'Thickness dependence of the static dielectric constant' with V.K.Srivastava, Physical Review, 1972 (Communicated)

6. 'An optically controlled electrode system for dielectric measurements of thin films' with V.K.Srivastava and V.K.Agarwal Presented in CSIR PRC convention held in April 1970 at Nainital (India).

7. 'Calculation of static dielectric constant of 'built-up' barium stearate films' with V.K.Srivastava and V.K.Agarwal, Proc. of Nuclear Phys. and Solid State Phys. Symp., Madurai (India), Dec. 1970, Vol. 3 pp. 131-134.

8. 'Calculation of Refractive index of molecular barium stearate films' with V.K.Srivastava, Presented in the U.G.C. Symp. on Thin Film Technology held at Waltair, India in Feb. '1972.

Note: In the first and seventh papers all the formulation and calculation has been done by the author. The contribution of other authors is only in the form of marginal discussion.