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HIGH FREQUENCY ELECTRICAL WAVES
CORRELATED WITH SOIL MICRO-STRUCTURE

by

RAGAA HAFEZ HELMY.

A thesis submitted for the degree of
Doctor of Philosophy
to
The City University, London.

October, 1976.

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ABSTRACT

The investigators interested in electrical dispersion of heterogeneous mixtures form two groups. The first group, which started in the last few decades of 19th century, resorted to microscopic models to depict the behaviour of mainly dilute suspensions of colloidal matter. Building on the results of these works, a second group of investigators started more recently using macroscopic models applied to rather concentrated systems such as consolidated soils.

A review of the literature on soil micro-structure and its characterization by the electrical dispersion method suggests the need for a reinterpretation of the associated electrical response data in order to account for some important aspects such as the very appreciable role of adsorbed water on clay. This requires the adoption of a more comprehensive macroscopic model, the elements of which reflect the properties of the microscopic components of the soil-water system.

While the researchers who used the electrical dispersion technique for soil investigation have attributed the main cause of electrical dispersion to one type or another of the relaxation mechanisms, the author believes in the possibility of various types of polarization and relaxation mechanisms taking place simultaneously within the soil-water system. Consequently, a broad spectrum of relaxation times should be expected.

Analysis of the available data suggests that at least one component of the soil-water system exhibits a frequency-dependant relaxation. This indicated that the adsorbed water phase could very well be the component responsible for such a phenomenon.

The experimental programme was designed to measure the dielectric constant and conductivity dispersion of saturated fine grained soils in the radio frequency range (10-110 MHz). Most of the compositional and micro-structural parameters of the soil-water-electrolyte system were deliberately and systematically changed to study their effects on the electrical responses of the system, and thus establishing the correlation between the electrical response and the soil micro-structure.

The electrical dispersion curves produced experimentally were analysed and compared with theoretical curves computed for the model. In most cases agreement was found to be more than satisfactory.

The present thesis is thus devoted to the development of an elaborate electrical model depicting the macroscopic and microscopic structures of the soil-water-electrolyte system, accounting for the critical role of adsorbed water, recognizing the possibility of simultaneous polarization contributions of various mechanisms, allowing for a frequency-dependent component, and capable of predicting the experimental observations. It is shown that the model is an efficient means of investigating the engineering behaviour and micro-structure of soil. This was achieved by deriving an expression relating the experimentally measurable characteristic time of the soil system to different micro-structural and compositional parameters of soil through a coefficient which the author calls "Micro-structure Electrical Modulus, M.E.M.". It is found that this modulus may describe the soil micro-structure in different directions in a numerical manner which permits a quantitative investigation of soil micro-structure. It may also be useful as a means of investigating the soil properties associated with hydraulic flow and wave propagation in different directions.

SYMBOLS

In selecting the symbols used in this thesis, an attempt was made to conform with the recommended symbols and nomenclature for soil mechanics. However, in some cases symbols were adopted to conform with usage in other disciplines or to avoid confusion. Whenever the same symbol is used to represent more than one item, the distinction should be clear from the text.

Symbols are normally defined where they first appear in the thesis; those which occur several times, along with their most commonly used dimensions, are listed below.

A	area, used with subscripts l and s to denote pore fluid and internal surface area of solid particles respectively.
A	shape factor.
AC	alternating current.
a,b,c	three axes of the soil particle.
C	capacitance (farad), used with subscripts o and t to denote empty capacitor and stray capacitance respectively.
c	concentration of electrolyte solutions (gram equiv./litre).
D	electric flux density (dielectric displacement).
DC	direct current.
d	distance, equivalent height.
E	electric field strength (volt/metre)
E'	local electric field strength.
e	electronic charge.
e	void ratio
exp	used for base of natural logarithms.

F	electric force (newton).
f	frequency (Hz).
f_c	characteristic or critical frequency.
f	subscript - denotes the strongly adsorbed layer.
f_d	subscript - denotes the strongly adsorbed layer parallel to the particle surface.
G	specific gravity of solid particles.
I	current (ampere).
i	unit imaginary ($=\sqrt{-1}$)
K	conductance (mho).
k	specific conductivity (mho/cm).
L	inductance (henry).
L, l	length (cm).
l	subscript - denotes pore fluid phase.
l_a	subscript - denotes a part of the pore fluid structurally associated with the solid and adsorbed phases.
M.E.M.	(M_E) Micro-structure Electrical Modulus.
$\bar{m}$	total moisture content (free and adsorbed).
N	number of elementary units per unit volume.
n	concentration (ion/cm ³).
P	polarization, used with subscripts e, a, d, i, and s to denote electronic, atomic, dipolar, interfacial, and static polarization respectively.
p	porosity.
p	volume fraction of suspended particles.
$\bar{p}$	linear porosity.
Q, q	electric charge (coulomb).
R	resistance (ohm).
r	distance.

S	specific surface area of solid particles (m^2/g).
T_θ	tortuosity coefficient.
T, t	time (day, sec.).
t_f	thickness of strongly adsorbed layer.
t_w	thickness of weakly adsorbed layer.
U_+ , U_-	mobility of charge carriers (+cations, -anions).
V	voltage (volt).
V	volume, used with subscripts f, l, la, w, and r to denote volumes of strongly adsorbed, pore fluid, associated pore fluid, weakly adsorbed, and solid phases respectively.
v	valence.
w	subscript - denotes weakly adsorbed layer.
wd	subscript - denotes weakly adsorbed layer parallel to the particle surface.
Y	admittance..
α	polarizability.
δ	infinitesimal distance.
ϵ	dielectric constant.
ϵ_0	static ϵ .
ϵ_∞	ϵ at very high frequencies.
ϵ^*	complex ϵ .
ϵ'	real part of ϵ .
ϵ''	imaginary part of ϵ .
ϵ_v	dielectric constant of free space (0.0885×10^{-12} farad/cm).
σ	charge density.
τ	relaxation time, characteristic time, or time constant.
ω	angular frequency (rad./sec).

CHAPTER 1

INTRODUCTION

Soil micro-structure comprises interparticle geometry (fabric) and interparticle forces (intrafabric features). The work of many investigators has lead to a better understanding of the effect of the micro-structural and compositional factors on the engineering properties of soils. Great strides have been made in the study of soil fabric using various direct methods such as the optical and electron microscopy, x-ray diffraction and ultrasonic pulse technique as well as in relating soil micro-structure to mechanical properties such as shrinkage, permeability, effective stress, sensitivity, and stress-strain behaviour; e.g., Bolt (1956) Foster (1972,1973), Lambe (1958,1960), Low (1961), Martin (1962), Mitchell (1956), Rosenqvist (1959,1968), Iida (1939), Nacci, et.al. (1967), and others. Unfortunately, the direct methods for determination of soil fabric are, except in special cases, difficult of quantitative expression, time consuming, and destructive in nature. Moreover, little information about the intrafabric features such as ion distribution, ion to surface bonding, ion mobility, adsorbed water characteristics, and rigid bonding which together with the fabric make up the total micro-structure of soil, can be inferred from such measurements.

Such deficiencies have led in many cases to the use of empirical and phenomenological relationships as well as the application of some fundamental theories to account for soil behaviour even beyond the scope within which these theories have been established. For instance, several attempts have been made to account for volume change tendencies of clays by means of the Gouy-Chapman diffuse double layer theory despite the fact that this theory was derived essentially for the case of dilute colloid suspensions and that the interactions between

different phases of a close packing of soil systems would complicate the problem and render the application of the Gouy-Chapman theory unwarranted.

Bolt (1956) used the Gouy-Chapman diffuse double layer theory to produce consolidation curves in fair agreement with experimental curves only in the case of clays exhibiting very strong colloidal properties. However, deviations from Bolt's results have been reported by Mitchell (1960) and are ascribed mainly to particle orientation.

Quigley and Thompson (1966) have observed fabric changes in natural marine clay during consolidation using x-ray diffraction methods. Foster (1972,1973) and Smart (1967) investigated the behaviour of kaolin fabric under shear stress using optical and electron microscope methods and demonstrated the usefulness of ultratome technique as a means of investigating fabric and fabric changes and their relationship to engineering behaviour.

Laughton (1957) has attempted to treat the general case of mineral particles in contact in a fluid of finite compressibility using the ultrasonic technique. Laughton suggested a 'structure bulk modulus' to account for the observed wave velocity changes. Morse (1952), has studied the wave propagation through various packing of uniform spheres and predicted that the sonic velocity should vary as the $1/3$ power of the confining pressure. Nacci, et al. (1967) investigated the influence of consolidated kaolin fabric on the elastic wave velocities using the ultrasonic pulse technique and suggested that the soil fabric and rigid bonding appear to be of primary importance in controlling the longitudinal wave velocity. For one clay fabric the longitudinal wave velocity varies linearly on a semi-logarithmic scale, with consolidation pressure, with the dispersed clay consistently giving the highest values.

Iida (1939), has shown the intimate relation between the propagation of elastic waves in soil and the soil system properties such as; the water content, closeness of packing, porosity, particle size, and the rigid bonding.

Murphy, et al. (1957) have investigated the effect of; porosity, amount of cementing material, type of cementing material, and type of interstitial fluid, on the longitudinal wave velocity through small synthetic cores. The wave velocity in liquid-filled cores of 10 percent porosity was approximately twice the velocity for cores of 20 percent porosity.

The studies of Roock, et al. (1967), Helmy (1972,1973), and Abouleid and Helmy (1974), have helped to establish the relation between the propagation velocity of mechanical waves through soil and soil strength.

Lambe (1958,1960) endeavoured to correlate the strength and sensitivity of clays with inter-particle forces and particle arrangements. A flocculated structure renders the clay more rigid than is the case with a dispersed one. Mitchell and Houston (1969), showed the importance of soil fabric and electrolyte concentration in influencing the sensitivity of clays. Gibson(1953) pointed out that the greater the activity of the clay mineral, the greater the contribution of cohesion to shear strength relative to that of friction.

Olsen (1962) has investigated the effects of different factors on hydraulic flow through saturated clays and concluded that the deviation from Darcy's law and the Kozeny-Carman equation is mainly due to different pore size distribution in the clay. Cluster structures are assumed to form and changes in permeability after consolidation are explained in terms of inter-cluster and intra-cluster void ratios.

Olsen derived an expression for the tortuosity of flow paths that depends among other factors on the direction of flow relative to that of consolidation pressure. Experimental results by Mitchell (1956) demonstrated the effect of particle orientation on permeability.

De (1970) reviewed the works of several investigators on the effect of soil micro-structure on the permeability, indicating that the flow of water through soil is enhanced in the direction of average particle alignment. Permeability decrease due to remoulding would be expected on the basis of the fabric change. As a result of remoulding, a more uniform pore distribution of particles results relative to that of undisturbed material. The average pore space is lower in the remoulded clay and thus the resistance to water permeation is higher resulting in lower permeability values than those in the undisturbed clays.

Many investigators have realised that the intrafabric features are dominated by the adsorbed water phase characteristics. Intensive studies have been devoted, therefore, to the adsorbed phase as a profoundly important constituent of the soil-water systems. Almost all the soil specialists agree that adsorbed water differs in properties from the pore free water. It is also recognized that the significance of the differences of the properties diminishes gradually with distance from the particle surface and eventually vanishes when the bulk water in pores is reached. Martin (1962), presented a comprehensive review of the studies of the adsorbed water on clay, and showed that two models have been suggested for the adsorbed water; solid or ice-like and two-dimensional fluid. Martin pointed out that dielectric measurements on clays could provide valuable data concerning the adsorbed phase. Admitting that the nature of adsorbed water remains

unknown, nevertheless, Martin favoured the two-dimensional liquid model.

Low (1961) presented a critical review of the literature on clay-water interaction and tried to elucidate the adsorbed phase in terms of a hypothetical molecular model. Low indicated that nowhere is the water structure so rigid that ions cannot diffuse through it and promote disorder; nor is it so rigid that it will not shear under stress. Nevertheless, it has a yield point that depends upon the proximity of adjacent mineral surfaces. Although the precise molecular arrangement of the water cannot be specified, it is not the same as that in ice.

Rosenqvist (1959) summarized the physico-chemical properties of soil-water systems and speculated even further by suggesting that a part of the water in a clay-water system should be considered as belonging to the mineral phase. The minerals thus consist of a central silicate skeleton with an outer part of aqueous composition. The presence of this outer part is the essential characteristic of the mineral phase in a clay-water system. Rosenqvist discussed in terms of this concept, some typical clay properties such as cohesion and plasticity.

Foster and Gazzard (1975) have investigated the effect on shear strength, consolidation, and consistency of clays due to rigid inter-particle bonding resulting from the introduction of different polymeric Aluminium hydroxy cations in solution into suspensions of kaolin prior to their laboratory sedimentation. Foster and Gazzard suggested the existence of four phases; free pore water, adsorption phase containing exchangeable cations, amorphous growth, and quasi-crystalline growth, and reported a significant increase in strength with time and cation type.

The preceding review suggests that:

- (1) In principle, quantitative predictions of the engineering properties of a soil specimen should be possible if all micro-structural and compositional factors can be represented and evaluated numerically.
- (2) The interparticle forces forming a component of the soil micro-structure are dominated by the adsorbed water phase characteristics. Any attempt to characterize soil-water systems and evaluate their engineering properties, to be successful, should represent the adsorbed water phase reasonably.
- (3) Present methods for the direct study of soil fabric such as electron microscopy and x-ray diffraction, are destructive in that samples must be cut up for examination. Indirect methods for the study of soil micro-structure such as measurements of pore water pressure, comparison of stress-strain characteristics, permeability measurement, and sensitivity are either destructive or time consuming.

Confronted by such situation, few geologists, geophysicists, and soil scientists, encouraged by the successful application of electrical methods in many fields of scientific research, resorted to such methods hoping to develop a new technique as an additional useful tool for the study of the soil micro-structure and the engineering behaviour of soils.

However, the job of those pioneer scientists has been rather difficult due to the fact that despite many attempts to relate the electrical properties of a heterogeneous mixture to those of its

components, the general theory of dielectrics is not yet sufficiently developed to explain the dielectric behaviour of such mixtures with adequate accuracy. . .

In the mean time, methods of soil investigation by the use of ultrasonic pulse technique are rapidly gaining ground, and due to the close similarity between these methods and the electrical dispersion technique methods, it is conceivable that by developing the correlation between the two techniques, very important and useful results may be achieved. Prospecting for ground water by induced electrical polarization (Vacquier, et al., 1957), propagation of electric pulses through earth materials (Bhattacharyya, 1957), and evaluating the electrical properties of soil in terms of the attenuation constant of a radio wave travelling along soil samples (Banerjee and Joshi, 1938), are examples of the type of research that would help to develop the correlation sought.

Clearly the correlation envisaged between electrical dispersion and ultrasonic techniques is a major project beyond the scope of the present investigation which is restricted to electrical dispersion.

In choosing the frequency range for the electrical dispersion investigation, the simplest type of electrical measurement would be of direct current conductivity. Measurements of this type in clay-water systems are complicated, however, by the fact that the prolonged application of a DC field across the soil causes electrokinetic coupling phenomena such as electro-osmosis, which may create irreversible changes in the system (Mitchell and Arulanandan, 1968). Use of alternating current fields minimises problems of this type. In this case, the measured responses depend on the frequency of the AC, and throughout this thesis the electrical responses of soil samples are measured in the radio frequency range; 10-110 MHz.

This thesis is devoted to the development of the dielectric dispersion technique as an additional nondestructive method for the study of the engineering behaviour of soils and the investigation of soil micro-structure. Therefore, it has as its objectives:

- (1) To present a critical review of the previous studies in order to summarize the current status of knowledge and development in this field.
- (2) To perform an experimental programme for investigating the effect of micro-structural and compositional factors on the electrical response of soil in the radio frequency range using specifically designed equipment to ensure the least disturbance to soil samples under test.
- (3) To develop an electrical model, analogous to soil-water systems, that meets the requirements stated earlier and is capable of predicting the experimental observations.

- (4) To derive a numerical micro-structure electrical modulus based on both the experimental observation and the theoretical model, and thus can be used to correlate the soil micro-structure with its experimentally measurable electrical response.

The author, for this formidable task, was appreciative of some recent work on the subject, especially by Arulanandan, Mitchell and Smith.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 DEFINITIONS

2.1.1 Electrical Forces

Coulomb's law may be stated as (Anderson, 1964):

$$F = A \cdot \frac{q_1 q_2}{\epsilon r^2} \cdot (\bar{a}) \quad \text{newtons} \quad (2.1.1)$$

where F is defined as the force between the charges q_1, q_2 and $(\bar{a})$ is a unit vector pointing from one charge away from the other, r is the distance between the charges and ϵ is a property of the medium called the dielectric constant by physicists and chemists and permittivity by electrical engineers.

A is a constant whose value will depend on the units used for charge, distance, and force. In the rationalized m.k.s system, A has the value $1/4\pi$ (Appendix I), then

$$F = \frac{q_1 q_2}{4\pi \epsilon r^2} (\bar{a}) \quad \text{newtons} \quad (2.1.2)$$

When A is made dimensionless, it necessarily implies units for the dielectric constant ϵ , i.e.

$$\epsilon \equiv \frac{(\text{coulombs})^2}{\text{newtons}(\text{metres})^2} \equiv \frac{(\text{Coulombs})^2}{\text{Joules metres}} \equiv \frac{\text{farads}}{\text{metres}}$$

2.1.2 Electric Field

A charge in the vicinity of a system of charges will, in general, experience a force. The region of influence of the charge is called an electric field, and its strength at a point is defined as the force per unit charge on a positive test-charge placed at that point. The electric intensity or "field strength" will, by definition, be a vector defined by

$$E = \frac{F}{\delta q}$$

where F is the force acting on the infinitesimal test-charge δq .

Thus, the field arising from a point charge q in a homogenous medium will be given by

$$E = \frac{q}{4\pi\epsilon r^2} \quad (\bar{a}) \quad \text{volts/metres} \quad (2.1.3)$$

2.1.3 Capacitors

An arrangement of two conductors (plates-electrodes) in close proximity, but insulated from one another, is called a capacitor. If a voltage V is applied to a capacitor it holds a charge Q such that (Daniel, 1967):

$$Q = CV$$

where C is the capacitance in farads.

The strength E of the electric field between the plates is equal to the potential gradient across the gap, i.e.

$$E = \frac{V}{d}$$

where d is the distance between the plates.

The capacitance C is directly proportional to the area A of the overlap of the plates and inversely proportional to d , i.e.

$$C \propto \frac{A}{d} \quad \text{and} \quad \frac{Q}{A} \propto \frac{V}{d} = \sigma \quad (2.1.4)$$

The quantity Q/A is the charge per unit area on each plate, and is referred to as the surface density of charge on the plates, σ .

It can be readily seen that

$$\epsilon = \frac{Cd}{A} \quad \text{farads/metres} \quad (2.1.5)$$

ϵ for a given medium must be found by experiment.

For the case of a vacuum between the plates, Eq.2.1.5 will give the value of dielectric constant for free space usually denoted by ϵ_v . Substitution of the appropriate values of units in Eq.2.1.2 gives

$$\epsilon_v = \frac{1}{36\pi \times 10^{11}} = 0.0885 \times 10^{-12} \text{ farads/cm}$$

Careful experimental measurements of ϵ_v give the same value. The capacitance C_0 of such an empty capacitor is determined by its dimensions (A and d) and thus called the geometrical capacitance.

$$C_0 = \epsilon_v \cdot \frac{A}{d}$$

$$= 0.0885 \times 10^{-12} \frac{A}{d} \quad \text{farads.} \quad (2.1.6)$$

Any other insulating medium introduced into the capacitor will reduce the electric field compared with its value in a vacuum, due to the neutralization of a part of the charges on the plates, and thus increasing its storage capacity Fig. 2.1.1

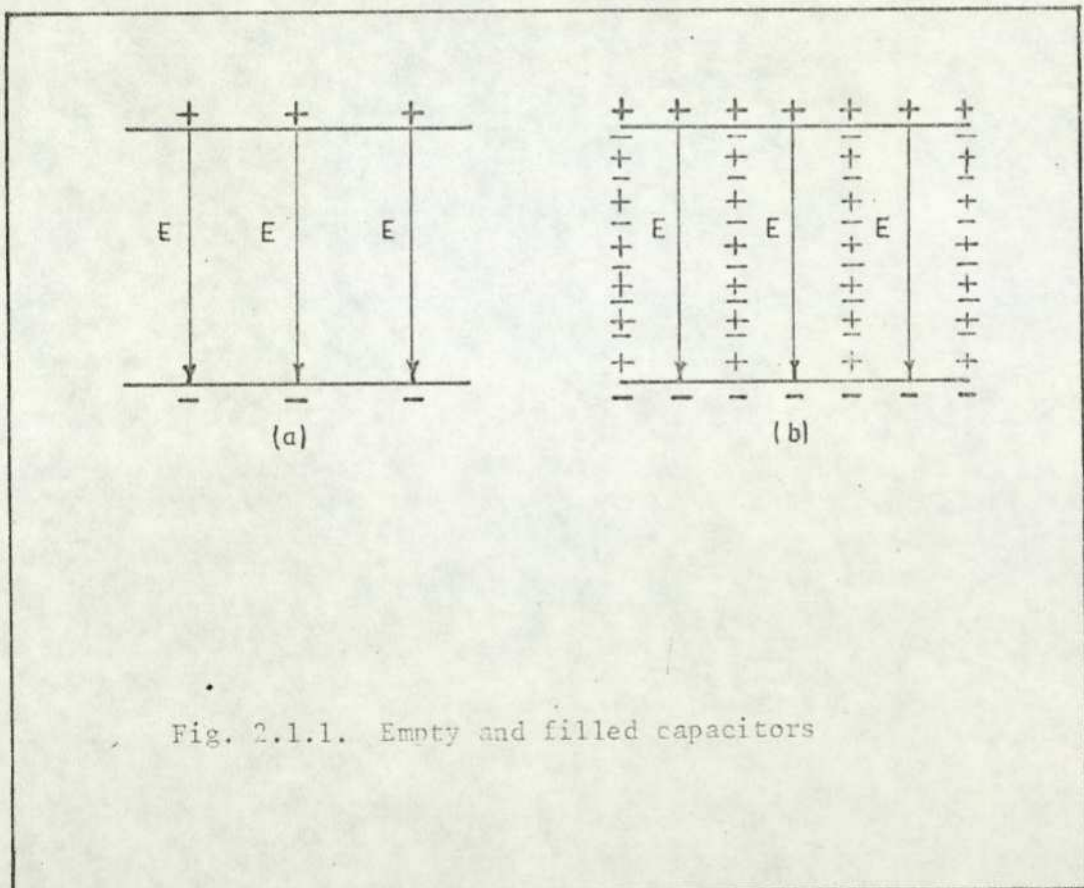


Fig. 2.1.1. Empty and filled capacitors

The dielectric constant ϵ of any insulating material, is therefore, greater than ϵ_v and the capacitance C of a capacitor filled with any insulating material is also greater than its geometrical capacitance C_o .

$$\frac{d}{A} = \frac{C}{\epsilon} = \frac{C_o}{\epsilon_v}, \text{ and}$$

$$C = \frac{\epsilon}{\epsilon_v} C_o = \epsilon_r C_o \quad (2.1.7)$$

where ϵ_r , known as the relative dielectric constant of the insulating material, is a dimensionless pure number equals 1.0 for a vacuum. The higher the value of ϵ or ϵ_r for a given material, the higher its ability to increase the capacitance of the capacitor. In engineering it is common to describe a material by its relative dielectric constant, and the word relative is often dropped and the symbol used is merely ϵ .

2.1.4 Dielectrics

Although a steady current cannot pass through an insulator, an electric field can; it is for this reason that an insulator is often referred to as a dielectric (Bennet, 1974). By contrast, a piece of metal acts as a screen to an electric field. In a metal some of the charges (electrons) are completely free to move; under the action of an electric field they will continue in motion until they have taken up positions that reduce the field inside the metal every-where to zero. Only while a current is flowing is there any electric field inside a conductor.

Thus, the study of dielectric materials sprang from the practical need for insulators which would not conduct the charge away. Amber, bees-wax, and glass were amongst the first practically-applied insulating materials.

For a given material, the insulating properties can be

described in terms of the dielectric strength expressed as the field which, when applied to the material, causes an uncontrollable current to flow through or across it. Also the ability of dielectric materials to increase the charge-storage capacity of a capacitor is of great importance. Like dielectric strength, this is a macroscopic characteristic described in terms of dielectric constant.

The applications of high-frequency current electricity, in connection with radio, increased the demands for capacitors of high capacity, high breakdown strength, and small size. To meet these requirements, many dielectric materials were examined and classified by their dielectric strength and dielectric constant, with a view to their use in this field.

2.1.5 Dielectric Polarization

In general, polarization includes all cases where, by the influence of an electric field, the positive and negative charges in a medium are slightly displaced (Böttcher, 1952).

The total polarization is the sum of contributions of various types of polarization mechanisms; electronic polarization, atomic polarization, orientation polarization, and interfacial polarization, as will be explained below.

2.1.6 Dielectric Relaxation

Every type of polarization mechanism is normally accompanied by losses in the dielectric material. The occurrence of dielectric loss can generally be understood as follows (van Beek, 1965): at very low frequencies the polarization easily follows the alternating field, thus its contribution to the dielectric constant (storage ability) is maximal, and theoretically no loss occurs. At very high frequencies the field alternates too fast for polarization to arise and there is no contribution

to the dielectric constant and no energy is lost in the medium.

Between these two extremes the polarization begins to lag behind the field, and energy is dissipated. . .

This lagging process is known as relaxation mechanism. It characterizes the decay of polarization after the sudden removal of a steady field and will also describe the building up of polarization towards its equilibrium value when a steady field is suddenly applied.

2.1.7 Dielectric Conductivity

It is sometimes convenient to use the concept of dielectric conductivity. It represents the sum of all the loss mechanisms in the material, and is a measure of the performance of a dielectric as an insulator.

2.1.8 Electrical Dispersion

Dielectric relaxation is the cause of anomalous dispersion in which the dielectric constant decreases and the conductivity increases with increasing frequency within the range of frequencies where the polarization process may operate, Fig. 2.1.2.

For a particular dielectric material several regions of electrical dispersion may be observed over the frequency range from 0 to microwave range, Fig. 2.1.3. At the lower end of the frequency spectrum there may be sufficient time between alternations of the electric field for many polarization mechanisms to contribute to the dielectric constant. However, as the frequency increases and the time between alternations decreases it may become impossible for certain polarization mechanisms to operate. This then leads to a decrease in the dielectric constant. The fact that different relaxation mechanisms cease to operate at different frequency ranges influences the form of the curve in Fig. 2.1.3.

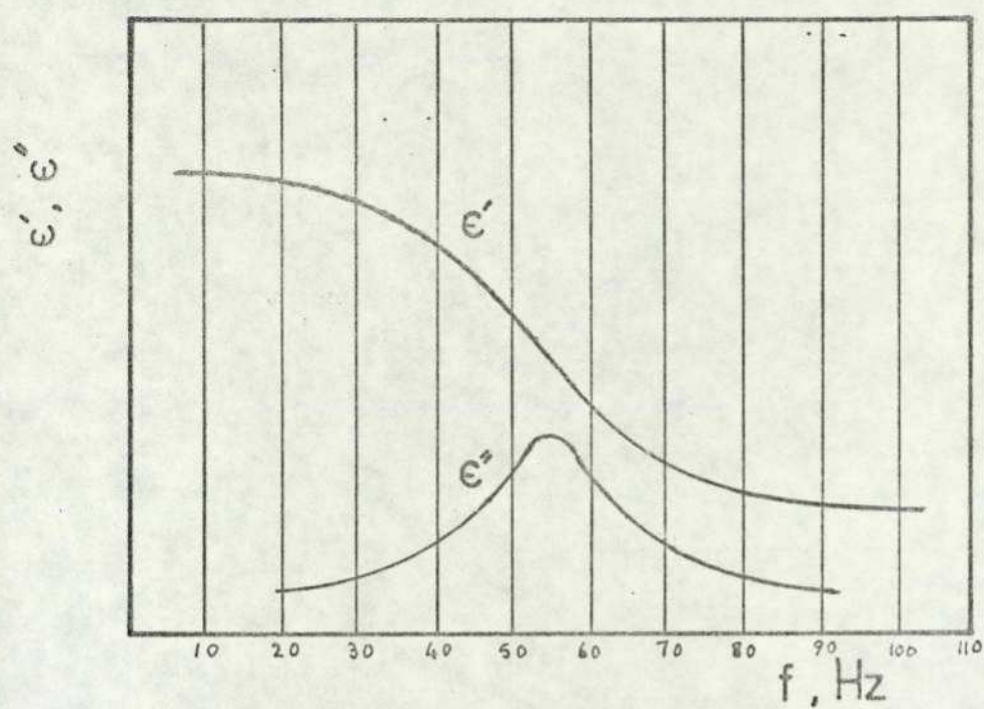


Fig. 2.1.2 Electrical Dispersion

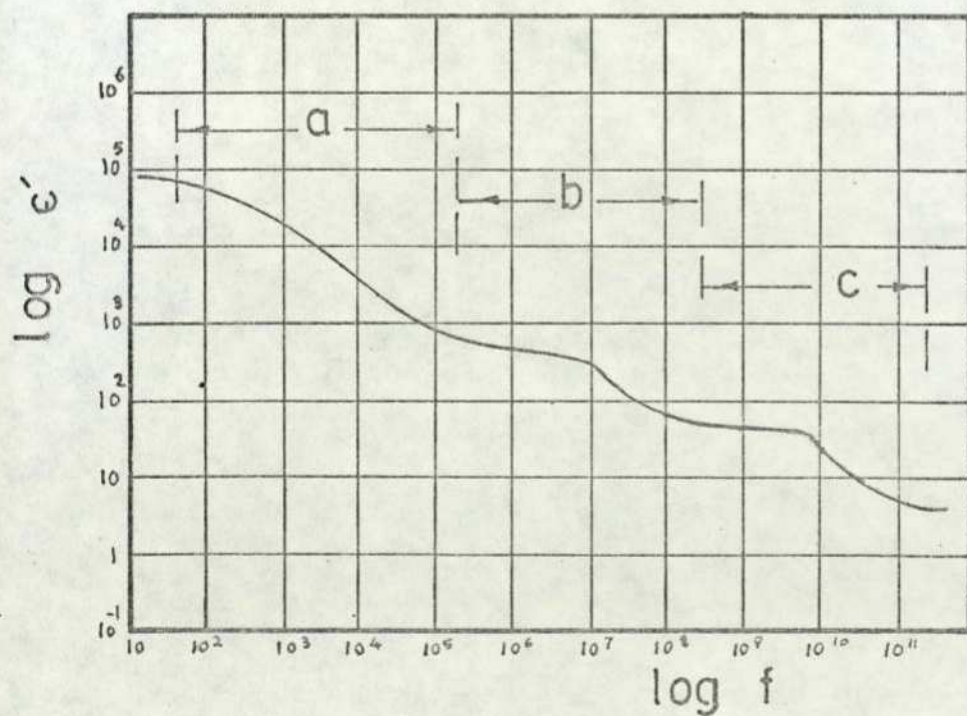


Fig. 2.1.3 Zones of anomalous dispersion

2.2 CHARACTERISTICS OF DIELECTRIC MATERIALS

2.2.1 Mechanisms of Polarization and Relaxation

2.2.1.1 Polarization

Matter, electrically speaking, consists of positive atomic nuclei surrounded by negative electron clouds. Upon the application of an external electric field the electrons are displaced slightly with respect to the nuclei; induced dipole moments result and cause the so-called electronic polarization of materials (von Hippel, 1954). This polarization is responsible for the refractive index and responds to a changing field in negligible time at all frequencies used for electrical measurements (Daniel, 1967), and hence may be considered as associated with elastic displacement of charges and not exhibiting any relaxation. Maxwell (1892) suggested that the electronic (or optical) dielectric constant is equal to the square of the refractive index. The electronic polarization is also called optical polarization to indicate that the characteristic or critical frequencies are usually in the optical region (Frohlich, 1949).

When atoms of different types form molecules, they will normally not share their electrons symmetrically, as the electron clouds will be displaced eccentrically towards the stronger atoms.

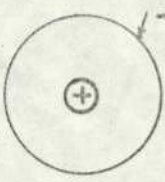
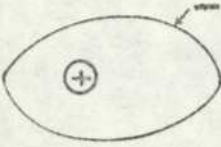
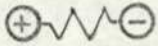
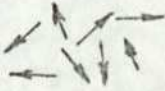
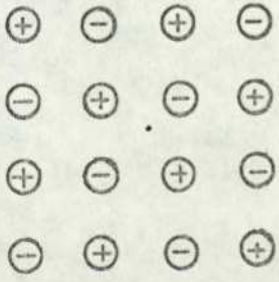
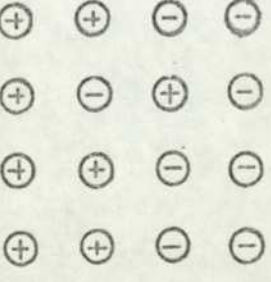
Thus atoms acquire charges of opposite polarity, and an external field acting on these net charges will tend to change the equilibrium positions of the atoms themselves. By this displacement (also assumed of elastic nature) of

charged atoms or groups of atoms with respect to each other, a second type of induced dipole is created; it represents the atomic polarization of the dielectric. The characteristic frequencies of the atomic polarization are usually in the infra-red region.

The asymmetric charge distribution between the unlike partners of a molecule gives rise, in addition, to permanent dipole moments which exist also in the absence of an external field. Such moments experience a torque in an applied field that tends to orient them in the field direction. Consequently, an orientation polarization (Debye, 1929) can arise.

These three mechanisms of polarization are due to charges that are locally bound in atoms, in molecules, or in the structure of solids and liquids. In addition, carriers that can migrate for some distance through the dielectric usually exist. When such carriers are impeded in their motion, either because they become trapped in the material or on interfaces, or because they cannot be freely discharged or replaced at the electrodes, space charges and a macroscopic field distortion result. Such a distortion appears to an outside observer as an increase in the capacitance of the sample, and is known as space charge polarization.

However, since such mechanism is promoted at electrodes or more generally at interfaces of mediums of different dielectric properties it could be termed interfacial

no field	field applied 	polarization mechanisms
		electronic
		atomic
		orientation
		interfacial (space - charge)
Fig. 2.2.1 Mechanisms of polarization		

polarization (or Maxwell-Wagner polarization).

Fig. 2.2.1 illustrates schematically the four polarization mechanisms.

The author believes that the total polarization of a sample could be the sum of contributions of more than one type of polarization mechanisms as long as these mechanisms can be induced in the frequency range applied. A successful model should allow, therefore, for the representation of every applicable polarization mechanism.

2.2.1.2 Relaxation

Several attempts have been made to represent and classify analytically the various types of relaxation mechanisms. Unfortunately none has been successful, and the most generally accepted description is by relating the relaxation to the associated polarization mechanism. It has been, therefore, justified to assume that the same function that describes the decay of polarization upon the removal of the steady field will also describe the building up of polarization towards its equilibrium value when a steady field is suddenly applied.

The simplest assumption in defining this function is to take the speed of approach to equilibrium as being proportional to the distance from equilibrium (Daniel, 1967), or in other words the decay is exponential with time.

It may also be summarized as being related to the time constant of polarization of a dielectric (Anderson, 1964). The reason of relating the relaxation mechanism to a time

constant is that at some critical (characteristic) frequency, f_c (Fig.2.2.2), the effect of the alternating field will cause the maximum loss, ϵ'' , in the dielectric medium. Since this time constant is a measure of the time lag, it is called the relaxation time. The time constant is thus equal to the reciprocal of this critical frequency and is a characteristic of the dielectric material. If the exponential decay function of polarization is valid, the relaxation time τ may be defined as the time in which this polarization reduces to $1/e$ times its original value, e being the natural logarithmic base, Fig.2.2.3. Theoretically, the time to complete decay would be infinity. However, there is practically no dielectric material that has a simple absolute relaxation time. This is due to the inhomogeneity of the dielectric micro-structures in general, the nature of polarization mechanisms, and the fact that more than one mechanism contribute to the total polarization simultaneously. It should then be expected that the relaxation will be distributed over a spectrum of times and the dielectric loss curve will be rather flatter. This is most significantly exhibited in case of heterogeneous dielectric mediums. The dielectric materials that show a spectrum of relaxation times may alternatively be described as exhibiting a frequency-dependent dielectric loss. The complicated and varied frequency dependence of the observed dielectric loss was historically an obstacle to the understanding of dielectric relaxation.

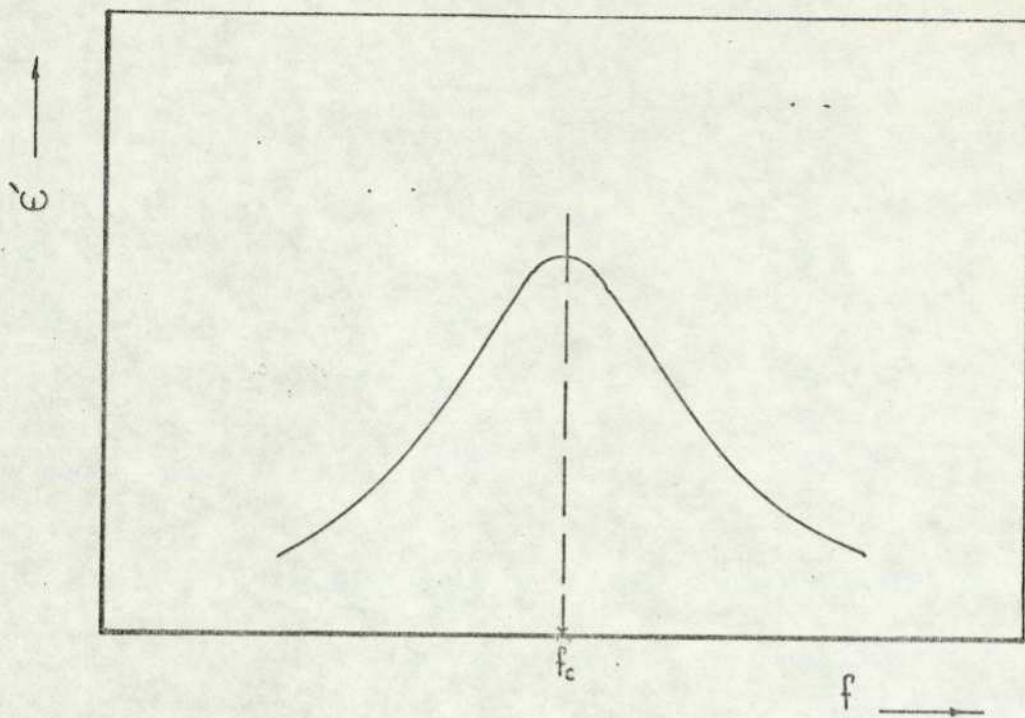


Fig. 2.2.2. Characteristic frequency f_c

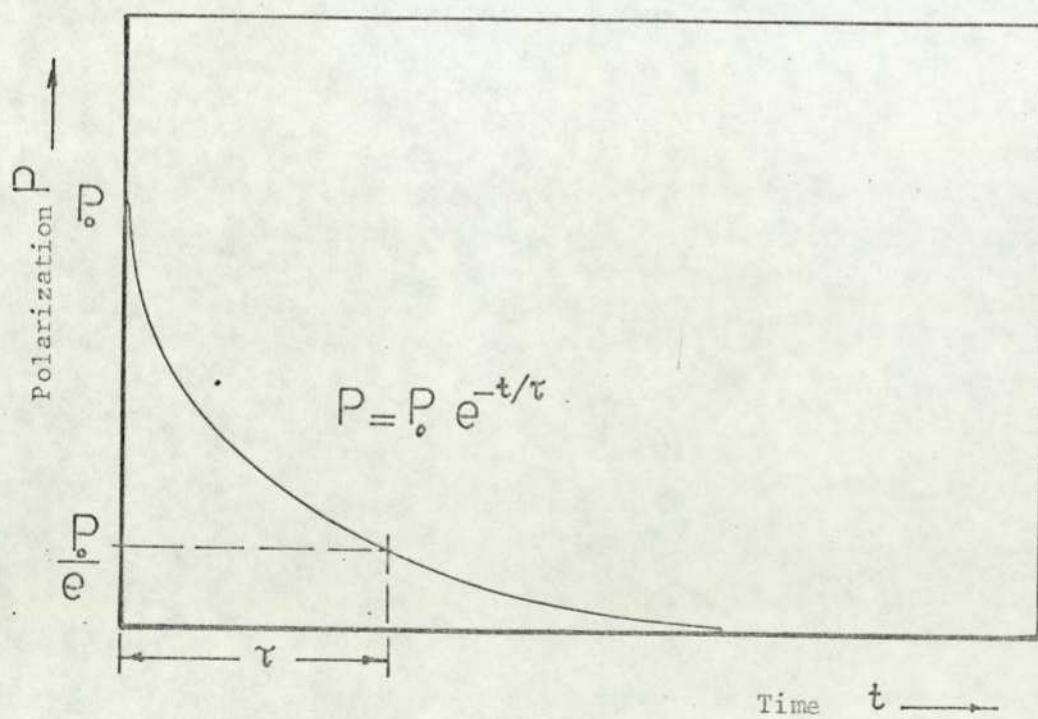


Fig. 2.2.3 Relaxation time τ

2.2.2 Dielectrics with Single Relaxation Time

Debye

According to Eq. 2.1.4, the charge density on the plates of a capacitor is given by $\sigma = Q/A$.

Elementary electrostatics show (Daniel, 1967) that the field and charge density are connected by

$$E = 4\pi\sigma_0 \quad (2.2.1)$$

where σ_0 is the charge density for the capacitor in vacuo. The factor 4π is due to the use of the m.k.s. system (Appendix I). If a dielectric is introduced into the capacitor, then

$$\sigma = \epsilon\sigma_0 \quad (2.2.2)$$

where ϵ is the dielectric constant, representing equilibrium after infinite time, of the dielectric material introduced.

In dielectric theory it is usual to introduce a field D as the electric flux density or dielectric displacement

$$D = 4\pi\sigma \quad (2.2.3)$$

where σ is the total charge density which is held on the plates by the combined action of the external field and polarization.

The polarization P is thus defined by

$$\sigma_0 + P = \sigma \quad (2.2.4)$$

as the charge density held on the plates by the internal displacement of charges. It is readily seen that

$$E + 4\pi P = D \quad (2.2.5)$$

Eq. 2.2.2 leads to

$$D = \epsilon E \quad (2.2.6)$$

Combining the last two equations gives a definition for the dielectric constant in terms of polarization, i.e.

$$(\epsilon - 1) E = 4\pi P \quad (2.2.7)$$

The polarization P implies a dipole moment, M , of the dielectric in the whole of the capacitor

$$M = PAd \quad (2.2.8)$$

so that P can also be defined as a dipole moment per unit volume.

This interpretation of P provides an entrance from the macroscopic into the molecular structure (Anderson, 1964).

This dipole moment per unit volume may be thought of as resulting from the additive action of N elementary dipoles per unit volume, each of average moment $\bar{\mu}$ (von Hippel, 1954), therefore

$$P = N\bar{\mu} \quad (2.2.9)$$

Furthermore, $\bar{\mu}$ may be assumed as proportional to a local electric field strength E' that acts on the particle

$$\bar{\mu} = \alpha E' \quad (2.2.10)$$

where α is called the polarizability, measuring the ease of displacement of the charges, and is proportional to what might be called a mean binding force acting upon the charges (Anderson, 1964). Thus α is the average dipole moment per unit field strength.

Eqs. 2.2.7, 9 and 10 give the two alternative expressions for the polarization, i.e.

$$\begin{aligned} 4\pi P &= (\epsilon - 1)E \\ P &= \alpha N E' \end{aligned} \quad (2.2.11)$$

linking the macroscopically measured dielectric constant to three molecular parameters, viz.; the number N of contributing elementary particles per unit volume, their polarizability α , and the locally acting electric field E' which will normally differ from the applied field E owing to the polarization of the surrounding dielectric medium.

Assuming that the four polarization mechanisms take place simultaneously, we may write both the total polarizability α and the total polarization P of a dielectric material as the sum of four terms, i.e.

$$\begin{aligned}\alpha &= \alpha_e + \alpha_a + \alpha_d + \alpha_i \\ P &= P_e + P_a + P_d + P_i\end{aligned}\quad \} (2.2.12)$$

where the suffices e, a, d, and i denote the electronic, atomic, orientation (or dipole) and space charge (or interfacial) respectively.

Introducing complex quantities (Appendix II) into Eq. 2.2.11:

$$4\pi P = (\epsilon^* - 1) E = \alpha^* N E' \quad (2.2.13)$$

where asterisk denotes complex quantities.

It is sometimes more convenient to regroup the polarization mechanisms according to the conditions under which they may occur.

Thus, assuming that infinite time is allowed for the charging of a dielectric in a capacitor while the external voltage is kept constant, the final charge density will be

$$\sigma = \epsilon_0 \sigma_0 \quad (2.2.14)$$

where ϵ_0 is the static dielectric constant. In this case the static polarization, P_s , will be given according to Eq. (2.2.7) by

$$(\epsilon_0 - 1)E = 4\pi P_s \quad (2.2.15)$$

If, however, E changes with time, then P at a given instant will generally differ from $P_s(E)$. A trend towards equilibrium implies that P will approach P_s and an assumption about the rate of change of P as a function of time will give a differential equation for $P(t)$, i.e.

$$\tau \frac{dP(t)}{dt} = P_s - P(t) \quad (2.2.16)$$

where τ is a constant having the dimension of a time. Since τ is a measure of the time lag it is called the relaxation time (Bottcher, 1952).

Knowing that both the electronic polarization P_e and the atomic polarization P_a respond to a changing field in negligible time at all frequencies used for electrical measurements, Eq. 2.2.15 may be rewritten

$$(\epsilon_0 - 1)E = 4\pi(\Delta P + P_\infty) \quad (2.2.17)$$

where P_∞ -- the contribution to P_s due to elastic displacements
 $= P_e + P_a$

ΔP -- the contribution due to all other displacements
 $= P_d + P_i$

Accordingly, an elastic dielectric constant ϵ_∞ may be defined by

$$(\epsilon_\infty - 1) E = 4\pi P_\infty \quad (2.2.18)$$

and Eq. 2.2.16 is then written

$$\tau \frac{d\Delta P}{dt} + \Delta P(t) = (\epsilon_0 - \epsilon_\infty) \frac{E(t)}{4\pi} \quad (2.2.19)$$

where the right-hand side of the equation is the equilibrium value of ΔP corresponding to $E(t)$, i.e. that value of ΔP which would be reached if the instantaneous value $E(t)$ of the field were applied for an infinite time.

For a periodic field of angular frequency ω ,

$$E^*(t) = E_0 e^{i\omega t}$$

the general solution of Eq. 2.2.19 is

$$\Delta P^*(t) = \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau} \frac{E_0}{4\pi} e^{i\omega t} \quad (2.2.20)$$

It follows that at any frequency ω , a dielectric constant $\epsilon^*(\omega)$ may be defined by:

$$\epsilon^*(\omega) - \epsilon_\infty = 4\pi \frac{\Delta P^*(\omega, t)}{E^*(\omega, t)}$$

thus

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega\tau}$$

Separating $\epsilon^*(\omega)$ or more generally ϵ^* to a real part ϵ' and an imaginary part ϵ'' :

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (2.2.21)$$

we have

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} \quad (2.2.22)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} \quad (2.2.23)$$

Eqs. 2.2.22 & 23 are usually called Debye equations. They were derived assuming that one single relaxation time was valid. The functions represented by these equations are illustrated in Fig. 2.2.4, plotted against $\log_{10} \omega$, for specific values $\epsilon_0 = 8$ and $\epsilon_\infty = 2$.

Experimentally, one measures usually the quantities ϵ' and the loss tangent:

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (2.2.24)$$

ϵ'' is sometimes called the dielectric loss factor because it describes the rate at which electrical energy is converted into heat in the medium.

The electrical behaviour of a material may also be expressed in terms of the admittance Y (Grant, 1941). The complex dielectric constant and complex conductivity are defined by the following equations:

$$Y = i\omega\epsilon^* = i\omega(\epsilon' - i\epsilon'') \quad (2.2.25)$$

$$Y = k^* = k' + ik'' \quad (2.2.26)$$

where k is the conductivity, then

$$k'(\omega) = \omega\epsilon'' \quad (2.2.27)$$

$$k''(\omega) = \omega\epsilon' \quad (2.2.28)$$

Eq. 2.2.27 defines the dielectric conductivity k' as a function of the angular frequency ω .

If, however, the material has a static or direct current conductivity k'_0 , Eq. 2.2.27 may be written in a more general form:

$$k' = k_0 + \omega \epsilon'' \quad (2.2.29)$$

According to Eqs. 2.2.22, 23 and 29 we have:

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1}{1 + \omega^2 \tau^2} \quad (2.2.30)$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (2.2.31)$$

According to Debye's assumption of a single relaxation time:

$$\tau = \frac{\epsilon_0 - \epsilon_\infty}{k_\infty - k_0} \quad (2.2.32)$$

where k_∞ is the conductivity at very high frequencies, then

$$\frac{k' - k_0}{k_\infty - k_0} = \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (2.2.33)$$

Plotting the left-hand sides of Eqs. 2.2.30, 31 and 33 against $\log \omega$ we obtain symmetrical curves as those of Fig. 2.2.4. The maximum of the loss curve is reached for $\log \omega \tau = 0$. Thus the angular frequency ω_c corresponding to the maximum dielectric absorption is:

$$\omega_c = \frac{1}{\tau} \quad (2.2.34)$$

The corresponding values ϵ'_c , ϵ''_c , and k'_c of ϵ' , ϵ'' , and k' respectively are obtained by substituting $\omega \tau = 1$ in equations 2.2.30, 31 and 33:

$$\epsilon'_c = \frac{\epsilon_0 + \epsilon_\infty}{2} \quad (2.2.35)$$

$$\epsilon''_c = \frac{\epsilon_0 - \epsilon_\infty}{2} \quad (2.2.36)$$

$$k'_c = \frac{k_0 + k_\infty}{2} \quad (2.2.37)$$

The frequency $f_c = \omega_c / 2\pi$, corresponding to the angular frequency ω_c is generally called the critical frequency. The corresponding wave length in vacuo is called the critical wave length λ_c . It is given by

$$\lambda_c = c / f_c = 2\pi c / \omega_c = 2\pi \tau \cdot c \quad (2.2.38)$$

where c is the velocity of light in vacuo (3×10^{10} cm/sec).

The logarithmic frequency scale has the advantage that the curves in Fig. 2.2.4 are symmetrical. This figure demonstrates the characteristics of the electrical dispersion. As frequency increases, the dielectric

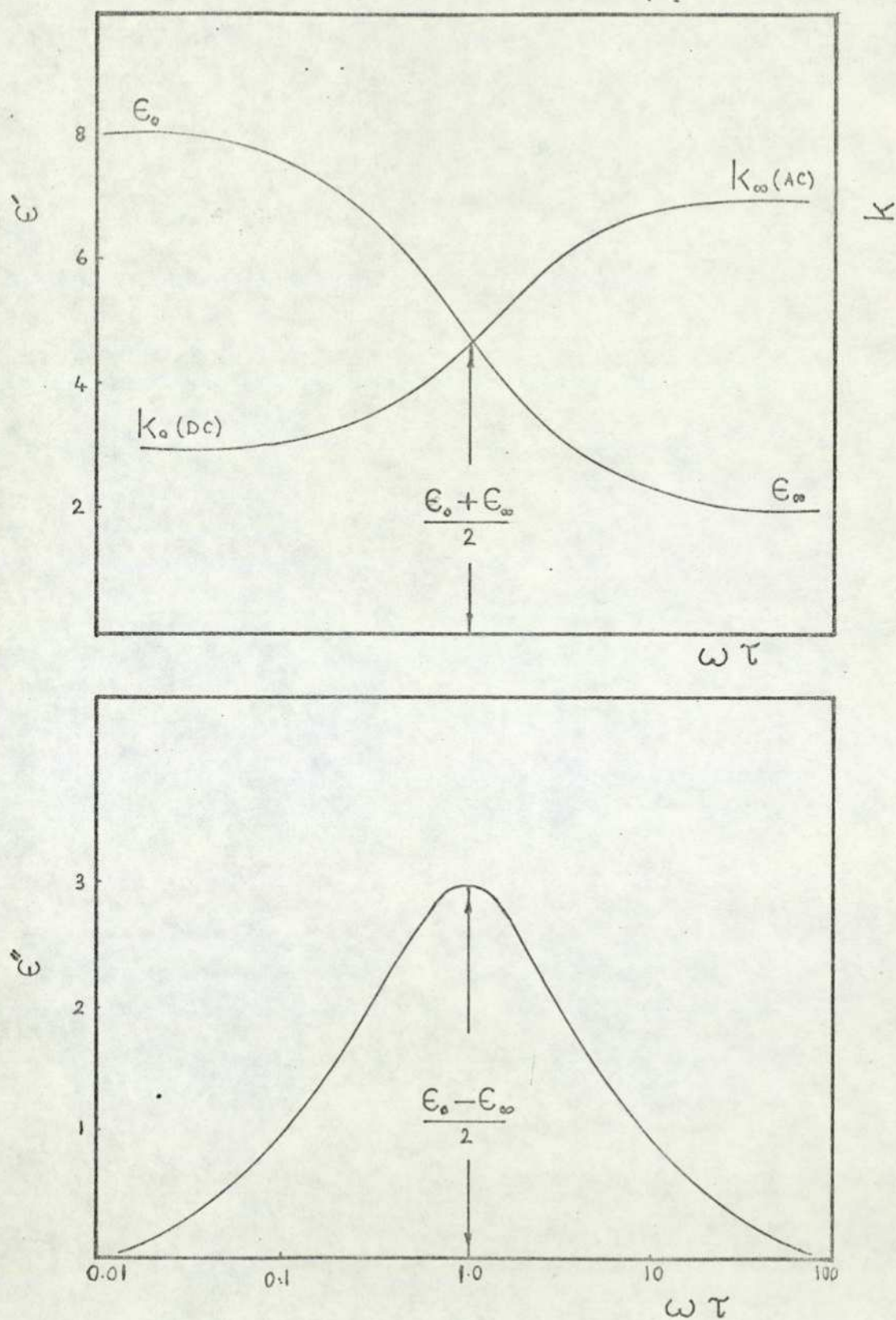


Fig. 2.2.4 Dielectrics with a single relaxation time

constant decreases from its highest value ϵ_0 at zero frequency (DC) to its lowest value ϵ_∞ at very high frequencies or theoretically at infinite frequency. The conductivity follows a reversed trend.

Another method of checking Debye equations (2.2.22 and 23), proposed by Cole and Cole (1941), is to construct an Agrand diagram or complex plane locus in which the imaginary part ϵ'' of the complex dielectric constant is plotted against the real part ϵ' , each point corresponding to one frequency, Fig. 2.2.5. From Debye equations we have:

$$\left(\epsilon' - \frac{\epsilon_0 + \epsilon_\infty}{2}\right)^2 + (\epsilon'')^2 = \left(\frac{\epsilon_0 - \epsilon_\infty}{2}\right)^2 \quad (2.2.39)$$

Thus by plotting ϵ'' versus ϵ' a semi-circle of radius $(\epsilon_0 - \epsilon_\infty)/2$ is obtained, its centre being on the abscissa at a distance $(\epsilon_0 - \epsilon_\infty)/2$ from the origin. The intersection points with the abscissa are characterized by $\epsilon' = \epsilon_\infty$ and $\epsilon' = \epsilon_0$.

An interesting point is that for given values of ϵ_0 and ϵ_∞ the Cole-Cole diagram is completely defined, provided Debye equations are valid, whereas the frequency range in which the dispersion occurs has no influence on the curve. Thus the ϵ''/ϵ' curve is independent of the value of the relaxation time (Bottcher, 1952).

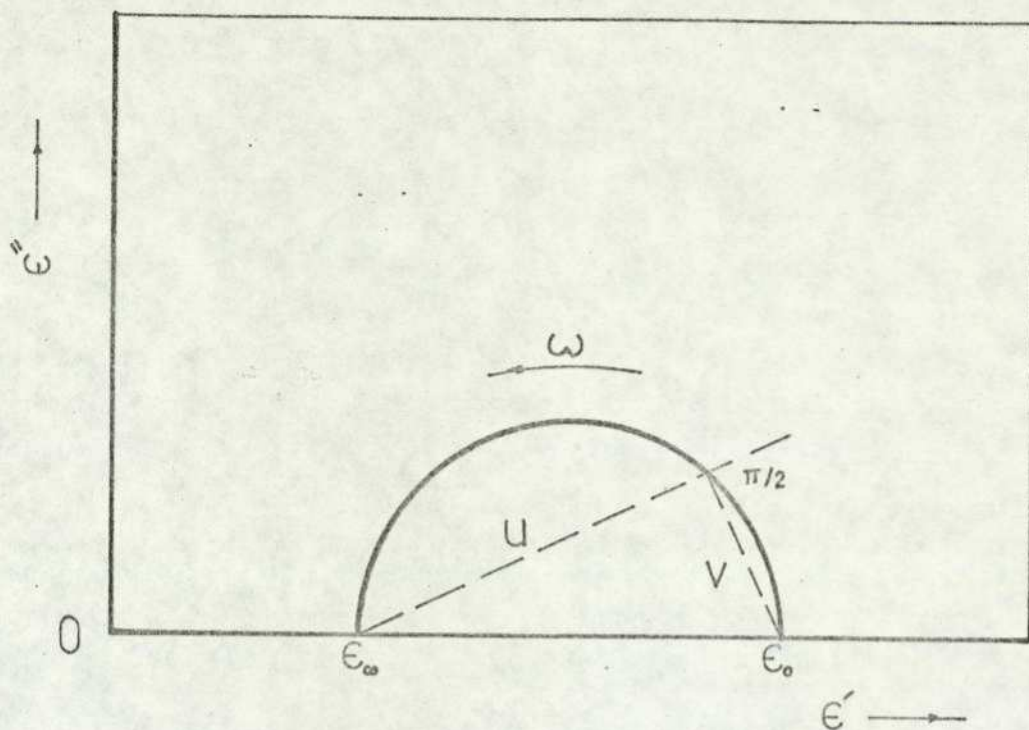


Fig. 2.2.5 Cole - Cole diagram (single τ)

2.2.3 Dielectrics with a Distribution of Relaxation Times

Cole and Cole

It has been mentioned already in 2.2.1.2 that there is practically no dielectric material that has a single relaxation time. In other words, the behaviour of a dielectric cannot be described by one relaxation time only. For this reason, the experimental ϵ' , k' , and ϵ'' versus $\log \omega$ curves only in exceptional cases conform with the Debye equations which were derived on the basis of one single relaxation time.

Generally the experimental curves (Fig.2.2.6) deviate considerably from the curves predicted by Debye equations. Usually the dispersion curve $\epsilon'/\log \omega$ is flatter and extends over a wider frequency range, while the dielectric loss curve $\epsilon''/\log \omega$ is broader and its maximum ϵ'' value is lower than the value ϵ''_c given by Eq. 2.2.36. It is also seen from Fig. 2.2.6 that the critical frequency of dielectric conductivity differs from that of the dielectric constant. The former being of higher value (lower relaxation time). However, the curves are still symmetrical.

Accordingly, it should be expected that the ϵ''/ϵ' curve will deviate from the semi-circle diagram of Fig.2.2.5. However, Cole and Cole (1941) have shown that generally the experimental curve is still a circular arc but with its centre below the abscissa.

The analytical expression for the circular arc locus is easily deduced by consideration of Fig.2.2.7. From simple geometry the angle $(1-\alpha)\pi/2$ between the vectors u and v in the complex plane is independent of the frequency and equal to half the central angle subtended by the arc. It therefore follows that

$$\begin{aligned} u + v &= \epsilon_0 - \epsilon_\infty \\ &= u[1 + f(\omega) e^{i(1-\alpha)\pi/2}] \end{aligned} \quad (2.2.40)$$

where $f(\omega)$ is a (real) undetermined function of the frequency and other parameters.

From the relation $e^{i(1-\alpha)\pi/2} = i^{(1-\alpha)}$ the last equation can be written

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + i^{(1-\alpha)} f(\omega)} \quad (2.2.41)$$

as the complex quantity u is simply $\epsilon^* - \epsilon_\infty$.

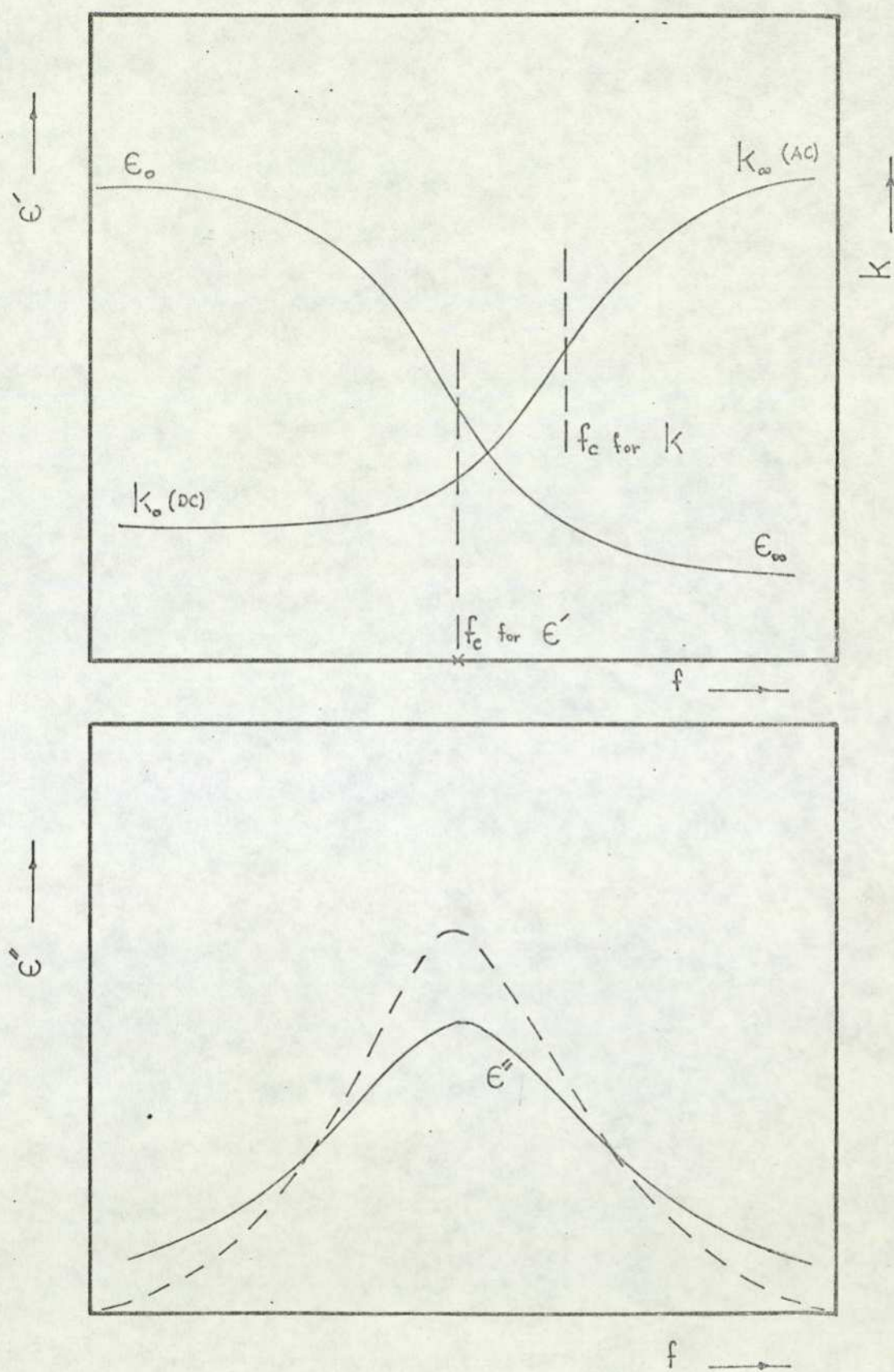


Fig. 2.2.6 Dielectrics with a distribution of τ

The dependence of the function $f(\omega)$ on the frequency is undetermined by this geometrical argument. From general consideration one can expect that this dependence will be of the form $\omega^{1-\alpha}$, as the complex form of ϵ^* results from the initial hypothesis of an applied field $E = E_0 e^{i\omega t}$. Any theory in which ω appears as the result of linear operations on the complex exponential must lead to the same functional dependence on ω as on the unit imaginary i so that

$$\epsilon^* - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \quad (2.2.42)$$

where the parameter τ_0 is left undetermined.

The real and imaginary parts ϵ' , ϵ'' of the complex dielectric constant as a function of frequency are given by

$$\epsilon' - \epsilon_\infty = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \left[1 - \frac{\sinh x(1-\alpha)}{\cosh x(1-\alpha) + \sin(\alpha\pi/2)} \right] \quad (2.2.43)$$

$$\epsilon'' = \frac{1}{2} (\epsilon_0 - \epsilon_\infty) \left[\frac{\cos(\alpha\pi/2)}{\cosh x(1-\alpha) + \sin(\alpha\pi/2)} \right] \quad (2.2.44)$$

where $x = \ln(\omega\tau_0)$

It is easily seen that Eqs. 2.2.43 and 44 reduce to the Debye equations (Eqs. 2.2.22 and 2.2.23) for $\alpha = 0$. For values of α greater than zero the dispersion region is broader and the maximum value of ϵ'' for $\omega = 1/\tau_0$ decreases.

If data are available only for ϵ' or ϵ'' alone as a function of frequency, the applicability of Eq. 2.2.42 can be determined by some standard curves given by Eqs. 2.2.43 and 44. It should be noted that ϵ' and ϵ'' are uniquely determined if either of them is known over the entire frequency range for which dispersion and absorption occur.

It has been found that the circular arc locus together with the equivalent analytic representation of Eq. 2.2.42 provide an excellent

description of the dispersion in a large number of dielectrics. This description requires the introduction of the single parameter α in addition to the constants ϵ_0 , ϵ_∞ , and τ_0 . The experimental results are thus completely described by these four quantities and the values found for a number of examples are listed in Appendix III (Cole and Cole, 1941). Nevertheless, some investigators (Arulanandan and Mitchell, 1968; Smith, 1971) while admitting the existence of a distribution of relaxation times, used the concept of "a mean relaxation time" in interpreting the experimental observations. This can be justified only at frequencies far remote from the region of relaxation frequency. At those frequencies, analysis based on a single relaxation time is usually adequate (Anderson, 1964).

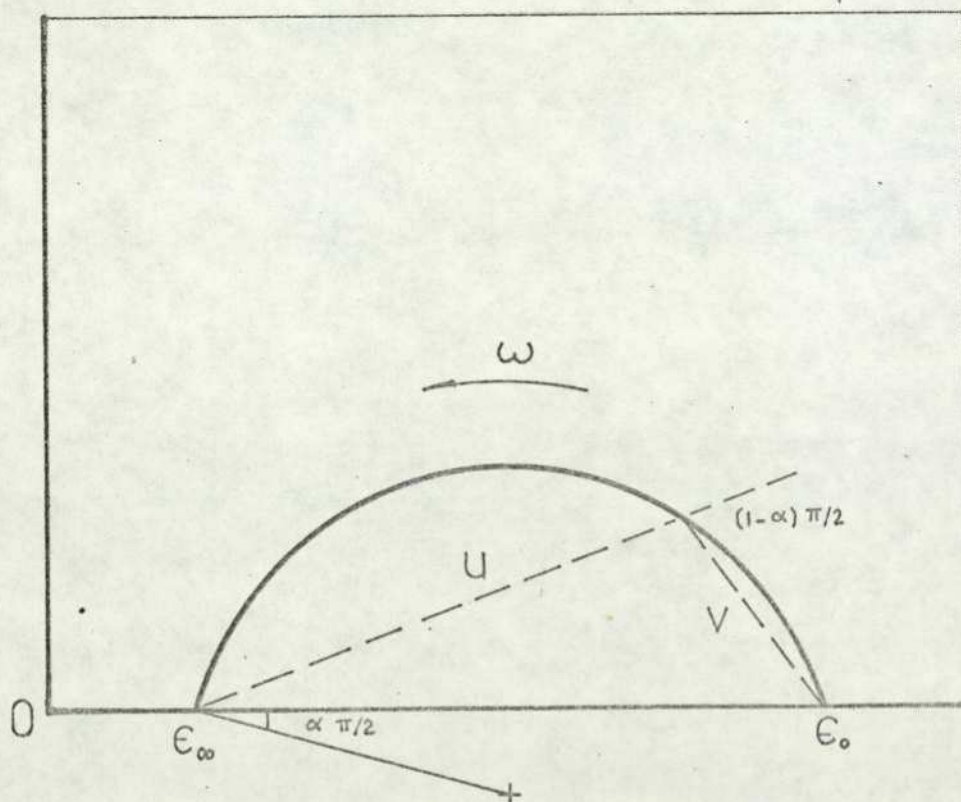


Fig. 2.2.7 Cole - Cole diagram (distributed τ)

The response of heterogenous dielectrics to a changing field is complicated by effects which would not occur in a homogenous material. In many cases these effects are negligible. In others they are important but cannot be treated theoretically because the systems in question contain too many unknown parameters. However, some of these cases have been extensively investigated, especially where the theoretical treatment of the complicating effects are relatively straightforward.

Dielectrics may consist of conglomerates of microscopic volume elements with different dielectric constants and conductivities. Such conglomerates may in practice be very complicated since dielectric constants as well as conductivities may be anisotropic, and conductivities need not be linear. If the wavelength of the alternating field is large compared with the dimensions of conducting bodies and if the conductivity of the inclusions is ohmic, the dielectric response of the heterogenous dielectric can, in principle, be derived in terms of the properties of the individual phases and the geometry of the system (Daniel, 1967).

2.3.1 Heterogeneity Solution

Interfacial, Space-charge polarization: Maxwell-Wagner

The fact that ions can move does not by itself guarantee a steady current flow. The ions have to migrate through the volume, to be discharged without the creation of disturbing deposits, and to be replaced without delay. These very stringent conditions are fulfilled only in rare cases. The accumulation of ions produces space charges and field distortions. If we add that the original ion type that moves through the lattice is, in general, not replaceable from the electrode and that chemical reactions and deposits alter the interfaces, a time-and-frequency dependence of the conduction should be the general rule.

On these bases, Maxwell (1892) considered the simplest geometrical case of a plate capacitor filled with n dielectrics of different conductivity to dielectric constant ratios arranged in layers parallel to the capacitor plates. Maxwell derived the differential equation for the field between the electrodes as a function of the current through the stratified dielectric. Maxwell investigated a microscopic model of a dilute suspension of spherical particles as well.

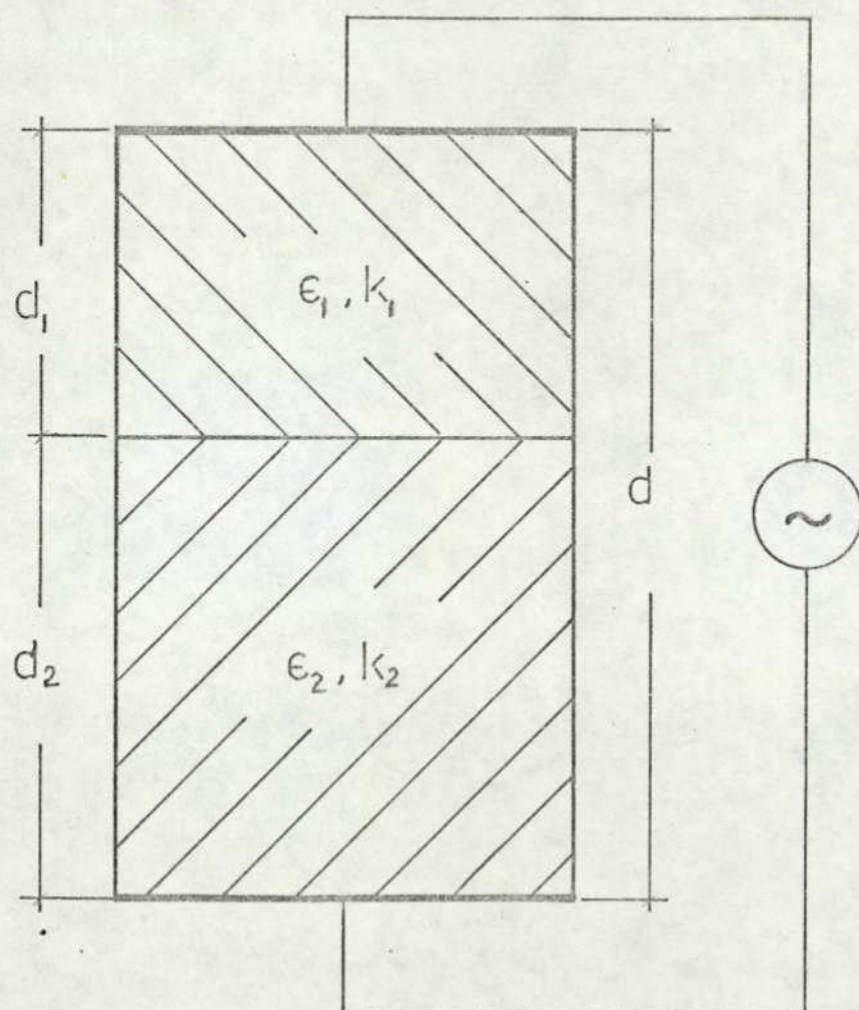


Fig. 2.3.1 Two-Layer Capacitor (Maxwell, 1892)

The most simple heterogenous system is the two-layer dielectric. Fig. 2.3.1 shows the two layers characterized by the dielectric constants of the compounds ϵ_1 and ϵ_2 , conductivities k_1 and k_2 , and thicknesses d_1 and d_2 . The two-layer system consists of two admittances Y_1 and Y_2 in series (Whitehead, 1927). Thus the total admittance Y

$$Y = \frac{Y_1 Y_2}{(Y_1 + Y_2)} \quad (2.3.1)$$

$$Y_1 = \frac{k_1 S}{d_1} + i\omega \frac{(\epsilon_1 \epsilon_v S)}{d_1} \quad (2.3.2)$$

$$Y_2 = \frac{k_2 S}{d_2} + i\omega \frac{(\epsilon_2 \epsilon_v S)}{d_2}$$

where S is the surface area of the sample Eqs. 2.3.1 & 2 give

$$\frac{Y}{S} = \frac{k_1 k_2 + i\omega \epsilon_v (\epsilon_1 k_2 + \epsilon_2 k_1) - \epsilon_1 \epsilon_2 \epsilon_v \omega^2}{(k_1 d_2 + k_2 d_1) + i\omega \epsilon_v (\epsilon_1 d_2 + \epsilon_2 d_1)} \quad (2.3.3)$$

The admittance of the whole sample is related to its composite parameters k, d , and ϵ^* by

$$\begin{aligned} Y &= \frac{kS}{d} + i\omega \epsilon_v \epsilon^* \frac{S}{d} \\ &= \frac{kS}{d} + i\omega \epsilon_v (\epsilon' - i\epsilon'') \frac{S}{d} \end{aligned} \quad (2.3.4)$$

Eqs. 2.3.3 and 4 lead to

$$\epsilon_0 = \frac{d(d_1 \epsilon_1 k_2^2 + d_2 \epsilon_2 k_1^2)}{(d_2 k_1 + d_1 k_2)^2} \quad (2.3.5)$$

$$\epsilon_\infty = \frac{d \epsilon_1 \epsilon_2}{(d_2 \epsilon_1 + d_1 \epsilon_2)} \quad (2.3.6)$$

$$\tau = \frac{\epsilon_1 d_2 + \epsilon_2 d_1}{d_2 k_1 + d_1 k_2} \quad (2.3.7)$$

$$k = \frac{d k_1 k_2}{d_2 k_1 + d_1 k_2} \quad (2.3.8)$$

The limiting dielectric constants are functions of the conductivities, dielectric constants, and thicknesses of the component layers as expected. The dielectric constant and loss factor are given by:

$$\epsilon' = \epsilon_0 + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau^2} \quad (2.3.9)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} + \frac{k}{\epsilon_v \omega} \quad (2.3.10)$$

These are exactly Debye equations (2.2.22 and 23) except that the loss factor Eq. 2.3.10 contains an additional term, dominant at low frequencies, owing to the conductivity of the sample k .

The two-layer model can be altered into n -layer model of two media or into a dispersion of particles of medium 1, distributed in a matrix of medium 2. As long as the relative amounts of media 1 and 2 remain the same, the complex dielectric constant stays unaltered. However, depending on its geometrical distribution in form of spheres, ellipsoids, bridging dendrites, or sheets extending perpendicularly to the field, the same amount of material causes very different relaxation spectra and a wide variation of relaxation times, Fig.2.3.2. (von Hippel, 1959).

From the molecular point of view, the part $(\epsilon_0 - \epsilon_\infty)$ of the dielectric constant can be explained by assuming that the two media contain mobile charge carriers of the densities N_1 and N_2 per unit volume, transporting charges e_1 and e_2 with mobilities U_1 and U_2 , then the two conductivities are given by

$$k_1 = N_1 e_1 U_1 \quad (2.3.11)$$

$$k_2 = N_2 e_2 U_2$$

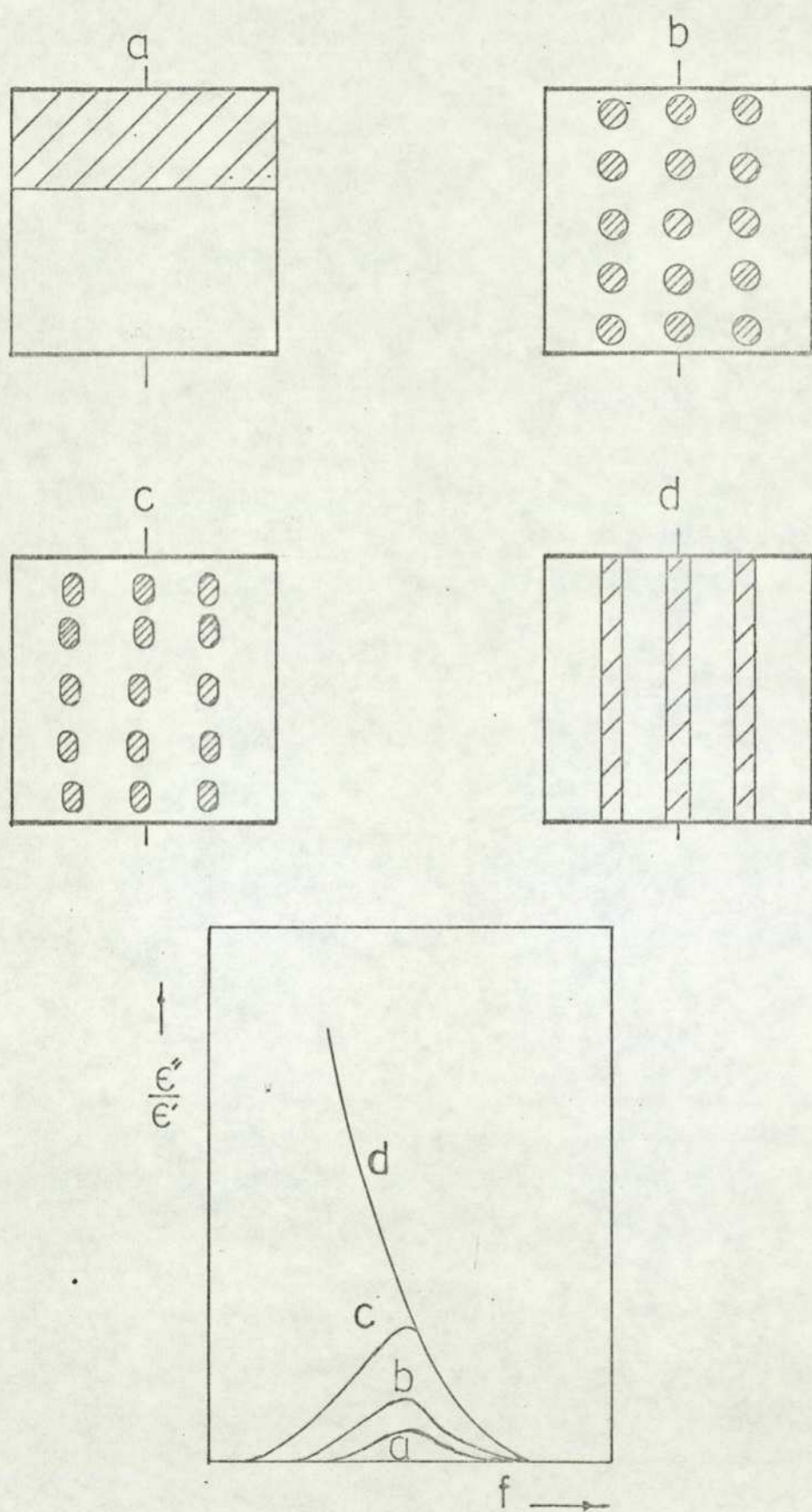


Fig. 2.3.2 Possible applications of the 2-layer model

Charges pile up at the interface between media (1) and (2) until constant current transfer is established and the static conductivity results as given by Eq. 2.3.8.

As frequency increases, this space charge (or interfacial) polarization begins to lag. Since the polarization P of the two-layer system is proportional to the applied field according to Eq. 2.2.11, it is possible to define the interfacial polarizability α_i by

$$4\pi P_i = \alpha_i N E' = (\epsilon^* - \epsilon_{\infty})E \quad (2.3.12)$$

hence

$$\alpha_i = \left[\frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau} + \frac{\sigma}{i\omega} \right] \frac{E_N}{N} \quad (2.3.13)$$

Wagner (1914) developed Maxwell's treatment by calculating the complex dielectric constant of the dilute suspension of spherical particles in an alternating field. The suspension was dilute enough to make electrostatic interaction negligible, and the spheres were assumed to be conductive (ϵ_2, k_2) dispersed in a material of comparatively low dielectric loss (ϵ_1, k_1). After this work, the dielectric loss due to interfacial polarization has been referred to as "Maxwell-Wagner".

Expressions for $\epsilon_o, \epsilon_\infty, k_o, k_\infty$, and τ of the model with p fractional volume of the suspended spheres, were derived as:

$$\epsilon_o = \epsilon_\infty + 9p \frac{(\epsilon_2 k_1 - \epsilon_1 k_2)^2}{(\epsilon_2 + 2\epsilon_1)(k_2 + 2k_1)^2} \quad (2.3.14)$$

$$\epsilon_\infty = \epsilon_1 \frac{(1+3p)(\epsilon_2 - \epsilon_1)}{\epsilon_2 + 2\epsilon_1} \quad (2.3.15)$$

$$k_\infty = k_1 \frac{(1+3p)(\epsilon_2 - \epsilon_1) + 9\epsilon_1(k_2 \epsilon_1^{-k_1} \epsilon_2)}{\epsilon_2 + 2\epsilon_1 (\epsilon_2 + 2\epsilon_1)^2} \quad (2.3.16)$$

$$k_o = k_1 \left(1 + 3p \frac{k_2 - k_1}{k_2 - 2k_1}\right) \quad (2.3.17)$$

$$\tau = \epsilon_o \frac{\epsilon_2 + 2\epsilon_1}{k_2 + 2k_1} \quad (2.3.18)$$

2.3.2 Discrete Phases Solution

(Adsorbed phase polarization: Murphy-Lowry)

In recent years many facts have been discovered which indicate that in most solid dielectrics direct-current conduction does not take place uniformly through the material as a whole but along paths of higher conductivity than the main part of dielectric. Since these paths are of sub-microscopic dimensions, the interfacial area of their boundaries should be large in comparison with their volume, and it would consequently be expected that the ions adsorbed by the interface between the conducting medium and the insulating medium may have important effects on the electrical properties of dielectrics (Murphy and Lowry, 1930).

Studies concerned with the polarization of the adsorbed phase usually refer to this phase in many names such as electric double layer, diffuse double layer, and ionic atmosphere.

Murphy and Lowry (1930) suggested that the essential form of the internal structures in the dielectric may be schematically illustrated as in Fig. 2.3.3, where the adsorbed water is regarded as a film of water containing a certain concentration of ions. In order to derive in a qualitative way the effect of the adsorption of ions, these authors attributed to the system the following properties:

- 1) The adsorbed ions are not rigidly fixed to certain points on the adsorbing surface, but can move over the surface under the influence of an externally applied electric field.
- 2) These ions cannot leave the particular structural unit by which they are adsorbed unless a certain threshold voltage gradient, which may be called the "desorption voltage", is

exceeded. In fact, forces which cause cohesion and adsorption are the bonds which prevent the ions from moving freely in the electric field but allow an elastic displacement of charges.

3) These ions are not equally strongly adsorbed to the surface, but are arranged in several layers which decrease in adsorption strength as a function of distance from interface, i.e., in accordance with the decreasing gradient of concentration of adsorbed ions, Fig. 2.3.4.

Therefore, the movement of the adsorbed ions when the field is applied is equivalent to a condenser charging current, and their return to the equilibrium distribution in the absence of the field to a discharge current. The reversible change in the distribution of ions produced by the application of a field may be regarded as equivalent in effect to dielectric polarization. However, owing to the fact that the solid particles with their adsorbed ions cannot move as a whole in the electric field, the adsorbed ions may produce a displacement current without producing a space charge. Free ions could not produce a displacement current without producing a space charge at the same time. In that way, the suggested mechanism differs from most theories of the effect of ions on dielectric absorption, i.e., the adsorbed ions do not form a space charge but produce a modified type of dielectric polarization.

On the basis of the interstitial mechanism of conduction and absorption described, Murphy and Lowry suggested that the dielectric loss may be divided into three main components corresponding to free ions, adsorbed ions, and molecules.

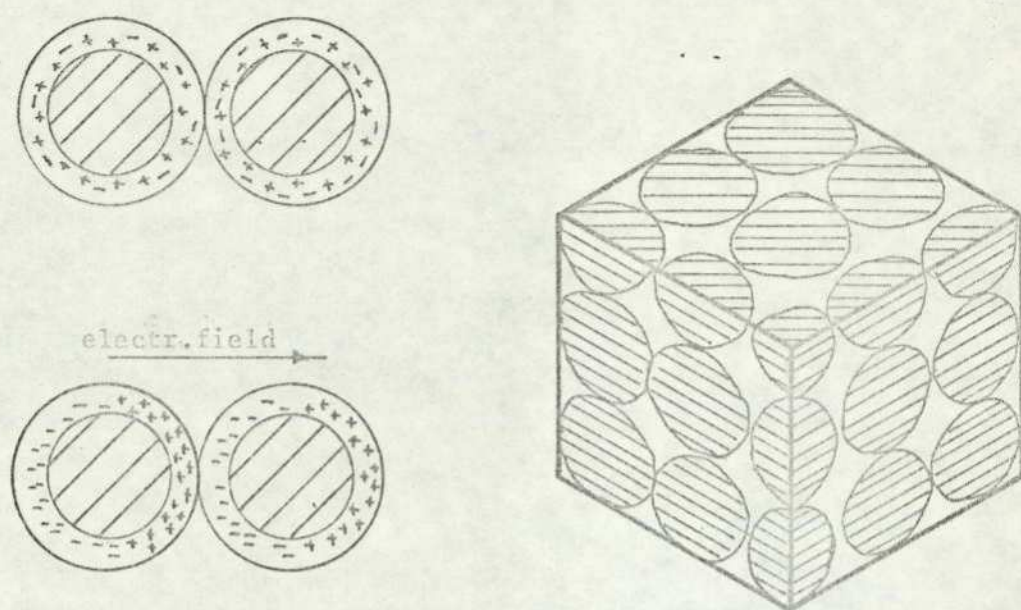


Fig. 2.3.3. Adsorbed layers in Dielectrics (Murphy & Lowry, 1930)

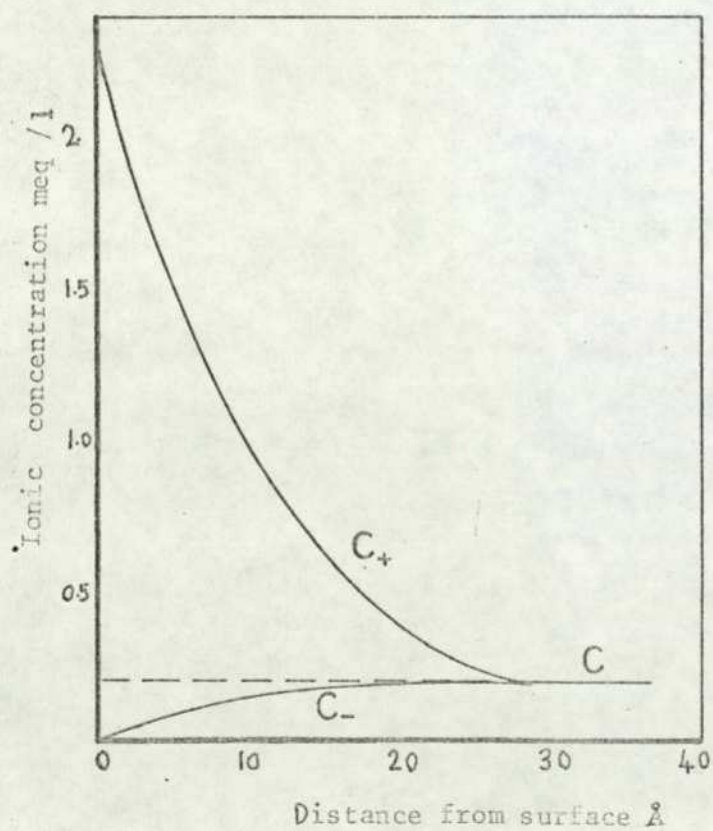


Fig. 2.3.4. Distribution of concentration in the adsorbed layer

Free ions can contribute to dielectric loss in several ways: by the constant direct current conductance which they produce; by the interactions between free ions; and by the non-uniformity in the resistance of the conduction paths.

Adsorbed ions will move back and forth on the surface of the structural unit by which they are adsorbed, under the influence of an alternating voltage applied to the system. The motion of these ions contributes to the alternating current conductance and capacity but not to the direct current conductance. It would be expected that the dielectric loss associated with this polarization of the ions adsorbed on the surface of a micelle or a crystallite would be greater than that associated with the polarization of a molecule because adsorbed ions probably share in the thermal motion as individuals, whereas the opposite charges of a molecule move as a whole in regard to thermal motion.

Molecular loss is due to the orientation of the permanent dipoles of molecules by an electric field. This orientation contributes to the dielectric polarization and is accompanied by the absorption of electrical energy as heat (Debye, 1924).

The existence of these several components of dielectric loss provides an alternative physical interpretation of the several characteristic time constants (relaxation times) introduced in the Maxwell-Wagner theory of dielectric absorption and loss to account for the experimental facts and attributed by Wagner to the presence of several different types of impurities in the dielectric.

All the above-mentioned considerations led Murphy and Lowry

to represent the structural unit of a solid dielectric with its adsorbed phase by the equivalent electrical network given by Fig.2.3.5, where each layer of adsorbed ions is represented by a capacitance in series with a resistance (see Sec. 2.4), both the capacitance and resistance being smaller the greater the distance from the interface. It follows that the time constants (relaxation times) of the layers are different and increase the closer the corresponding layer to the interface.

The equivalent parallel capacitance of the adsorbed layer is

$$C = C_m + \frac{C_1}{1 + (\omega R_1 C_1)^2} + \dots + \frac{C_n}{1 + (\omega R_n C_n)^2} \quad (2.3.19)$$

and the equivalent parallel conductance

$$K = \frac{1}{R_{DC}} + \frac{R_1 (\omega C_1)^2}{1 + (\omega R_1 C_1)^2} + \dots + \frac{R_n (\omega C_n)^2}{1 + (\omega R_n C_n)^2} \quad (2.3.20)$$

where C_m is the capacitance due to dielectric polarization of the molecules; $C_1, C_2, \dots, C_n$ are the capacitances due to the redistribution of the adsorbed ions; $R_1, R_2, \dots, R_n$ are the resistances equivalent to the frictional resistances which impede the process of forming a polarized distribution of the adsorbed ions in layers 1, 2, ..., n respectively; and R_{DC} is the direct current resistance.

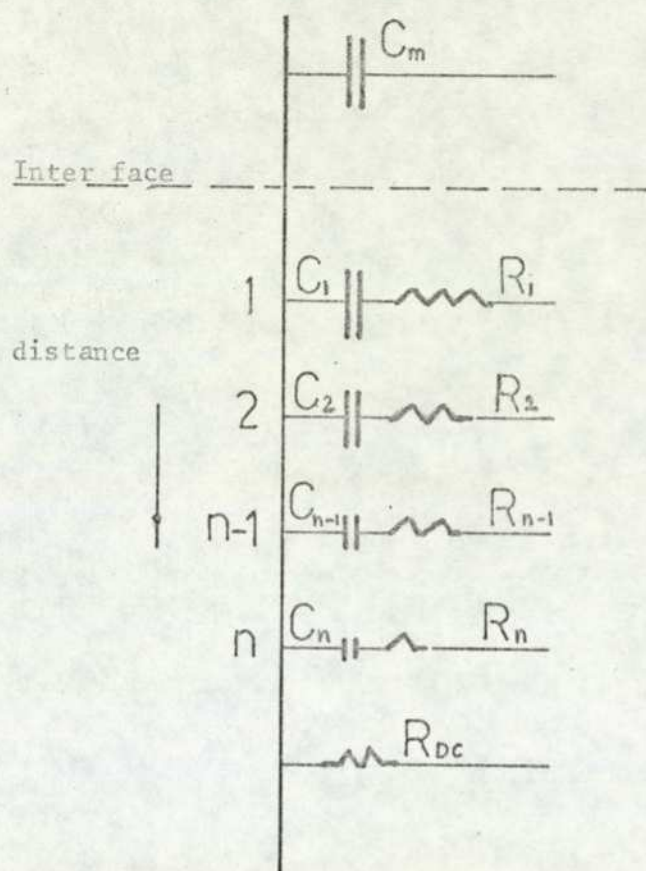


Fig. 2.3.5. Equivalent Circuit of the adsorbed layer

(Murphy & Löwry, 1930)

2.4 ELECTRICAL NETWORK ANALOGY

Analogy between electrical systems and various physical and mechanical systems often provides a useful means of analysis and interpretation of the experimental behaviour of these systems (Pain, 1968; Richart, et al., 1970; Armstrong, et al., 1971; Bardeen, 1949; Hodge, et al., 1975). For instance, it is a feature of the dielectric relaxation that the relationships involved obey the same mathematical formalism as those of electrical circuits consisting of capacitances, resistances and inductances, that is, passive electrical networks. Certain passive networks are mathematical analogues to certain dielectric materials. Therefore, it is often convenient to represent the properties of dielectrics exhibiting dispersion by means of an electrical circuit. Analogue circuits for dielectrics mostly contain only capacitances and resistances. However, it will be shown that accurate representation of experimental results requires more complicated equivalent circuits.

Simple electrical networks can be used for the analysis of macroscopic behaviour only. The mathematical treatment of all macroscopic phenomena that can be governed by a differential equation of the type (2.2.16) is obviously identical, and solutions can be translated from one physical system to another (Olson, 1958). There are many cases in which data of macroscopic systems may complement those of microscopic ones.

Assume a gas or liquid or amorphous solid of given volume v , subject to a pressure p , the change of volume due to the pressure being

$$x = v(p) - v(p_0) \quad (2.4.1)$$

where p_0 is a standard pressure. Then x obeys an equation of type (2.2.16). In the equivalent circuit, an inductance L represents a quantity M of dimension gcm^{-4} called "inertance", a capacitance C

represents an acoustical capacitance C_A of dimension $g^{-1} cm^4 sec^2$, and a resistance R represents an acoustical resistance R_A of dimension $g cm^{-4} sec^{-1}$. The inertia in this case, as in all mechanical cases, is due to a mass.

In a gas the acoustical system is essentially periodic dominated by the inertia term. However, in liquids and particularly in soft solids the damping may be the dominant influence. In those cases the material and its properties may be described without reference to the inertia term. Here the mathematics is quite analogous to the case of an RC network. The relevant properties are usually measured by the application of periodic pressure waves, using the techniques of ultrasonics.

2.4.1 Basic Electrical Elements

Fig.2.4.1 shows the three basic elements used in electrical circuits, along with their phasor diagrams (Purcell, 1965)

2.4.1.1 Resistance R

$$R = \frac{V}{I} \quad \text{ohms} \quad (2.4.2)$$

where V is the voltage in volts, and I is the current in amperes. Eq. 2.4.2 is an expression of Ohm's law, it applies at any instant of time since current and voltage are in phase. It can thus be used in case of DC as well as AC.

The power P absorbed by a pure resistance and converted to heat is given by

$$P = I^2 R = \frac{V^2}{R} \quad (2.4.3)$$

2.4.1.2 Capacitance C

A capacitive element is one which has the ability to store an electrical charge. Current passes through the conductors leading to the capacitor only when the charge on the capacitor changes. Thus, in a DC circuit no current passes to the capacitor after it has become charged. The amount of charge in a capacitor is related to the current by

$$Q = CV$$

$$I = \frac{dQ}{dt} = C \frac{dV}{dt} \quad (2.4.4)$$

where C is the capacitance in farads, Q is the charge in coulombs, and I is the current in amperes.

For an alternating voltage $V = V_o \sin \omega t$, we have

$$I = C\omega V_o \sin \left(\omega t + \frac{\pi}{2} \right) \quad (2.4.5)$$

Thus, in a capacitor, the current leads the voltage by a phase angle equals $\pi/2$.

2.4.1.3 Inductance L

An inductive element consists of a coil having zero resistance surrounded by a magnetic field due to the current passing through it. Any change in current will change the magnetic field and induce a voltage in the coil, which tends to oppose the change in current. The relationship for an inductive element is given by

$$I = \frac{1}{L} \int V dt \quad (2.4.6)$$

where L is the coil inductance in henrys.

For an alternating volt

$$I = \frac{V_o}{\omega L} \sin \left(\omega t - \frac{\pi}{2} \right) \quad (2.4.7)$$

Thus, in an inductor, the current lags the voltage by a phase angle equals $\pi/2$.

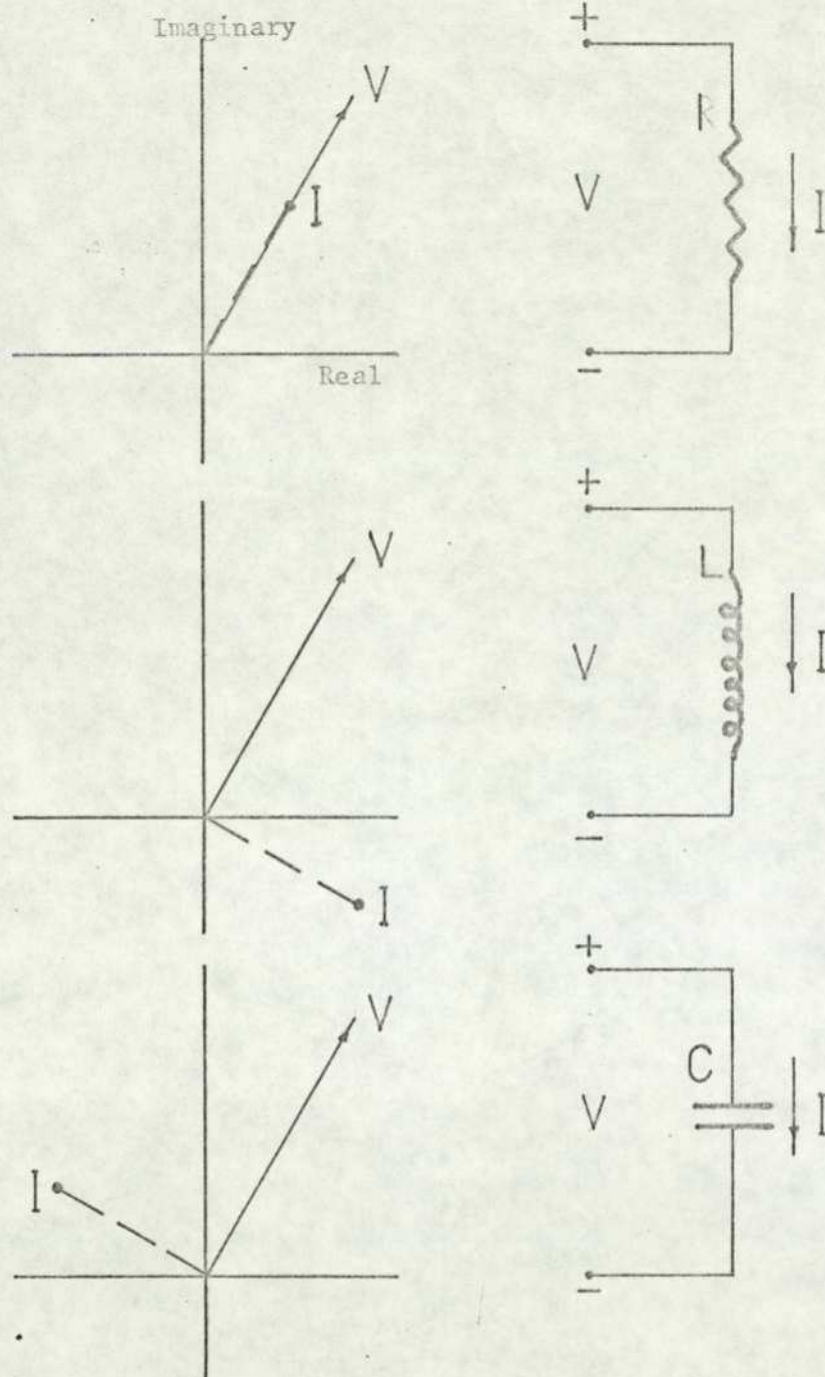


Fig. 2.4.1. The three basic electrical elements

2.4.1.4 Impedance and Admittance Z & Y

These two terms are used to describe the characteristics of an electrical circuit. The impedance Z is defined by the ratio of the voltage amplitude to the current amplitude as a function of the frequency. The admittance Y is the reciprocal of Z .

In view of the phase difference between the current and the voltage for capacitors and inductors, it is convenient to introduce complex notations and express the impedance and admittance in vector form.

The properties of the three basic circuit elements are summarized below:

Symbol	Impedance Z (ohm)	Admittance $Y = 1/Z$ (1/ohm) or (mho)
R	R	$\frac{1}{R}$
C	$\frac{1}{i\omega C}$	$i\omega C$
L	$i\omega L$	$\frac{1}{i\omega L}$
	$V = ZI$	$I = YV$

Any circuit can be built up from the three basic elements. When elements or combinations of elements are connected in parallel, it is convenient to use the admittance, for in that case admittances add. In case of series combinations, the use of impedance is more convenient.

2.4.2 Elementary Circuits

2.4.2.1 Single Relaxation Time

It is well known (von Hippel, 1954) that static fields as well as electromagnetic waves are greatly influenced by the polarization and magnetization of dielectrics. This interplay between fields and matter leads to measuring techniques for determining ϵ^* (called permittivity for electrical circuits instead of dielectric constant) and μ^* (complex magnetic permeability). What really happens in dielectrics the macroscopic theory cannot reveal. Thus, it is customary to visualize the material as equivalent to a two-terminal network of lumped circuit components.

The current-voltage diagram of a capacitor dielectric at one frequency only, allows any number of circuit interpretations. The simplest equivalent picture would be that the capacitor housing contains an ideal condensor (loss free) C and a resistor R in series or in parallel combination Fig. 2.4.2. Comparing the responses of the two arrangements to a sinusoidal voltage we obtain:

Series Arrangement (2.4.8)

$$V = IR + \frac{1}{C} \int I dt \quad (a)$$

$$\dot{V} = I \left(R + \frac{1}{i\omega C} \right) \quad (b)$$

$$Z = \frac{V}{I} = R + \frac{1}{i\omega C} \quad (c)$$

Parallel Arrangement (2.4.9)

$$I = \frac{V}{R} + C \frac{dV}{dt} \quad (a)$$

$$= V \left(\frac{1}{R} + i\omega C \right) \quad (b)$$

$$Y = \frac{I}{V} = \frac{1}{R} + i\omega C \quad (c)$$

In terms of the complex permittivity, a capacitor of the geometrical capacitance C_0 has the admittance (see Appendix II)

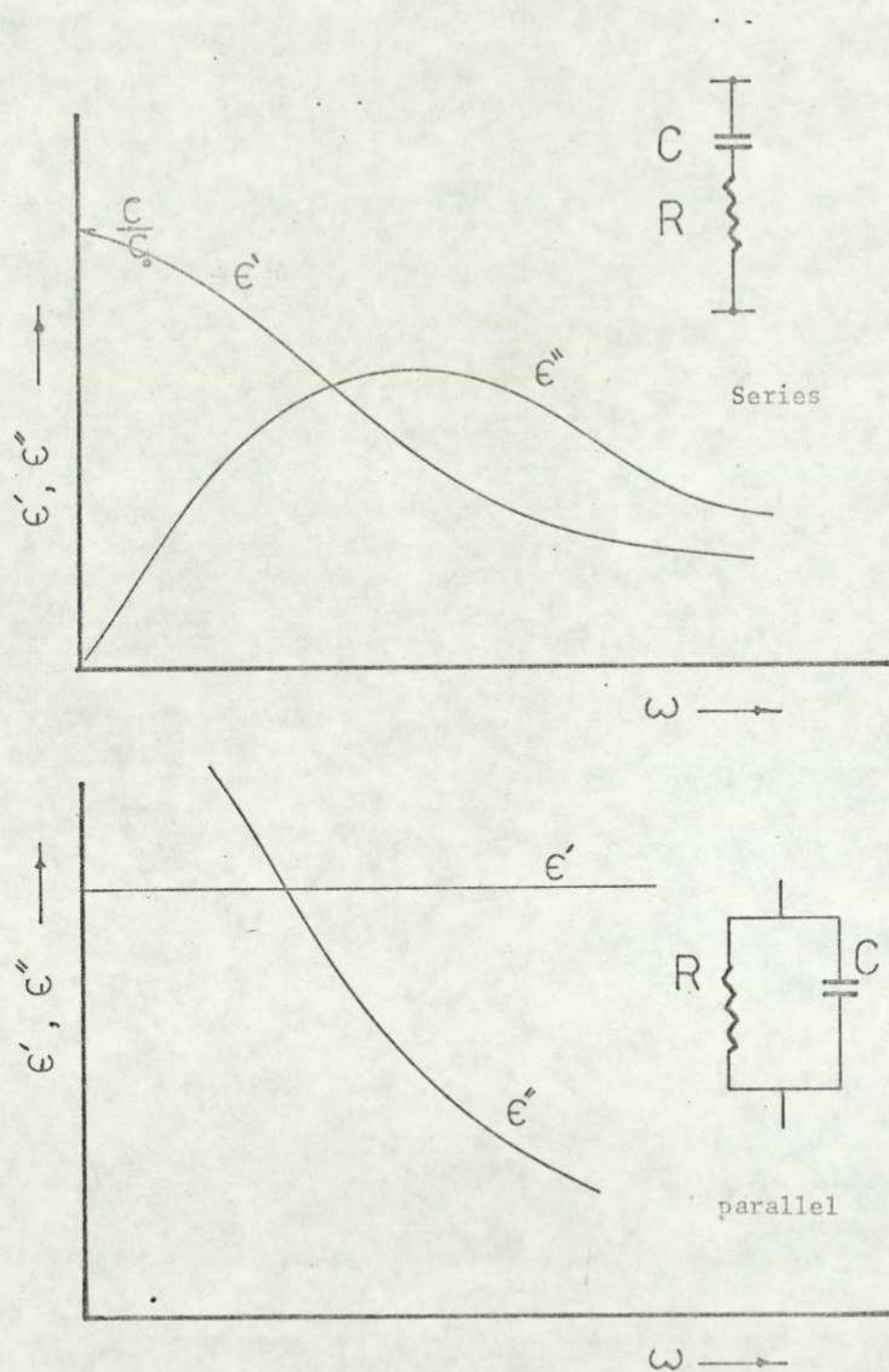


Fig. 2.4.2. Elementary equivalent circuits
of dielectrics

$$Y = \frac{1}{Z} = \frac{I}{V} = (i\epsilon' + \epsilon'')\omega C_0 \quad (2.4.10)$$

By equating the admittance of the two circuit arrangements to this expression, we arrive at the equivalent values for the relative permittivity, loss factor, and loss tangent:

<u>Series Arrangement</u> (2.4.11)	<u>Parallel Arrangement</u> (2.4.12)
$\epsilon' = \frac{C}{C_0 [1 + (\omega RC)^2]} \quad (a)$	$\epsilon' = \frac{C}{C_0} \quad (a)$
$\epsilon'' = \frac{\omega RC^2}{C_0 [1 + (\omega RC)^2]} \quad (b)$	$\epsilon'' = \frac{1}{\omega RC_0} \quad (b)$
$\tan \delta = \omega RC \quad (c)$	$\tan \delta = \frac{1}{\omega RC} \quad (c)$

Obviously, as Fig. 2.4.2 shows, the frequency dependence of these two elementary circuits has completely different trends. Proper combinations of both circuits may therefore produce a variety of response curves with maxima or minima of the loss tangent which may fit an actually measured frequency characteristic when neither of the elementary circuits will.

Figs. 2.4.3 and 2.4.4 show two typical examples: the frequency characteristics of water and of the capacitor fluid, Pyranol (a mixture of isomeric pentachlorodiphenyls). Obviously, even a simple three-element equivalent circuit may provide a relatively good fit over an appreciable frequency range. That the equivalence between the lumped circuit and the dielectric material is a purely formal one is demonstrated in Fig. 2.4.5 by the alternative placing of the series capacitance. The two circuits are undistinguishable by two-terminal measurements.

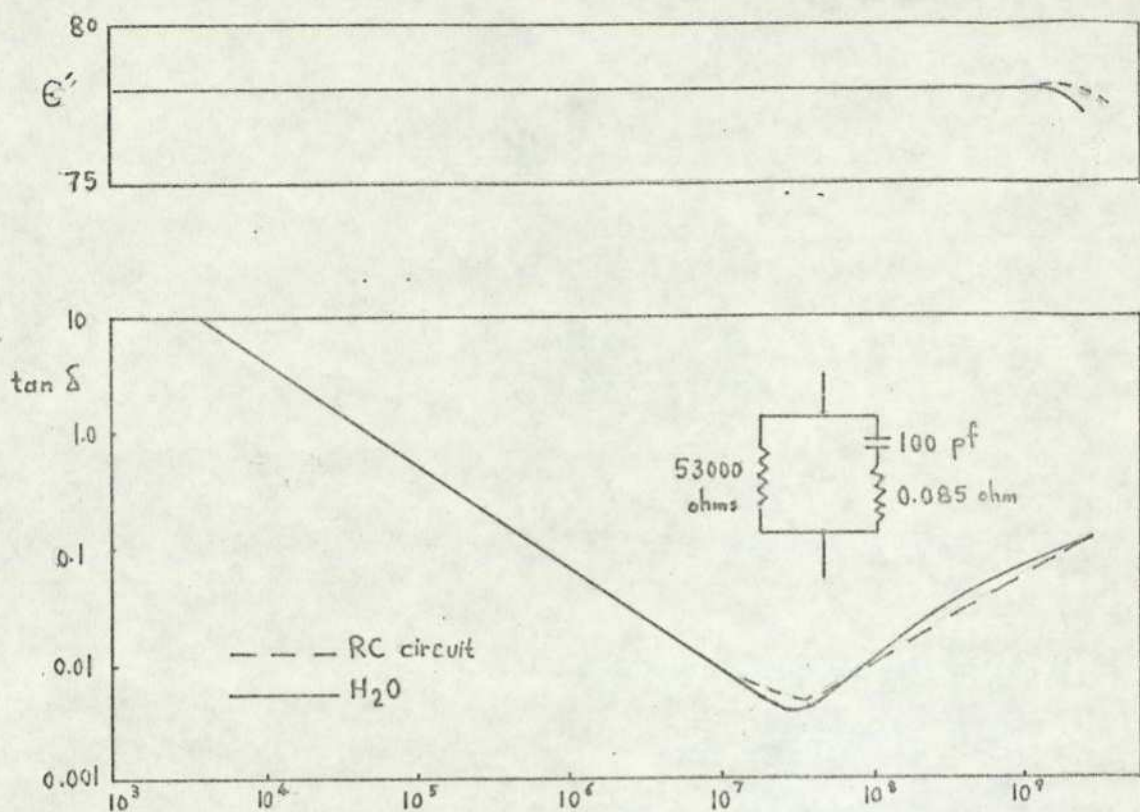


Fig. 2.4.3 Frequency response and equivalent circuit of water

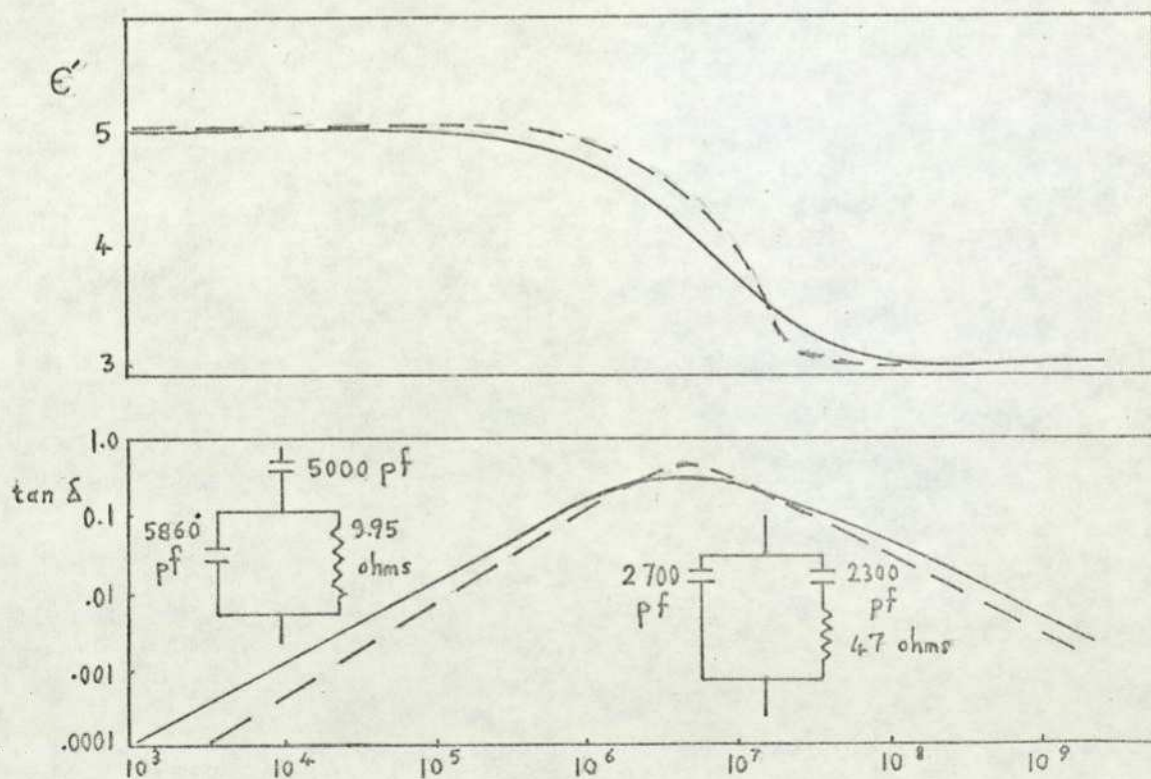


Fig. 2.4.4 Frequency response and equivalent circuit of Pyranol

The network shown in Fig. 2.4.5 may represent the simplest type of polar dielectrics. Its admittance

$$Y = i\omega C_1 + \frac{1}{Z_2} \quad (2.4.13)$$

where

$$Z_2 = R_2 + \frac{1}{i\omega C_2}$$

If the capacitor C_2 is charged to a voltage V_0 and then the circuit shorted across the $R_2 C_2$ combination, the voltage V_2 across the capacitor will decrease as a function of time and cause a current flow $C_2 dV_2/dt$ through the resistor. Hence, for the partial circuit $R_2 C_2$, the transient equation holds

$$R_2 C_2 \frac{dV_2}{dt} + V_2 = 0 \quad (2.4.14)$$

with the solution

$$V_2 = V_0 e^{-t/R_2 C_2} \quad (2.4.15)$$

The voltage drops exponentially with a relaxation time

$$\tau_2 \equiv R_2 C_2 \quad (2.4.16)$$

Introducing τ_2 into Eq. 2.4.13 and separating the real from the imaginary part, we obtain for the network admittance the expression

$$Y = \frac{\omega^2 C_2 \tau_2^2}{1 + \omega^2 \tau_2^2} + i\omega C_1 + \frac{i\omega C_2}{1 + \omega^2 \tau_2^2} \quad (2.4.17)$$

By equating Eq. 2.4.17 to Eq. 2.4.10, the relative dielectric constant and loss of the equivalent circuit become

$$\epsilon' = \frac{C_1}{C_0} + \frac{C_2}{C_0} \frac{1}{1 + \omega^2 \tau_2^2} \quad (2.4.18)$$

$$\epsilon'' = \frac{C_2}{C_0} \frac{\omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (2.4.19)$$

hence its complex relative permittivity

$$\epsilon^* = \frac{C_1}{C_0} + \frac{C_2}{C_0} \frac{1}{1 + i\omega \tau_2} \quad (2.4.20)$$

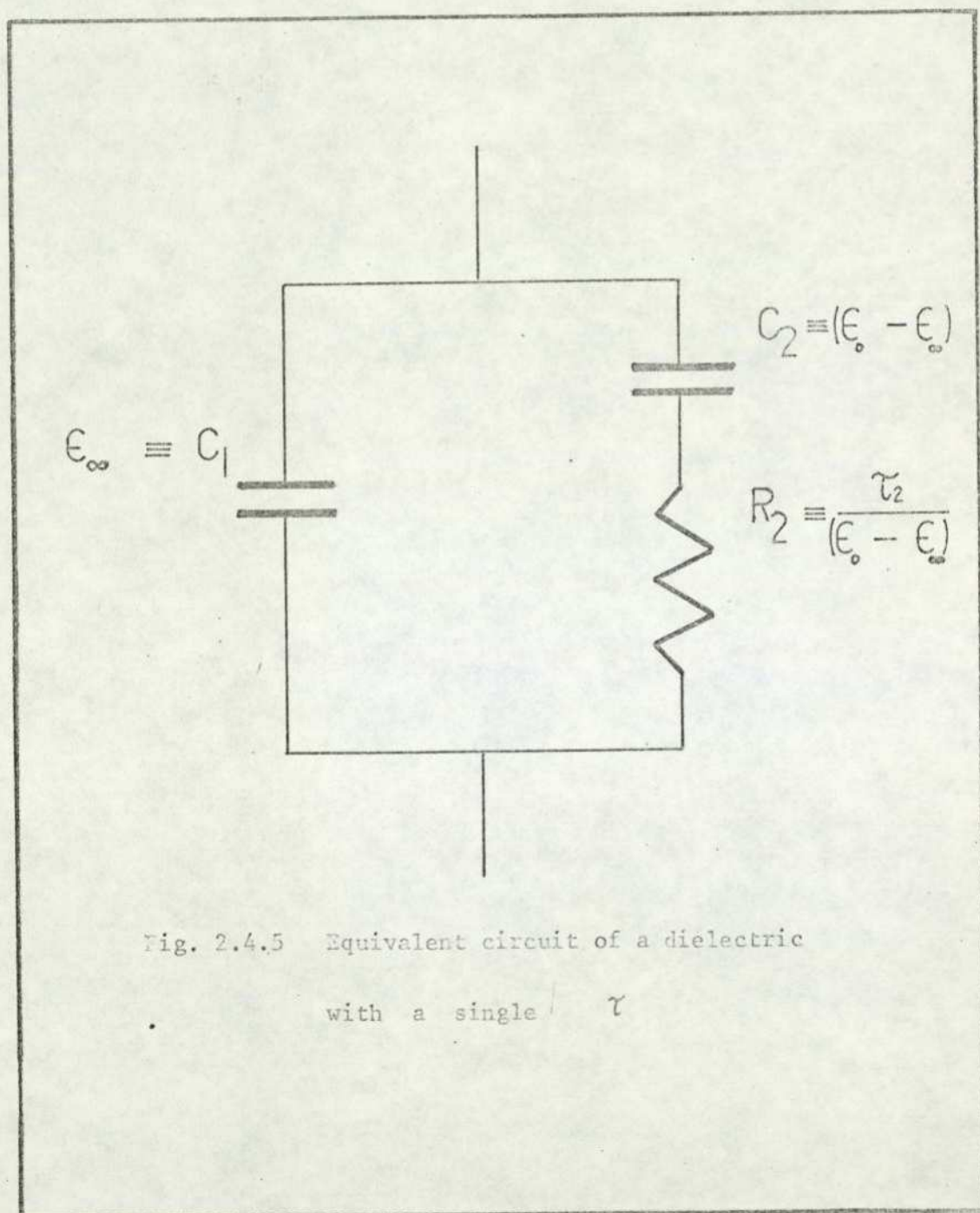


Fig. 2.4.5 Equivalent circuit of a dielectric
with a single τ

For the series branch R_2C_2 alone, the loss tangent

$$\tan \delta_2 = \omega \tau_2 \quad (2.4.21)$$

but the by-pass capacitor C_1 reduces the overall loss tangent by carrying more current as the frequency increases, therefore

$$\tan \delta = \frac{\tan \delta_2}{1 + \frac{C_1}{C_2} (1 + \omega^2 \tau_2^2)} \quad (2.4.22)$$

Expressions for ϵ_0 at zero frequency and ϵ_∞ at infinite frequency can be obtained by substituting values of the frequency in equations 2.4.18 and 2.4.19, then

$$\epsilon_0 \equiv \frac{C_1}{C_0} + \frac{C_2}{C_0} \quad (2.4.23)$$

$$\epsilon_\infty \equiv \frac{C_1}{C_0} \quad (2.4.24)$$

$$\epsilon_0 - \epsilon_\infty \equiv \frac{C_2}{C_0} \quad (2.4.25)$$

Eqs. 2.4.18-20 thus become

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + \omega^2 \tau_2^2} \quad (2.4.26)$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_\infty) \omega \tau_2}{1 + \omega^2 \tau_2^2} \quad (2.4.27)$$

These are typical Debye equations 2.2.22 and 23.

The complex permittivity Eq. 2.4.20 can be written

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + i\omega \tau_2} \quad (2.4.28)$$

The loss factor reaches its maximum $(\epsilon_0 - \epsilon_\infty)/2$ at the critical frequency given by

$$\omega_c = \frac{1}{\tau_2} \quad (2.4.29)$$

Plotted on a logarithmic frequency scale (Fig.2.2.4) the loss factor describes a symmetrical, bell-shaped absorption band centered at ω_c and covering about two decades above and below this value, whereas ϵ' traverses a falling, S-shaped characteristic limited

essentially to the range of one decade on both sides of the critical frequency. It is easily seen that this characteristic corresponds to the electrical response of a dielectric of the Debye type, that is, with one relaxation time and thus its ϵ''/ϵ' diagram is a semi-circle (see Fig. 2.2.5)

2.4.2.2 Distribution of Relaxation Times

It was shown that the simple three-element circuit in Fig. 2.4.5 may satisfactorily represent a dielectric with a single relaxation time. When, as is often the case, the material has a spread of relaxation times, a more complicated equivalent circuit is needed. In such circuits, the resistor of the elementary circuit is replaced by a complex impedance which is a function of frequency (Cole and Cole 1941), Fig. 2.4.6.

In this circuit the capacitance C_1 represents the polarization at very high frequencies (ϵ_∞), while the capacitance C_2 corresponds to the polarization (ΔP , Eq.2.2.17) set up only for low frequencies ($\epsilon_0 - \epsilon_\infty$). The complex impedance is given by

$$Z = \frac{\tau_0 (i\omega\tau_0)^{-\alpha}}{\epsilon_0 - \epsilon_\infty} \quad (2.4.30)$$

This impedance has the striking property that, while the resistance and reactance components are functions of the frequency, the phase angle is a constant independent of the frequency and equal to $\alpha\pi/2$.

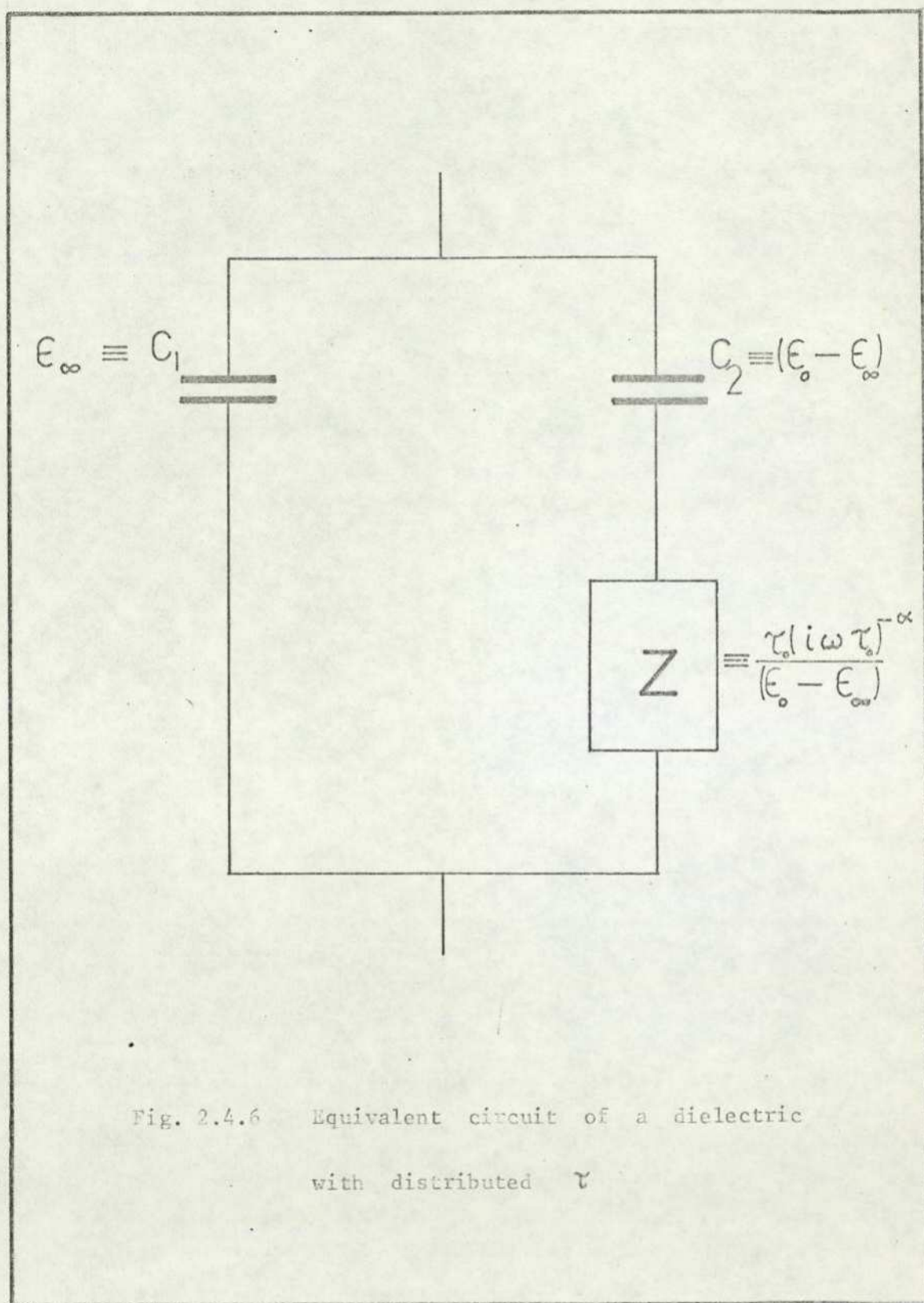
Impedance of the series branch of this circuit

$$Z_2 = \frac{1}{i\omega C_2} + Z = \frac{1 + i\omega C_2 Z}{i\omega C_2} \quad (2.4.31)$$

and its admittance

$$Y_2 = \frac{1}{Z_2} = \frac{i\omega C_2}{1 + i\omega C_2 Z} \quad (2.4.32)$$

Total admittance of the circuit



$$\begin{aligned}
 Y &= Y_2 + i\omega C_1 \\
 &= \frac{i\omega C_2}{1 + i\omega C_2 Z} + i\omega C_1
 \end{aligned}
 \tag{2.4.33}$$

Introducing the complex expression for admittance

$$Y = i\omega \epsilon^* = \frac{i\omega C_2}{1 + i\omega C_2 Z} + i\omega C_1
 \tag{2.4.34}$$

thus

$$\epsilon^* = \frac{C_2}{1 + i\omega C_2 Z} + C_1$$

Substituting values of C_1 , C_2 , and Z

$$\epsilon^* = \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega T_0)^{1-\alpha}} + \epsilon_\infty
 \tag{2.4.35}$$

This is the same expression of equation 2.2.42 representing a dielectric with a distribution of relaxation times. The locus of its permittivity in the complex plane is a circular arc with end points on the axis of reals and centre below this axis (see Fig.2.2.7).

2.4.3 Equivalent Networks

2.4.3.1 Systems of parallel circuits in Series

The network in Fig. 2.4.7 formed of two parallel elementary circuits in series, is usually used as equivalent to the Maxwell-Wagner two-layer capacitor. As will be shown in Chapter 3, the generalization of this network to n parallel circuits in series is also used as analogous to n -layer dielectric systems. Analysis of such networks is essentially similar to that of the 2-layer model.

The steady-state solution when an AC voltage $V = V_0 \exp(i\omega t)$ is applied, can be derived as follows:

Admittances Y_1 and Y_2 of the two elementary circuits

$$Y_1 = \frac{1}{R_1} + i\omega C_1, \quad Y_2 = \frac{1}{R_2} + i\omega C_2 \quad (2.4.36)$$

Total admittance of the circuit

$$Y = \frac{I}{V} = \frac{Y_1 Y_2}{Y_1 + Y_2} \quad (2.4.37)$$

The time constant τ of the circuit in terms of the time constants

$$\tau_1 = R_1 C_1 \quad \text{and} \quad \tau_2 = R_2 C_2 \quad (\text{see Eq. 2.4.16})$$

of the two individual circuits is given by (von Hippel, 1954)

$$\tau = \frac{R_1 \tau_2 + R_2 \tau_1}{R_1 + R_2} \quad (2.4.38)$$

hence the admittance may be rewritten

$$Y = \frac{1}{R_1 + R_2} \frac{(1 + i\omega \tau_1)(1 + i\omega \tau_2)}{1 + i\omega \tau} \quad (2.4.39)$$

Introducing the complex expression for admittance

$$Y = i\omega \epsilon^*, \quad \text{then}$$

$$\epsilon^* = \frac{\tau_1 + \tau_2 - \tau + \omega^2 \tau_1 \tau_2 \tau}{(R_1 + R_2)(1 + \omega^2 \tau^2)} \quad (2.4.40)$$

which changes from its static value at $\omega = 0$

$$\epsilon_0 = \frac{\tau_1 + \tau_2 - \tau}{(R_1 + R_2)} \quad (2.4.41)$$

to its value as $\omega \rightarrow \infty$

$$\epsilon_{\infty} = \frac{\tau_1 \tau_2}{(R_1 + R_2)\tau} \quad (2.4.42)$$

Introducing ϵ_0 and ϵ_{∞} into Eq. 2.4.40

$$\epsilon' = \epsilon_{\infty} \left(1 + \frac{K}{1 + \omega^2 \tau^2} \right) \quad (2.4.43)$$

$$\text{where } K = \frac{(\tau_1 + \tau_2 - \tau)\tau - \tau_1 \tau_2}{\tau_1 \tau_2} = \frac{\epsilon_0 - \epsilon_{\infty}}{\epsilon_{\infty}} \quad (2.4.44)$$

The loss factor is thus given by

$$\epsilon'' = \epsilon_{\infty} \left(\frac{K\omega\tau}{1 + \omega^2 \tau^2} + \frac{\tau}{\omega\tau_1\tau_2} \right) \quad (2.4.45)$$

and the complex permittivity

$$\epsilon^* = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau} + \frac{\sigma}{i\omega} \quad (2.4.46)$$

$$\text{where } \sigma = \frac{1}{R_1 + R_2} \quad (2.4.47)$$

A comparison of these expressions with those of section 2.3.1, shows that the network of Fig. 2.4.7 represents successfully the Maxwell-Wagner two-layer system. The permittivity is indistinguishable from that of the simple orientation polarization of Debye theory, and the loss factor contains an additional term dominant at low frequencies because of the resistor branch $R_1 + R_2$.

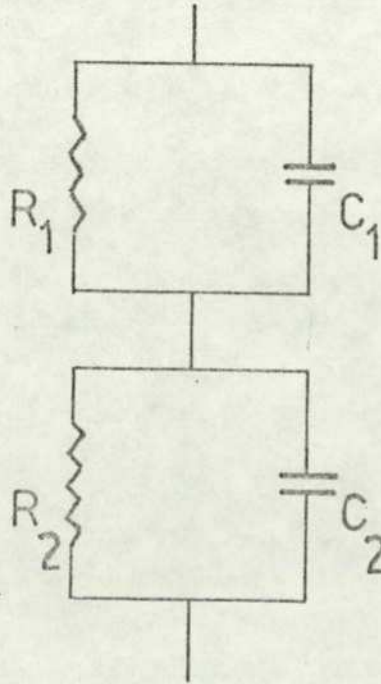
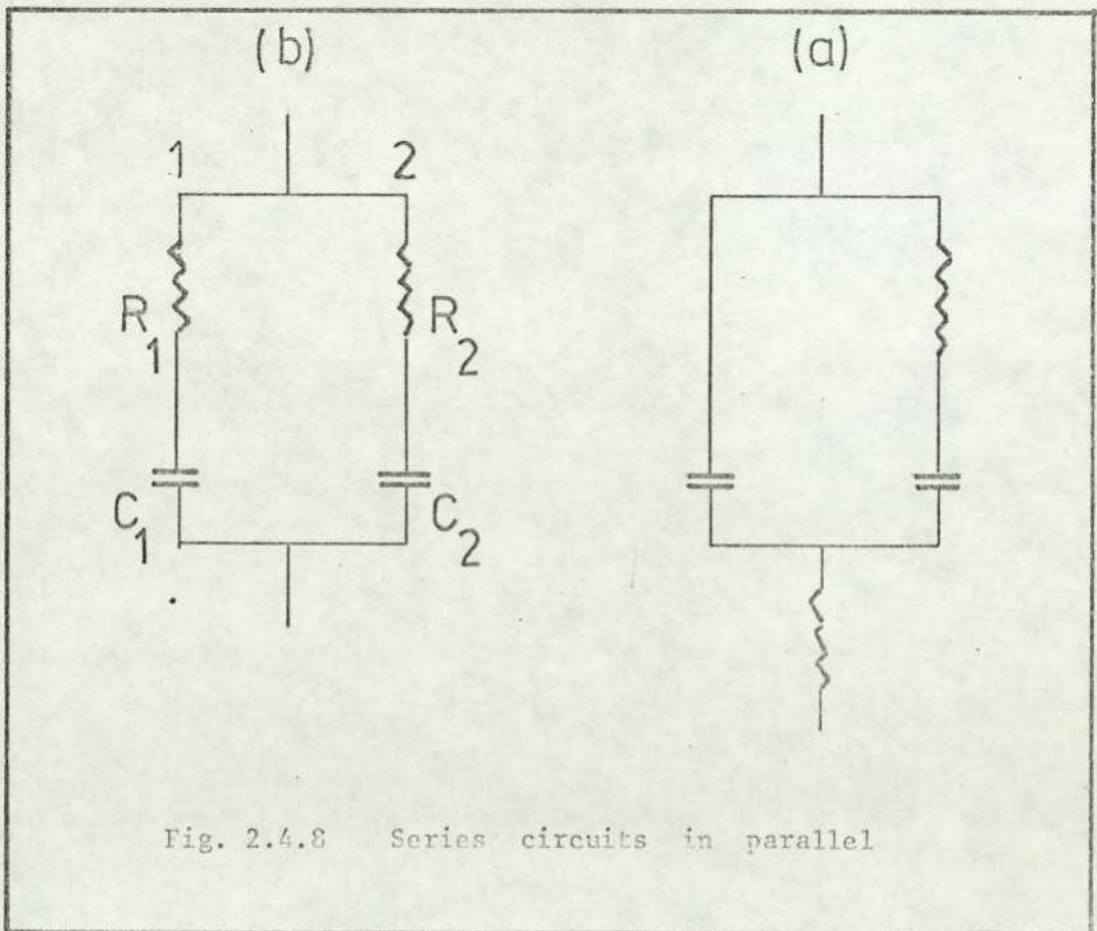


Fig. 2.4.7 Parallel circuits in series

2.4.3.2 Systems of series circuits in parallel

It is always possible (Guillemin, 1953) to represent a given network such as that shown in Fig. 2.4.8(a) by an equivalent one, such as that shown in Fig. 2.4.8(b), where each branch can be described by a first-order differential equation, so that a differential equation of the n th order is replaced by n differential equations of the first order each with a constant relaxation time. Circuits which are defined as equivalent in this sense behave in the same way with regard to any voltage applied to their terminals.



The admittances Y_1 and Y_2 of branches 1 and 2 of the network in Fig. 2.4.8 (b) in terms of $K_1 = 1/R_1$ and $K_2 = 1/R_2$, are

$$Y_1 = \frac{i\omega C_1}{1 + i\omega C_1 R_1} = \frac{\omega^2 C_1^2 R_1}{1 + (\omega C_1 R_1)^2} + \frac{i\omega C_1}{1 + (\omega C_1 R_1)^2} \quad (2.4.48)$$

$$Y_2 = \frac{i\omega C_2}{1 + i\omega C_2 R_2} = \frac{\omega^2 C_2^2 R_2}{1 + (\omega C_2 R_2)^2} + \frac{i\omega C_2}{1 + (\omega C_2 R_2)^2}$$

Since the total admittance $Y = Y_1 + Y_2$, and by complex admittance expression and separating real and imaginary quantities, we get

$$\epsilon' \epsilon_v = \frac{C_1}{1 + (\omega C_1 R_1)^2} + \frac{C_2}{1 + (\omega C_2 R_2)^2} \quad (2.4.49)$$

$$= \frac{C_1}{1 + \omega^2 \tau_1^2} + \frac{C_2}{1 + \omega^2 \tau_2^2} \quad (2.4.50)$$

$$K = \frac{\omega^2 C_1^2 R_1}{1 + (\omega C_1 R_1)^2} + \frac{\omega^2 C_2^2 R_2}{1 + (\omega C_2 R_2)^2}$$

$$= \frac{\omega^2 C_1 \tau_1}{1 + \omega^2 \tau_1^2} + \frac{\omega^2 C_2 \tau_2}{1 + \omega^2 \tau_2^2} \quad (2.4.51)$$

in which

$$\tau_1 = R_1 C_1$$

$$\tau_2 = R_2 C_2$$

It is easily seen that these expressions can be extended to apply for any number of circuit branches or layers, and the physical meaning of replacing the differential equation of n th order by n differential equation of the first order is readily understood.

2.5 SUMMARY AND DISCUSSION

The preceding theoretical review of the dielectric behaviour may be summarized as follows:-

- 1) In addition to the four well known mechanisms of polarization (electronic, atomic, orientation, and space-charge polarization), the adsorbed phase polarization suggested by Murphy and Lowry (1930) seems to be a very convincing explanation of the dielectric behaviour of systems in which adsorption phenomenon takes place.
- 2) In homogenous dielectric materials, neither the space-charge polarization nor the adsorbed phase polarization will take place, and knowing that both the electronic and atomic polarizations do not exhibit relaxation in the frequency ranges used for electrical measurements, it is concluded that the electric dispersion in homogeneous dielectrics is attributed solely to orientation polarization.

Since the relaxation of homogeneous dielectrics is attributable to one polarization mechanism only it is expected to be described by one single relaxation time. However, there is practically no dielectric material that has one single relaxation time, and according to the accuracy required, the investigation should be based on the more realistic concept of distribution or spectrum of relaxation times (Cole and Cole, 1941).

- 3) In mixtures or heterogeneous dielectrics, all types of polarization may take place and the electrical dispersion may be associated with orientation, space-charge, or adsorbed phase polarization. In general the total polarization is the sum of contribution of various polarization mechanisms,

and so is the dielectric dispersion. Consequently the dielectric behaviour of heterogeneous systems is rather complicated. However, as proved by van Beek (1965), the general results of all dielectric dispersion theories can be written as equations of the simple Debye type.

If we add that the additional type of polarization, viz, the adsorbed phase polarization, which is adopted in this thesis, may also be formalised as Debye equations, the handling of the complicated behaviour of heterogeneous dielectrics is considerably simplified. One exception should be underlined at this point, that in the heterogeneous dielectrics, an additional conductivity term, due to the combined conductivity of the individual phases of the material, usually appears in conductivity formulae of dielectric theories other than the Debye theory.

4) The electrical network analogy often supplies a convenient method of investigating the dielectric behaviour of materials. The electrical properties of matter may be represented by a parallel or a series combination of a capacitance C and a resistance R . The type of combination is not indicative of a mechanism, transformation from one to the other being readily effected by use of equations 2.4.8-12.

However, such a simple RC circuit can merely represent a dielectric with one relaxation time. Due to the distribution of relaxation times the dispersion curves representing the RC circuit do not conform with experimentally observed curves. The greater the distribution of relaxation times, the poorer will be the agreement between the calculated and

measured curves. Accurate representation of the experimental results requires a more complicated equivalent circuit in which the resistance R is replaced by a complex impedance which is a function of frequency.

Thus an accurate equivalent circuit for the dielectric is only possible, with fixed components, at a single frequency in the region near the relaxation frequency. Far removed from this region, the equivalent circuit calculated on the basis of a single relaxation time is adequate.

Therefore, the assumption that both components of the Maxwell model of two-layer capacitor are loss-free and have well-defined dielectric constants without dispersion in the frequency region considered would justify the representation of each phase by a simple RC circuit, i.e., one with a single relaxation time.

CHAPTER 3

REVIEW OF PREVIOUS STUDIES

It has been shown in the last chapter that although the electrical response of homogeneous dielectrics may be adequately described by Debye theory and the Cole-Cole modification for the distribution of relaxation times, yet there is no single quantitative theory of sufficient generality to account for all the observations on the mixtures or heterogeneous dielectrics. The most prominent theories of heterogeneous dielectrics are the Maxwell-Wagner theory of space-charge polarization and the adsorption phase polarization theory.

The electrical properties of soil-water-electrolyte systems, which are heterogeneous systems by all accounts, have been studied by many investigators on the bases of the above mentioned two theories in connection with analogous electrical network models. The previous studies are, therefore, reviewed in this order.

3.1 STUDIES BASED ON MAXWELL-WAGNER THEORY

Although the Maxwell-Wagner effect is of considerable practical interest, its theoretical treatment does not appear to have been extended beyond the two simple systems considered by Wagner, viz., a stratified body and a dilute suspension of spheres (Frike, 1953).

A formalistic prototype of interfacial polarization is the Maxwell-Wagner two-layer capacitor, discussed in section 2.3.2, and usually represented by an equivalent network of two parallel RC circuits in series (Section 2.4.3.1).

Volger (1960) generalized the two-layer model to a multi-layer one represented by a multi-circuit in series electrical network. The limiting dielectric constants $\epsilon_0, \epsilon_\infty$ are also given by a form of Debye equations (2.2.22 & 23) and the loss factor ϵ'' has an additional conductivity term.

Two-layer and many-layer systems often supply good descriptions of compressed or sintered polycrystalline samples in which surface barriers exist between adjacent particles, or of samples with surface layers of different properties. It is easily shown that a system consisting of a number of layers of the same material, separated by layers of another substance, behaves as a two-layer system. In other words, the sequence of the layers does not influence the dielectric behaviour of the system (van Beek, 1965).

Sometimes a two-layer system does not produce a Maxwell-Wagner effect, namely when $\epsilon_0 - \epsilon_\infty = 0$, which leads to the condition

$$\epsilon_{2k_1} = \epsilon_{1k_2} \quad (3.1.1)$$

Also for some values of the ratio (thickness x conductivity) for the two layers, the frequencies of maximum loss may vary widely and it is often worth while to estimate whether Maxwell-Wagner losses might interfere in practical cases.

Adsorbed water would not seem to produce high losses, when considered in terms of two-layer systems. However, Hasted (1961) has shown that adsorbed water often produces very high dielectric losses, and that the inhomogeneity of comparatively non-polar solid systems containing water may result in a Maxwell-Wagner conductivity in the kilocycle range which shows frequency dependence similar to the Debye relaxation. Losses may also be produced at higher frequencies when its conductivity has been enhanced by dissolved electrolyte.

Successful experiments to test Wagner's theory were performed by Hammon (1953) on mixtures consisting of a non-polar base material (paraffin wax) and small percentages of a slightly conducting solid (copper phthalocyanine) or liquid "impurity". Two types of dispersion of the solid impurity were studied, one using discrete spheres and the other using a fine powder covering the surfaces of large grains of the base material. For the discrete spheres, good agreement with Wagner's theory was obtained. The results for the powdered solid impurity and the liquid impurity show that such mixtures can give rise to dielectric loss factors that increase slowly with decreasing frequency over a wide frequency range, and finally merge with the loss due to DC conductivity. Hammon concluded that at least for non-polar dielectrics, the small loss factors and DC charging currents frequently observed may be due to conducting impurities present as a separate phase.

Sillars (1937) made the first step to enlarge Maxwell-Wagner model to take into account the large variety of possible shapes of

inclusions that cannot be regarded, even approximately, as spheres. He considered the case of a dilute suspension of spheroid shaped particles, but simplified matters by assuming that the conductivity of the dispersing medium is $k_1 = 0$, i.e. an insulating medium. The spheroids were assumed to be ellipsoids with axis 'a' in the field direction and equal axes 'b = c' at right angles to the field. In this way the geometry of the heterogeneous dielectric is represented by only two variables, namely, the fractional volume of spheroids 'p' and the axial ratio a/b.

In the static case and for $k_1 = k_2 = 0$ the field inside and outside the spheroid can be derived from the field theory, i.e.

$$\epsilon_1 E_1 = \epsilon_2 E_2 \quad (3.1.2)$$

where E_1 and E_2 are the normal components of the field at the interface between the dielectric 1 and 2. For $k_2 \neq 0$ surface charges are held at the interface of magnitude given by

$$\sigma = (\epsilon_1 E_1 - \epsilon_2 E_2) \epsilon_v \quad (3.1.3)$$

where σ and E are in practical units, ϵ_1 and ϵ_2 in e.s.u. The field E_2 within the spheroid is zero in the static case, but not so in the dynamic case, since surface charges are adjusted towards equilibrium by means of currents flowing in the conductive medium. This is the case even if k_1 as well as k_2 is finite.

For periodic fields when the normal components at the interface may be represented by the complex quantities

$$E_1^*(t) = a^* e^{i\omega t}, \quad E_2^*(t) = b^* e^{i\omega t} \quad (3.1.4)$$

we may calculate the surface charge carried by conduction as

$$\begin{aligned}\sigma^*(t) &= \int (k_1 E_1^* - k_2 E_2^*) dt \\ &= (k_1 E_1^* - k_2 E_2^*) \frac{1}{i\omega}\end{aligned}\quad (3.1.5)$$

Eq. 3.1.3 may be rewritten for periodic fields

$$\sigma^*(t) = (\epsilon_1 E_1^*(t) - \epsilon_2 E_2^*(t)) \epsilon_v \quad (3.1.6)$$

which together with Eq. 3.1.5 give

$$\left(\epsilon_1 \epsilon_v + \frac{k_1}{i\omega} \right) E_1^* = \left(\epsilon_2 \epsilon_v + \frac{k_2}{i\omega} \right) E_2^* \quad (3.1.7)$$

which is a generalization of Eq. 3.1.2

The relationship between the field applied to a capacitor containing the heterogeneous dielectric and the polarization in the dielectric is required to define the problem. The task of deriving this relationship is much simplified if $k_i = 0$, that is the inclusions are embedded in a perfect dielectric. In this case, all the power dissipated occurs in the inclusions and the complex dielectric constant of the heterogeneous dielectric can be deduced from the power loss. To derive the power loss Sillars used Ohm's law, so that, W , the power loss per unit volume of the inclusion is

$$W = \frac{1}{2} k_2 |E_2^*|^2 \quad (3.1.8)$$

where E_2^* ..the field within the inclusion, may be calculated using Eq. 3.1.7

For a heterogeneous dielectric as defined, Sillar's calculation leads to a complex dielectric constant of Debye type, namely

$$\epsilon = \epsilon_\infty - \frac{\epsilon_1 N}{1 + (\omega \tau)^2} \quad (3.1.9)$$

$$\epsilon'' = \frac{\epsilon_1 N \omega \tau}{1 + (\omega \tau)^2} \quad (3.1.10)$$

where ϵ_∞ , N and τ are quantities which involve a dimensionless function $\lambda(a/b)$ of the axial ratio. This function has been evaluated by Sillars; it equals unity for a layered dielectric $(a/b) = 0$ and 3 for spheres $(a/b) = 1$. The expressions for N and ϵ_∞ are

$$\tau = \frac{\epsilon_1(\lambda - 1) + \epsilon_2}{k_2/\epsilon_v} \quad (3.1.11)$$

$$N = P \frac{\lambda^2 \epsilon_1}{\epsilon_1(\lambda - 1) + \epsilon_2} \quad (3.1.12)$$

$$\epsilon_\infty = \epsilon_1 \left[1 - P \frac{\lambda(\epsilon_2 - \epsilon_1)}{\epsilon_1(\lambda - 1) + \epsilon_2} \right] \quad (3.1.13)$$

Similar to Wagner's equations for the dilute system, Sillar's are independent of the size of the particle. The relaxation time is also independent of particle volume concentration but dependent on particle shape.

Khradly and Jackson (1953) investigated the effect of neglecting the electrostatic interaction between conducting particles in Sillar's treatment. They considered two and three dimensional arrays of conducting spheres, cylinders, etc. in a loss free dielectric, and gave a formula for the complex dielectric constant ϵ^* of a composite dielectric containing a cubic array of spheres

$$\frac{\epsilon^*}{\epsilon_1} = \frac{(1-3p) \frac{\epsilon_2^* - \epsilon_1}{\epsilon_2^* + 2\epsilon_1}}{(1-3p) \frac{\epsilon_2^* - \epsilon_1}{\epsilon_2^* + 2\epsilon_1}} \quad (3.1.14)$$

where

$$\epsilon_v \epsilon_2^* = \epsilon_2 \epsilon_v + \frac{k_2}{i\omega} \quad (3.1.15)$$

Eq. 3.1.14 is a generalization of Eqs. 3.1.9 & 10 and reduces to the latter as $p \rightarrow 0$.

Khradly and Jackson verified Eq. 3.1.14 experimentally for an artificial dielectric consisting of one layer of spheres arranged in a square array. They found that, up to $p=0.1$ the calculation without electrostatic interaction gives moderately good agreement while above $p=0.3$ even Eq. 3.1.14 does not give very good agreement.

Dryden and Meakins (1957), Pauly and Schwan (1959), and Hanai (1961), independently considered a model in which the volume concentration is not dilute. They derived the dispersion equations for systems of conducting spheres that are surrounded by a thin conducting shell and suspended in a conducting medium. The formulae were verified for particle concentration up to about $p=0.3$ where the agreement with theory was very poor. The formulae are again of the Debye type (van Beek, 1965) with a relaxation time

$$\tau = \frac{\epsilon_{\infty} [2\epsilon_1 + \epsilon_2 - p(\epsilon_2 - \epsilon_1)]}{2K_1 + K_2 - p(K_2 - K_1)} \quad (3.1.16)$$

and limiting dielectric constants

$$\epsilon_0 = \epsilon_{\infty} + \frac{9P(1-P)(\epsilon_1 K_2 - \epsilon_2 K_1)^2}{[2\epsilon_1 + \epsilon_2 - p(\epsilon_2 - \epsilon_1)]^2 [2K_1 + K_2 - p(K_2 - K_1)]^2} \quad (3.1.17)$$

$$\epsilon_{\infty} = \epsilon_1 \frac{2\epsilon_1 + \epsilon_2 + 2P(\epsilon_2 - \epsilon_1)}{2\epsilon_1 + \epsilon_2 - p(\epsilon_2 - \epsilon_1)} \quad (3.1.18)$$

and limiting conductivities

$$K_0 = K_1 \frac{2K_1 + K_2 + 2P(K_2 - K_1)}{2K_1 + K_2 - p(K_2 - K_1)} \quad (3.1.19)$$

$$K_{\infty} = K_0 + \frac{9P(1-P)(\epsilon_1 K_2 - K_1)^2}{[2\epsilon_1 + \epsilon_2 - p(\epsilon_2 - \epsilon_1)]^2 [2K_1 + K_2 - p(K_2 - K_1)]^2} \quad (3.1.20)$$

These expressions are independent of particle size or shape. However, the relaxation time is seen to be a function of the particle volume concentration.

Fricke (1953) presented a more general treatment of suspensions with respect to the effect of particle shape and orientation by introducing a shape factor formula that depends on the particles orientation with respect to the applied field. He first considered the case of a dilute suspension of ellipsoids and then extended the treatment to more concentrated suspensions. The latter case was treated on the basis of a semi-theoretical general conductivity equation derived assuming that the effective internal field acting upon a suspended particle is equal to the average field in the suspending fluid.

In the case of a dilute suspension, equations obtained for k and ϵ showed that a suspension of ellipsoids having one of the principal axes parallel with the field, is characterized by a single Debye type dispersion zone. When the axes are oriented at random, there are three such dispersion zones, the electric behaviour of the suspension being the same as that of an even mixture of the three principal orientations of the ellipsoids. The same trends were suggested to apply in the case of more concentrated suspensions.

Assuming homogeneous ellipsoids (axis $2a \geq 2b \geq 2c$) (ϵ_2, k_2) distributed in a homogeneous medium (ϵ_1, k_1), Fricke derived expressions for the two cases:

1) The axis $2a$ is parallel with the external field,

$$K_{\infty} - K_0 = \frac{P(1-P)(1+x_i)^2 (K_2 \epsilon_1 - K_1 \epsilon_2)^2}{B(K_{12}) [B(\epsilon_{12})]^2} \quad (3.1.21)$$

$$\epsilon_0 - \epsilon_{\infty} = \frac{P(1-P)(1+x_i)^2 (K_2 \epsilon_1 - K_1 \epsilon_2)^2}{[B(K_{12})]^2 B(\epsilon_{12})} \quad (3.1.22)$$

$$B(K_{12}) \equiv K_2 + x_i K_1 - P(K_2 - K_1)$$

$$B(\epsilon_{12}) \equiv \epsilon_2 + x_i \epsilon_1 - P(\epsilon_2 - \epsilon_1)$$

x_i - is a form factor for different axial ratios with the field parallel to the x_i axis. Fricke reported values of x_i for different cases both numerically and graphically.

2) The ellipsoids assuming a random orientation.

$$K_o = K_2 + \frac{(K_1 - K_2)(1-P)}{1+L} \quad (3.1.23)$$

$$\epsilon_o = \epsilon_2 + \frac{(\epsilon_1 - \epsilon_2)(1-P)}{1+S} \quad (3.1.24)$$

$$L = \sum_i \frac{K_1 - K_2}{K_2 + x_i K_1} \cdot \frac{P}{3}$$

$$S = \sum_i \frac{\epsilon_1 - \epsilon_2}{\epsilon_2 + x_i \epsilon_1} \cdot \frac{P}{3}$$

$$K_o = K_2 + \frac{(K_1 - K_2)(1-P)}{(1+S)} + \frac{(1-P)(K_2 \epsilon_1 - K_1 \epsilon_2)(\epsilon_1 - \epsilon_2)N}{(1+S)^2} \quad (3.1.25)$$

$$\epsilon_o = \epsilon_2 + \frac{(\epsilon_1 - \epsilon_2)(1-P)}{(1+L)} + \frac{(1-P)(\epsilon_2 K_1 - \epsilon_1 K_2)(K_1 - K_2)M}{(1+L)^2} \quad (3.1.26)$$

$$N = \sum_i \frac{x_i + 1}{(\epsilon_2 + x_i \epsilon_1)^2} \cdot \frac{P}{3}$$

$$M = \sum_i \frac{x_i + 1}{(K_2 + x_i K_1)^2} \cdot \frac{P}{3}$$

It is seen that the dispersions are functions of bulk properties, particle volume concentration, particle shape and orientation. As Fricke pointed out, the system is characterized by dispersion regions inside each of which, it behaves quantitatively like a Debye dipole system.

Polder and van Santeen (1947) have attempted to extend Sillar's theory by taking into consideration the effect of interaction of

particles. The effective dielectric constant was calculated for a material consisting of a medium in which solid particles or empty holes with various dielectric constants are packed together and in which the individual particles or holes were assumed to be ellipsoids.

De Loor (1956) reviewed the formulae of the dielectric constant of mixtures and discussed the relaxation behaviour. He suggested expressions for shape depolarization factor A in accordance with those given by Fricke (1953).

Bruggeman (1935) introduced a scheme to investigate the effect of the concentration of dispersed particles in the immediate neighbourhood of the particle under consideration. In this scheme, the initially low concentration is gradually increased by infinitesimal additions of dispersed component (ϵ_2). In the course of this process, the dielectric constant of the medium around a particle slowly changes from (ϵ_1) of the dispersing medium to the final value (ϵ) of the whole system. This technique enabled Bruggeman to derive the formula

$$p = 1 - \frac{\epsilon_2 - \epsilon}{\epsilon_2 - \epsilon_1} \left(\frac{\epsilon_1}{\epsilon_2} \right)^{1/3} \quad (3.1.27)$$

for the dielectric constant ϵ of the mixture in terms of the volume fraction p of the dispersed component.

Looyenga (1965) used a similar method to that of Bruggeman and suggested that the formula

$$p = \frac{\epsilon^{1/3} - \epsilon_1^{1/3}}{\epsilon_2^{1/3} - \epsilon_1^{1/3}} \quad (3.1.28)$$

gives the closest fit with the experimental results.

Basu and Arulandan (1973) investigated the influence of micro-structure and compositional factors on the radio-frequency electrical properties of clay-water-electrolyte system and suggested a classification chart for the identification of swell potential of soils. They reported that the magnitude of dielectric dispersion, $\Delta \epsilon$, is a measure of mainly the clay mineral composition and percentage clay content while the water content, cation type, pore fluid concentration, flocculation and dispersion, and particle orientation (with respect to the direction of current flow) have a second order effect.

These authors considered the cause of dielectric dispersion as follows: In a two-component system (clay particles and solution), such as a saturated clay-water-electrolyte system, current density varies from point to point since the ratio of conductivity to dielectric constant is different for each of the two components. Charges, therefore, accumulate at the interface between the clay particle and the surrounding solution (Maxwell-Wagner). Since this build-up of charges takes time, as the frequency is increased, there will be less time for the charges to accumulate at the interface, which in turn decreases the system's ability to store electrical potential energy, and thus decreases the dielectric constant.

Okonski (1960) treated the dielectric behaviour of colloidal particles by introducing the concept of surface conductivity. The effects of the excess conductivity arising from mobility of ions at the interface, and - with thin ion atmospheres - the charge transport due to counterions, may be expressed in terms of a two-dimensional conductivity. Formulation of an adequate theory of the dielectric constant and conductivity of systems such as colloidal dispersion, requires treatment of the charge carriers in the solvent, in the ion atmosphere, and in the dispersed phase.

Okonski assumed that the surface conductivity, λ , is composed of two parts:

λ_s - the contribution of the charge carriers in the surface such as ions, electrons, and holes, given by

$$\lambda_s = \sum_i N_i v_i U_i \quad (3.2.1)$$

where N_i is the number of carriers of type i per unit surface area, v_i the valence of the ion, and U_i its mobility.

λ_a - the contribution to the conductivity due to the ion atmosphere, given by

$$\lambda_a = \int_{-\infty}^0 (K'_1 - K_1) dy + \int_0^{\infty} (K'_2 - K_2) dy \quad (3.2.2)$$

where k_1 , k'_1 , k_2 and k'_2 are the bulk conductivities at large distance and arbitrary closer distance from the interface of phase 1 and 2 respectively, and y is the distance from the interface. Thus, the total surface conductivity λ is given by

$$\lambda = \lambda_s + \lambda_a \quad (3.2.3)$$

In an alternating electric field, the surface charge density is assumed to undergo a time variation as the result of two processes:

- 1) The transport of ions to and from an element of surface as a result of the bulk conductivities of the two media.
- 2) The transport of ions along the surface as a result of surface conductivity.

The time derivative of the surface charge density may, therefore, be written as the sum of the contributions of the two processes 1) and 2) when they occur simultaneously.

Okonski suggested that the effect of the surface conductivity λ is exactly equivalent to an increase of the bulk conductivity k_2 of the dispersed spheres by the particle surface conductivity, thus

$$k_s = k_2 + k'_s \quad (3.2.4)$$

where k_s may be regarded as the effective volume conductivity of a particle electrically equivalent to the model comprising the volume conductivity k_2 and the surface conductivity k'_s given by

$$k_s = 2 \frac{\lambda}{a} \quad (3.2.5)$$

in the case of a spherical particle of radius a .

Okonski derived the expression for the complex dielectric constant of the a suspension of spheres as

$$\epsilon^* = \epsilon_1 \left[1 - \frac{p}{3} (\epsilon_s^* - \epsilon_1^*) (\epsilon_s + 2\epsilon_1) \right]^{-1} \quad (3.2.6)$$

where p is the fractional volume of the spherical particles 2 dispersed in medium 1 and ϵ_s^* is the complex dielectric constant of the equivalent sphere with surface conductivity, given by

$$\epsilon_s^* = \epsilon_2 + \frac{4\pi K_s}{i a} \quad (3.2.7)$$

where $i = \sqrt{-1}$

For insulating media, i.e., $k_1 = 0$; the relaxation time is given by

$$\tau = \frac{a(\epsilon_2 + 2\epsilon_1)}{8\pi \lambda} \quad (3.2.8)$$

confirming a result given earlier by Okonski (1955).

Okonski demonstrated the effects of surface conductivity on the internal field, the induced polarization, the dielectric constant and dispersion, and the conductivity of dilute systems. He pointed out that the term λ_s describing a part of the surface conductivity (Eq. 3.2.1), is general and may include a contribution from the probable displacement of the adsorbed or bound ions. Such displacement has been discussed earlier by Kirkwood and Shumaker (1952).

Consistent values of the surface conductivity of colloidal particles have been reported by several investigators:

O'Konsiki (1960); in the order of 10^{-9} mho
 Schwan, et al. (1963); between 10^{-9} and 10^{-8} mho
 Schwarz (1963); in the order of 10^{-9} mho
 van Olphen (1957); between 3.2 and 5.8×10^{-9} mho (for Na bentonite)
 Bloksma (1957); in the order of 10^{-8} mho
 Fricke & Curtis (1936); in the order of 10^{-9} mho

Schwan, et al. (1962), showed that the mere introduction of a surface conductivity would be inadequate to explain the very high dielectric constants observed experimentally in many systems at low frequencies. Their data for polystyrene particles in KCl solution together with those of Fricke and Curtis (1937) for kaolin and pyrex particles in dilute KCl solution, could only be explained by the introduction of a frequency-dependent surface conductance component.

Therefore, the surface conductance is composed of two parts, one being independent of and the other dependent on frequency. Schwan, et al. (1962) suggested that the frequency-dependent component changes approximately in proportion with the conductivity of the dispersing medium, while the magnitude of the conductivity dispersion is almost independent of the ionic strength of that medium.

Assuming negligible particle conductivity ($k_2 = 0$), and that $dk_s/a \ll k_1$ (d = thickness of the double layer), the results were

$$K_o = K_1 \frac{1-P}{1+0.5P} + \frac{dK_s}{a} \cdot \frac{4.5P}{(1+0.5P)^2} \quad (3.2.9)$$

$$\epsilon_o = \epsilon_\infty + \frac{d\epsilon_s}{a} \cdot \frac{4.5P}{(1+0.5P)^2} \quad (3.2.10)$$

Schwarz (1962) added that the effect of ionic diffusion in the double layer should be included in the theory as a capacitive part of the surface admittance. He thus, replaced the dielectric constant of the particles, ϵ_2 , by the expression

$$\epsilon_2 + \frac{2K_s\tau}{\epsilon_v(1+i\omega\tau)} \quad (3.2.11)$$

where the relaxation time τ is given by

$$\tau = \frac{a^2}{2UkT} \quad (3.2.12)$$

where k is the Boltzmann constant, and T is the absolute temperature. Thus, τ is related to the ionic diffusion in the double layer.

Miles and Robertson (1932) have proposed very early that the electric properties of colloidal particles with an electric double layer might be explained in terms of a model involving a sphere surrounded by a concentric shell of higher conductivity, and developed equations for the complex conductivity of a dilute system.

Muir (1954) investigated the dielectric loss properties of the water films adsorbed upon the minerals kaolinite, halloysite, meta-halloysite, and talc over the frequency range 2.5 kc/s to 25 Mc/s. Two varieties of relaxation absorption maxima were observed. One type varies its frequency position, but not its magnitude, with increasing water content, and was attributed to a complete first water layer adsorbed upon a surface of hydroxyle groups. The second type remains in one frequency position but increases in magnitude with increasing water content, and was attributed to a first layer of water being adsorbed upon a surface of oxygen atoms.

Goldsmith and Muir (1960), in a similar work, suggested that the dielectric absorption is due to the conductivity of the adsorbed layers arising from the solution of ions in the first, or first few layers of water adsorbed.

Weiler and Chaussidon (1968) studied the surface conductivity and dielectric properties of montmorillonite gels and suggested that the field action is zero in the direction of the small axis of the platelet but maximum along the long axis so that the motion of the charge carriers is essentially tangential to the platelet. The counterions were considered to be disturbing elements in the water layers structure, thus creating a number of lattice defects able to transport the current. They reported values of the surface conductance of the order of magnitude of 10^{-9} mho.

Mitchell and Arulandan (1968) investigated the relation between electrical dispersion and soil structure in order to determine to what extent the electrical properties of soils might be useful for the study of the influence of microstructure and compositional factors on soil behaviour. These authors have shown that the dielectric constant and conductivity of saturated clay-water-electrolyte systems in the low-frequency range (zero to 10^5 C/S) vary with frequency in a manner dependent on a number of factors. The principal factor influencing the dielectric constant appears to be the ease with which the adsorbed layers of cations surrounding the clay particles can be polarized. This in turn depends on the strength with which the cations are bonded to the surface and the distance through which they can be displaced. The difference between the AC and DC conductivity relates primarily to the amount and type of electrolyte and the difference in cation and anion mobilities. Mitchell and Arulandan suggested that the micro-structural and compositional parameters influence the dielectric and conductivity

response in a numerically significant way.

In another paper, the same authors (Arulandan and Mitchell 1968) investigated the dielectric dispersion of clay-water-electrolyte systems at low-frequency range (30 C/S to 10^5 C/S). They examined several processes of polarization in an attempt to explain the observed data and concluded that the bound ion polarization could explain some of the results. However, Arulandan and Mitchell pointed out that the theory, like most of the other theories, does not consider effects on the electrical properties caused by some important factors such as particle orientation; degree of binding of the ions to the surface, and electrolyte concentration.

3.3 STUDIES BASED ON ANALOGOUS MODELS

It was suggested by Wyllie and Southwick.(1954) that the specific conductance of an aggregate of conductive particles saturated with a conducting electrolyte was compatible with an equivalent resistance model comprising three elements in parallel, Fig.3.3.1.

The three components of specific conductance were:

- 1) An element, K_1 , comprising particles and solution in series with each other.
- 2) An element, K_2 , consisting of particles in sufficiently close contact with one another to form continuously conducting paths.
- 3) An element, K_3 , consisting of fluid filling the interstices between the particles.

In other words, the simple square model of Fig. 3.3.1 (b), was substituted for the complicated geometry of the porous medium Fig.3.3.1 (a).

Sauer, et al.(1955) used the simplified three-element model to explain their observations on the DC conductance of porous plugs containing conductive material (ion exchange resin spheres saturated with electrolyte solutions).

These authors derived an expression for the conductance of the system as follows:

Consider a resistor model, 1 cm x 1 sq. cm, as shown in Fig. 3.3.1, which is to represent the resistance of 1 cc. of the porous material saturated with interstitial solution. In Fig.3.3.1, a, b, and c represent the fractional cross sections of elements 1, 2, and 3, respectively, and d is the length parameter shown in the same figure.

If k_r and k_s are the specific conductances (mho cm^{-1}) of the solid resin and the interstitial solution, respectively, the conductances,

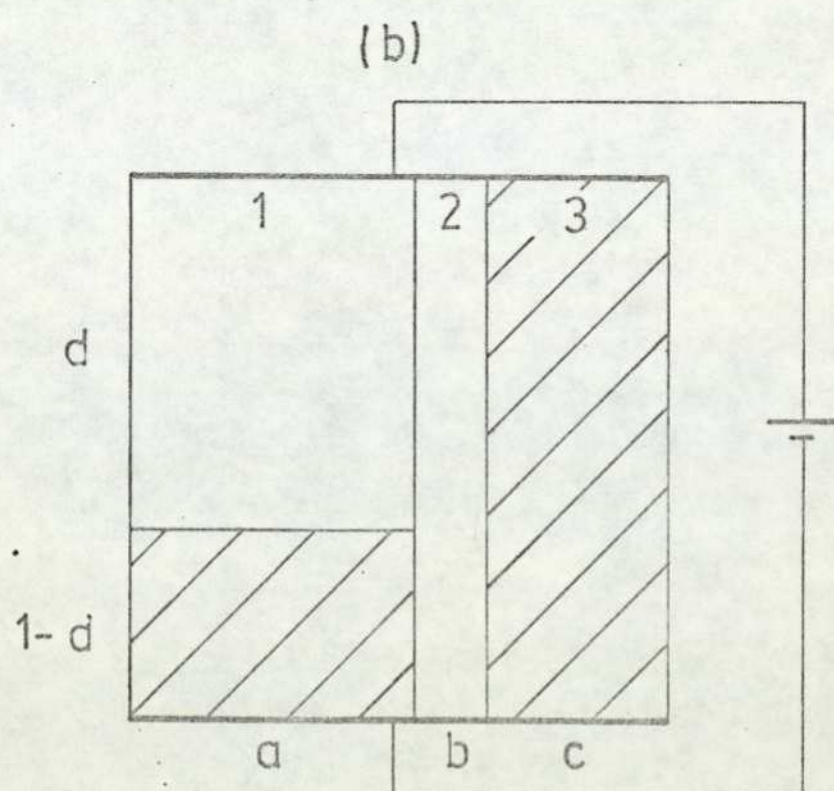
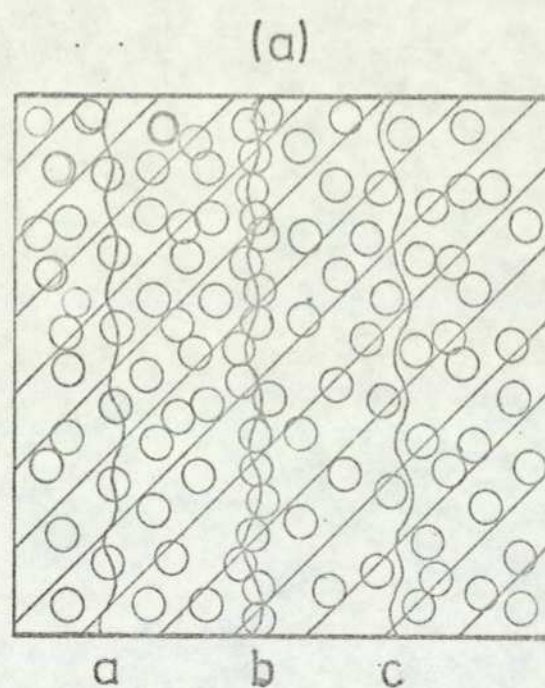


Fig. 3.3.1 Three-element DC resistor model

K_1 , K_2 , K_3 of the three elements are given by

$$\frac{1}{K_1} = \frac{(1-d)/a}{k_s} + \frac{d/a}{k_r} = \frac{x}{k_s} + \frac{y}{k_r} \quad (3.3.1)$$

$$K_1 = \frac{k_r k_s}{k_r(1-d)/a + k_s d/a} = \frac{k_r k_s}{x k_r + y k_s} \quad (3.3.2)$$

$$K_2 = b k_r = \frac{k_r}{z} \quad (3.3.3)$$

$$K_3 = c k_s = \frac{k_s}{F} \quad (3.3.4)$$

where x , y , and z have been defined by

$$x \equiv \frac{(1-d)}{a}, \quad y \equiv \frac{d}{a}, \quad z \equiv \frac{1}{b} \quad (3.3.5)$$

and c has been set equal to $1/F$; F is the formation factor which would characterize the system if the solids were nonconductive.

If solids are nonconductive, only element 3 contributes to the conductance, and the specific conductance of the system is then k_s / F . Since $a+b+c=1$, then

$$\frac{1}{x+y} + \frac{1}{z} + \frac{1}{F} = 1 \quad (3.3.6)$$

The (specific) conductance, K_0 (mho/cm), of the system containing conductive solids is the sum of the conductances of the three elements

$$K_o = K_1 + K_2 + K_3$$

$$= \frac{k_r k_s}{k_r(1-d)/a + k_s d/a} + b k_r + c k_s$$

$$= \frac{k_r k_s}{x k_r + y k_s} + \frac{k_r}{z} + \frac{k_s}{F} \quad (3.3.7)$$

Therefore, to determine K_o , it was required to obtain values of x , y , z , and F .

From Eq. 3.3.7 it is seen that for $k_s = 0$

$$K_o = \frac{k_r}{z} \quad (3.3.8)$$

Thus the intercept of the K_o/k_s plot on the ordinate gives z if k_r is known.

Also by differentiating Eq. 3.3.7 for constant k_r

$$\frac{dK_o}{dk_s} = \frac{x k_r^2}{(y k_s + x k_r)^2} + \frac{1}{F} \quad (3.3.9)$$

For $k_s = 0$, Eq. 3.3.9 reduces to

$$\frac{dK_o}{dk_s} = \frac{1}{x} + \frac{1}{F} \quad (3.3.10)$$

Thus the slope of the K_o/k_s plot at $k_s = 0$ gives $\frac{1}{x} + \frac{1}{F}$

When $k_s \gg k_r$, i.e., at high solution concentrations, it follows from Eq. 3.3.7 that

$$K_o \approx k_r \left(\frac{1}{y} + \frac{1}{z} \right) + \frac{k_s}{F} \quad (3.3.11)$$

The intercept of the approximate straight line defined by Eq.3.3.11 extrapolated to a value of $k_s = 0$ is, therefore, $k_r(\frac{1}{y} + \frac{1}{z})$

As a first step, approximate values of x , y , z , and F computed from Eqs.3.3.8, 10 & 11 were substituted in Eq.3.3.7 to give a calculated K_o/k_s . These initial values of x , y , z , and F served as starting points in a trial and error procedure aimed at obtaining better agreement between theoretical and experimental curves.

In order to determine the conductance k_r of the wet resin from a plot of k_w as abscissa against K_o as ordinate (the same scale being used for plotting both K_o and k_s), a line intersecting the plot was drawn through the origin at 45° to the abscissa. The intersection of this line with the plot clearly gives the point at which $k_w = K_o$, defined as the "isoconductance point". At the isoconductance point, the specific conductances of the system and of the interstitial solution are equal (Dakshinamurti, 1960). In other words, the presence of the resin leaves the conductance of the solution unaffected. Accordingly, at this point $k_r = k_s$. The isoconductance point method is illustrated in Fig.3.3.2.

Sauer, et al. suggested that the concept of three-parallel-element model may be useful for characterising pore structure of sedimentary rocks, wood fibres, and soil aggregates.

Sachs and Spiegler (1964) used the three-element (parallel current paths) model to derive expressions for the dielectric constant and conductivity of the porous conductive plugs in the radio frequency range (20-90 MHz). Each element or layer was described by a parallel circuit of capacitor and resistor (Fig.3.3.3). The theoretical electrical

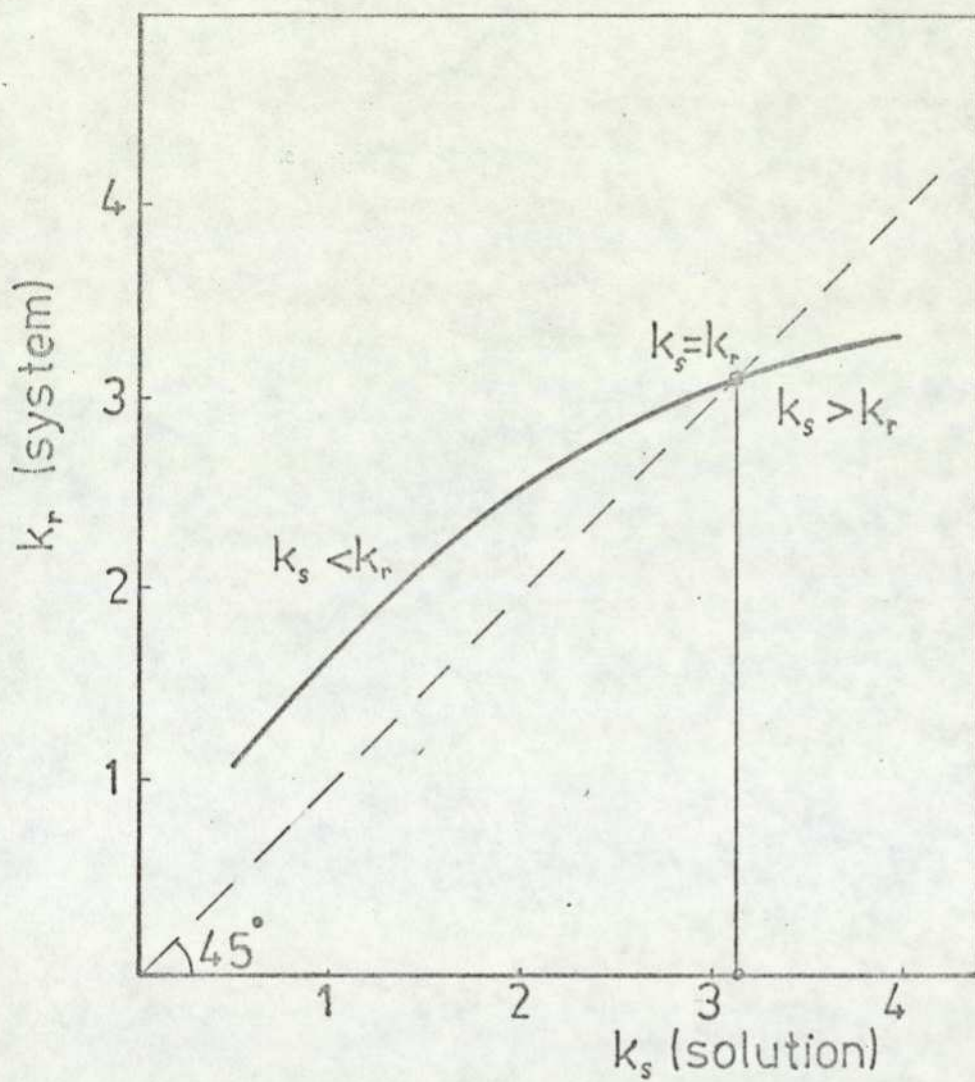


Fig.3.3.2 Isoconductance point method

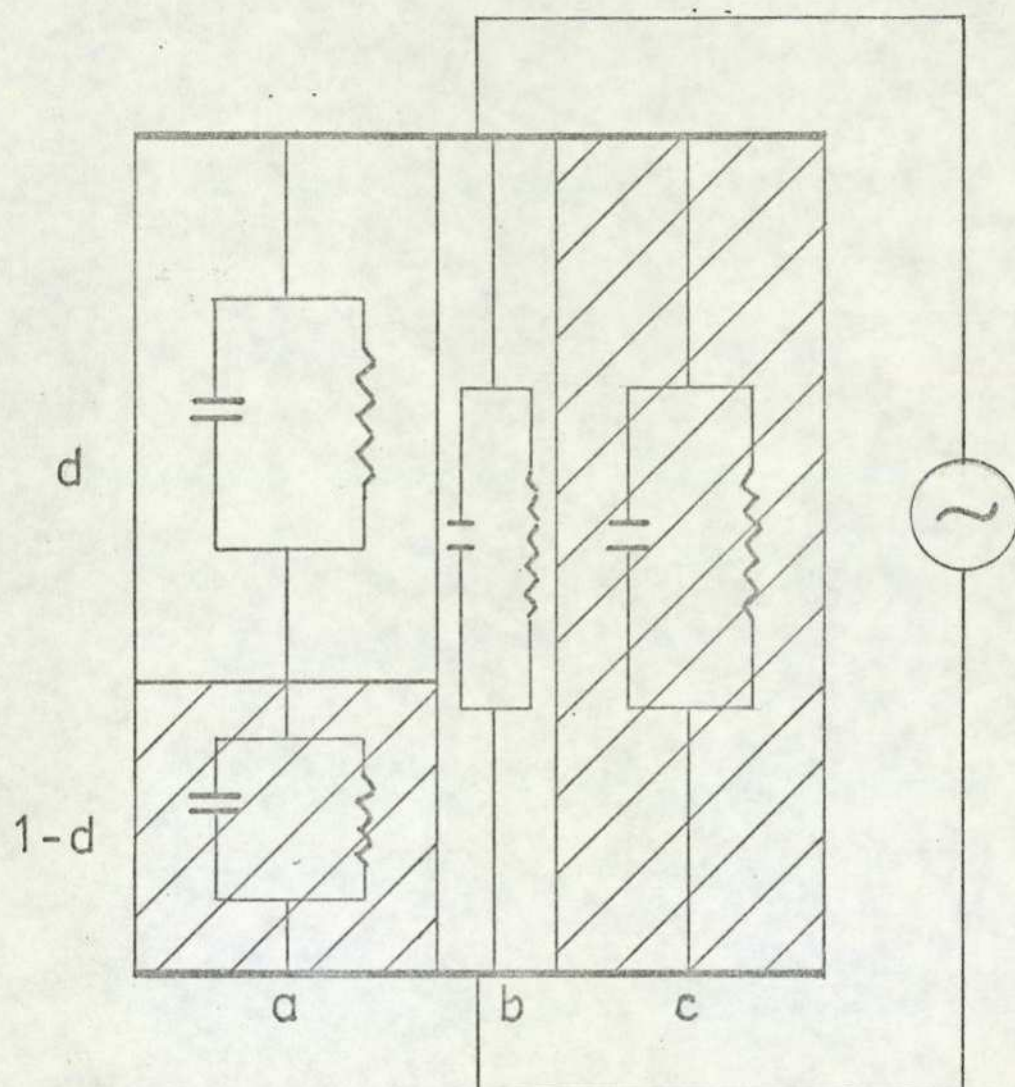


Fig. 3.3.3. Three - element AC network model

response of the model was determined as follows:

The specific admittance, Y , of the system is the sum of the admittances Y_1 , Y_2 , and Y_3 of the three elements 1, 2, and 3 respectively

$$Y_1 = \left[\frac{1-d}{(a k_s + i\omega a \epsilon_v \epsilon_s)} + \frac{d}{(a k_r + i\omega a \epsilon_v \epsilon_r)} \right]^{-1} \quad (3.3.12)$$

$$Y_2 = b k_r + i\omega b \epsilon_v \epsilon_r \quad (3.3.13)$$

$$Y_3 = c k_s + i\omega c \epsilon_v \epsilon_s \quad (3.3.14)$$

$$Y = Y_1 + Y_2 + Y_3$$

where ω is the angular frequency.

Separating imaginary and real parts (LePage 1952), the following expressions for the dielectric constant ϵ' and the specific conductivity k of the system are obtained

$$\epsilon' = \frac{a}{d(1-d)S} \left[\frac{\epsilon_r k_s^2}{1-d} + \frac{\epsilon_s k_r^2}{d} + \omega^2 \epsilon_v^2 \left(\frac{\epsilon_r \epsilon_s^2}{1-d} + \frac{\epsilon_s \epsilon_r^2}{d} \right) \right] + b \epsilon_r + c \epsilon_s \quad (3.3.15)$$

$$k = \frac{a}{d(1-d)S} \left[\frac{k_r k_s^2}{1-d} + \frac{k_s k_r^2}{d} + \omega^2 \epsilon_v^2 \left(\frac{k_r \epsilon_s^2}{1-d} + \frac{k_s \epsilon_r^2}{d} \right) \right] + b k_r + c k_s \quad (3.3.16)$$

$$S \equiv \left(\frac{k_s}{1-d} + \frac{k_r}{d} \right)^2 + \omega^2 \epsilon_v^2 \left(\frac{\epsilon_s}{1-d} + \frac{\epsilon_r}{d} \right)^2 \quad (3.3.17)$$

In addition to the use of isoconductance point method in determining the conductance k_r of the wet resin, Sachs & Speigler used another indirect method to determine the dielectric constant of the solid wet resin. The value of the dielectric constant of the system at the highest frequency used (ϵ_∞), was taken as ϵ_r . An expression for ϵ_∞ was derived from Eq. 3.3.15, i.e.,

$$\epsilon_\infty = \frac{a \left(\frac{\epsilon_r \epsilon_s^2}{1-d} + \frac{\epsilon_s \epsilon_r^2}{d} \right)}{d(1-d) \left(\frac{\epsilon_s}{1-d} + \frac{\epsilon_r}{d} \right)} + b \epsilon_r + c \epsilon_s \quad (3.3.18)$$

Arulandan and Mitra (1970) applied the three-element electrical network model to clay-water-electrolyte systems in the radio frequency range (0.5×10^6 to 10^8 Hertz), as an attempt to characterise such systems in terms of the micro-structural and compositional factors. Realizing that this model has been originally suggested for ion-exchange resin solution systems, these authors resorted to an optimization computer programme to determine the values of the geometrical parameters of the model, a , b , c , d ($c = 1-a-b$) as well as the material constants, ϵ_r , k_r , and k_s such that the frequency dispersions of the dielectric constant and conductivity calculated from Eqs. 3.3.15-16 fit the experimental results as well as possible. The remaining parameter, ϵ_s , was kept constant. In order to use the optimization programme, initial values for the parameters were needed. Therefore, Arulanandan and Mitra assumed approximate initial values as follows:

ϵ_s - the dielectric constant of solution as equal to that of pure water (78)

b - the contact area of particles was taken 0.01

c - the area of pore fluid cross-section was taken as $(2/3) \times$ porosity.

d - the height of the solid part of element 3 (particle - solution in series) was assumed 0.5.

k_r - the conductivity of wet particles was assumed a value close to the isoconductivity value as suggested by Sauer, et al. (1955)

ϵ_r - the dielectric constant of wet particles was assumed a value obtained from Eq. 3.3.18 using the dielectric constant of the soil at 10^8 Hertz, where the dielectric constant levels off, as a value for ϵ_∞ (Sach, et al., 1964), and $a = 1-b-c$.

Although Arulanandan and Mitra (1970) noted that the choice of six seemingly random parameters might be enough to fit almost any set of curves and that the physical meaning of the results would seem doubtful, yet they suggested that only the three independent geometrical

parameters were genuine unknowns.

Smith (1971), in a work very similar to that of Arulandan and Mitra (1970), applied the three-element electrical network model to clay-water-electrolyte systems in the radio frequency range ($10^6 - 10^8$ Hertz). Smith suggested that the model could be used to represent numerically the heterogeneous nature of saturated porous systems in terms of the geometrical parameters of the model.

Smith investigated the ability of the model to measure the compositional and fabric changes associated with the curing of kaolinite soil-cement and reported that, contrary to current interpretations, the major portion of the hydration of the cement particle occurs during the first few days of curing. Smith, therefore, suggested that the macroscopic model may find value as an indicator test for relative strength increases in soil-cement.

Although Smith concluded that the relaxation mechanism causing dielectric and conductivity dispersion in the system under consideration is of the Maxwell-Wagner type, yet he has used the concept of wet particles as representing the single phase of solids, and suggested that the primary particles in the consolidated clay mass are arranged in clusters, packets or domains.

The work of Smith was summarized and reported in a later paper by Arulanandan and Smith (1973).

Backer and Watillon (1973) investigated the dielectric constant and conductivity dispersion of pyrex-water-electrolyte systems in the frequency range (5 Hertz - 10^7 Hertz) using an equivalent electrical network model. In this model, Fig.3.3.4, Backer and Watillon represented the electrodes effect by a capacitance which decreases to a negligible

value at high frequencies, and the self inductance of the cell and transmission line by an inductance which increases to a considerable value only at high frequencies.

Analysis of the experimental data led these authors to characterise the dielectric dispersion as a Debye mechanism. Backer and Watillon suggested that the double layer (at the electrodes) may be considered as a third phase of the system.

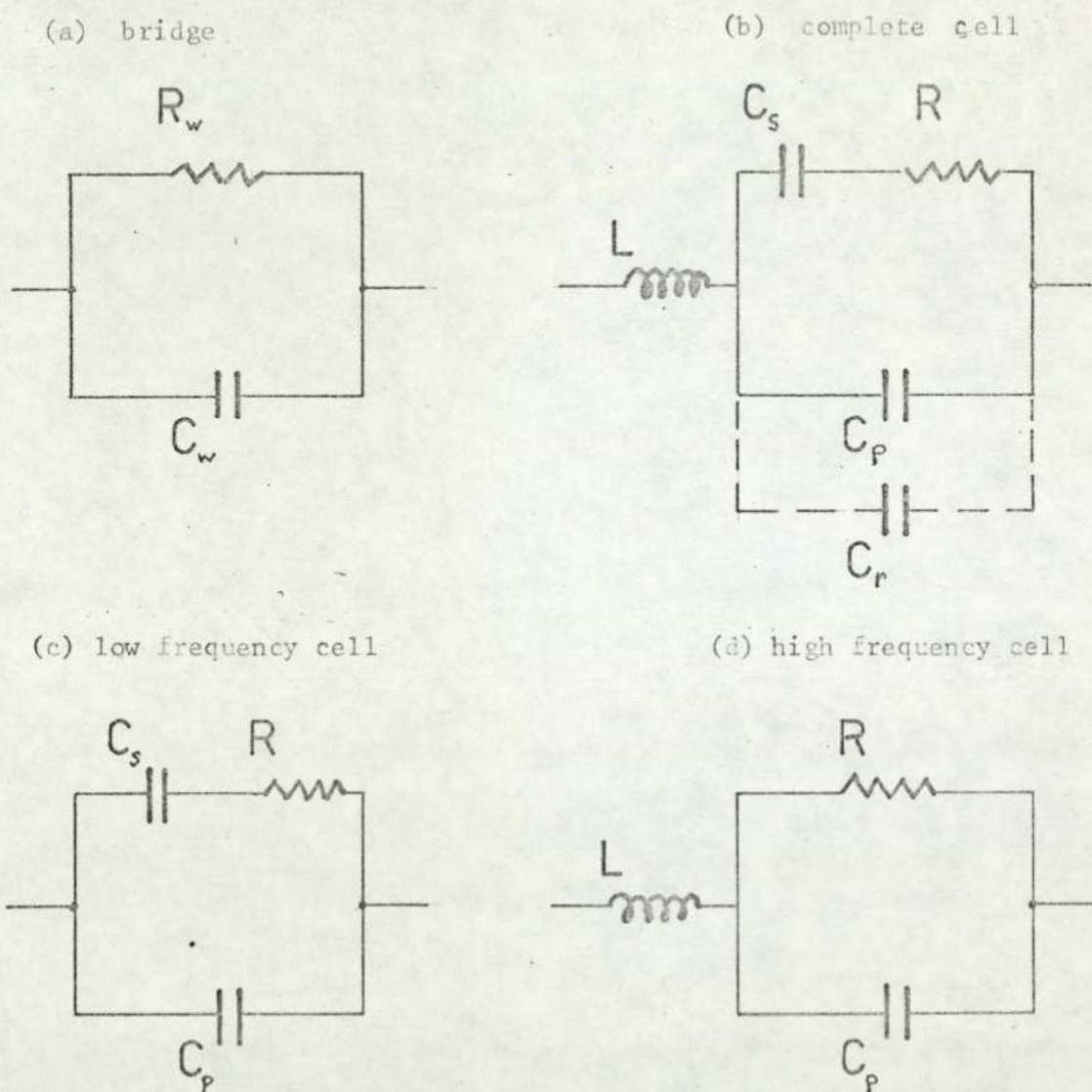


Fig. 3.3.4 Equivalent circuit of porous plugs

(Backer & Watillon, 1973)

3.4 DISCUSSION

The review of previous studies shows that the present situation in the field of soil investigation by the electrical dispersion technique is rather chaotic. This thesis will be an attempt at clarification.

The application of the electrical dispersion technique to the specific field of consolidated soil-water-electrolyte system has been carried out by a few investigators, namely; Basu and Arulanandan(1973), Mitchell and Arulanandan(1968), Arulanandan and Mitra(1970), Scharlin (1971), and Smith(1971).

Basu and Arulanandan(1973) described the electric dispersion in soil systems in terms of Maxwell-Wagner theory, Mitchell and Arulanandan(1968) attributed the dispersion to the adsorbed phase polarization, and all the other investigators resorted to electrical network analogous models.

In fact all the soil investigations by electrical network analogy were based on one and the same three-element model which was originally suggested by Wyllie and Southwick(1954). To apply the model to the complicated field of soil systems, several assumptions were inevitable resulting in possible inaccuracies which arose from the following specific considerations:

- 1) To represent the nonconductive solid phase by an RC electrical circuit whose conductivity is $1/R$, the solid particles were described as "wet particles" whose electrical properties cannot be directly determined, and thus more assumptions became necessary.

In fact these wet particles are equivalent to the solid particles together with the adsorbed layer, and, therefore, a model that specifically and adequately represents the admittedly very important adsorbed layer (on fine grained soils) would be more advantageous.

2) To allow for a solution layer in series combination with the solid phase, it was suggested that the primary particles in the clay mass are arranged in clusters, packets or domains.

In consolidated clays, however, the cluster structure would not be the general case, and the existence of unequal pore sizes and discontinuous interstitial spaces is probably a more general description. Such a description may lead to a similar conclusion to that of the earlier workers, that is, a part of the pore solution is in series combination with the solid phase, without, however, implying that the soil system has a cluster structure. The solid phase of the model will then be in series combination (see Sec.4.1.2) with a layer of the pore solution whose volume may be determined in terms of factors such as porosity, particle shape, orientation, internal surface area, adsorbed layers thickness, and rigid bonding.

3) A third element in the three-element model adopted by earlier workers was considered to be the current path through solid particles in contact with each other, and values of the contact area were reported as 0.01 - 0.02 of the total area of the cross-section of the soil sample (Smith, 1971).

If it was possible that such a path through solid particles could exist, it would probably be a nonconductive path since the solid particles are assumed to be nonconductive, and if these solid particles were also considered to be "wet particles", it would be rather difficult to distinguish between the current path through these wet particles and that through the solution and particles in series.

Furthermore, suggesting that the clay possesses a clustered structure does not agree with the assumed current path through contact areas of particles, and renders the sum of all contact areas far below

the reported values and of quite a negligible magnitude. It is relevant to note that Olsen(1961) derived a relationship for the conductivity of a clustered system by considering three current flow paths: a) through the large pores between the clusters; b) through a path that alternately passes through and between the clusters; and c) through a path that passes through the clusters at their points of contacts. Olsen then concluded that the contribution of the third path has to be ignored after finding it to be negligible when contact areas between the clusters are less than 10 per cent.

4) The theoretical response of the three-element model is independent of the direction of flow of electric current through the sample, and the use of an optimization computer programme to determine the parameters of the model that fit the experimental observation would not give much credit to the model itself. This can be easily demonstrated by the ability of the optimization programme to compute two groups of parameters that fit the two different electrical dispersion curves obtained experimentally in two different directions of one sample represented by the same model.

CHAPTER 4

DEVELOPMENT OF A NEW MODEL

4.1 SOIL-WATER-ELECTROLYTE SYSTEM

4.1.1 Phases of the System

The preceding review indicates that the soil-water-electrolyte system may be reasonably divided into three phases:

4.1.1.1 The solid phase

This represents the solid particles of the soil. Its volume can be determined theoretically from the void ratio value or from the total water content, comprising both the free and adsorbed water, in the case of saturated soils.

For saturated soils, the void ratio

$$e = \frac{\bar{m} \times G}{100} \quad (4.1.1.)$$

where $\bar{m}$ is the total moisture content (per cent), G is the bulk density of the solid particles. The porosity p is given by

$$p = \frac{e}{1 + e} \quad (4.1.2)$$

The volume of solid particles, V_r , in a unit volume of soil

$$V_r = 1 - p \quad (4.1.3)$$

The internal surface area of particles A_s , in a unit volume of soil

$$A_s = V_r \cdot G \cdot S \quad (4.1.4)$$

where S is the specific surface area of particles (per unit weight).

4.1.1.2 The pore fluid phase

This is the liquid filling up the pores in soils. It is described as free or unaffected by the electrostatic or other forces of the solid particles, and it constitutes a part of the total moisture in the soil.

The volume of the total moisture, V_m , in a unit volume V of soil is given by:

$$V_m = p \times e = V - V_f \quad (4.1.5)$$

where e is the average density of pore fluid and adsorbed water.

If V_d is the volume of the adsorbed phase, then the volume of the pore fluid V_f is given by

$$V_f = V_m - V_d \quad (4.1.6)$$

4.1.1.3 The adsorbed phase

This is the part of soil moisture in close proximity to the particle because of the electrostatic and other forces of the solid particles. It, therefore, has an important influence on the behaviour of fine grained soil in general and a significant impact on its electrical properties. This phase may be found in literature under many names such as; electric double layer, diffuse double layer, ionic double layer, electrical diffuse layer, and ionic atmosphere, which causes confusion. Therefore, throughout this thesis, it will be referred to as "adsorbed layer" for it is believed that this is the most relevant name.

The characteristics of the adsorbed layer may be summarized as follows:

4.1.1.3.1 It comprises mainly adsorbed cations and water molecules. In clays, where the particle surface is principally possessed of a negative charge, the counterions are cations, and the water molecules are adsorbed by three mechanisms one of which is due to hydrogen bonding to the clay surface and two due to dipolar attraction to the adsorbed cations and to the negatively charged surface.

4.1.1.3.2 The concentration of adsorbed cations and the strength of adsorption decrease sharply with the distance from the clay surface. However, for the purpose of the investigation it is considered to be an advantage if the adsorbed phase is assumed to be subdivided into two layers, having no distinct boundary between them.

1) Strongly adsorbed layer

This is the innermost part of the adsorbed layer close to the surface in which most of the counterions are concentrated and the adsorption forces exert their stronger influence. The thickness t_f of the strongly adsorbed layer may be estimated as; the radius of a hydrated adsorbed cation, the thickness of two water monomolecular layers, or $5\text{\AA}$. The significantly different properties of this layer from those of water are attributed mainly to the more ordered structure of the adsorbed molecules despite the fact that counterions tend in some cases to disrupt this order. It is generally described as having either a two-dimensional fluid or a solid-like (ice) structure. The surface area covered by this layer may be assumed as equal to the internal surface area A_s (Eq.4.1.4), thus its volume V_{fd} is given by

$$V_{fd} = t_f \times A_s \quad (4.1.7)$$

2) Weakly adsorbed layer

The remaining part of the adsorbed layer represents an intermediate layer between the strongly adsorbed layer and the pore fluid. Its thickness may be considered as approximately equal to the "characteristic length" in the Debye-Huckel theory (Mitchell, 1961) of strong electrolytes (which is appreciated as strictly applicable to dilute colloidal suspensions), i.e.

$$t_w = \left(\frac{\epsilon k T}{8\pi n e^2 v^2} \right)^{1/2} \quad (4.1.8)$$

where t_w is the thickness of the weakly adsorbed layer, ϵ is the dielectric constant of this layer, n the electrolyte concentration in ions/cm³, e is the electronic charge, v is the valence of ions, k is Boltzmann constant, T is the absolute temperature.

The author, after numerous application of this formula, suggests the following modification in order to account for the high local concentration of counterions in the close proximity of the clay surface and also for the inevitable existence of co-ions (usually anions in the case of clay) within the adsorbed layer.

$$t_w = \left(\frac{\epsilon k T}{8\pi n e^2 v^2} \right)^{1/2} \cdot C \quad (4.1.9)$$

where $C = \ln(10^3 N) \left(\frac{v_1 + v_2}{2} \right)^{1/2}$

in which N is the normality of the pore fluid, v_1 and v_2 are the valencies of counterion and co-ion respectively.

Similar to the strongly adsorbed layer, the volume V_{wd} of the weakly adsorbed layer may be defined as

$$V_{wd} = t_w A_s \quad (4.1.10)$$

4.1.1.3.3 The total volume V_d of the adsorbed layer may be given theoretically as the sum of its two sub-layers given by Eqs.4.1.7 and 10.

$$\begin{aligned} V_d &= V_{fd} + V_{wd} \\ &= (t_f + t_w) A_s \\ &= t A_s \end{aligned} \quad (4.1.11)$$

where t is the total thickness of the adsorbed layer.

This thickness has been reported by different authors in a wide range of values, as for example:

Terzaghi and Peck(1948),	$t = 50 - 1000 \text{ \AA}$
Foster(1948),	$t = 4 \text{ \AA}$
Baver,et al(1961),	$t = 8 \text{ \AA}$ (kaolin), $68 \text{ \AA}$ (montmorillonite)
Spiel(1940),	$t = \text{several hundred angstroms}$
Grim(1968),	$t = 7.5$ (Na montmorillonite)

Almost all the values of t obtained in this investigation, by applying the suggested equation 4.1.9, are inside one hundred angstroms with the vast majority of them less than $30 \text{ \AA}$.

4.1.2 Geometrical Representation of the System

Fig.4.1.1 shows a unit volume of the soil system divided into the three phases described above, i.e., the solid phase, V_s , the pore fluid phase, V_f , and the adsorbed phase, V_d (comprising the two sublayers; strongly adsorbed, V_{fd} , and weakly adsorbed, V_{wd}), all in parallel. Knowing that the adsorbed layers are physically associated with the solid phase, since the pore fluid is expelled under mechanical pressure while the adsorbed layers are not, it would be more relevant to redistribute the three phases so that the adsorbed layers will be in series with the solid phase to form a three-layer phase in parallel with the pore fluid, Fig.4.1.2.

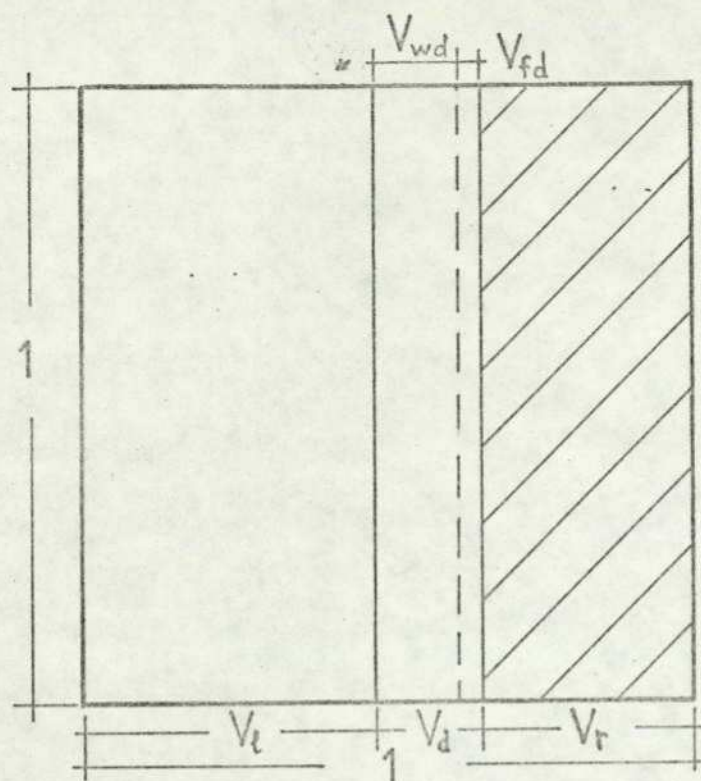


Fig. 4.1.1. Volumetric distribution of a unit volume of soil

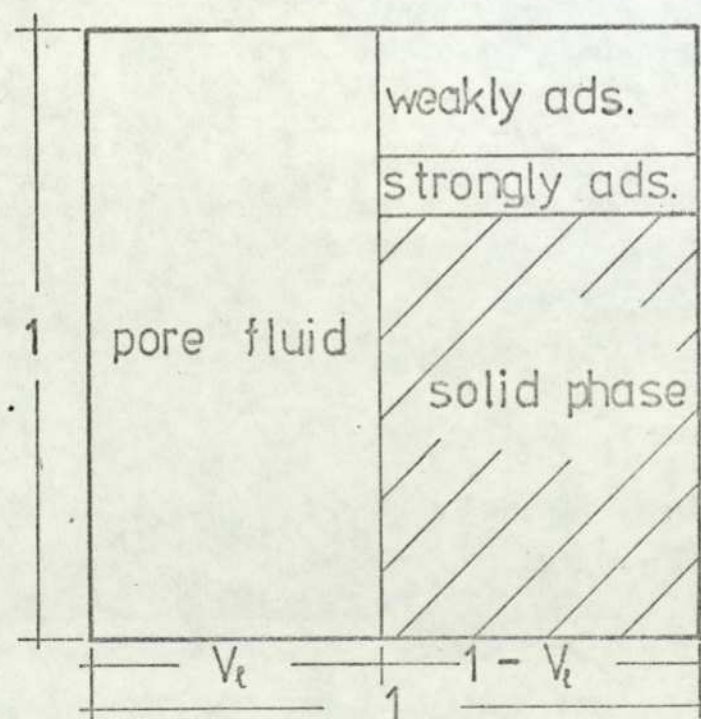


Fig. 4.1.2 Geometrical arrangement of phases

Furthermore, knowing that the geometry of the system has a significant effect on its electrical response, it is necessary to represent the geometrical configuration of the system in three dimensions. For this purpose a geometrical arrangement which is in agreement with the basic concepts of Maxwell-Wagner two-layer and n-layer model is proposed. In such models, the sequence of layers or the dispersion of particles has no effect on the complex dielectric constant of the system as long as the relative amounts of media 1 and 2 remain the same (see Secs. 2.3.1 & 3.1).

Therefore, the author introduces the concept of "linear porosity" which may be defined as the linear component of the volume porosity if it was resolved in three mutually perpendicular directions.

If for simplicity we assume that the volume porosity is equally distributed over the three dimensions, the linear porosity, $\bar{p}$, will be given by (Fig.4.1.3)

$$\bar{p} = 1 - (1 - p)^{1/3} \quad (4.1.12)$$

where p is the volume porosity.

The solid phase then becomes a cube of volume = $(1-p)$, and from the geometry of Fig.4.1.3 it is seen that:

$$d_f = (1 - p)^{1/3} = 1 - \bar{p} \quad (4.1.13)$$

$$d_f = V_f / (1 - \bar{p})^2 \quad (4.1.14)$$

$$d_w = V_w / (1 - \bar{p})^2 \quad (4.1.15)$$

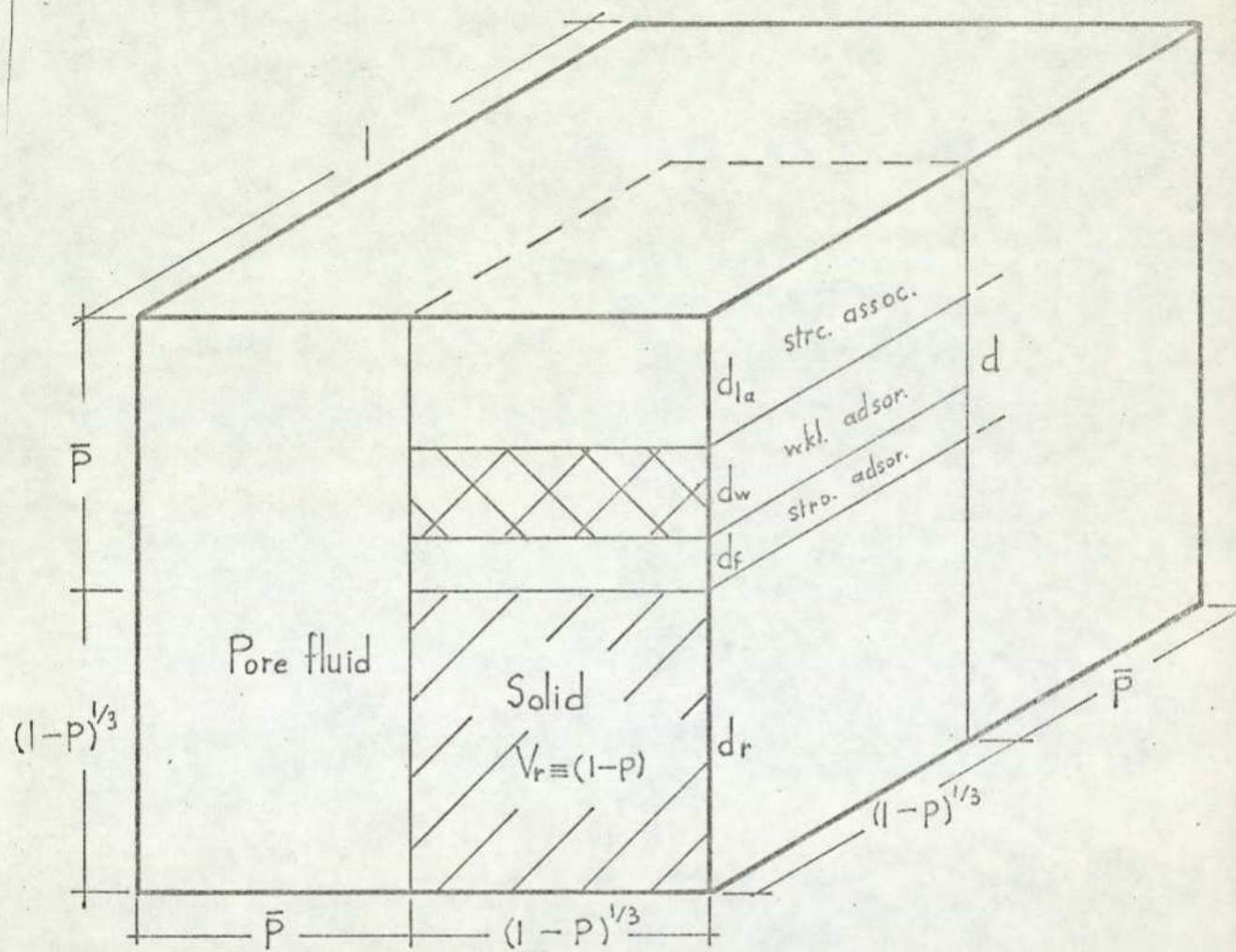


Fig. 4.1.3. Geometrical representation of soil systems

$$d = d_f + d_w = V_d / (1 - p)^{2/3} \quad (4.1.16)$$

$$d_{la} = \bar{p} - d \quad (4.1.17)$$

where d_f , d_f , d_w , d , and d_{la} are respectively the equivalent heights of the solid phase, the strongly adsorbed layer, the weakly adsorbed layer, the total adsorbed layer, and a geometrically or structurally associated part of the pore fluid which may be regarded as in series with the solid and adsorbed phase. Therefore, the system may be geometrically described as a four-layer combination (composite phase) in parallel with the pore fluid phase (Fig.4.1.3).

It should be noticed that the structurally associated pore fluid layer is not necessarily regarded as being attracted to the particle surface in any way, on the contrary, according to the assumptions made in this thesis, it is considered as completely electrostatically free. This also does not presuppose that the primary particles in the clay mass are arranged-packets, clusters, or domains, as suggested by some investigators (Smith,1971). However, the inter-layer or inter-structural-unit water in some clay minerals (e.g. montmorillonite) would be considered as a part of the structurally associated pore fluid layer.

4.1.3 Electrical Properties of the Different Phases

4.1.4.1 Pore fluid phase

Fig.4.1.3 shows that the cross-sectional area, A_1 , of the equivalent pore fluid element is given by

$$A_1 = \bar{p} (2 - \bar{p}) \quad (4.1.18)$$

The capacitance, C_1 , of this phase is given by (Sec.2.1)

$$C_1 = \epsilon_1 \epsilon_v \bar{p} (2 - \bar{p}) \quad (4.1.19)$$

where ϵ_1 is dielectric constant of the pore fluid, which depends on the concentration and type of ions (Hasted,1973). For solutions whose concentrations are of the order of 1 molar, ϵ_1 is lower than the dielectric constant of pure water by a few per cent. In the limit of low concentration the dependence of ϵ_1 upon concentration c was approximated by a linear relationship:

$$\epsilon_1 = \epsilon_{sw} + \delta c \quad (4.1.20)$$

where δ is a negative quantity known as the dielectric decrement (Appendix III), and ϵ_{sw} represents the static dielectric constant of water.

The conductance, K_1 , of this phase is given by

$$K_1 = k_1 \bar{p} (2 - \bar{p}) \quad (4.1.21)$$

where k_1 is the specific conductivity of the pore fluid, which depends on the concentration, valence, and mobility of ions, and may be calculated (Garside, et al., 1962) by

$$k_1 = \frac{c(u_+ + u_-)}{1000} \quad (4.1.22)$$

where c is the concentration of the solute in gramme equivalent/litre, u_+ , u_- are ion conductances or ionic mobilities of cations and anions respectively (Appendix III).

The associated pore fluid layer has the following electrical components (Sec.2.1)

$$C_{la} = \epsilon_l \epsilon_v (1 - \bar{p})^2 / d_{la} \quad (4.1.23)$$

$$K_{la} = k_l (1 - \bar{p})^2 / d_{la} \quad (4.1.24)$$

where C_{la} and K_{la} are the conductance and capacitance of the associated pore fluid layer respectively.

4.1.3.2 Solid phase

Fig.4.1.3 shows that the cross-sectional area of the equivalent solid phase is $(1-p)^{2/3}$ and its height is $(1-p)^{1/3}$. Therefore, the capacitance, C_r , and conductivity, K_r , of this phase are given by:

$$C_r = \epsilon_r \epsilon_v (1 - \bar{p}) \quad (4.1.25)$$

$$K_r = k_r (1 - \bar{p}) \quad (4.1.26)$$

where ϵ_r and k_r are the dielectric constant and conductivity of the solid particles respectively.

ϵ_r values for soil particles have been reported by several investigators in the range of 2-10 (Low,1961; Hasted,1973; Banerjee,1938) and a value of 10 - 4 is adopted throughout this thesis.

k_r is known to be practically negligible for dry soil particles. However, for an absolutely general representation, the

solid phase is described by the two electrical components. k_T in this case is assumed to be of the order of magnitude of 1×10^{-16} mho/cm.

4.1.3.3 Adsorbed phase

4.1.3.3.1 Introduction

Two types of polarization mechanisms may take place within the adsorbed layers. The first is due to the formation of the so-called molecular capacitor (van Olphen, 1963), by the accumulation of counterions and water molecules on the charged surface of particles, whereas the second is due to the adsorbed phase polarization (Murphy and Lowry, 1930) as the applied field tends to displace counterions and molecules which are "anchored" to the surface.

In view of these characteristics, the author suggests the concept of dual representation of the adsorbed layers:

1) Perpendicular to the surface of the particle, an element representing the adsorbed layer, and in series combination with the solid particles phase, will have the two electrical components;

A capacitance which is essentially attributed to an instantaneous polarization of negligible relaxation time, i.e., it persists at all frequencies.

A conductance which in the direction perpendicular to the particle surface may be mainly attributed to electrons.

2) Parallel to the surface of the particle, an element representing the adsorbed layer, and in parallel combination with the two other phases, viz., the solid phase and the pore fluid phase, will have two electrical components:

A capacitance which is essentially attributed to a time and frequency dependent polarization, having different relaxation times for different adsorbed layers depending on their distance from particle surface, the size of the adsorbed ions, and the strength of the adsorptive forces. Because of its time dependency, this capacitance almost vanishes at high frequencies.

A conductance which is the sum of various contributions. In the direction parallel to the particle surface; the concentration, mobility, and valence of counterions; the characteristics of particle surface as influenced by the mineral type, the particle size and shape, the extent of particle lattice defects, the rigid bonding and cementing agents; the void ratio, and the orientation of particles with respect to the direction of current, may all affect the adsorbed layer conductivity.

However, another factor that may add to the complexity of the conductivity of the adsorbed layer is the possibility that some of the adsorbed ions may be able to escape from the "adsorptive anchors" and become desorbed or transformed into free ions that would contribute to direct current conductivity. It is thus seen that this conductance is voltage and frequency-dependent, and therefore, may explain the observed phenomena of the frequency-dependent component of surface conductance (Schwan, et al., 1962 & Schwarz, 1962).

On this basis, the author suggests that the adsorbed layer element, parallel to the particle surface may be represented by a complex impedance (Cole and Cole, 1941), and that a coefficient should be introduced to account for the various factors contributing to the parallel to the surface conductivity. This coefficient, which may be called the "Tortuosity Coefficient" is discussed below.

4.1.3.3.2 Tortuosity coefficient

Assuming an idealized model similar to that of Olsen(1962), a Tortuosity coefficient, T_θ , defined as the length of the actual path of current per unit length along the applied field vector, is proposed (Appendix IV). T_θ is given by

$$T_\theta = [1 + \delta' \sin^2 \theta' (2 + \delta')]^{1/2} \quad (4.1.27)$$

where

$$\theta' = \frac{1}{2} (1 + n) \theta \quad (4.1.28)$$

$$\delta' = \frac{1}{2} (2 - \alpha) \delta \quad (4.1.29)$$

where θ is the angle between the direction of the applied field and the normal to the applied consolidation pressure which is assumed to be the preferred orientation of the plate-like particles, and δ is the difference in length between the actual path and corresponding unit path length along the direction of the field. n is an "orientation coefficient" which depends on the valence v of counterions, their concentration N (normality), degree of rigid bonding B , and a shape factor A . It is proposed to express n exponentially by

$$n = \exp. - 0.25(v + N + 1/B + 1/A) \quad (4.1.30)$$

where B is given the value of vane strength (ton/m^2),

$$A = \frac{a + b}{2c} \quad (4.1.32)$$

a , b , and c are the lengths of the particle three principal axes. α is a "linearity coefficient" which depends on the consolidation pressure P (kg/cm^2), duration of consolidation T (days), and the pH value, and is given by

$$\alpha = \exp. - 0.001(P + T + 14 \text{ pH}) \quad (4.1.33)$$

The somewhat empirical expressions given for n and α are introduced to facilitate analysis and correlation of the data. Further statement and discussion on their development are given in chapters 7 & 8.

4.1.3.3.3 Strongly adsorbed layer

1) Perpendicular to the particle surface

The molecular capacitance of this layer is given by (Davies, et al., 1963).

$$C_f = \epsilon_f \epsilon_v A_s / t_f \quad (4.1.34)$$

where ϵ_f is the dielectric constant of the strongly adsorbed layer which is known to be very low and of the order of magnitude of the dielectric constant of ice (Palmer, et al., 1952), i.e., $\epsilon_f = 3-5$ in the mega Hz range (Auty and Cole, 1952).

However, in view of the geometrical consideration discussed above this layer is lumped in an element thickness d_f (Eq. 4.1.14), and a cross-sectional area $(1-\bar{p})^2$, therefore

$$C_f = \epsilon_f \epsilon_v (1-\bar{p})^2 / d_f \quad (4.1.35)$$

It should be noticed that the principle applied in deriving this equation is the same principle applied in Maxwell stratified capacitor (See Sec. 3.1), i.e., the sequence of the layers does not influence the dielectric behaviour of the system (van Beek, 1965).

The conductivity of this layer may be given by

$$K_f = k_1 (1-\bar{p})^2 / d_f \quad (4.1.36)$$

2) Parallel to the particle surface

The dielectric constant, ϵ_{fd} , of this layer may be estimated by making use of the approximate formula (Hasted, 1973)

$$\epsilon_{fd} = \epsilon_{sw} [1 - (b/t_f^4)] \quad (4.1.37)$$

where ϵ_{sw} is the static dielectric constant of water, t_f is the thickness of the layer in angstroms, $b = 163 \times 10^{-32} \text{ \AA}^4$.

Therefore, the static capacitance, C_{fd} , of this layer is given by

$$C_{fd} = \epsilon_{fd} \epsilon_v d_f \quad (4.1.38)$$

The complex impedance, Z_f , of this layer may be determined by using Eq. 2.4.30 (Cole and Cole, 1941). In this case $\epsilon_\infty = 0$, and

$\epsilon_0 = C_{fd} / \epsilon_v$, then

$$Z_f = \frac{\tau (i\omega\tau)^{-\alpha}}{C_{fd}/\epsilon_v} \quad (4.1.39)$$

where τ and α the relaxation time and the distribution factor respectively of the layer, their values are dependent on the properties of the layer and are expected to be of the same order of magnitude as those of ice.

Since the strongly adsorbed layer does not contribute to the DC conductivity of the system and the capacitance C_{fd} of this layer vanishes at high frequencies (see Sec. 4.1.3.3.1), the equivalent electrical components of this layer, C_{fd} and Z_f , can be determined from Eqs. 4.1.38 and 39 by assuming reasonable values for α and τ (Appendix III).

4.1.3.3.4 Weakly adsorbed layer

1) Perpendicular to the particle surface

The capacitance of this element may be calculated by making use of the following set of equations (van Olphen, 1963):

The charge, σ_1 , of the strongly adsorbed layer may be given by

$$\sigma_1 = \frac{N_1 v e}{1 + (N_A / M n) \exp[-(v e \Phi_f + \Psi) / k T]} \quad (4.1.40)$$

in which N_1 is the number of adsorption spots on 1 cm^2 of the surface, N_A is Avogadro's number, M is the molecular weight of the solvent, Φ_f is the potential on the border between the strongly and weakly adsorbed layers, and Ψ is the specific adsorption potential of the counterions at the surface.

For the strongly adsorbed layer, we find

$$\sigma_0 = \epsilon_f (\Phi_0 - \Phi_f) / 4 \pi t_f \quad (4.1.41)$$

in which σ_0 and Φ_0 are the charge density and the potential at the particle surface.

Furthermore, the charge of the weakly adsorbed layer is given by (Delahy, 1965)

$$\sigma_2 = 2 (\epsilon_w n k T / 2 \pi)^{1/2} \sinh(v e \Phi_f / 2 k T) \quad (4.1.42)$$

Finally,

$$\sigma_0 = \sigma_1 + \sigma_2$$

The capacitance, C_w , of this adsorbed layer is directly obtained by differentiating Eq. 4.1.42 with respect to Φ_f (Grahame, 1947).

$$C_w = (\epsilon_w n v^2 e^2 / 2 \pi k T)^{1/2} \cosh(v e \Phi_f / 2 k T) \quad (4.1.43)$$

where n is the concentration of pore fluid, and ϵ_w is dielectric constant of the weakly adsorbed layer which may be calculated as ϵ_1 of the pore fluid Eq.4.1.20.

Alternatively C_w may be calculated according to the geometrical model of the system

$$C_w = \epsilon_w \epsilon_v (1 - \bar{p})^2 / d_w \quad (4.1.44)$$

In the same way the conductance K_w of this layer is given by

$$K_w = k_w (1 - \bar{p})^2 / d_w \quad (4.1.45)$$

2) Parallel to the particle surface

In analogy to the strongly adsorbed layer, the capacitance, C_{wd} of the weakly adsorbed layer is given by

$$C_{wd} = \epsilon_{wd} \epsilon_v d_w \quad (4.1.46)$$

where ϵ_{wd} is determined by the same expression (4.1.37).

The DC conductivity of the whole adsorbed phase parallel to the particle surface is attributed solely to the conductivity of the weakly adsorbed layer, K_{wd} , which is significantly affected by the tortuosity coefficient, T_θ , of the system in the direction of flow of the electric current. It is therefore given by the expression

$$K_{wd} = \lambda A_s / T_\theta^2 (1 - \bar{p})^2 \quad (4.1.47)$$

where λ is the specific surface conductivity of the solid particles which is of the order of magnitude of 10^{-9} mho (see Sec.3.2), and T_θ is the tortuosity coefficient (Eq.4.1.27).

4.2 DEVELOPMENT OF THE ELECTRICAL MODEL

The preceding section shows that the soil-water-electrolyte systems may be reasonably represented by micro-structural and compositional elements and parameters. Therefore, the representation of these elements and parameters by analogous electrical elements would be acceptable, as long as the representation is seen to be relevant and the electrical network is consistent with the experimental observations.

4.2.1 Equivalent Electrical Elements

4.2.1.1 Pore fluid phase

This phase is represented by a simple RC parallel circuit. This is justified by the fact that the critical frequency and consequently the dispersion would be out of the frequency range used. The values of the capacitance, C_1 , and resistance (reciprocal of the conductance K_1) are already determined by Eqs. 4.1.19 & 21.

The part of the pore fluid which is associated with the other two phases, is also represented by a simple RC parallel circuit of capacitance C_{1a} and conductance K_{1a} as given by Eqs. 4.1.23 & 24.

4.2.1.2 Solid phase

The critical frequency of the solid material is known to be in the kilo-cycle range, i.e., it is far removed from the frequency range used in this investigation (Keymenlen, 1956; Keymenlen, et al., 1957). Therefore, the solid phase is well represented by an RC parallel circuit. Values of the capacitance, C_r , and the conductance, K_r , are given by Eqs. 4.1.25 & 26.

4.2.1.3 Adsorbed phase

4.2.1.3.1 Strongly adsorbed layer

Normal to the particle surface, this layer is represented by an RC parallel circuit whose components are given by Eqs. 4.1.35 & 36. However, as was shown in 4.1.3.3.1 the conductance of this layer normal to the particle surface is mainly attributed to electrons and therefore it may be neglected. In this case the RC circuit is reduced to a capacitance C_f .

Parallel to the particle surface, this layer exhibits the adsorbed phase polarization and is represented by a circuit including a complex impedance element as given by Eqs. 4.1.38 & 39.

4.2.1.3.2 Weakly adsorbed layer

Similarly to the strongly adsorbed layer, the weakly adsorbed layer is represented by two circuits. Normal to the particle surface the weakly adsorbed layer is represented by a capacitance C_w , whereas parallel to the particle surface, a series RC circuit whose components are given by Eqs. 4.1.46 & 47 is suggested.

4.2.2 Equivalent Electrical Network

Fig. 4.2.1 shows the electrical network model that represents all the micro-structural and compositional parameters discussed so far.

The electrical response of this model may be determined as follows:

Element 1: Comprises the four parallel circuits in series array.

Elementary network analysis (Guillemin, 1953) shows that a series array of parallel circuits may be expressed in terms of an equivalent series combination of a resistance and a reactance. Therefore, the impedance,

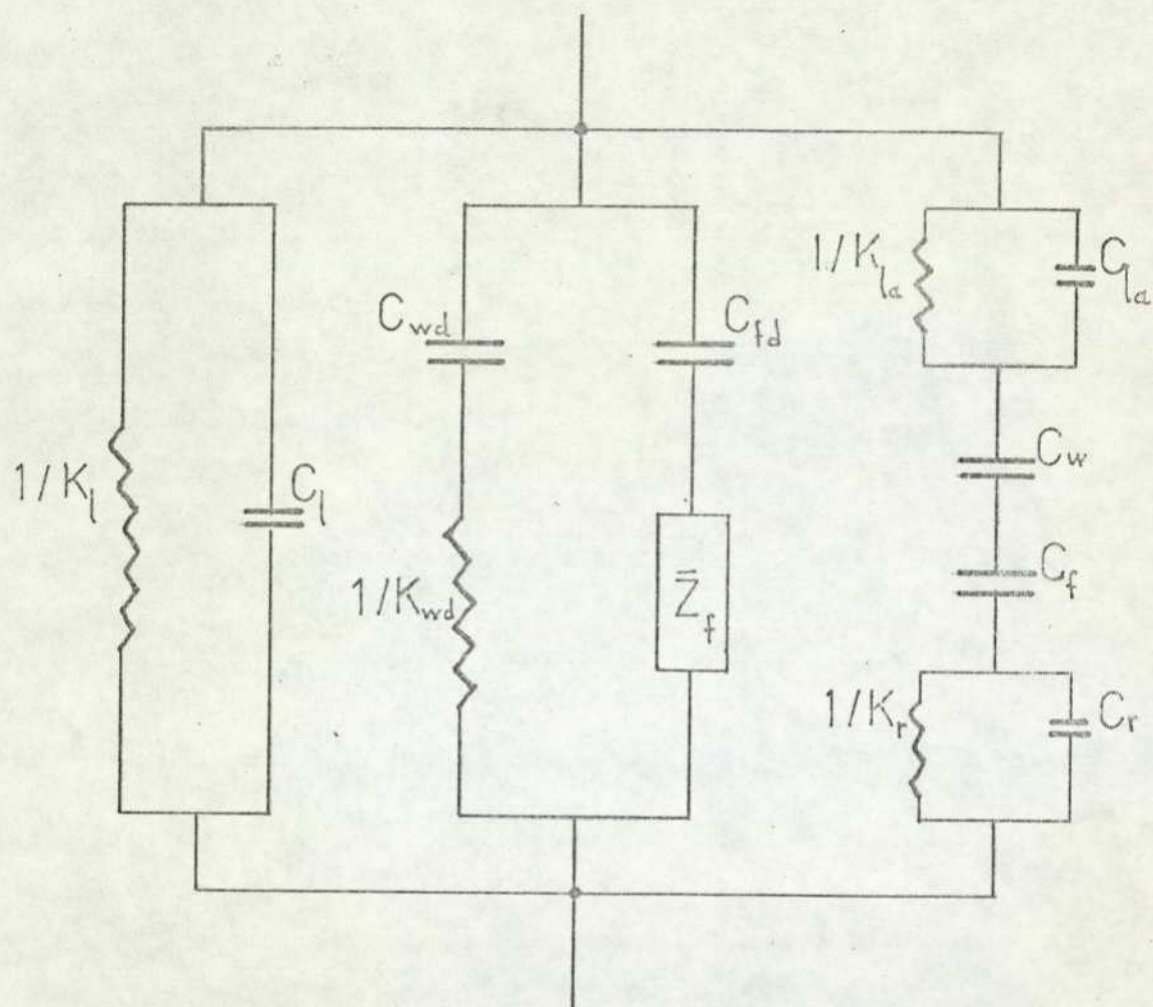


Fig. 4.2.1 The new electrical network model
proposed by the author

Z , of element 1 may be determined by the following equations.

$$Z = X - i\omega Y \quad (4.2.1)$$

$$X = \frac{K_r}{K_r^2 + (\omega C_r)^2} + \frac{K_{la}}{K_{la}^2 + (\omega C_{la})^2} \quad (4.2.2.)$$

$$Y = \frac{C_r}{K_r^2 + (\omega C_r)^2} + \frac{1}{\omega^2 C_f} + \frac{1}{\omega^2 C_w} + \frac{C_{la}}{K_{la}^2 + (\omega C_{la})^2} \quad (4.2.3)$$

The equivalent series capacitance, C_c , and conductance, K_c , of element 1 are

$$C_c = \frac{1}{\omega^2 Y} \quad (4.2.4)$$

$$K_c = \frac{1}{X} \quad (4.2.5)$$

The equivalent parallel capacitance and conductance $\bar{C}_c$ and $\bar{K}_c$ of this element are thus

$$\bar{C}_c = \frac{C_c K_c^2}{K_c^2 + (\omega C_c)^2} \quad (4.2.6)$$

$$\bar{K}_c = \bar{C}_c \omega^2 C_c / K_c \quad (4.2.7)$$

Element 2: The strongly adsorbed layer in the direction parallel to the particle surface.

According to equations 4.1.38 & 39, the capacitance, $\bar{C}_f$, and conductance, $\bar{K}_f$, of this layer may be given by:

$$\bar{C}_f = \frac{1}{2} C_{fd} \left[1 - \frac{\sinh x(1-\alpha)}{\cosh x(1-\alpha) + \sin(\alpha\pi/2)} \right] \quad (4.2.8)$$

$$\bar{K}_f = \frac{\omega}{2} C_{fd} \left[\frac{\cos(\alpha\pi/2)}{\cosh x(1-\alpha) + \sin(\alpha\pi/2)} \right] \quad (4.2.9)$$

where $x = \ln(\omega\tau_0)$

Element 3: The weakly adsorbed layer in the direction parallel to the particle surface. This is represented by a series circuit whose components C_{wd} and K_{wd} are given by Eqs.4.1.46 & 47.

The equivalent parallel capacitance, $\bar{C}_w$, and the equivalent parallel conductance, $\bar{K}_w$, of this circuit are given by:

$$\bar{C}_w = \frac{C_{wd} K_{wd}^2}{K_{wd}^2 + (\omega C_{wd})^2} \quad (4.2.10)$$

$$\bar{K}_w = \bar{C}_w \omega^2 C_{wd} / K_{wd} \quad (4.2.11)$$

Element 4: The pore fluid phase.

This is a simple RC circuit whose components C_1 and K_1 are given by Eqs.4.1.23 & 24.

Finally, the capacitance, C_m , and conductance K_m , of the whole network model are readily given according to Eqs.4.1.23 - 24, 4.2.6-11, by:

$$C_m = \bar{C}_c + \bar{C}_f + \bar{C}_w + C_1 \quad (4.2.12)$$

$$K_m = \bar{K}_c + \bar{K}_f + \bar{K}_w + K_1 \quad (4.2.13)$$

from which the dielectric constant, ϵ'_m , and the dielectric loss factor, ϵ''_m , are found

$$\epsilon'_m = \frac{C_m}{\epsilon_v} \quad (4.2.14)$$

$$\epsilon''_m = \frac{K_m}{\omega \epsilon_v} \quad (4.2.15)$$

Expressions 4.2.13-15 for K_m , ϵ'_m , and ϵ''_m , are the theoretical electrical responses of the suggested electrical network model. They have been compared, in accordance with conventional practice, with the observed experimental responses of the physical system (clay-water-electrolyte) in order to assess the validity of the model. Such evaluation of the applicability of the model is presented in Chapter 7.

CHAPTER 5

EXPERIMENTAL PROGRAMME

5.1 EXPERIMENTAL EQUIPMENT AND PROCEDURE

5.1.1 Apparatus

The measuring instrument is an "RX Meter", type 250B (Boonton Radio Corporation, Division of Hewlett-Packard, Rockway, New Jersey). It is a bench type, self-contained instrument designed to permit measurement of equivalent parallel resistance and parallel reactance of two-terminal networks over the frequency range of 500 kHz to 250 MHz. The instrument includes a continuously tuned oscillator, high frequency bridge (Schering), mixer, amplifier-detector, null indicating meter, and regulator power supply (Fig.5.1.1). The frequency ranges are in 8 bands; 0.5 to 1 MHz, 1 to 2 MHz, 2 to 4 MHz, 4 to 9 MHz, 9 to 21 MHz, 21 to 48 MHz, 48 to 110 MHz, and 110 to 250 Mhz.

Resistance measurement range : 15 to 100,000 ohms.

Capacitance measurements range : 0 to 20 pF.

Inductance measurement range : 0.001 μ H to 100 mH.

5.1.2 The Electrical Measurement Cell.(Fig.5.1.2)

The cell is based on the well-known principle of vectorial subtraction of impedences measured at different electrode distances (Mandel and Jenard,1963). In this manner the impedance of the transmission line and electrode polarization effects can be eliminated from the final results. Therefore, the main feature of the cell and its connections is that the path length of the current is kept constant

irrepective of the inter-electrode distance and that the geometry of the transmission line remains almost unchanged.

The cell (1) is made of a hollow perspex cylinder (inner diameter 16mm, outer diameter 50mm, and height 50mm) designed as a part of the consolidation mould (Section 5.1.3) to avoid any disturbance to the soil sample when the cell is connected to the RX Meter after consolidation, Fig.5.1.3. The elements of the transmission line are made of brass and the two electrodes (5,7) are entirely plated with platignum. An O-ring, fitted to a thin plate having a grooved edge (13), is placed under the lower electrode to ensure water tightness.

A scale is engraved on both the upper electrode post (6) and the vertical post (9). These scales together with the perspex flange (2), which is graduated and can be screwed onto the lower electrode post (4), to act as a micrometer, are used to produce any required variation in the length of the transmission line. If, for instance, the upper electrode is lowered a distance L to reduce the sample height the same length L , then the horizontal rod (8) can be lowered a distance $L/2$ to compensate for the change in the length of the transmission line (Fig. 5.1.8).

A perspex three-pronged cap (3), which can glide along the upper electrode post, helps to align the upper electrode quickly, to trim the extruded part of the sample easily, and to fix the whole assembly in position when it is engaged in the three notches in the upper end of the cell.

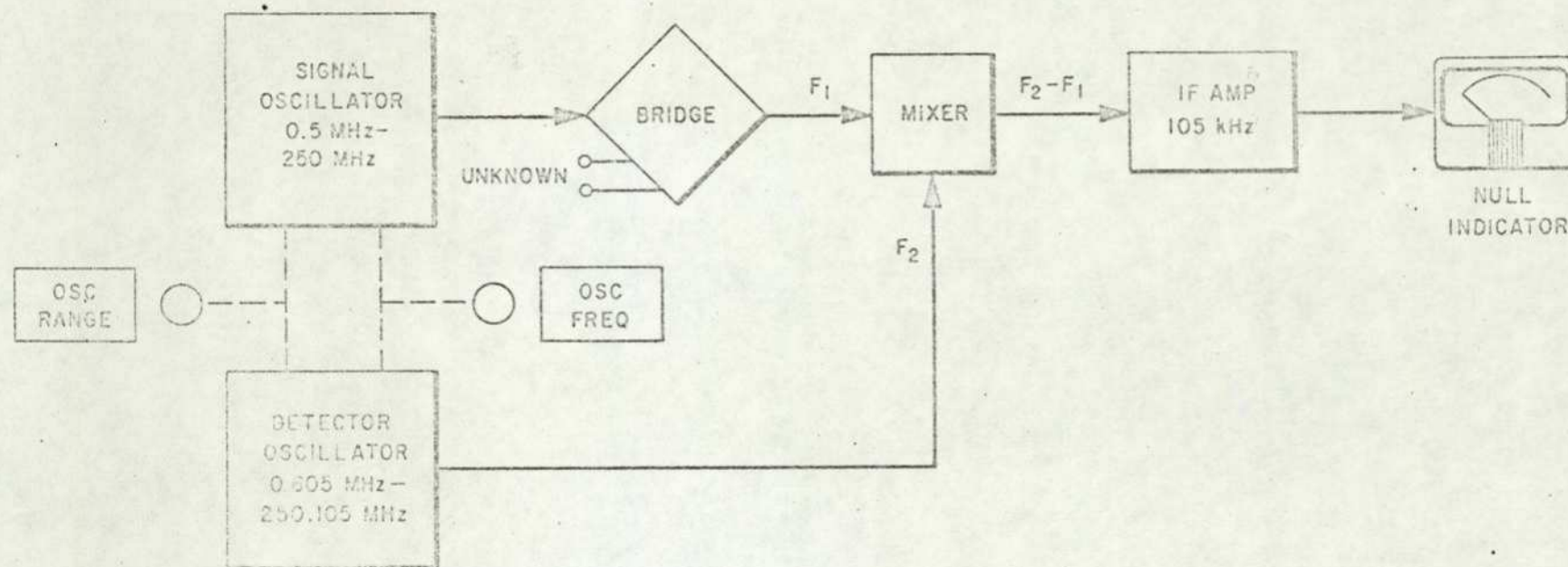
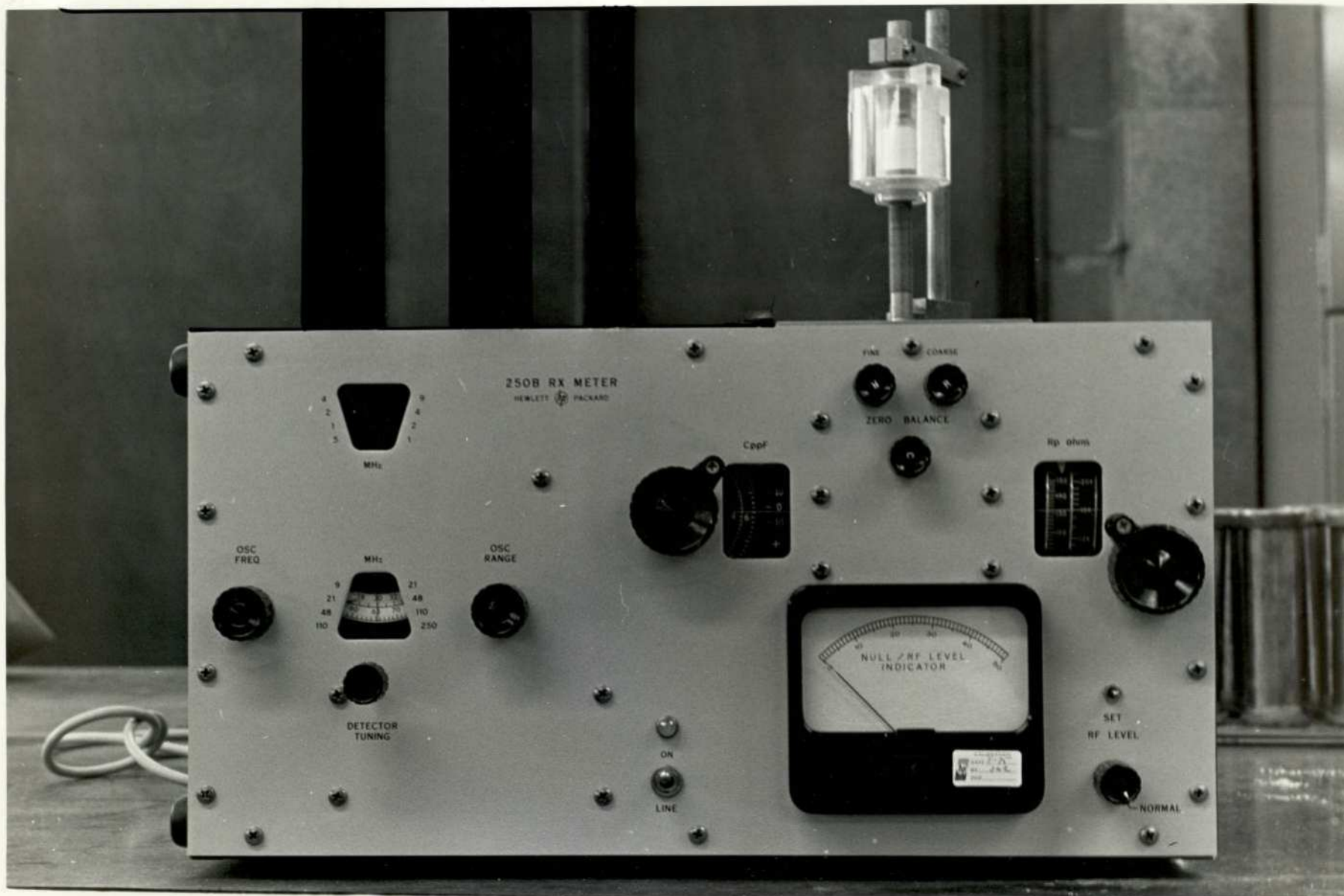
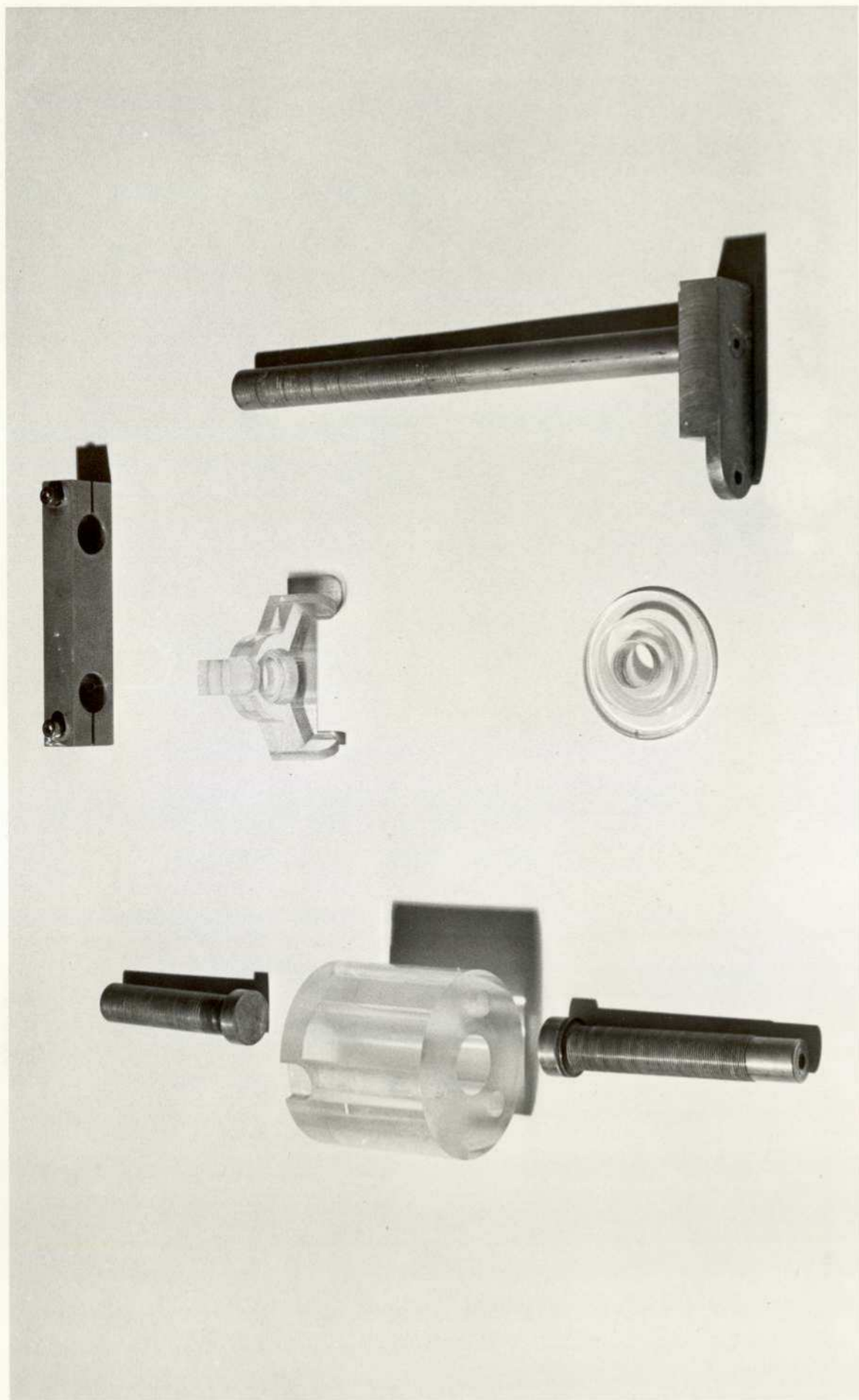


Fig. 5.1.1 RX Meter block diagram.





5.1.3 The Consolidation Mould. (Fig. 5.1.4)

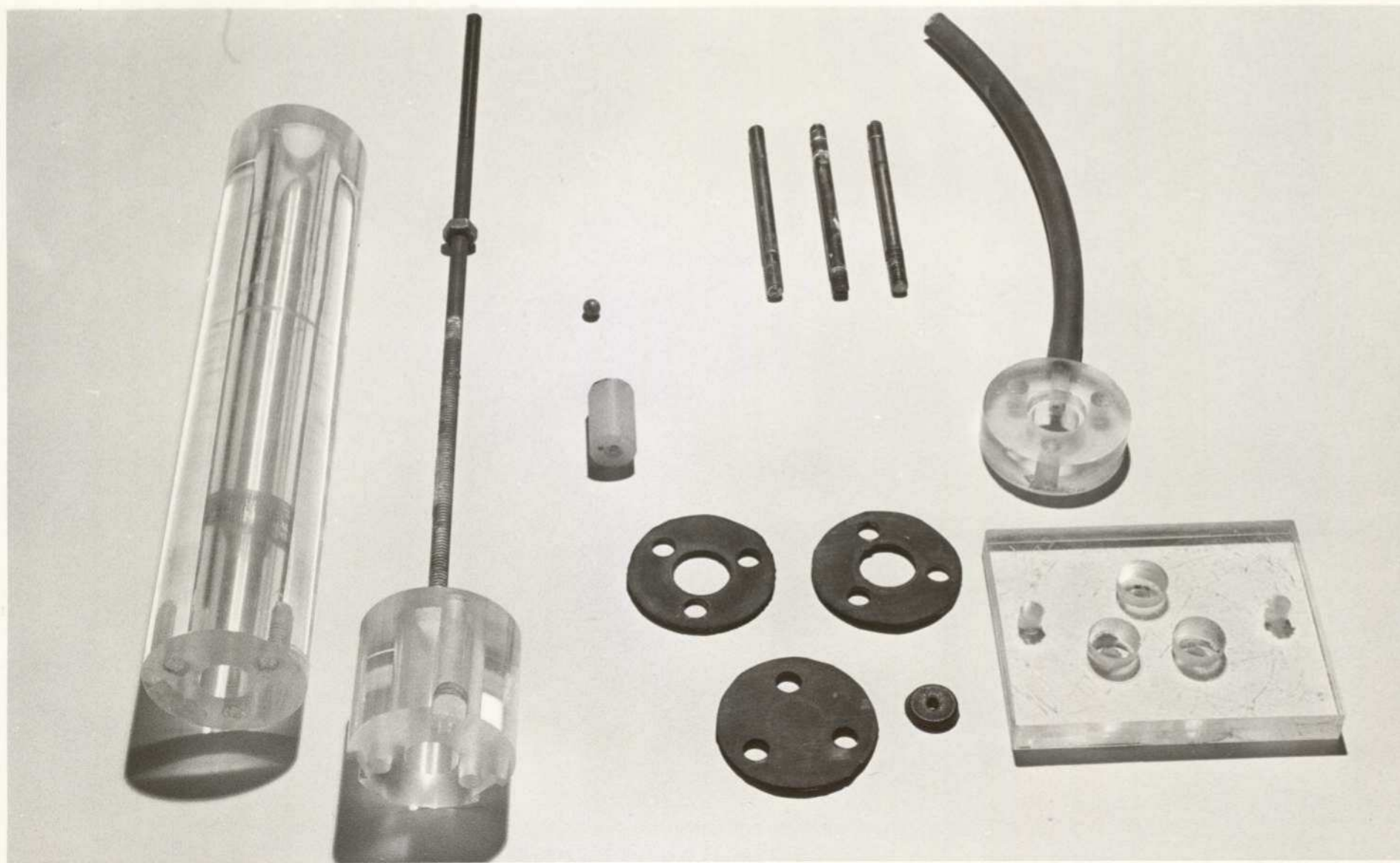
A consolidation mould which included the electrical measurement cell was designed and twelve of these moulds were made for the purposes of this project.

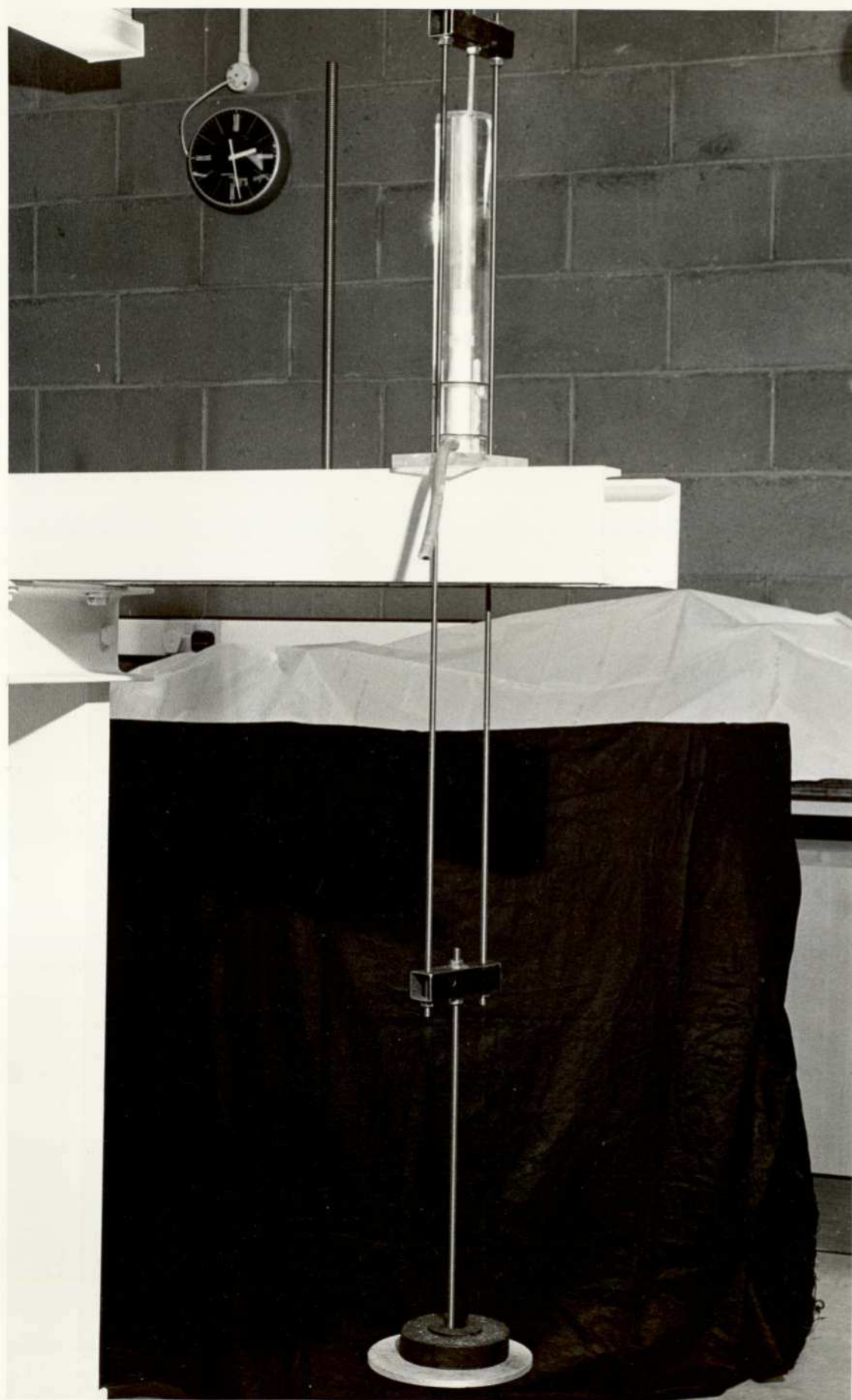
The main mould comprised a three-section (1,2 & 3) perspex clamped to a perspex base plate (4) with three screws (6) and three rubber washers (5):

Section 1 is the consolidation chamber, 2 is the electrical cell and 3 has a recess to house the lower porous stone below which drainage channels are formed with an outlet connected to a rubber tube.

The consolidation loads are applied through a piston (9) (poly-ethylene provided with grooves, holes, filter paper, etc.), stirrups (10) and a hanger (11), Fig.5.1.5.

Apart from the twelve consolidation moulds described, a large oedometer developed at The City University-Soil Mechanics Laboratory (Figs. 5.1.6 & 7) has been used to prepare samples for the particle orientation experiments (Section 5.2.6).





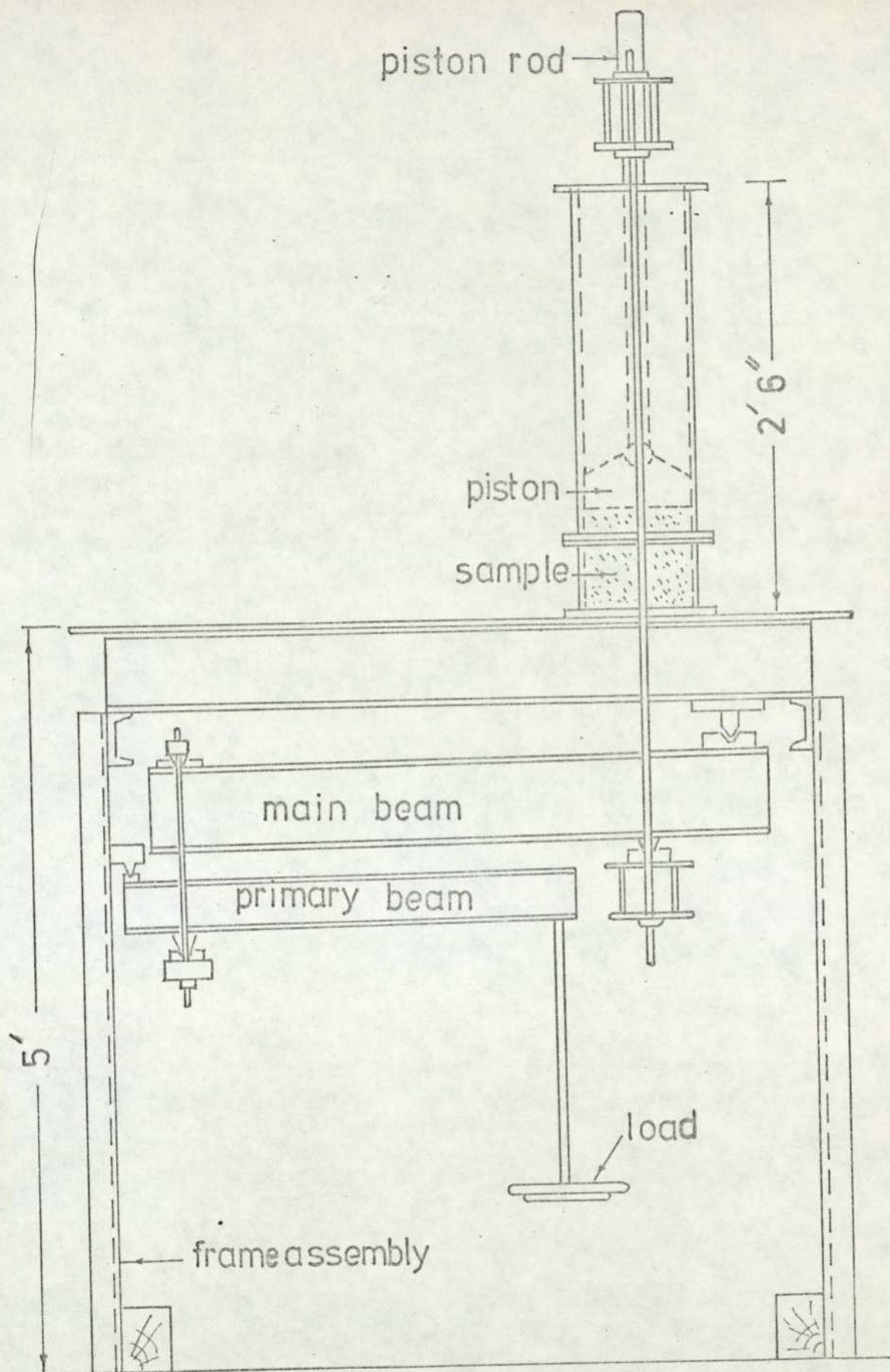
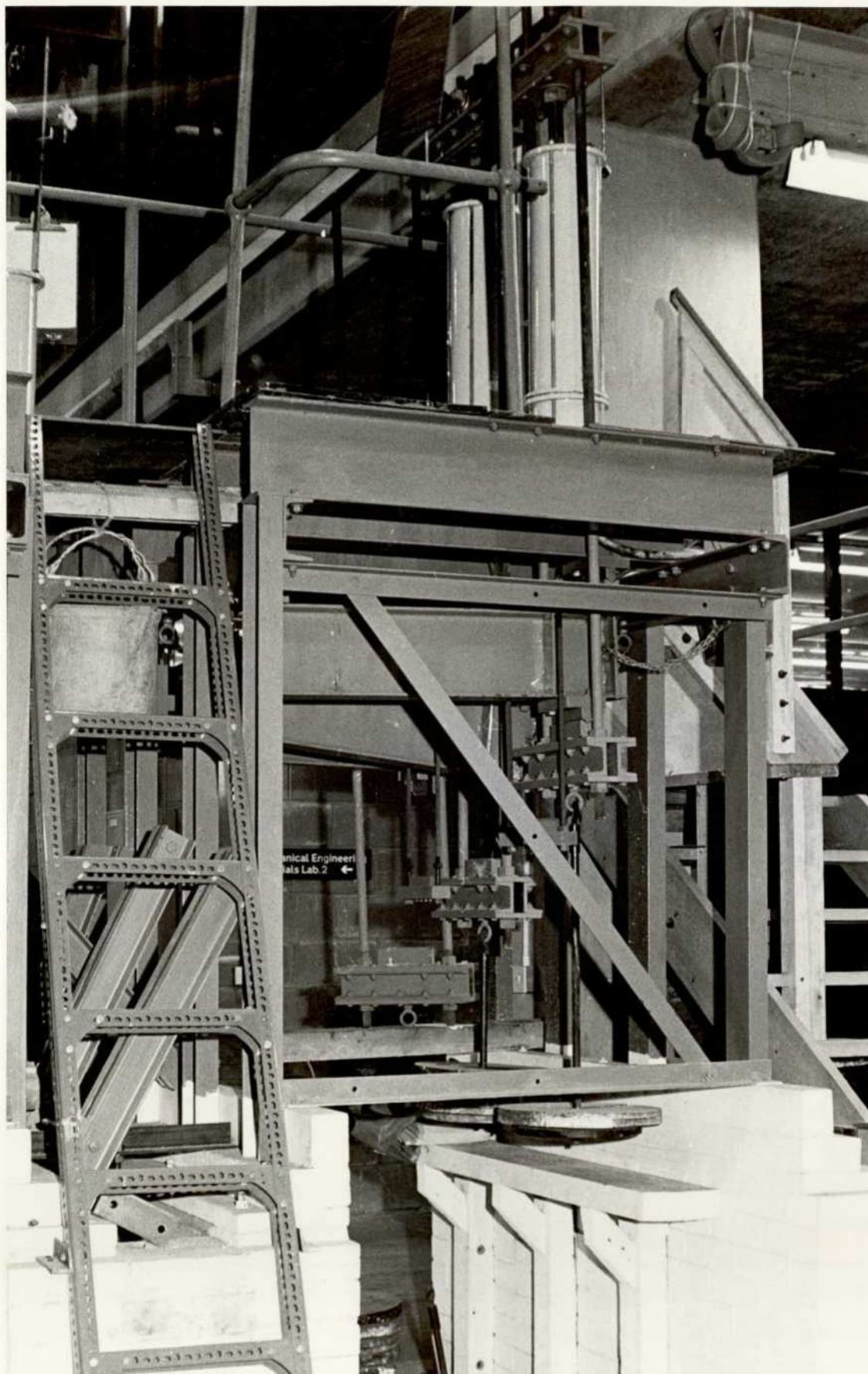


Fig. 5.1.6 6" - diameter oedometer (not to scale)



5.1.4 Procedure

After a sample had been allowed to completely consolidate under the final load increment without any change in sample height for at least three days, the electrical cell was trimmed away from the other two sections with a wire cutter and was thus ready for the electrical measurements to be performed according to the following procedure:

5.1.4.1 The cell and transmission line were connected to the binding posts of the RX Meter which had been adjusted to the required frequency.

5.1.4.2 The C_p and R_p controls were adjusted alternately until a final null point was reached. The equivalent parallel resistance and capacitance were read from the dials.

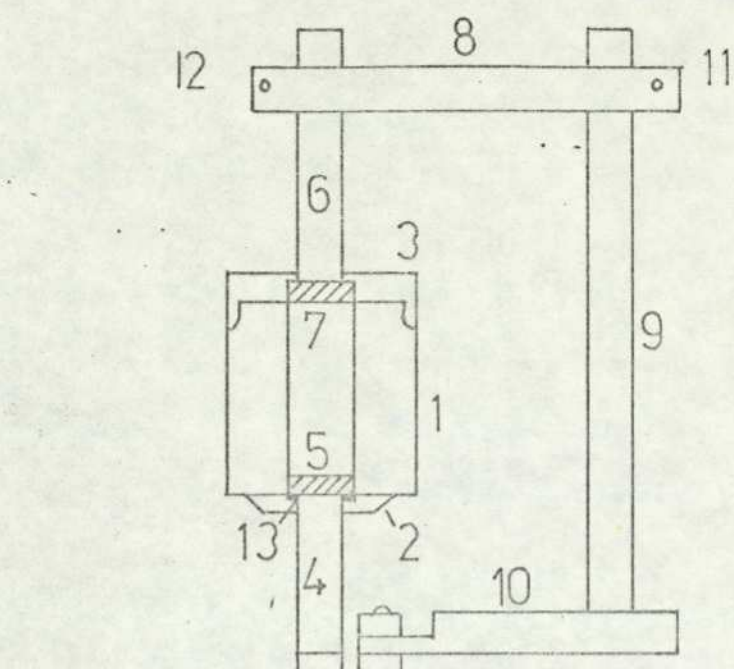
5.1.4.3 Steps 1 and 2 were repeated for each of the eleven frequencies chosen for this investigation (10 to 110 MHz at 10 MHz intervals).

5.1.4.4 To reduce the height of the sample by a length L

(Fig.5.1.8):

- 1) The horizontal rod (8) was slightly swivelled about the vertical post (9).
- 2) The perspex flange (2) was screwed downward by a distance ($L/2$).
- 3) The cell was pushed downward to rest back on the flange, and so the sample was extruded by a length ($L/2$) out of the top of the cell
- 4) The extruded part of the sample was trimmed by a wire cutter.
- 5) The horizontal rod (8) was lowered along the vertical post (9) until the upper electrode again touched the top of the cell. Rod (8) was then locked in position by the screw (11).
- 6) To complete the total reduction in sample height (L), steps 2) and 3) were repeated for another length ($L/2$) of the sample.
- 7) The screw (12) was unlocked, the upper electrode lowered to reach the cell top, and the screw (12) locked again.
- 8) The horizontal rod (8) was swivelled back and with the help of the three-pronged cap (3), the upper electrode was aligned in position at the top of the soil sample.

5.1.4.5 Steps 1 to 3 were repeated for the new sample height as well as for each of the other sample heights (usually 3-4 heights for each soil sample) which were prepared by repeating step 4 to reduce the sample height.



RX Meter

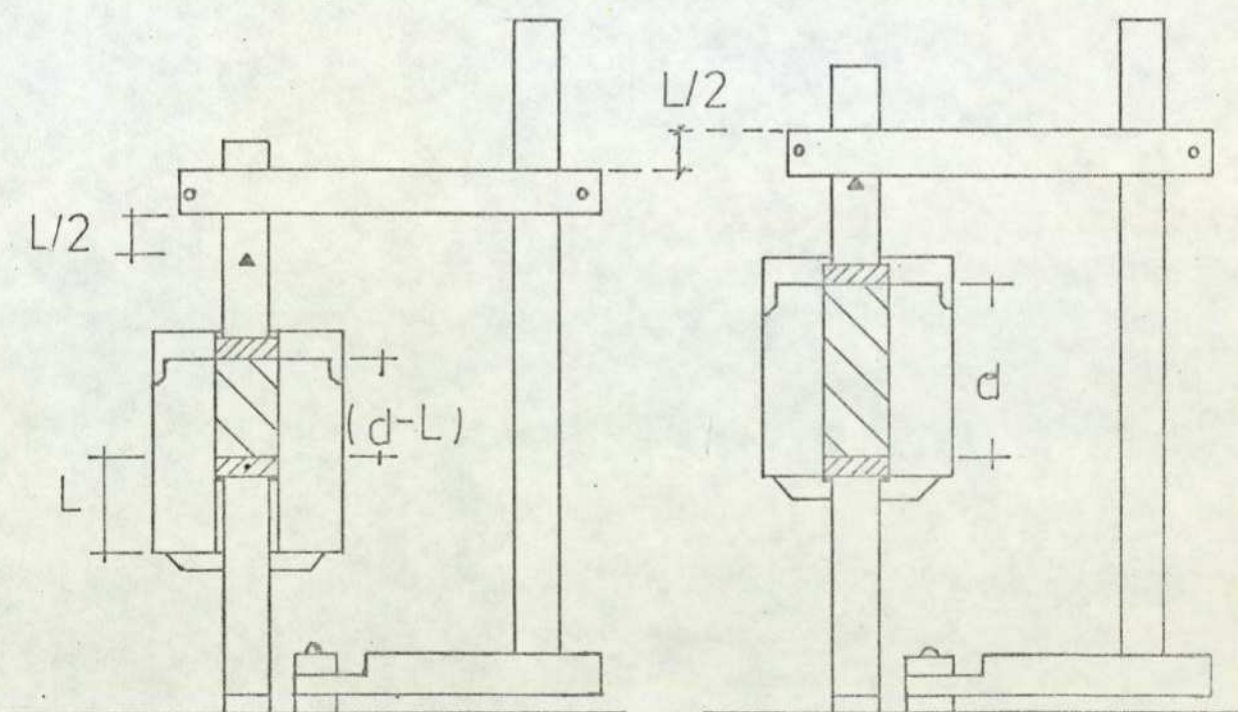


Fig. 5.1.8. Variation of sample height at
constant transmission line lengths

5.2 MATERIALS AND EXPERIMENTAL PARAMETERS

5.2.1 Clay Mineral

5.2.1.1 Kaolin

The soil used in the majority of the experiments was a kaolinite clay. It was supplied as a paper clay by English Clays Lovering Pochin Company - St. Austell, under the trade name of "Supreme". The particles of this material have a characteristic plate-like irregular hexagonal shape. Its properties are listed in Table 5.2.1. Further information about the "Supreme" kaolin was obtained by Foster and De (1970) using a fractionation method by sedimentation and electron microscopy (Table 5.2.1, Figs. 5.2.1 & 2).

Table 5.2.1 : "Supreme" Kaolin Properties

A. Typical chemical analysis

	%
Si O ₂	46.6
Al ₂ O ₃	38.3
Fe ₂ O ₃	0.49
Ti O ₂	0.05
Cu O	0.2
Mg O	0.2
K ₂ O	0.68
Na ₂ O	0.07

B. Classification after fractionation (Foster and De, 1970)

Liquid limit	69.3
Plastic limit	53.6
Plasticity index	15.7
Activity	0.23
Uniformity coeff.	1.9

C. Particle form factors (Foster and De, (1970)

Length/width 1.1

Length/thickness 12

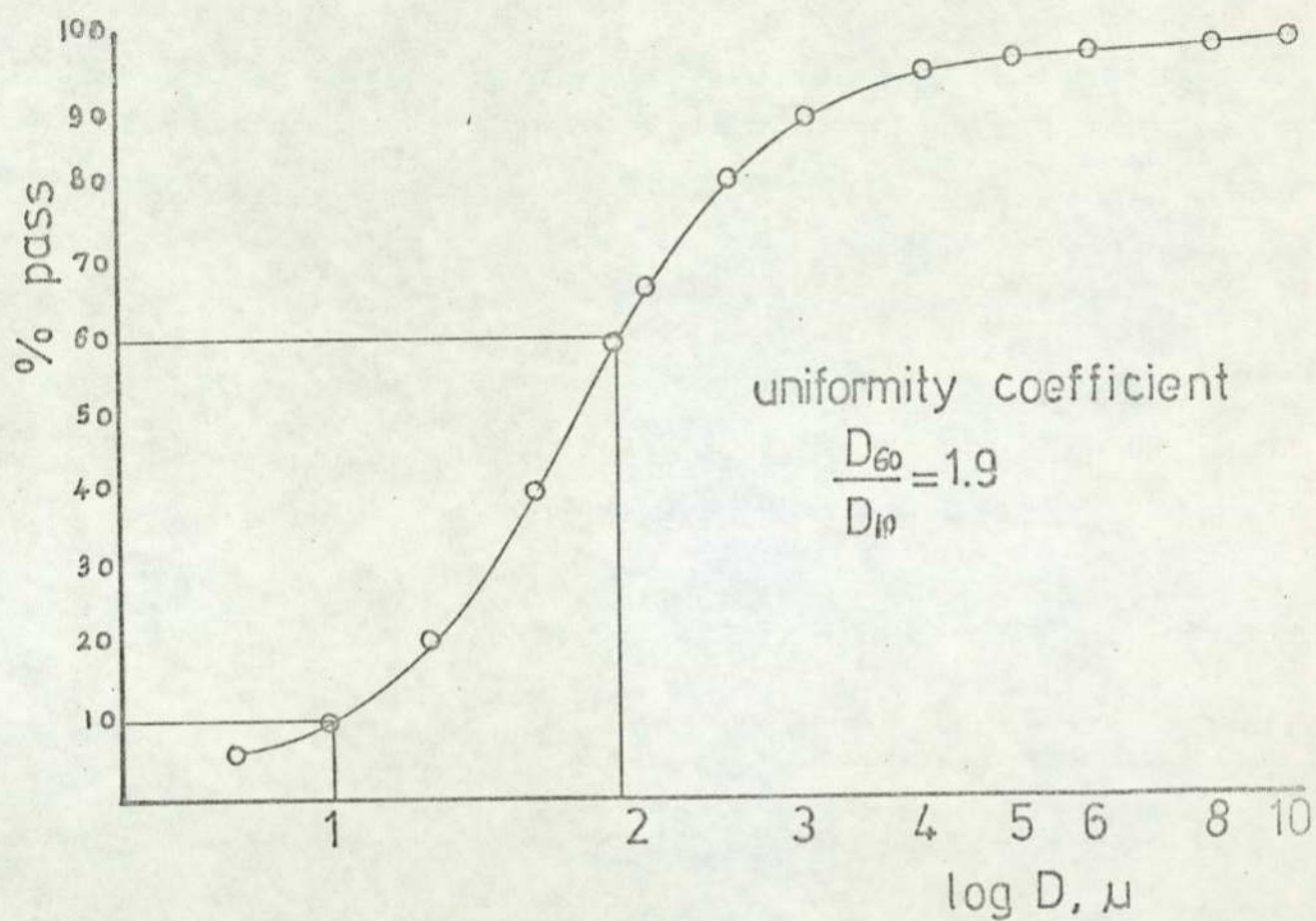
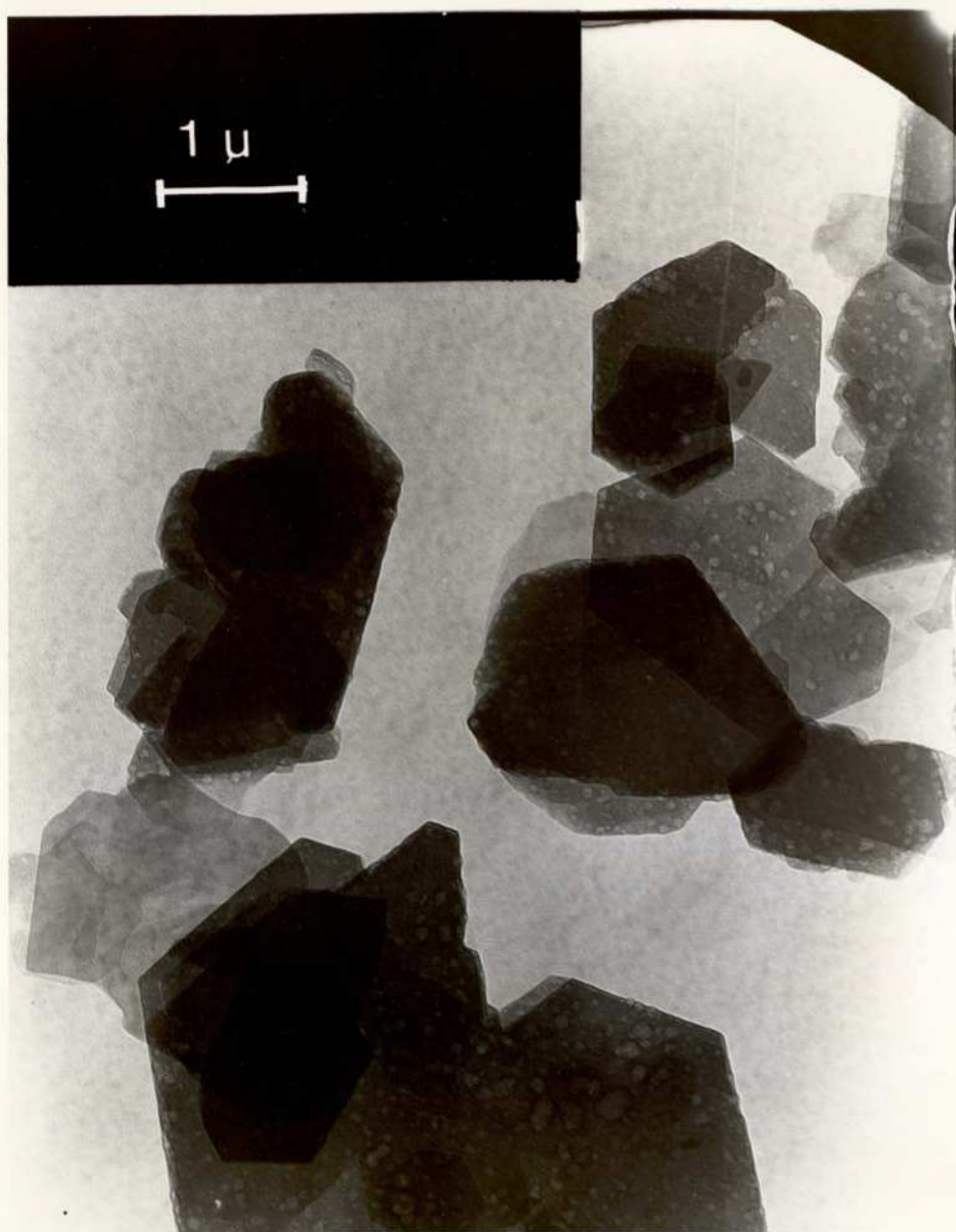


Fig. 5.2.1 Particle size distribution of fractionated kaolin
 (Foster, et al., 1971)



5.2.1.2 Montmorillonite

The montmorillonite was supplied by Laporte Industries Company - Bedfordshire, under the trade name of Fulbent 570. This material is a sodium bentonite and its structural unit comprises an aluminium layer between two tetrahedral layers of silicon and oxygen with sodium ions attached to the outer layers as exchangeable cations. The particles of this material have a characteristic thin plate-like shape. Its properties are listed in Table 5.2.2.

Table 5.2.2 "Fulbent" Montmorillonite Properties

A. Typical chemical analysis

	%
Si O ₂	56.0
Al ₂ O ₃	15.0
Fe ₂ O ₃	6.5
Na ₂ O	5.0
Mg O	3.5
Ca O	2.5
Ti O ₂	0.5
K ₂ O	0.5

B. Other typical properties

True density	2.6 g/cc
Liquid limit	400-500%
Plastic limit	55-60%
pH of 5% suspension	10.4
Cation exchange capacity	88 m eq/100g
Median particle size (fully, hydrated)	0.2 micron

C. Typical sieve analysis

Dry-passing	
100 BSS	96.2
200 BSS	84.6
300 BSS	71.8
Wet-Passing	
200 BSS	99.3
300 BSS	99.0

The liquid limit of "Fulbent" montmorillonite has been determined, for the purpose of this investigation, using a cone penetrometer and was found to be 390.

5.2.1.3 Slate Dust

The slate dust was supplied by Penrhyn Quarries, Gwynedd-North Wales, under the trade name of "Fullersite". This material is produced by crushing and milling the slate. Its particles are flaky

and angular, but not particularly elongated. The properties of "Fullersite" slate powder are given in Table 5.2.3.

Table 5.2.3 "Fullersite" Slate Powder Properties

A. Typical chemical analysis

	%
Si O ₂	58.56
Al ₂ O ₃	19.23
Fe ₂ O ₃	8.92
Mg O	2.11
Ca O	1.68
Ti O ₂	0.8
K ₂ O	0.34
Na ₂ O	0.16

B. Other typical properties

True density	2.84 g/cc
pH of water extract	7.4
specific surface area	0.819 sq.m/g

C. Typical sieve analysis

Passing BSS	%
72	100
85	99.7
100	99.5
120	99.0
150	98.0
170	97.0
200	95.0

The liquid limit of "Fullersite" slate powder has been determined for the purpose of this investigation, using a cone penetrometer and was found to be 26.5%.

Lewin, et al. (1970) reported the following experimental data on slate dust:

L.L 29% - P.L 18% - True density 2.78 g/cc.

5.2.1.4 Mica

The mica powder was supplied by Mineral and Services Co., Derby - U.K. The properties of this material are given below

A. Typical chemical analysis

	%
Si O ₂	45.08
Al ₂ O ₃	34.40
K ₂ O	10.41
Fe ₂ O ₃	2.04
Na ₂ O	.8
Mg O	.68
Ti O ₂	.66
Ca O	.5

B. Other typical properties

True density	2.85
pH	7.0

5.2.2. Cation Valence

Three electrolytes of different cation valencies (1,2 & 3) were used:

- 1) Sodium Chloride Na Cl
- 2) Calcium Chloride Ca Cl₂
- 3) Aluminium Chloride AlCl₃

Other factors were kept constant for the three samples;

Clay mineral : kaolin

Water content (initial) : 200%

Electrolyte concentration : 1.0 N

Consolidation pressure : 7.0 kg/cm²

5.2.3 Cation Concentration

Three different concentrations of the same electrolyte solution were used :

- 1) 0.01 N Ca Cl₂
- 2) 0.1 N Ca Cl₂
- 3) 1.0 N Ca Cl₂

Other factors were kept constant;

Clay mineral : kaolin

Water content (initial) : 200%

Consolidation pressure : 7.0 kg/cm²

5.2.4 pH Value

Three electrolytes of different pH values were used:

- 1) pH 13.4 (Na OH)
- 2) pH 7.0 (Na Cl)
- 3) pH 0.35 (H Cl)

Other factors were kept constant;

Clay mineral : kaolin

Water content (initial) : 200%

Electrolyte concentration : 1.0 N

Consolidation Pressure : 7.0 kg/cm^2

5.2.5 Consolidation Pressure-Water Content

Nine samples were prepared in three different initial water contents and consolidated at three different consolidation pressures :

Consolidation pressure (kg/cm^2) : 3.5, 7.0, 14

Initial water content (%) : 100, 200, 400

The clay mineral of the nine samples was kaolin. Values of the initial water contents were chosen in the order 1.33, 2.66, and 5.33 times the liquid limit of kaolin "Supreme".

5.2.6 Particle Orientation

One sample was consolidated using the six inches diameter oedometer (fig.5.1.6 & 7), from which three cylindrical specimens were cut in three different directions. A soil lathe was used to cut the sample to fit in the electrical measurement cell.

The three orientations of the samples are :

- 1) The longitudinal axis-parallel to the consolidation direction
- 2) The longitudinal axis — perpendicular to the consolidation direction.
- 3) The longitudinal axis-at 45° to the consolidation direction.

5.2.7 Rigid Bonding

Nine samples were prepared using, for the electrolyte, three different types of polymeric aluminium hydroxy cations in solutions having three different concentrations, Table 5.2.4.

Cation type : Large cation (LC), Medium cation (MC), Small cation (SC)

Concentration to give number of mono-molecular adsorbed layers :

0.33 , 1 , 2

Other factors were kept constant;

Clay mineral : kaolin

Water content (initial) : 200%

Consolidation pressure : 7.0 kg/cm²

pH : 5.2 (a minimum value recommended (Foster,1976) to prevent an undesirable effect of hydrogen ions on the bonding process produced by the polymeric aluminium hydroxy cations. Buffering to control pH was achieved by/titration with sodium acetate)

The effect of ageing was investigated by repeating electrical measurements on samples at different time intervals :

Time intervals (days) : 15, 35, 160.

Table 5.2.4 Samples for Rigid Bonding Experiments

Cation type	Concent. m. Layers	Molar Ratio OH/Al	0.1N NaOH (Litres)	0.2M AlCl ₃ 6H ₂ O	Distilled water (Litres)	Wt. kaolin (kg)	M/C (%)	pH solution
LC	0.33	2.5	0.3825	0.0765	0.441	0.450	200	5.5
MC	0.33	1.5	0.027	0.009	0.264	0.150	200	5.2
SC	0.33	0.5	0.009	0.009	0.282	0.150	200	5.2
LC	1.0	2.5	0.3825	0.0765	0.459	0.150	300	5.2
MC	1.0	1.5	0.0765	0.0255	0.198	0.150	200	5.2
SC	1.0	0.5	0.0255	0.0255	0.249	0.150	200	5.2
			0.3N NaOH	0.6M AlCl ₃ 6H ₂ O				
LC	2.0	2.5	0.255	0.051	0.306	0.150	200	5.2
MC	2.0	1.5	0.051	0.017	0.232	0.150	200	5.2
SC	2.0	0.5	0.017	0.017	0.266	0.150	200	5.2

5.3 REPRESENTATION OF THE EXPERIMENTAL RESULTS

5.3.1 The Stray Capacitance caused by the Cell

The parasitic impedance between the cell and the instrument takes the form of a parallel stray capacitance, C_t . Such capacitance may make an important contribution to the measured values of the electrical responses of samples and should, therefore, be determined and excluded from the results by appropriate corrections.

It has been suggested (Smith, 1971) that the stray capacitance for a similar cell in the radio frequency range is independent of the frequency, while in another work (Sachs, et al., 1970), C_t was found dependent on the inter-electrode distance but of negligible variation with frequency in the range 0-50 MHz at constant electrode distance. However, in the present investigation, it was found that the stray capacitance C_t is dependent on the inter-electrode distance as well as on the frequency. Values of C_t were determined at different electrode distances and frequencies (Appendix V).

The empty cell is connected to the RX Meter at electrode separation l . The instrument is balanced at frequency f and the capacitance C_p° is recorded. R_p° is naturally infinite since there is void space between the electrodes. Then

$$C_p^\circ = C_t + C_o \quad (5.3.1)$$

which according to Eq.2.1.6 can be written

$$C_p^\circ = C_t + \frac{\epsilon_v A}{l} \quad (5.3.2)$$

where C_o is the capacitance of the empty cell at the frequency f and electrode separation l , and A is the electrode area. The measurements are repeated for a range of values of l and f . A graph is then

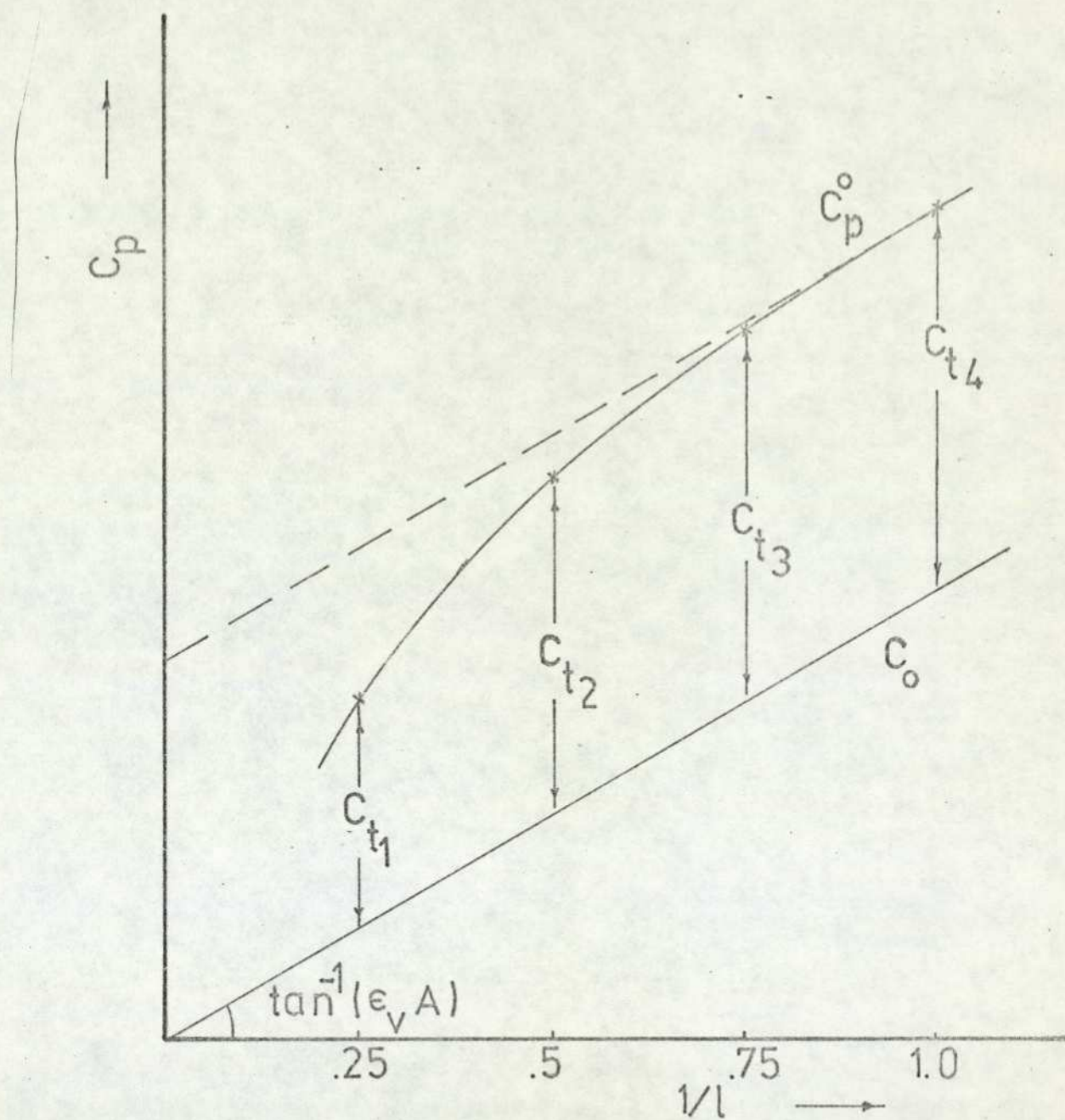


Fig. 5.3.1 Stray Capacitance of the cell.

plotted for C_p° against $1/l$, Fig.5.3.1, at each frequency. A straight line is drawn through the origin at a slope of $\epsilon_0 A$ to represent the capacitance C_0 . C_t for a given electrode separation l is given by the difference of ordinates of C_0 and C_p° at $1/l$. The assumption that C_t is independent of l (Smith, 1971) implies that the C_p° graph is a straight line parallel to C_0 and intercepts the C_p° axis at the constant value of C_t , whereas the assumption that C_t is independent of frequency (Sachs, et al. 1970) implies that the C_p° graphs are the same at different values of frequency. However, the experimental observations did not give evidence that either of the two assumptions obtained.

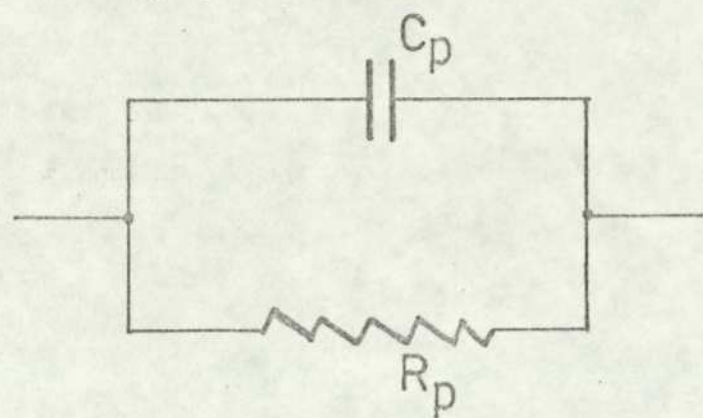
For example; C_t at $l = 4$ cm and $f = 10$ MHz, was found 2.73 p .

C_t at $l = 4$ cm and $f = 110$ MHz, was found 2.86 p .

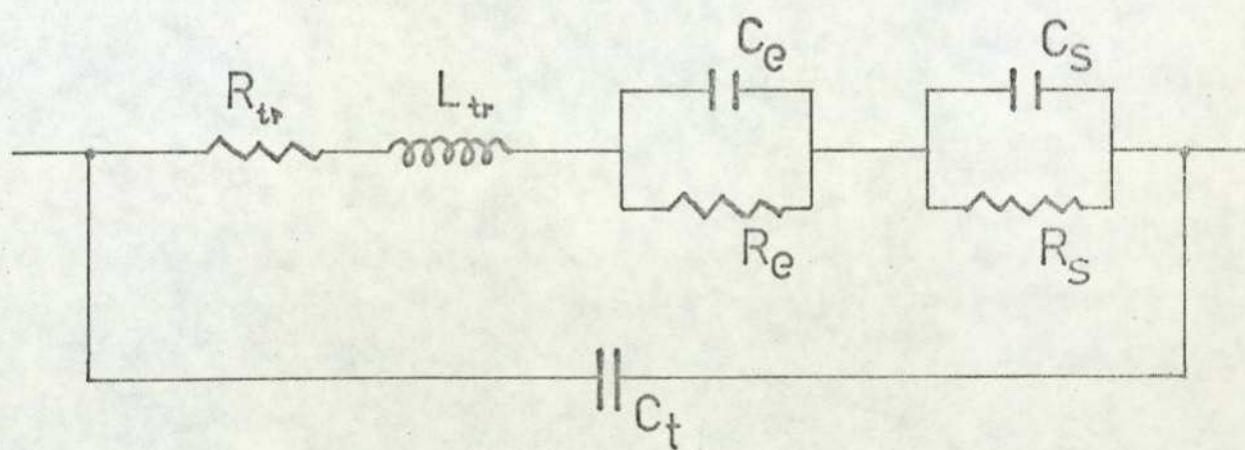
C_t at $l = 1$ cm and $f = 110$ MHz, was found 3.37 p .

5.3.2 The Impedance of the Transmission Line

The RX Meter yields results which are read in terms of parallel resistance R_p and positive (or negative) parallel capacitance C_p . An R_p reading is a direct indication of the effective parallel resistance component of the unknown impedance effective at the RX Meter binding posts, and a C_p reading indicates directly the effective parallel capacitance of the associated capacitive impedance. Therefore, the RX Meter measures the above values as they obtain at its binding posts (Fig.5.3.2a), i.e., equivalent to a network (Fig.5.3.2b) which includes the true resistance and capacitance of the sample (R_s , C_s) the parallel stray capacitance C_t , the series impedance of the transmission line (R_{tr} , C_{tr}), and a series impedance due to electrode polarization (R_e , C_e).



(a)



(b)

Fig. 5.3.2 Equivalent circuit for cell
and transmission line

The equivalent series combination to the network of the cell and transmission line (Fig. 5.3.2b) and also to the parallel circuit (Fig. 5.3.2a), may be expressed in terms of a resistance X (in ohms) and a reactance Y (in henries) (Sachs, et al., 1970) such that

$$X = \frac{1/R_p}{(1/R_p)^2 + \omega^2(C_p - C_t)^2}$$

$$= \frac{1/R_e}{(1/R_e)^2 + \omega^2 C_e^2} + \frac{1/R_s}{(1/R_s)^2 + \omega^2 C_s^2} + R_{tr} \quad (5.3.3)$$

$$Y = \frac{(C_p - C_t)}{(1/R_p)^2 + \omega^2(C_p - C_t)^2}$$

$$= \frac{C_e}{(1/R_e)^2 + \omega^2 C_e^2} + \frac{C_s}{(1/R_s)^2 + \omega^2 C_s^2} - L_{tr} \quad (5.3.4)$$

For a sample of length l , these two equations may be written

$$X = R + \alpha l \quad (5.3.5)$$

$$Y = -L + \beta l \quad (5.3.6)$$

where we define

$$\alpha \equiv \frac{1/R_s}{1/R_s^2 + (\omega C_s)^2} \quad (5.3.7)$$

$$\beta \equiv \frac{C_s l}{1/R_s^2 + (\omega C_s)^2} \quad (5.3.8)$$

and

$$R \equiv \frac{1/R_e}{1/R_e^2 + (\omega C_e)^2} + R_{tr} \quad (5.3.9)$$

$$L \equiv -\frac{C_e}{1/R_e^2 + (\omega C_e)^2} + L_{tr} \quad (5.3.10)$$

From which

$$R_s = \frac{\alpha^2 + \beta^2}{\alpha/l} \quad (5.3.11)$$

$$C_s = \frac{\beta/l}{\alpha^2 + \beta^2} \quad (5.3.12)$$

Measurements are repeated for different values of sample length and from plots of X and Y against l Fig.5.3.3, α and β can be determined for different frequency values. Thus the impedance components of both the transmission line and electrodes are eliminated in the calculation of the sample electrical properties.

Values of R_s and C_s as given by Eqs. 5.3.11 & 12 are used for the evaluation of the dielectric constant ϵ' , the conductivity k' , and the dielectric loss factor ϵ'' according to Eqs.2.1.6, 2.4.12

$$\epsilon' = \frac{C_s l}{\epsilon_v A} \quad (5.3.13)$$

$$k' = \frac{l}{R_s A} \quad (5.3.14)$$

$$\epsilon'' = \frac{l}{R_s A \omega \epsilon_v} \quad (5.3.15)$$

Throughout the experimental programme, electrical response values, R_p and C_p , were measured for a number of sample heights (3 to 4), so that 3 to 4 points could be determined for each of the graphs X/l and Y/l . As expected, straight lines were obtained for each frequency

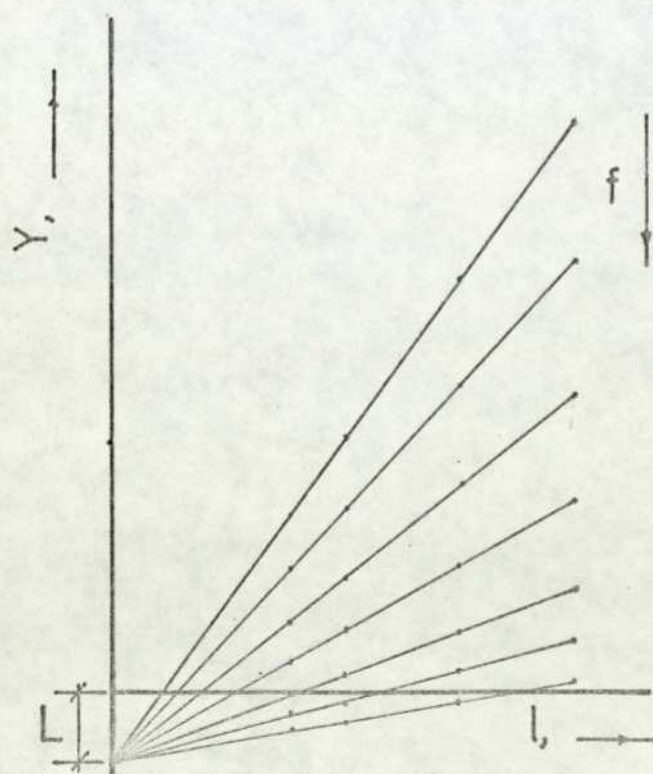
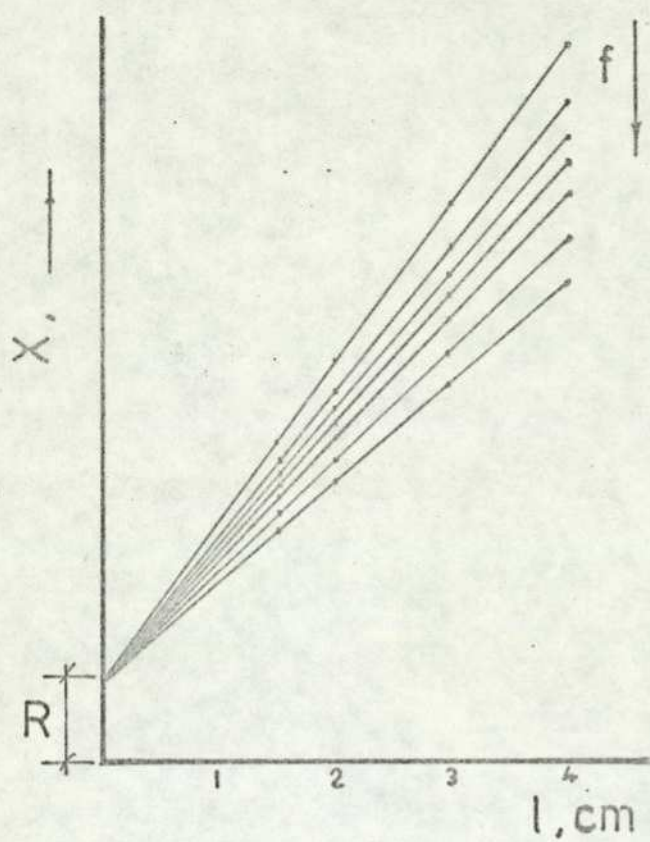


Fig. 5.3.3. Impedance components of the transmission line

(α , β , R and L are the slopes and intercepts on the X and Y axes respectively), which allowed R_s and C_s to be evaluated from equations 5.3.11 & 12. The precision of the straight lines obtained and the consistency of R and L with frequency, lend support to the assumption of the frequency and length dependent stray capacitance C_t used in equations 5.3.3 & 4 and confirms the accuracy of measurements. Values obtained for the impedance components of the transmission line and electrode polarization are :

$$R = 20 \text{ ohms.}, \quad L = 0.116 \times 10 \text{ henries}$$

It is easily seen from Eqs. 5.3.13 & 14 that the specific capacitance and specific conductance of the soil sample are given by

$$C_s = \epsilon' \epsilon_v \quad (5.3.16)$$

$$k_s = k' \quad (5.3.17)$$

The results obtained by the whole experimental programme are given in Appendix V.

5.3.3 Electrical Dispersion Curves

The final step was to represent graphically the behaviour of the dielectric constant ϵ' and conductivity k' as the frequency f changes. In accordance with common practice, the experimentally obtained values of ϵ' and k' were plotted against $\log f$. The dispersion curves obtained by the whole experimental programme are given in Chapter 6.

ANALYSIS OF THE EXPERIMENTAL RESULTS

6.1 CLAY MINERAL

The effect of the clay mineral on the electrical properties of the clay-water system, as obtained experimentally, is given in Figs 6.1.1 & 2. Four different fine grained soils were investigated, viz., kaolinite, montmorillonite, slate dust, and mica.

In general, the four soil samples exhibit electrical dispersion in their response over the frequency range used, i.e., the radio frequency range.

The dispersion curves show that the dielectric constant ϵ' , the conductivity k , the dielectric dispersion $\Delta \epsilon$, and the conductivity dispersion Δk , all increase in the sequence.

slate dust < kaolin < Mica < montmorillonite.

It should be noticed that this is the same sequence of increase in the values of other properties such as; the cation exchange capacity, the liquid limit, the specific surface area, and others.

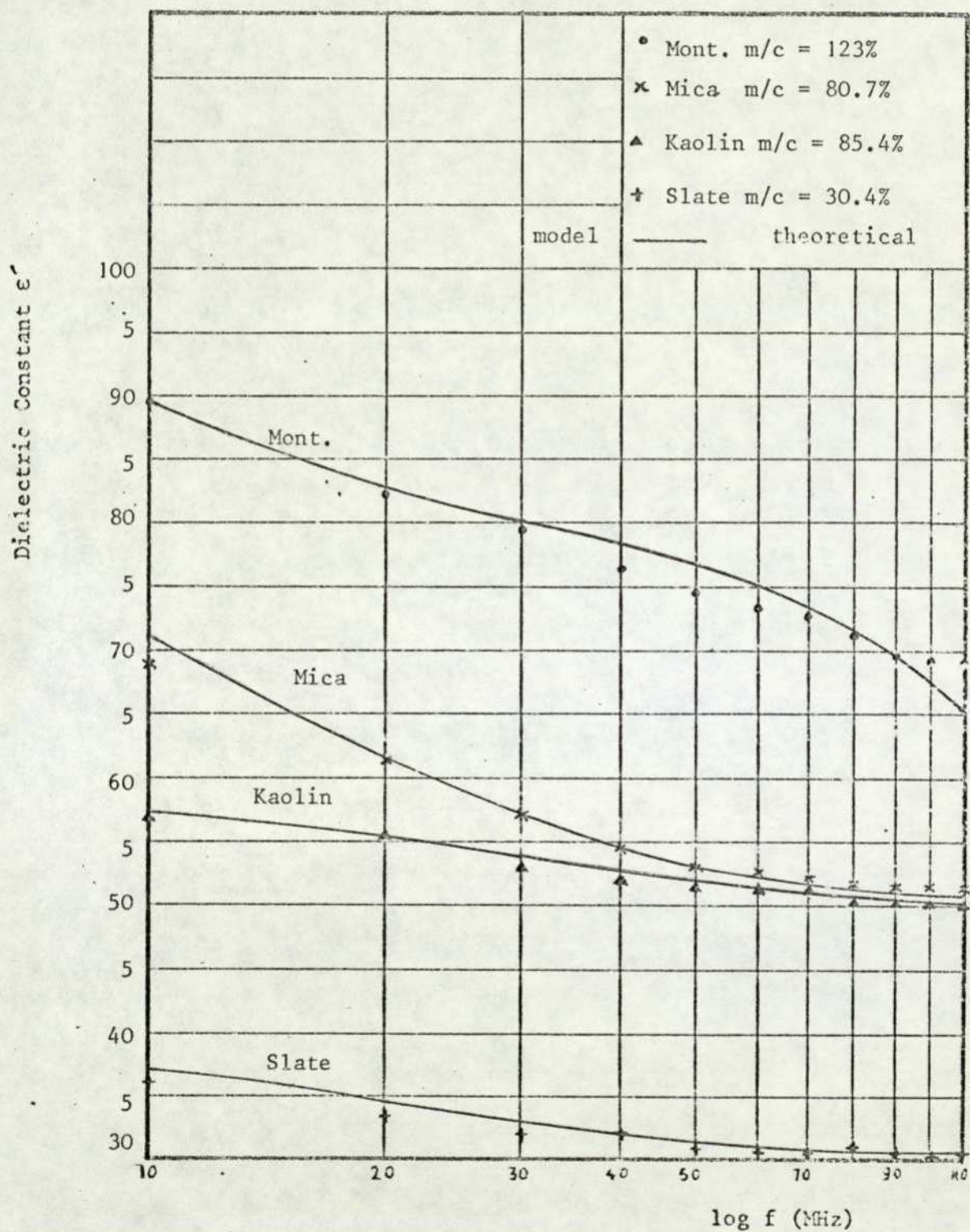


Fig. 6.1.1 Dielectric Dispersion - Clay Mineral

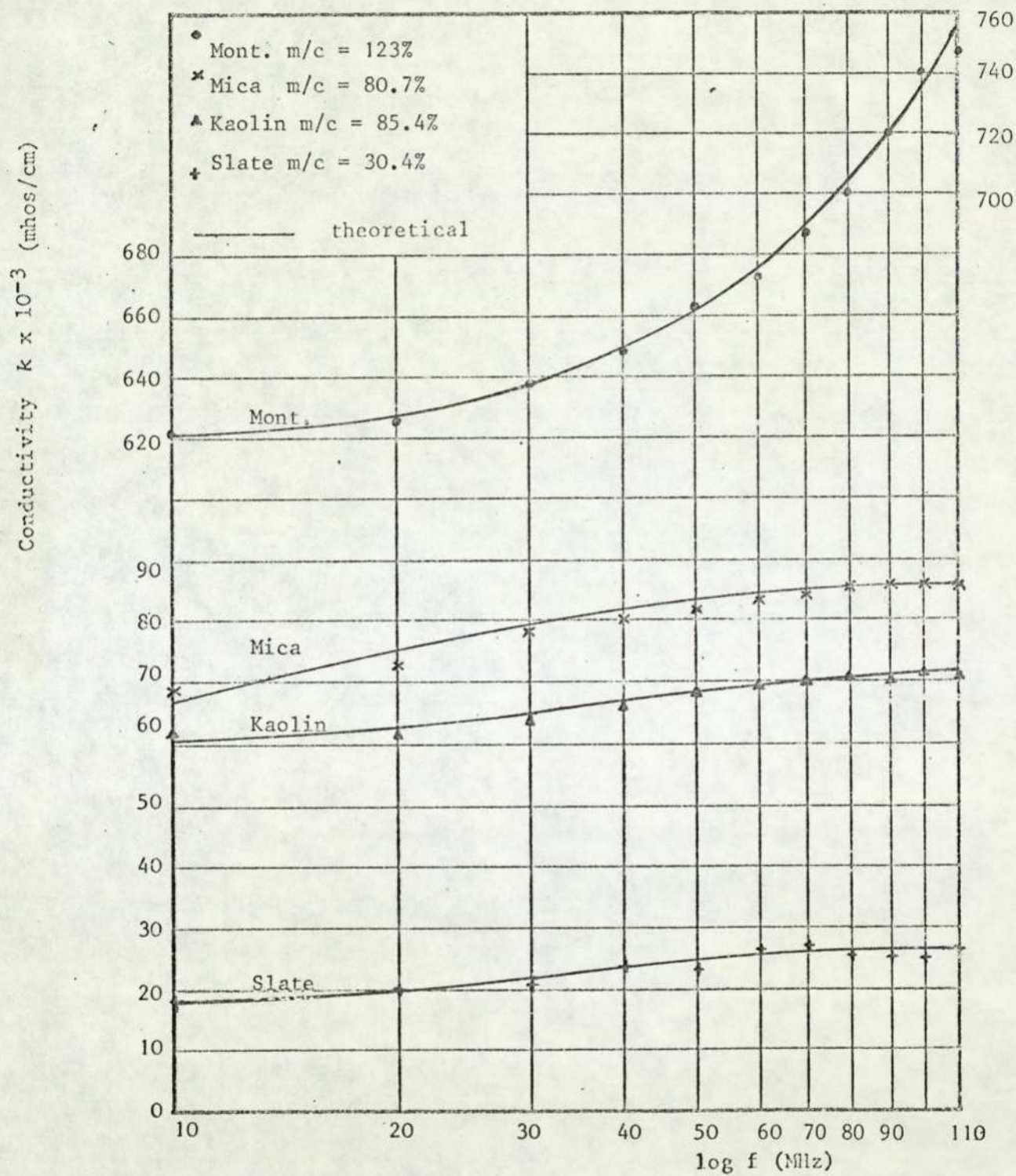


Fig. 6.1.2 Conductivity Dispersion -- Clay Mineral

6.2 CATION VALENCE

The effect of cation type on the electrical properties of the clay-water-electrolyte system is shown in Figs. 6.2.1 & 2. Three electrolytes of different cation valencies, i.e., monovalent (sodium), divalent (calcium), and trivalent (aluminium).

It is clear that the system exhibits electrical dispersion of both the dielectric constant and conductivity in the radio-frequency range and that the electrical responses of the clay-water-electrolyte system follow the trend :

As the valence of the cation increases.

- 1) the dielectric constant increases,
- 2) the conductivity increases,
- 3) the dielectric dispersion slightly increases & then decreases,
- 4) the conductivity dispersion increases.

The variation of dielectric dispersion with cations valence suggests that there might be a critical cation valence at which the trend would be reversed.

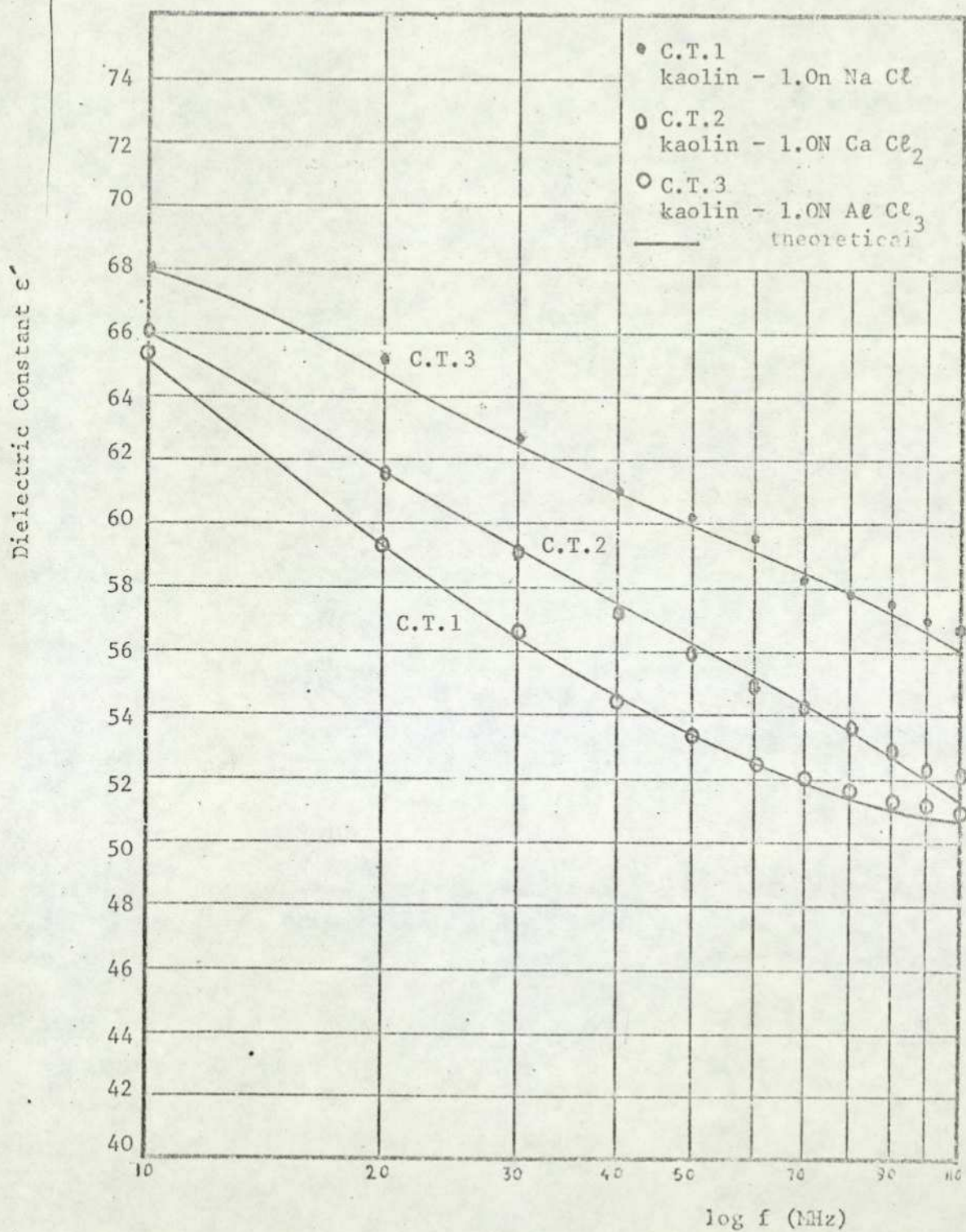


Fig. 6. 2.1 Dielectric Dispersion- Cation Valence

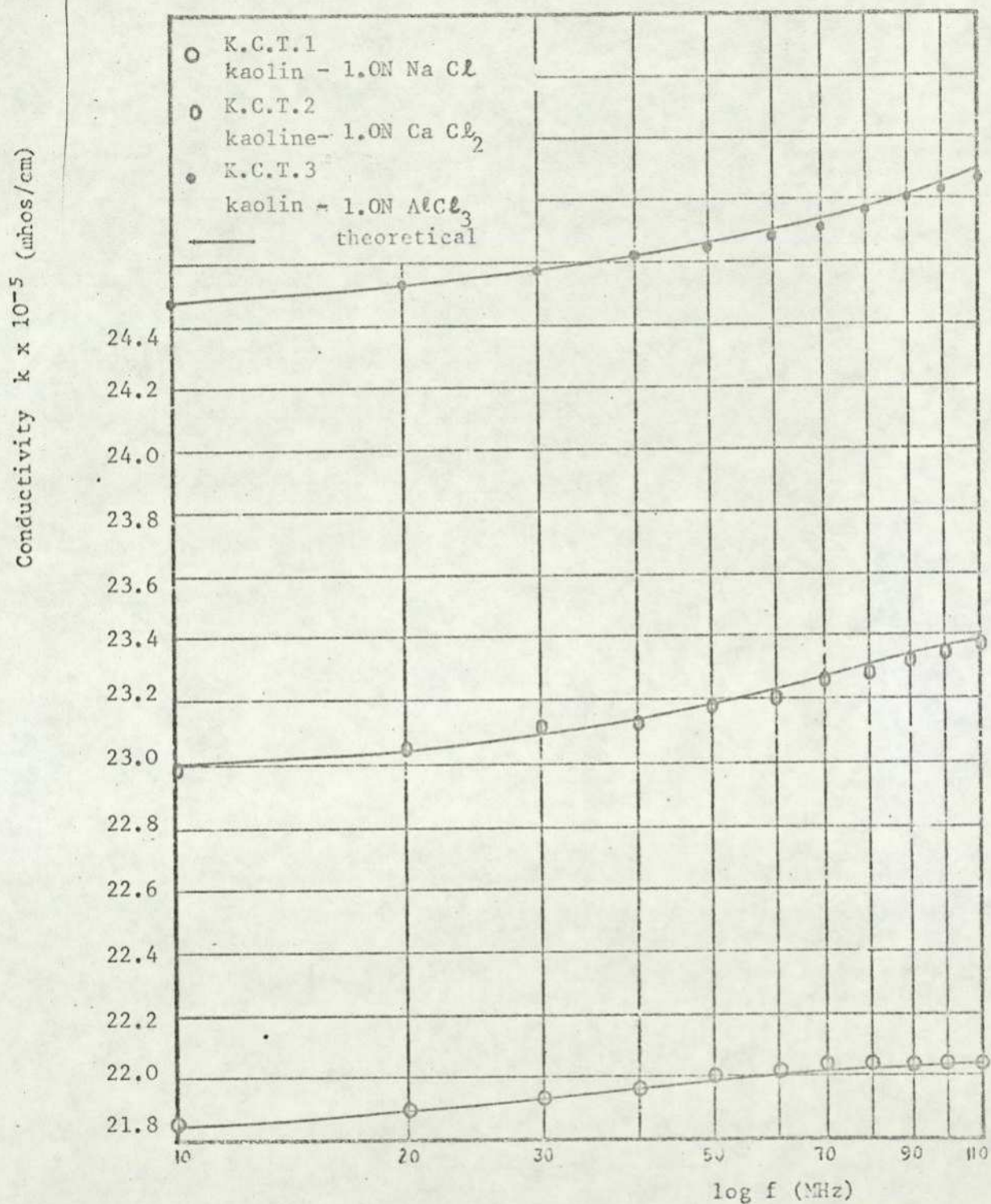


Fig. 6.2.2 Conductivity Dispersion - Cation Valence

6.3 CATION CONCENTRATION

Figs 6.3.1 & 2 show the effect of the cation concentration on the electrical response of the clay-water-electrolyte system. The same electrolyte solution (Ca Cl_2) was used in three different concentrations; 0.01 N, 0.1 N, and 1.0 N.

Typical electrical dispersions are obtained in the radio frequency range. The electrical properties follow the trend :
As the concentration of the electrolyte increases

- 1) the dielectric constant increases,
- 2) the conductivity increases,
- 3) the dielectric dispersion slightly increases, and
- 4) the conductivity dispersion increases.

This is the same trend observed in the case of cation type variation (Sec.6.2).

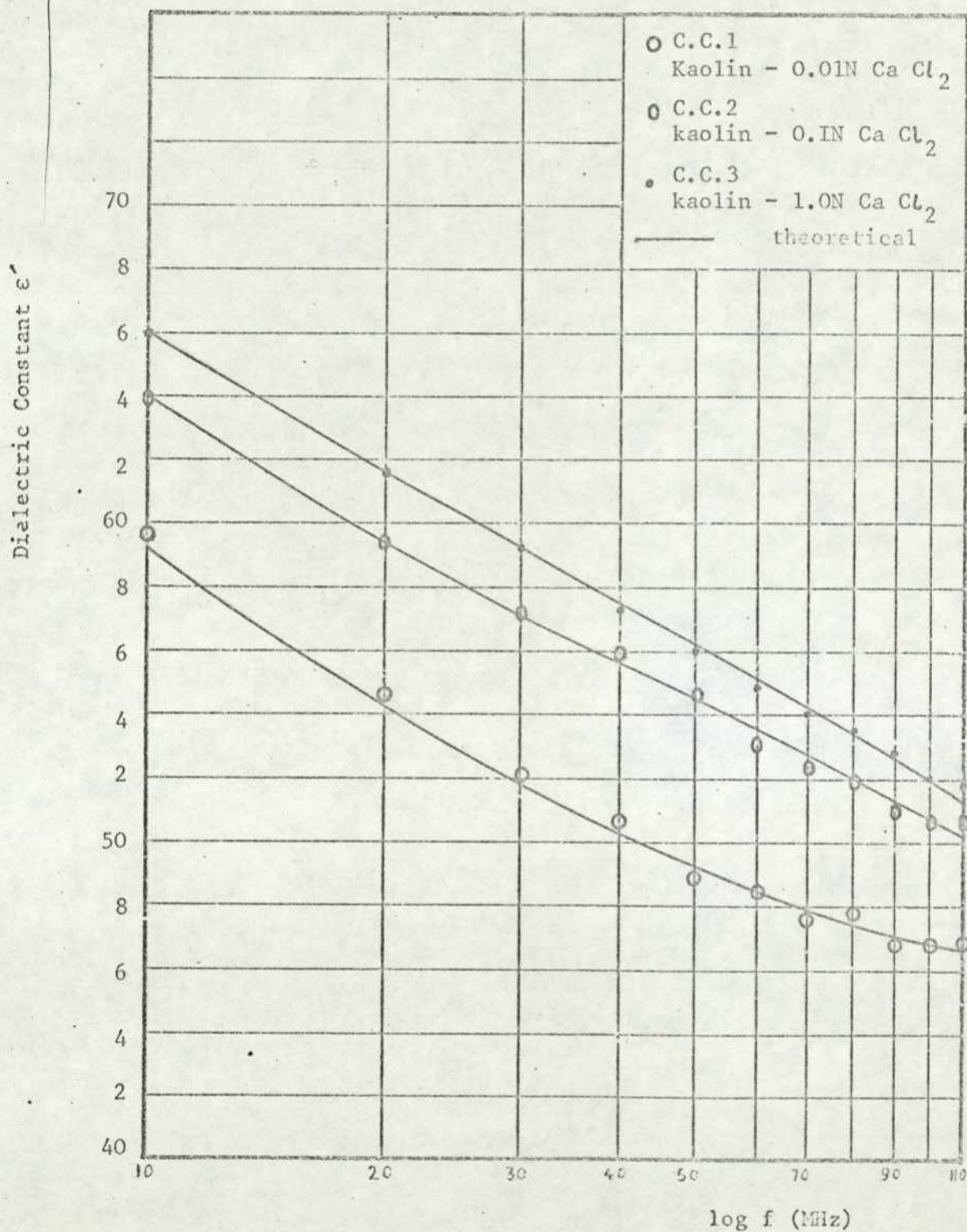


Fig. 6.3.1 Dielectric Dispersion - Cation Concentration

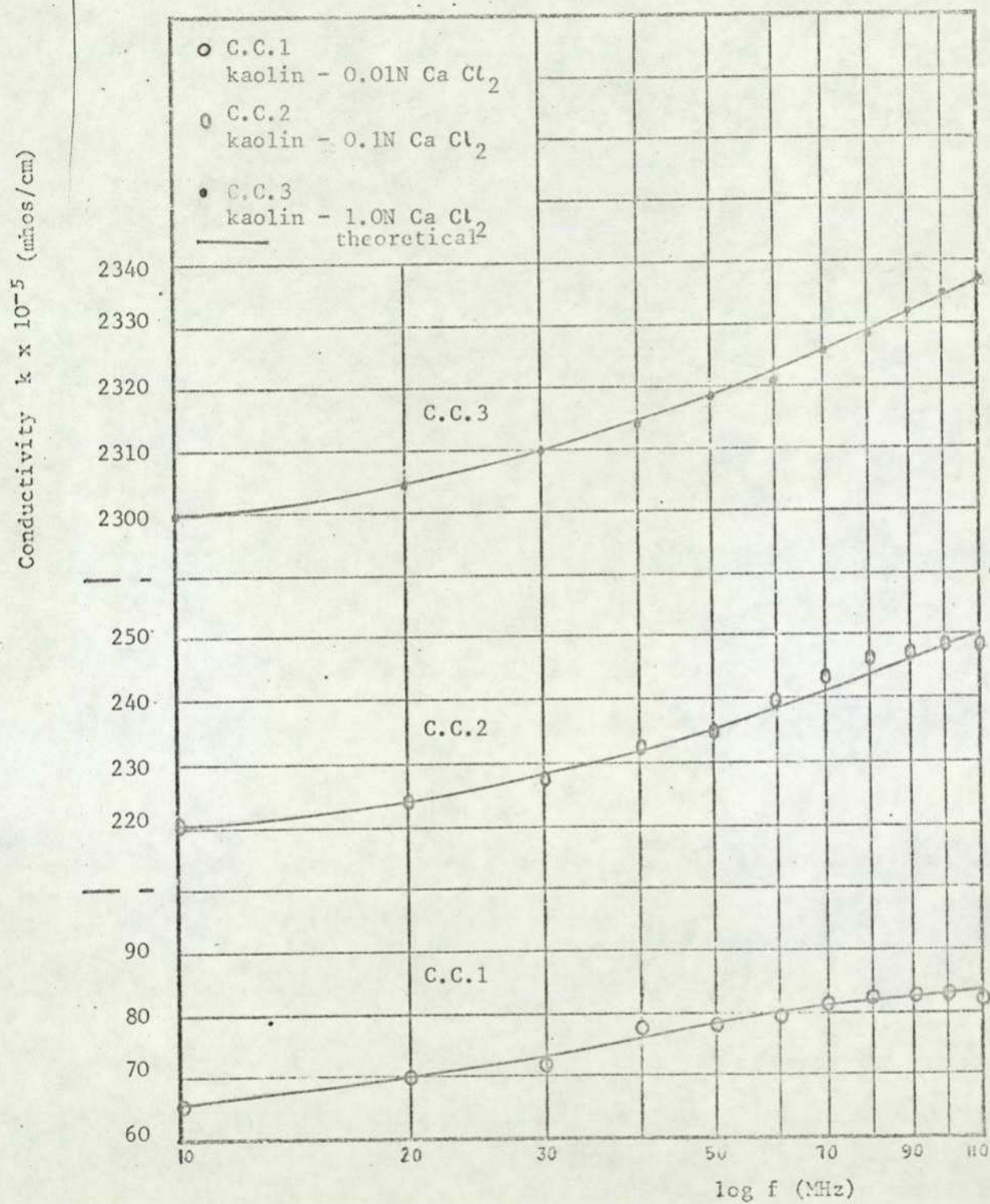


Fig. 6.3.2 Conductivity Dispersion - Cation Concentration

6.4 pH VALUE

Figs 6.4.1 & 2 show the effect of electrolyte pH value on the electrical properties of the clay-water-electrolyte system. Three electrolytes of different pH values were used to prepare samples of kaolin for electrical dispersion tests. (Na OH : pH 13.4, Na Cl : pH 7.0, HC : pH 0.35)

Examination of the dispersion curves shows, in addition to the familiar dispersion characteristics, that :

As the pH value of the electrolyte increases

- 1) the dielectric constant increases,
- 2) the conductivity increases,
- 3) the dielectric dispersion decreases
- 4) the conductivity dispersion decreases as pH values approach neutrality (pH = 7) and then increases.

This is the same trend observed in the case of clay mineral variation (Sec.6.1) with the exception of the variation in the dielectric dispersion.

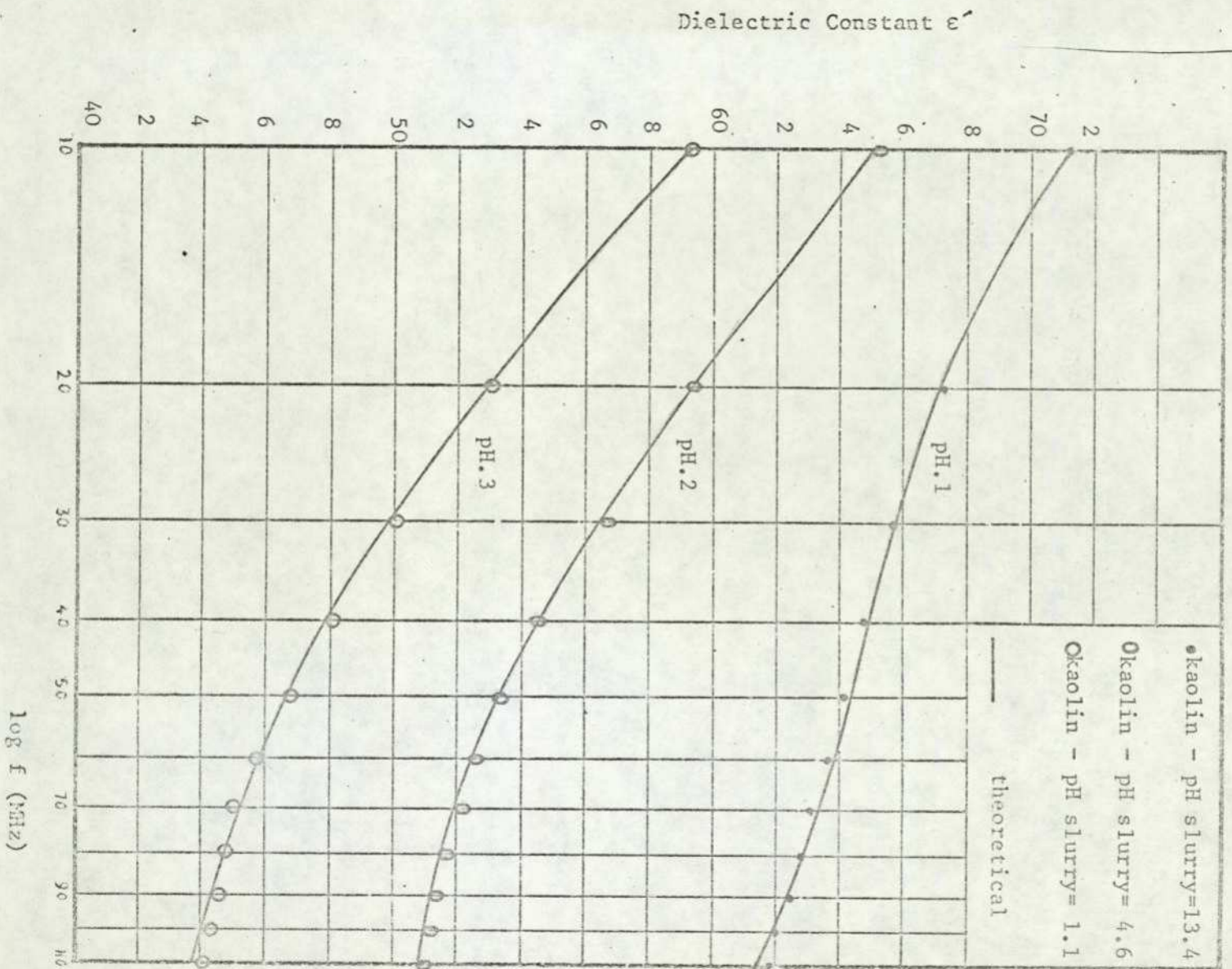


Fig. 6.4.1 Dielectric Dispersion - pH Value

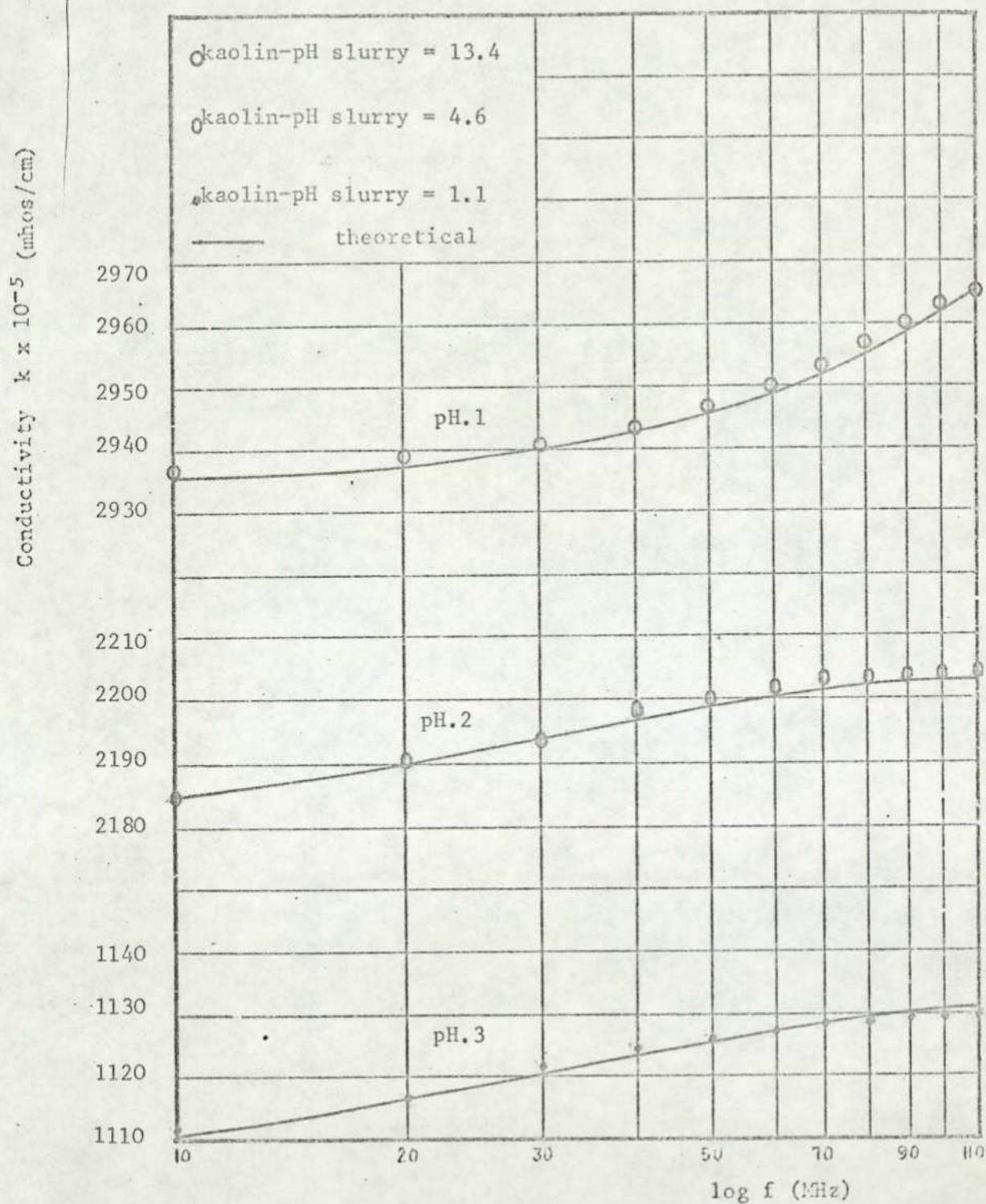


Fig. 6.4.2 Conductivity Dispersion -

6.5 CONSOLIDATION PRESSURE - WATER CONTENT

The effects of consolidation pressure and water contents on the electrical properties of the clay-water system are shown in Figs. 6.5.1-6. Three different consolidation pressures (3.5, 7.0, 14 kg/cm²) and three different initial water contents (100, 200, 400%) were used to prepare nine samples of kaolin.

Figs. 6.5.1-4 show that electrical properties of the clay-water system vary in a characteristic manner:

As either the consolidation pressure decreases or the water content increases

- 1) the dielectric constant increases
- 2) the conductivity increases
- 3) the dielectric dispersion decreases (inconsistent)
- 4) the conductivity dispersion increases (slightly)

This is in agreement with the results of all other investigations on the subject (Mitchell and Arulanandan, 1968; Hasted, 1973).

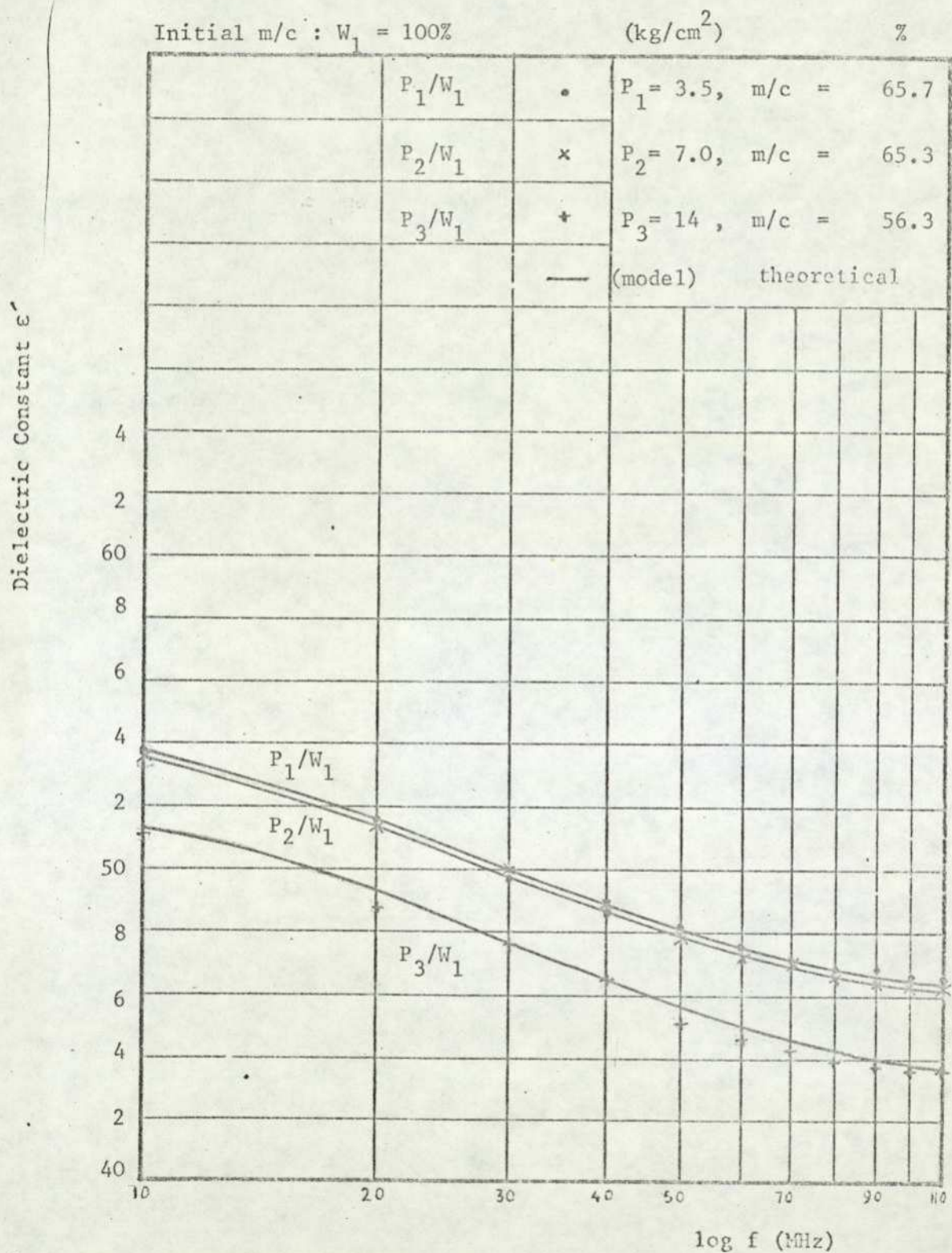


Fig. 6.5.1 Dielectric Dispersion - Consolidation Pr & m/c

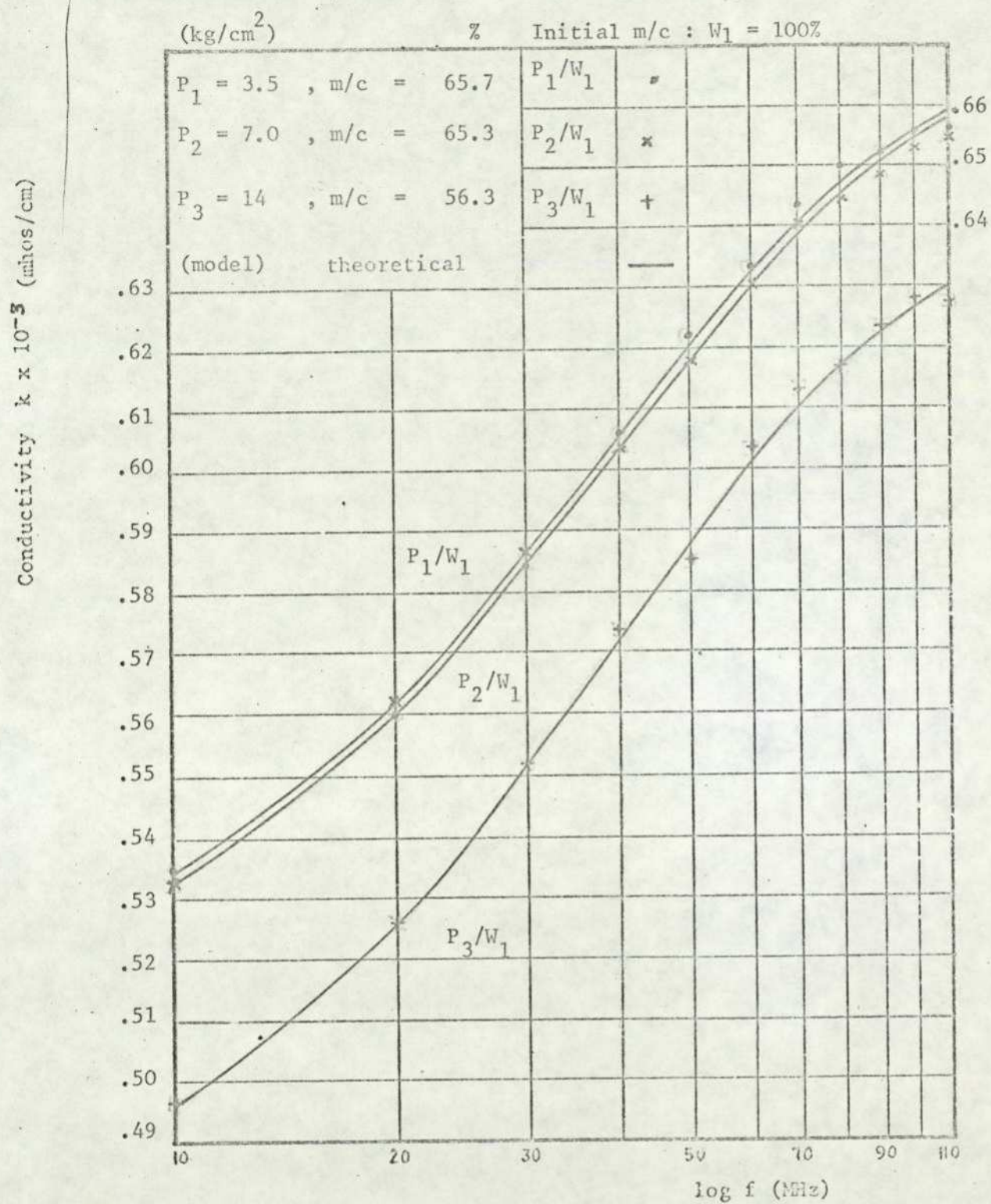


Fig. 6.5.2 Conductivity Dispersion - Consolidation Pr. & m/c

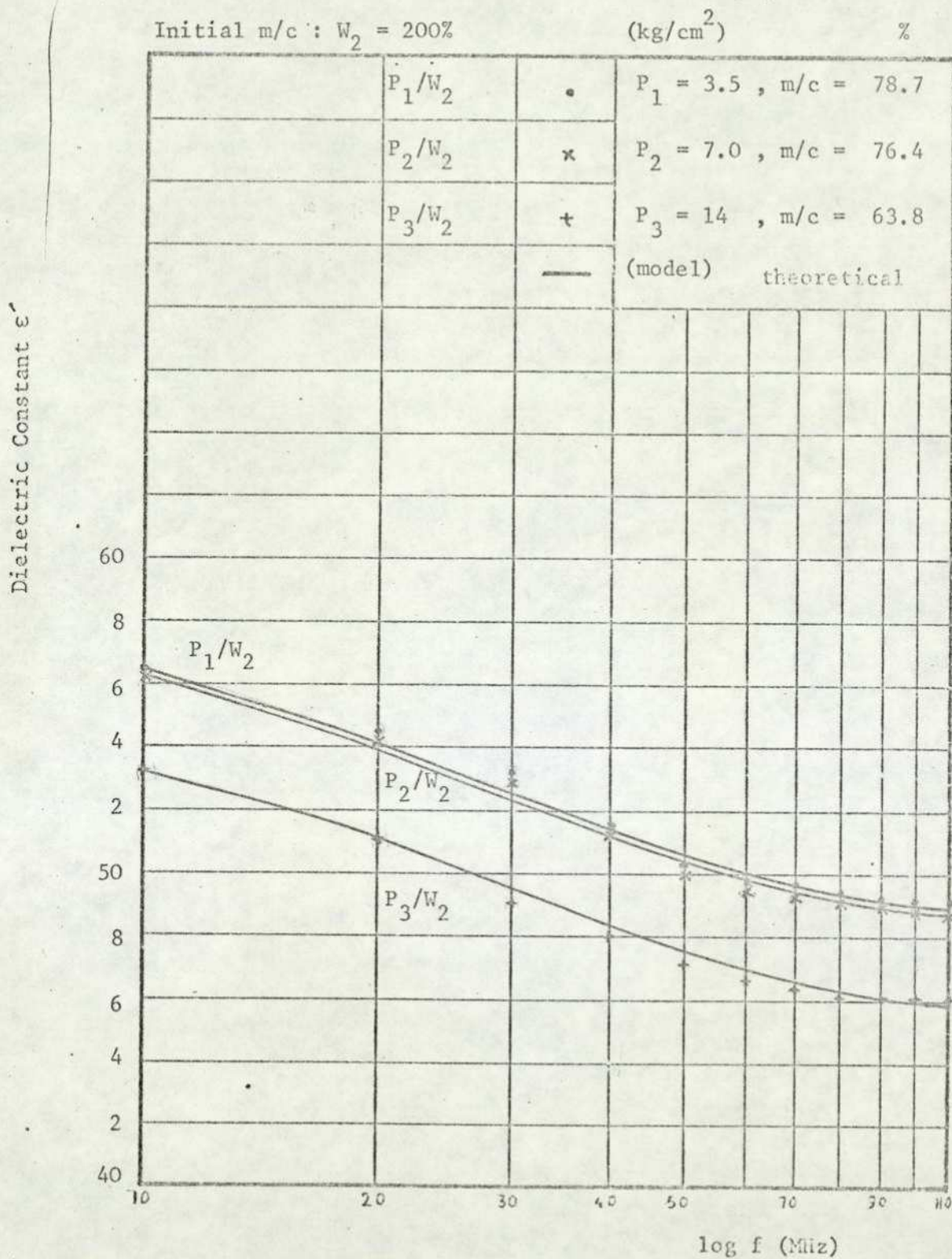


Fig. 6.5.3 Dielectric Dispersion - Consolidation Pr. & m/c

Conductivity $k \times 10^{-5}$ (mhos/cm)

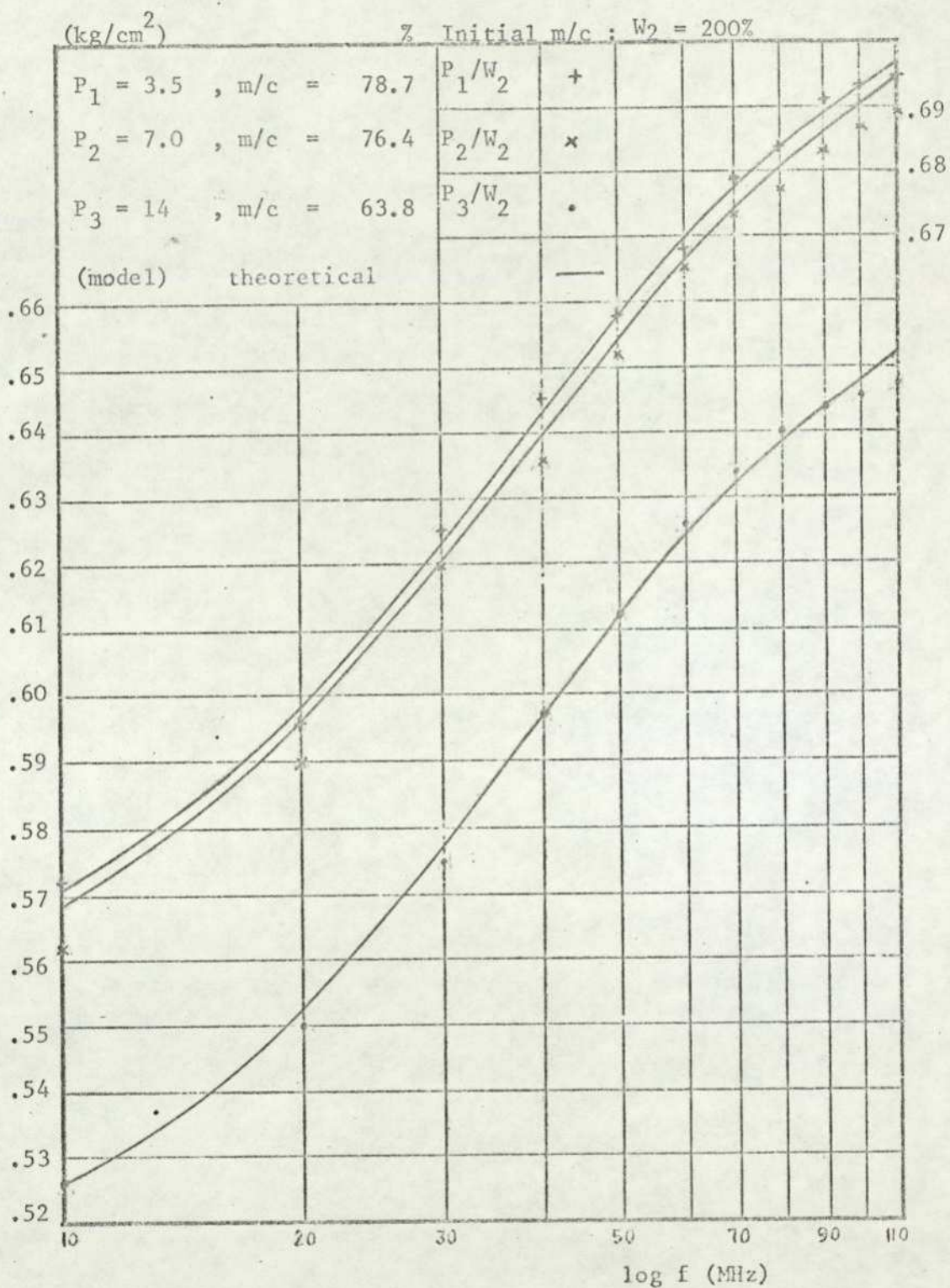


Fig. 6.5.4 Conductivity Dispersion - Consolidation Pr. & m/c.

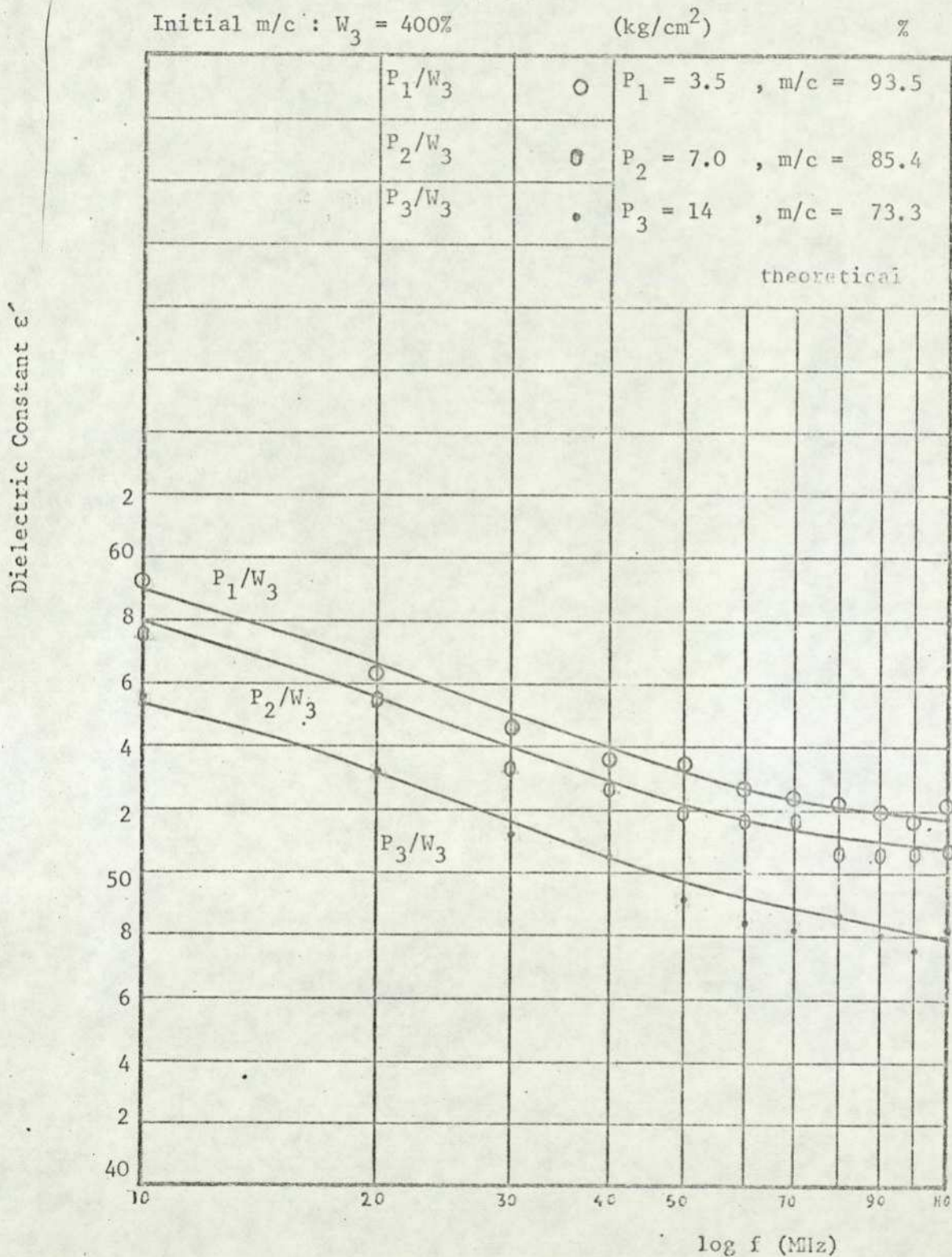


Fig. 6.5.5 Dielectric Dispersion- Consolidation Pr. & m/c

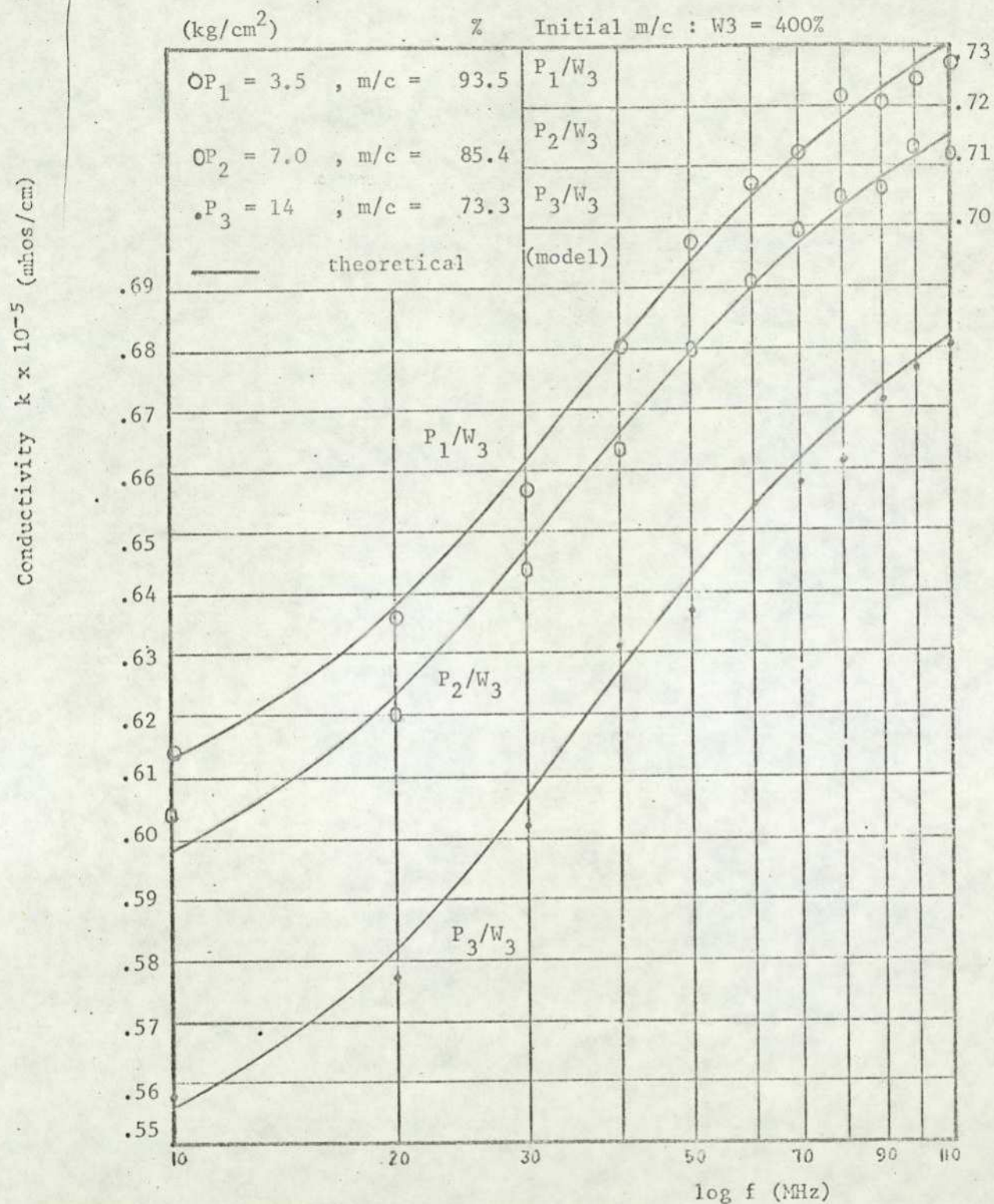


Fig. 6.5.6 Conductivity Dispersion - Consolidation Pr. & m/c

6.6 PARTICLE ORIENTATION

The effect of particles orientation on the electrical properties of clay-water-electrolyte system is shown in Figs.6.6.1 & 2. Three cylindrical sub-samples were cut with their longitudinal axes in different orientations with respect to the direction of consolidation pressure (parallel, perpendicular, and at 45°).

The electrical properties change with the direction of current path such that the dielectric constant ϵ , the conductivity K , the dielectric dispersion $\Delta \epsilon$, and the conductivity dispersion ΔK , all increase in the sequence parallel to the direction of consolidation < inclined < perpendicular. It is relevant that these orientations indicate at the same time the angle between the direction of flow of the current and the preferred orientation of the long axis of particles.

This is consistent with the results of all other investigations on the subject (Basu and Arulanandan,1973, Smith,1971).

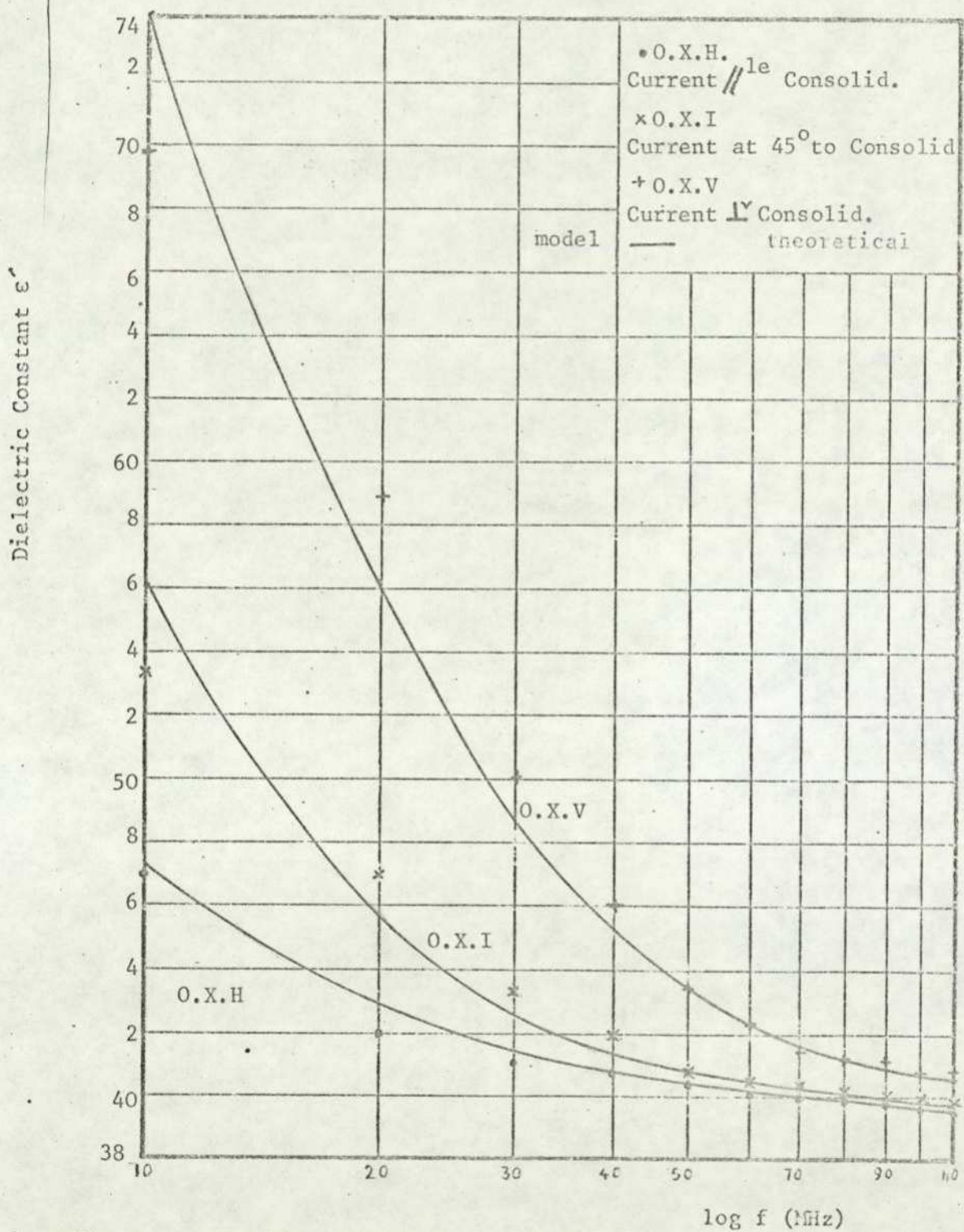


Fig. 6.6.1 Dielectric Dispersion- Particle Orientation

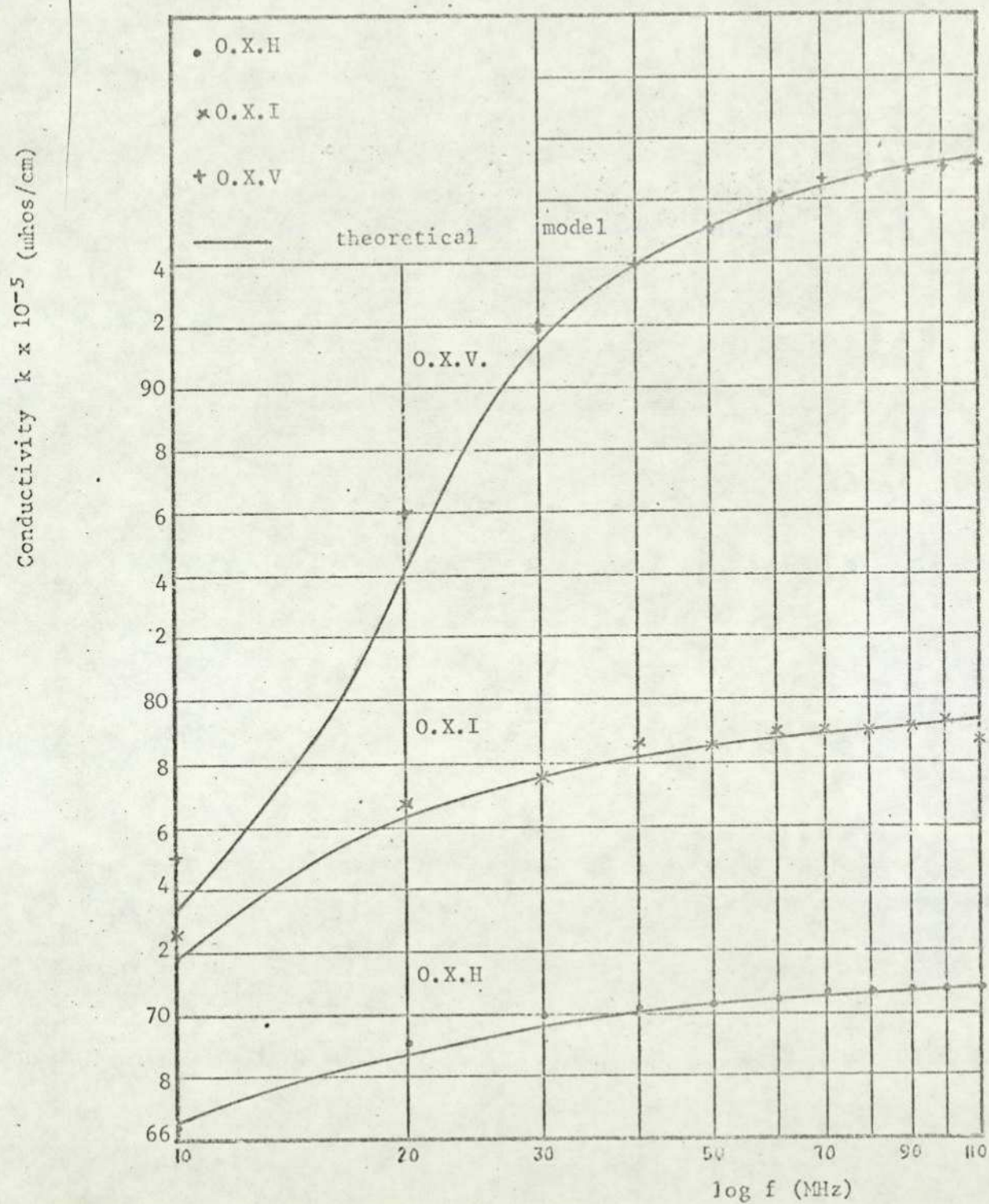


Fig. 6.6.2 Conductivity Dispersion - Particle Orientation

6.7 RIGID BONDING

Figs. 6.7.1-2 show the effect of variation in rigid bonding strength on the electrical properties of the clay-water-electrolyte system. Three types of polymeric aluminium hydroxy cation solutions (small, medium, and large cation) in three different concentrations (0.33, 1, 2 monomolecular layers) were used to prepare nine samples for electrical dispersion tests.

1) The variation in the electrical properties follows the trend :

As the cation size decreases

- a) the dielectric constant decreases,
- b) the conductivity decreases,
- c) the dielectric dispersion decreases, and
- d) the conductivity dispersion decreases

2) Figs. 6.7.3 -4 show the effect of ageing on the electrical properties of the same nine soil samples used for rigid bonding effect. It can be seen that as time lapses

- a) the dielectric constant decreases
- b) the conductivity decreases
- c) the dielectric dispersion decreases, and
- d) the conductivity dispersion decreases.

It is relevant that as the size of the polymeric aluminium hydroxy cation decreases, the rigid bonding strength increases, and in all cases the rigid bonding strength increases with time.

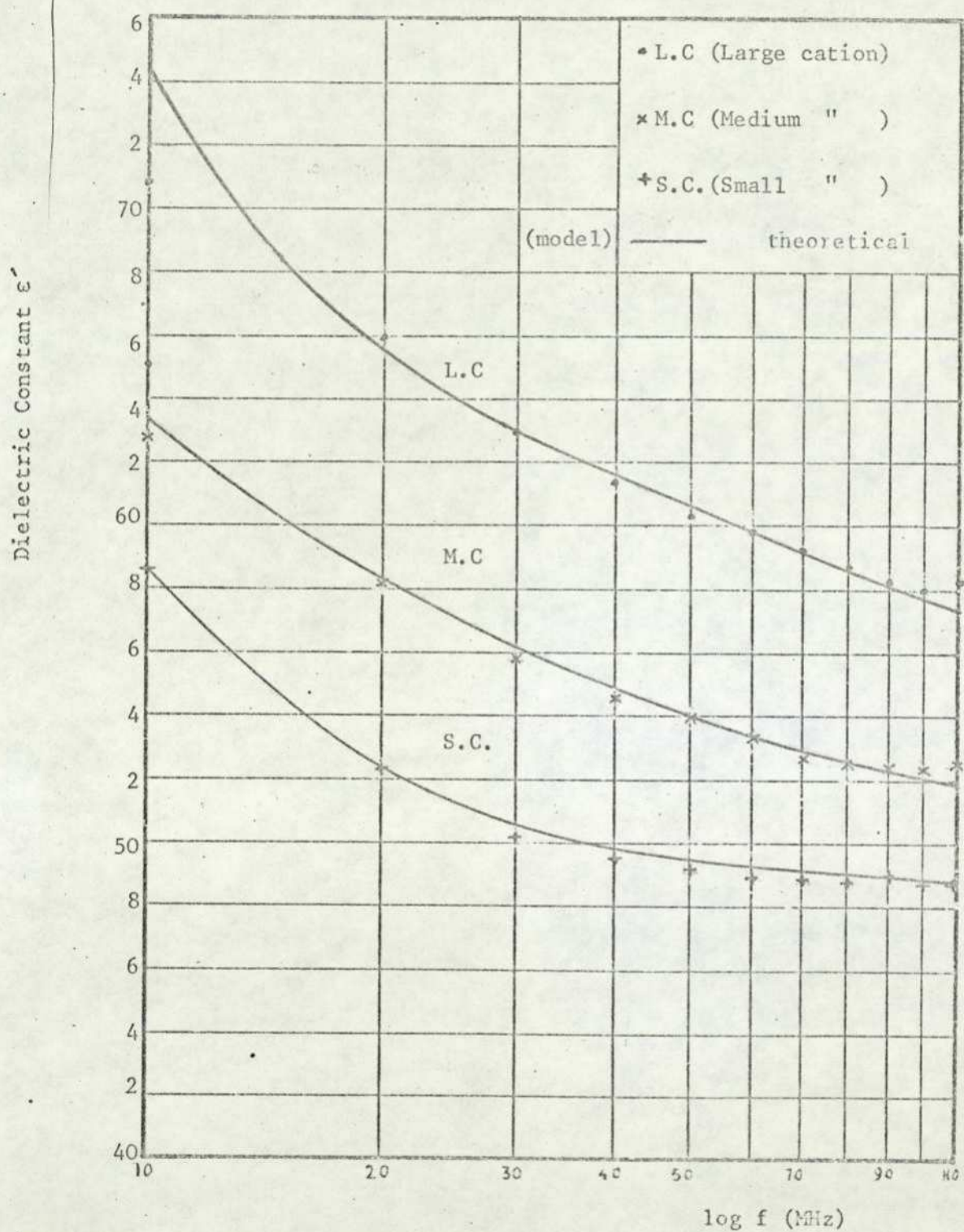


Fig. 6.7.1 Dielectric Dispersion - Rigid Bonding

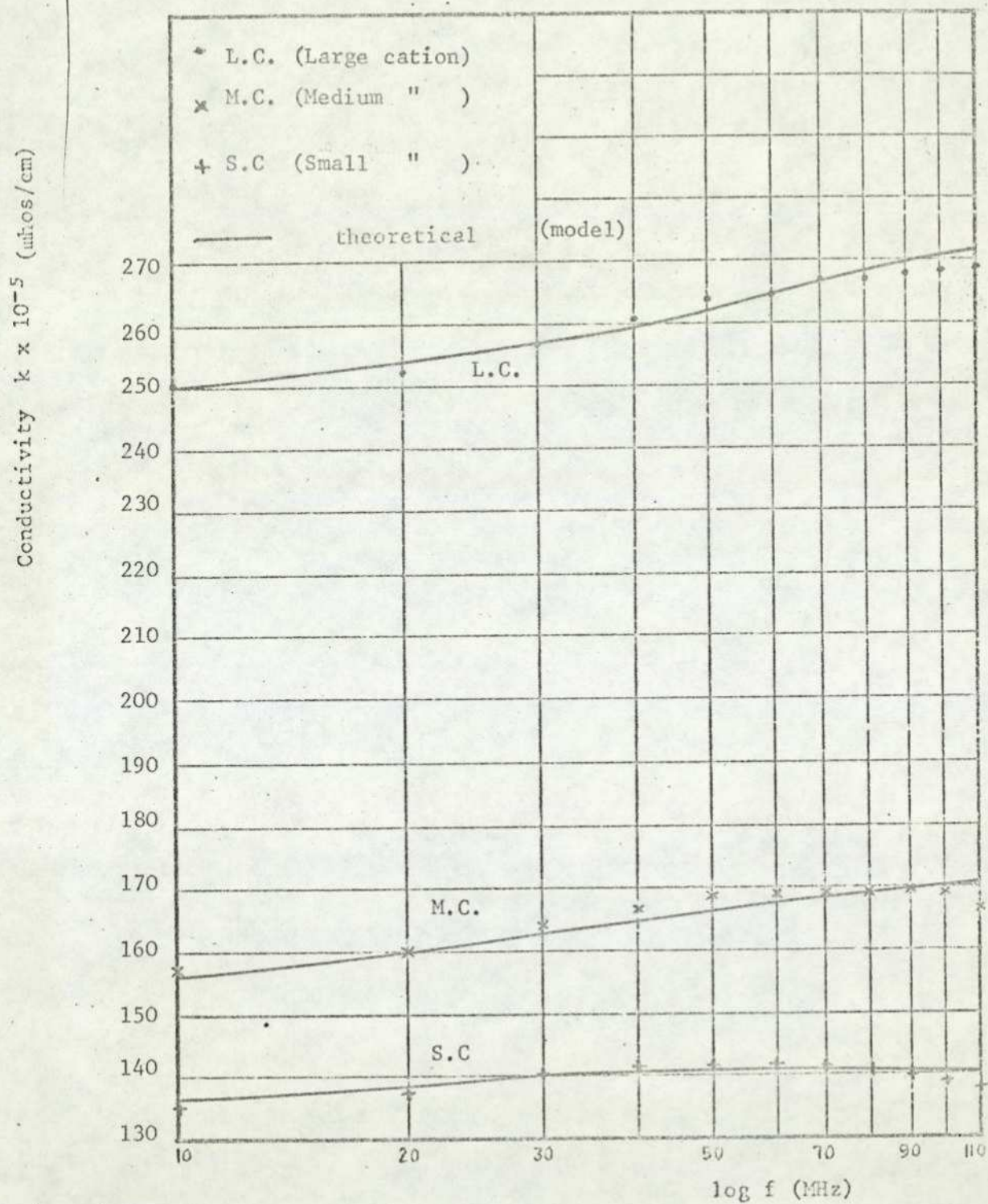


Fig. 6.7.2 Conductivity Dispersion - Rigid Bonding

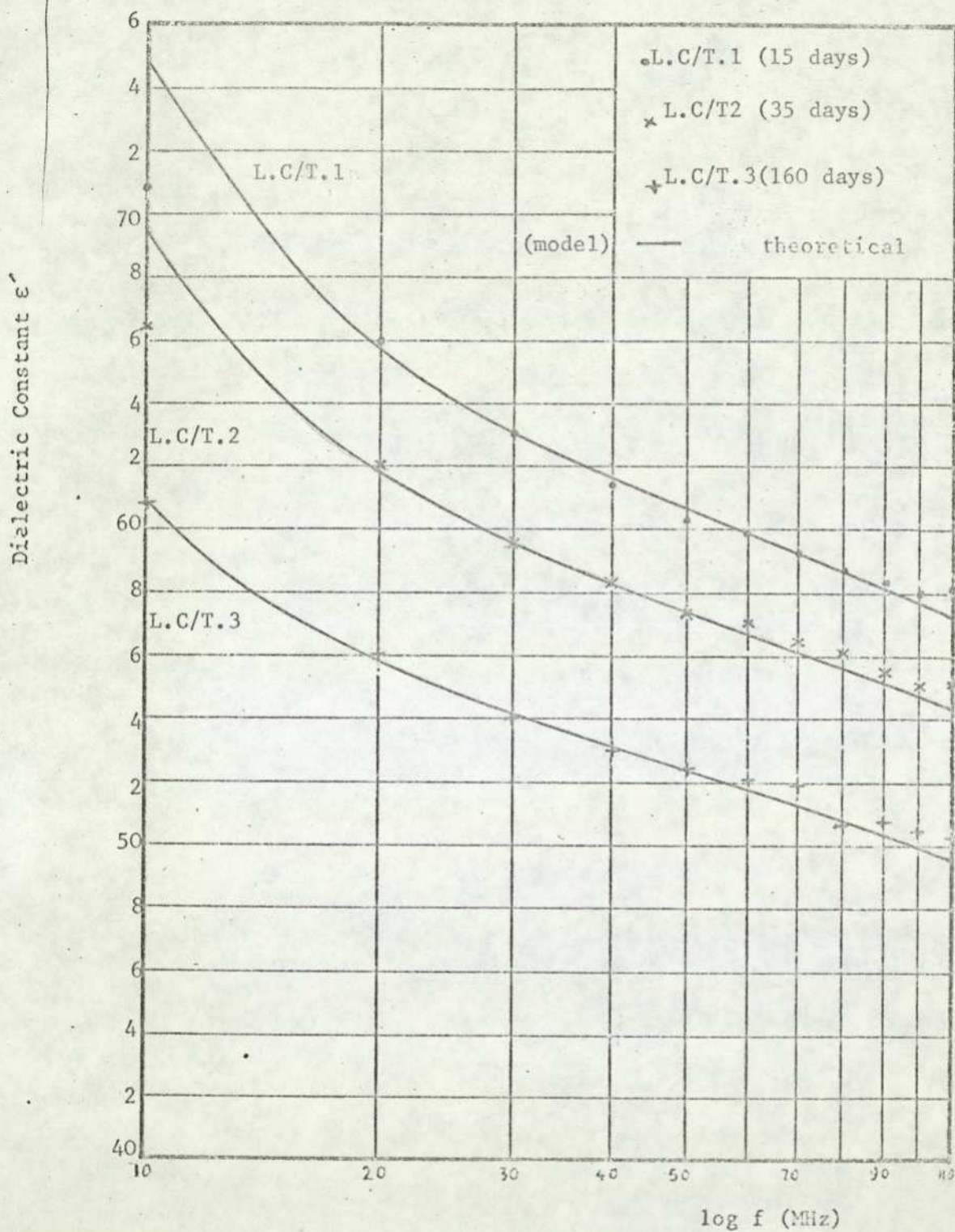


Fig. 6.7.3 Dielectric Dispersion - Rigid Bonding

Conductivity $k \times 10^{-5}$ (mhos/cm)

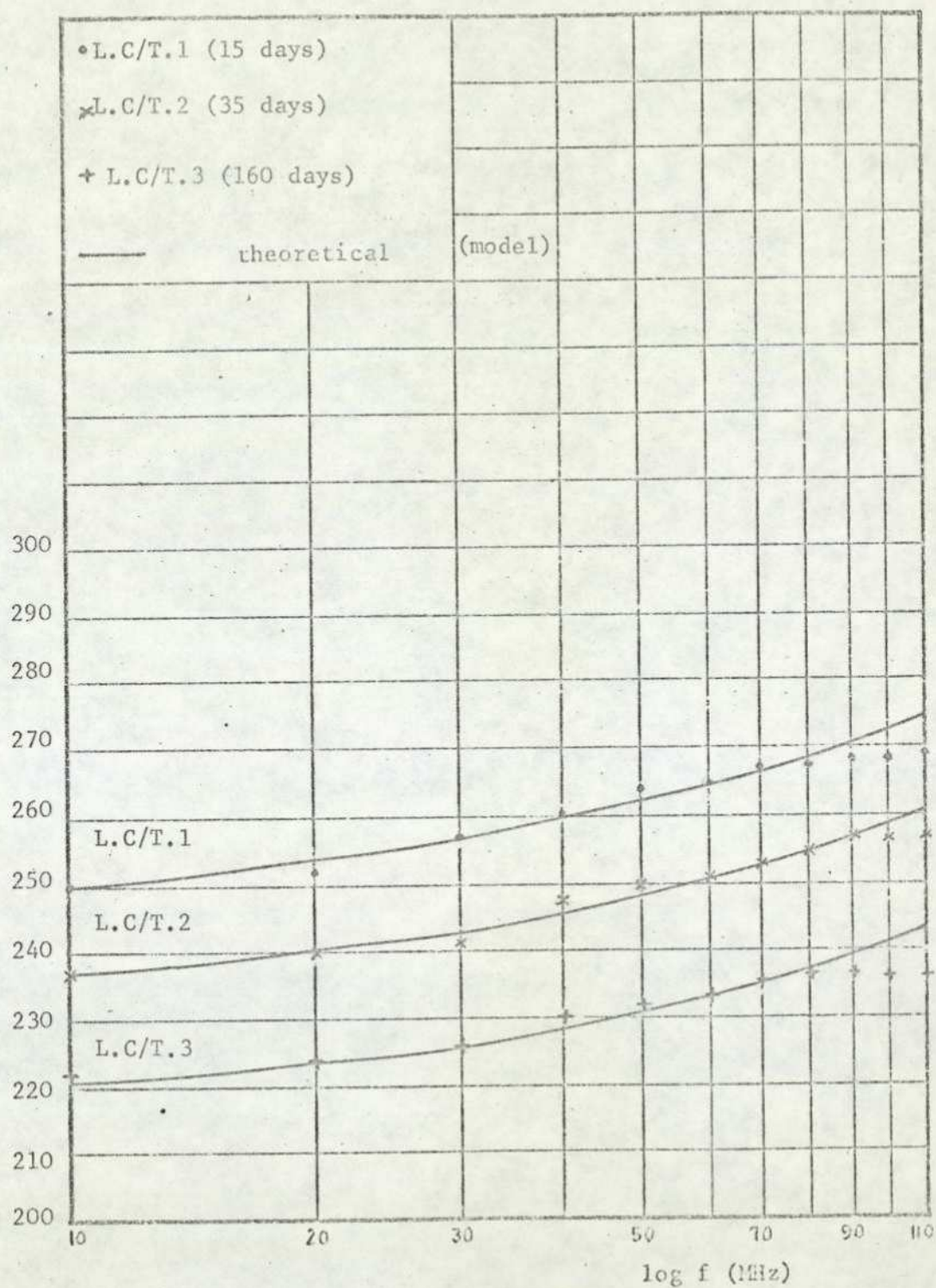


Fig. 6.7.4 Conductivity Dispersion - Rigid Bonding

6.8 SUMMARY AND DISCUSSION

The effects of different experimental parameters on the electrical properties of soil-water-electrolyte system, i.e.; the dielectric constant ϵ , the conductivity k , the dielectric dispersion $\Delta \epsilon$, and the conductivity dispersion Δk , are summarized in Table 6.8.1

Table 6.8.1 : Effect of Different Parameters on Electrical Properties

S.	Parameters-variation	Effect on electrical properties			
		ϵ	k	$\Delta \epsilon$	Δk
1.	Clay mineral(c.e.c.)increases	increases	increases	increases	increases
2.	Cation valence increases	increases	increases	increases*	increases
3.	Cation concentration increases	increases	increases	increases*	increases
4.	pH increases	increases	increases	decreases*	increases*
5.	Water content increases (consolidation pressure decreases)	increases	increases	decreases*	increases*
6.	Angle between current direction and particles long axis increases	decreases	decreases	decreases	decreases
7.	Rigid bonding increases	decreases	decreases	decreases	decreases

* slight variation or inconsistent

The experimental results summarized in Table 6.8.1 indicate that :

6.8.1 The increase of cation exchange capacity of the clay mineral or the pH value of the electrolyte produces an increase in the three components of the electrical response, i.e., ϵ , K , and ΔK .

It is well known (Michaels,1959;Schofield,et al.,1949;1954; De 1974) that at high pH values the positive charges on the clay particles edges decrease and thus the surface density of negative charge increases,

i.e. the cation exchange capacity of the clay particles increases. Therefore, the increase in c.e.c. of the clay mineral or the pH value of electrolyte solution will have a similar effect as indeed is confirmed by the present experimental observation.

Perhaps the most inconsistent results are those of the dielectric dispersion. This is probably due to the fact that various factors are affecting $\Delta \epsilon$ simultaneously and in different ways in addition to the possibility that a number of these factors might have a critical value after which the trend of their effect is reversed.

The increase of the other three components of the electrical properties; ϵ , k , and Δk , is probably due to the increase of water content associated with soil system as the c.e.c. of clay mineral or pH value of electrolyte increases. This is evident by the values of final water contents obtained in those experiments which were as follows:

Slate dust	-	final m/c	30.4%
Kaolinite	-	final m/c	65.4%
Montmorillonite	-	final m/c	122.6%
pH 0.35	-	final m/c	52.8%
pH 7.0	-	final m/c	60.8%
pH 13.4	-	final m/c	78.3%

6.8.2 The increase of cation valence or cation concentration causes an increase in ϵ , k , and Δk , while the variation of the dielectric dispersion was inconsistent.

The behaviour of $\Delta \epsilon$ is explained by the fact that the thickness

of the adsorbed layers decreases as the cation valence or concentration increases and consequently the capacitances parallel to the particle surface decrease resulting in a decrease of the dielectric dispersion. In the mean time, the increase of the conductivity of the weakly adsorbed layer causes an increase in the dielectric dispersion resulting in a possible inconsistency in the overall result.

The increase in k and Δk is probably due to the increase of concentration and valence of cations in the pore fluid phase (Harris, et al., 1957), while the increase in the dielectric constant may be attributed to the increase of the capacitances normal to particle surface caused by the thinner adsorbed layers (Schofield, 1947, Bolt, 1955). These capacitances are known to be essentially loss free and thus contribute to the dielectric constant rather than to the dielectric dispersion.

6.8.3 As the consolidation pressure increases the water content reduces and it is found that ϵ , k , and Δk decrease, whereas $\Delta\epsilon$ slightly increases.

The reduction in water content implies a reduction in the pore fluid and thus the relative contribution of the transport of electric current through the solution becomes less. Knowing that when the pore fluid is essentially pure water, the contribution of both the solid and adsorbed water phases to the components of the electrical response is minimal, it should be expected that ϵ , k , $\Delta\epsilon$, and Δk will increase as the water content increases.

However, due to the fact that the critical frequency of pure water dipolar relaxation is significantly remote from the radio frequency range (17 GHz), the dielectric dispersion would be entirely in the composite phase (solid, normally adsorbed, and structurally

associated). Therefore, as the water content increases, the composite phase decreases, and thus a factor opposite to that mentioned above will tend to reduce $\Delta \epsilon$ and Δk with an overall result confirming the experimental observation.

6.8.4 The decrease of the four components of electrical response with the increase in the angle between the direction of flow of electric current and the preferred orientation of the long axis of the plate-like particles, is obviously due to the corresponding increase in the tortuosity of the current path.

6.8.5 As the rigid bonding strength increases, either by the type of cation (polymeric aluminium hydroxy cation) or by ageing, a corresponding decrease in the four components of electrical response, ϵ , K , $\Delta \epsilon$, and ΔK , is observed.

In fact the increase in rigid bonding is associated with three other effects:

- 1) an increase in the tortuosity of electric current path
- 2) a decrease in the effective surface area of the charged particles
- 3) a decrease in the free pore water content as the amorphous growth and quasi-crystalline growth develop (Foster et al., 1975)

It has been shown in this chapter that these three effects cause a decrease in the electrical response components.

However, it may be noticed that the higher rigid bonding strength is caused by the smaller polymeric aluminium hydroxy cation which is known to be of higher valence (Hsu et al., 1964) and thus should be expected

to raise the components ϵ , K , and ΔK (Sec.6.2). Probably, the above mentioned three effects overshadow the effect of valence, which reduces as these cations become incorporated in an amorphous solid coating (Foster, et al., 1975).

VALIDITY OF THE NEW MODEL7.1 PROCEDURE FOR INVESTIGATING THE MODEL'S VALIDITY

The suggested new model for the soil system was applied to all the soil samples that have been experimentally investigated in this thesis in order to evaluate the model's ability to predict the experimental observations. The procedure is presented in the following order:

7.1.1 Experimental data of the soil sample

Clay mineral (I)

Electrolyte type (I) and Concentration (I)

pH of : Electrolyte (I), Slurry (D), and Extract (D)

Consolidation pressure P (I)

Final water content W (D)

These are all experimental parameters of the soil sample under consideration, in which:

I $\equiv$ Independent variable

D $\equiv$ Dependent variable

7.1.2 Calculated Data of the Sample

Void ratio (e), is given by Eq.4.1.1

Porosity (p), is given by Eq.4.1.2

Internal surface area (A_s), is given by Eq.4.1.4

Specific surface area S may be determined by different methods

(van Olphen, 1963): Computation from particle dimensions, computation from crystallographic dimensions, direct determination from vapor-adsorption data, and determination by negative adsorption (Schofield, 1947).

Consistent results are reported according to these methods:

kaolin, S; 15-18 m^2/g (Schofield, et al., 1954).

11-17 m^2/g (Murray, et al., 1959).

11 m^2/g (Olsen, 1962).

bentonite, S; $800 \text{ m}^2/\text{g}$ (Schofield, et.al., 1948).

$750 \text{ m}^2/\text{g}$ (van Olphen, 1963).

Values of $S = 15 \text{ m}^2/\text{g}$ for kaolin and $S = 750 \text{ m}^2$ for bentonite are used in this thesis.

Tortuosity coefficient (T), is determined by Eq.4.1.27.

Thickness of the strongly adsorbed layer (t_f)

As mentioned before (Sec. 4.1.1.3) t_f is determined by:

(a) the radius of the hydrated adsorbed cation (Davies and Rideal, 1968).

(b) 10 angstroms (Rosenqvist, 1959).

(c) two monomolecular layers of adsorbed water or 5 angstroms (van Olphen, 1963).

The value of $t_f = 5$ angstroms is used in most of the cases investigated in this thesis.

Thickness of the weakly adsorbed layer (t_w)

This is given by Eq. 4.1.9.

7.1.3 Calculated Data of the Model

Geometrical parameters

The linear porosity ($\bar{p}$), is given by Eq. 4.1.12, and is equivalent to the width of the pore fluid phase.

Equivalent height of the solid phase element (d_r) is given by Eq.4.1.13 and at the same time equals the width of the composite phase.

Equivalent height of the strongly adsorbed layer (d_f) is given by Eq.4.1.14

Equivalent height of the weakly adsorbed layer (d_w) is given by Eq.4.1.15.

Equivalent height of the associated pore fluid layer (d_{1a}) is given by Eq.4.1.17.

Electrical parameters

Capacitance of the pore fluid phase (C_f) is given by Eq.4.1.19.

Conductivity of the pore fluid phase (K_f) is given by Eq.4.1.21.

Capacitance of the solid phase (C_r) is given by Eq.4.1.25.

Conductivity of the solid phase (K_r) is given by Eq.4.1.26.

Capacitance of the strongly adsorbed layer, in the direction perpendicular to the soil particle surface (C_{fd}) is given by Eq.4.1.35.

Capacitance of the weakly adsorbed layer, in the direction perpendicular to the soil particle surface (C_w) is given by Eq.4.1.44.

Capacitance of the associated pore fluid layer (C_{fa}) is given by Eq.4.1.23.

Conductivity of the associated pore fluid layer (K_{fa}) is given by Eq.4.1.24.

Capacitance of the strongly adsorbed layer, in the direction parallel to the surface of the soil particle (C_{fd}) is given by Eq.4.1.38, and the complex impedance of this layer

in the same direction (Z_f) is given by Eq. 4.1.39.

Capacitance of the weakly adsorbed layer, in the direction parallel to the surface of the soil particle (C_{wd}) is given by Eq.4.1.46, and the conductivity of this layer in the same direction (K_{wd}) is given by Eq.4.1.47.

7.1.4 Computed theoretical electrical response of the model

Theoretical electrical responses of the model (ϵ'_m , K_m , and ϵ''_m) were computed from Eqs.4.2.13-15 for different samples at different frequencies by substituting the relevant values of the model parameters. The results are listed in Appendix V.

7.1.5 Graphical representation of the theoretical responses

Theoretical responses of the model were plotted as graphs of ϵ' and K_m against $\log f$. The experimental observations for the different samples were plotted together with the corresponding theoretical graphs to help in a direct comparison as shown in Chapter 6, Figs.

7.2 DISCUSSION

The results obtained by the application of the proposed model, show clearly that the electrical network of the model provides theoretical responses which are consistent with the experimental observations. The agreement between the theoretical and experimental results lends support to the concepts which have been introduced in developing the model. These concepts reflect important differences between the new model and the other model which has been frequently adopted by several investigators (Basu and Arulanandan, 1973; Smith, 1971; Sachs, et. al., 1964) since it was first suggested by Wyllie and Southwick (1954).

The main concepts that were used in developing the new model and which at the same time constitute the above mentioned differences may be outlined as follows:-

- 7.2.1 The representation of the adsorbed phase, which should not, by any means, be neglected in a clay-water-system. Therefore, instead of the not very well defined "wet particle" element, the new model incorporates two discrete elements representing the solid phase and the adsorbed layers in series combination.
- 7.2.2 The recognition of the possibility of simultaneous polarization contributions of various mechanisms instead of a unique type of polarization mechanism. While an interfacial polarization (Maxwell-Wagner, 1914) may take place at the interfaces of different phases, an adsorbed phase polarization (Murphy and Lowry, 1930) may develop along the particle surface as well as an orientation polarization (Debye, 1924) within different phases and around the points of adsorption.
- 7.2.3 The representation of a frequency-dependent component of admittance by a component of the strongly adsorbed layer parallel to the particle surface with a distribution of relaxation time (Cole and Cole, 1941), rather than a single relaxation time or a mean relaxation time.

- 7.2.4 The introduction of a "tortuosity coefficient" whose value depends among other factors on the angle between the direction of the electrical current and that of the preferred orientation of the long axis of the particles, and thus providing a means of interpretation of the variation of the electrical properties of soils with the direction of current. Such variation has been observed and reported by many investigators (Arulanandan and Mitchell, 1968; Arulanandan and Smith, 1973).
- 7.2.5 The proposal of empirical numerical expressions to account for every factor that was expected to have an effect on the electrical properties. Despite the empiricism of these expressions, they have nevertheless the merit of describing effects which are relevant to the phenomena investigated and therefore permit the introduction of these effects into the analysis of the data. It is appreciated that these expressions although useful as initial approximation may be subject to further improvement.

ELECTRICAL RESPONSE IN RELATION
TO SOIL MICRO-STRUCTURE

8.1 INTRODUCTION

Several attempts have been made to correlate the electrical properties of soil systems with the internal structure of these systems. The investigators interested in this subject are from different disciplines, and perhaps the petroleum engineers were first to realise the importance of such correlation.

Archie (1942) suggested a "formation resistivity factor", F , to describe the type and character of the formations penetrated in the exploitation of oil and gas reservoirs. He proposed the empirical expression

$$F = p^{-m} \quad (8.1.1)$$

where p is the porosity and m is the slope of the line representing the relationship between F and p as determined experimentally.

From a study of many groups of data, Archie reported that m has been found to range between 1.8 and 2.0 for consolidated sandstones.

Patnode (1949), reported a value of $m = 1.6$ for aqueous slurries of raw attapulgite clay and powdered silica.

Following a rather extensive experimental study on a variety of both consolidated and unconsolidated porous beds and structures, Macmullin and Muccini (1956) developed a dimensionless relation between the hydraulic radius r_h , viscous flow permeability p , and F

$$F = r_h^2 = C \cdot p \quad (8.1.2)$$

where the mean value of the constant C is 3.66. The expected error in calculating any of the three parameters from the other two is 17.6%.

The formation factor F has been called also the "Resistivity Factor" by Cornell and Katz (1953), while Carman (1956) used the term "Tortuosity Factor" to denote (porosity/F).

Meredith and Tobias (1962), reviewed the studies on the conductivity in consolidated systems and concluded that because of the complexity of the problem, it can be treated only by empirical equations of rather limited validity.

Patnode and Wyllie (1950), in their work on the quantitative interpretation of electric log data, defined the "formation factor" as the ratio of the resistivity of the formation 100 percent saturated with brine, to the resistivity of the brine, and thus it expresses the texture of all the solid constituents of the rock. Noticing that F was not independent of the resistivity of the saturating solutions, these authors attributed a part of the conduction current to "wet clay" components. Therefore, Patnode and Wyllie suggested that the soil system is analogous to a two-element in parallel resistor model, one element being the current path through the solution while the other element represents the conductance of current by the "wet solid" particles. The conductance, K_0 , of the two-element model is the sum of the conductances of the two elements

$$\begin{aligned} K_0 &= K_1 + K_2 \\ &= \frac{kr}{z} + \frac{ks}{F} \end{aligned} \quad (8.1.3)$$

where kr, ks are the specific conductivities of the wet solid

particles and the solution respectively, and z is a function of the volume fraction of solid particles. It is easily seen that the two-element model and its conductance expression (Eq.8.1.3) are equivalent to the three-element model (Sec.3.3) and its corresponding expressions (Eqs.3.3.3 & 4) if element 1 in the latter was omitted.

Winsauer and McCardell (1953) attempted to extend the two-element model to account for the so-called "ionic double layer", and assumed that the conductance of this layer was in parallel combination with the solution phase. Therefore, the specific conductivity of the solution phase, k_s , in Eq.8.1.3 was replaced by the sum of two components, i.e.

$$k_s = k_p + k_d \quad (8.1.4)$$

where k_p & k_d are the conductivities of the pore fluid and the adsorbed layer respectively.

Combination of Eq.8.1.3 with Eq.8.1.4 gives

$$K_o F = k_p + k_d \quad (8.1.4)$$

where the specific conductivity of the solid particles, k_p , is zero as the particles were no more assumed to be wet.

Experimental results reported by Winsauer and McCardell assuming F to be 3500 in one case and 4000 in another, showed that there was some uncertainty as to the actual magnitude of the adsorbed layer conductivity because of uncertainty as to the value of F . Nevertheless, the results indicated that there was an increase in the adsorbed layer conductivity as the solution concentration increased up to about 1.0 normal above which the trend was gradually reversed. Similar results were reported by Berg (1952) and Wyllie (1952).

8.2.1 Theoretical Considerations

It has been shown in chapter 4 that the electrical theoretical responses of the soil system can be determined by Eqs.4.2.12 & 13 of the new model proposed by the author and in chapter 7 it was demonstrated that these theoretical responses are in good agreement with the experimental observations.

Careful examination of Eqs.4.2.12 & 13 leads to the conclusion that the pore fluid phase has no effect on the electrical dispersion and that the composite phase which includes the normal components of the adsorption phase of soil systems has a negligible effect on the electrical dispersion which is, therefore, attributed solely to those adsorbed layers which form the parallel components of the adsorption phase. Also the expressions of the electrical components of the two adsorbed layers show that only the weakly adsorbed layer is affected by the geometrical arrangement of the solid particles described by the tortuosity coefficient T_θ , Eq.4.1.47.

Therefore, rearranging Eqs. 4.2.12 & 13.

$$\bar{C}_w = C_m - (\bar{C}_c + \bar{C}_f + C_1) \quad (8.2.1)$$

$$\bar{K}_w = K_m - (\bar{K}_c + \bar{K}_f + C_1) \quad (8.2.2)$$

and by substituting for C_m and K_m of the model by the experimentally measured values of C_s and K_s of the soil sample

(see Eq.5.3.16 & 17),

$$C_w = C_s - (\bar{C}_c + \bar{C}_f + C_1) \quad (8.2.3)$$

$$K_w = K_s - (\bar{K}_c + \bar{K}_f + K_1) \quad (8.2.4)$$

values of C_w and K_w of the weakly adsorbed layer can be determined individually at each frequency used in the experimental programme. Therefore, these values are regarded as the experimentally determined values of the capacitance and conductance of the weakly adsorbed layer.

On the other hand, the theoretical capacitance, C_{wd} , and conductance, K_{wd} , of this layer are given by Eqs.4.1.46 & 47

$$C_{wd} = \epsilon_{wd} \epsilon_v \frac{twAs}{(1-p)^{2/3}}$$

$$K_{wd} = \frac{\lambda As}{(1-p)^{2/3} T\theta^2}$$

The series RC element (of the model) which represents the weakly adsorbed layer of the soil system, has the theoretical electrical components C_{wd} and $R_{wd} = 1/K_{wd}$, while the experimentally determined components of this layer, C_w and K_w , are given by Eqs.8.2.3 & 4.

Therefore, the characteristic time, τ_w , of the weakly adsorbed layer can be determined both theoretically and experimentally.

According to Eq.3.3. , the characteristic time of a series RC circuit is given by

$$\tau = R.C = \frac{C}{K}$$

Therefore the theoretical τ_w is determined by

$$\tau_w = \frac{C_{wd}}{K_{wd}} = T\theta^2(\epsilon_{wd} \epsilon_v tw)/\lambda \quad (8.2.5)$$

which at the same time equals the experimental $[\tau_w]$

$$\tau_w = \frac{C_w}{K_w} = [\tau_w] \quad (8.2.6)$$

Eqs.8.2.5 & 6 give the very important result of correlating the coefficient T_θ which describes the tortuosity of the current path and thus the geometry of the particle arrangement with the experimentally measurable characteristic time which is an electrical property of the system.

It is seen that the coefficient T_θ which has been so far termed the tortuosity coefficient is now expressed, by Eq.8.2.5, in terms of almost all the micro-structural parameters (inter-particle geometry and inter-particle forces). Therefore, it is more relevant to call this coefficient the "Micro-structure Electrical Modulus, M.E.M." which will be denoted M_E and is equal to T_θ such that Eq.8.2.5 can be written

$$\tau_w = M_E^2 (\epsilon_{wd} \epsilon_v t_w) / \lambda$$

$$\text{or } M_E = [\tau_w \lambda / (\epsilon_{wd} \epsilon_v t_w)]^{1/2} \quad (8.2.7)$$

8.2.2 The "Micro-structure Electrical Modulus, M.E.M." in relation to the parameters of soil systems.

In view of the theoretical derivation of Eq.8.2.7, M.E.M. may be defined as the ratio of the characteristic time of the soil sample to its characteristic time if the pores were uniform equi-diameter cylinders with their axes parallel to the direction of electric current flow. M_E is therefore a dimensionless number.

8.2.2.1 In order to use the M.E.M. as a measure of the soil micro-structure, the M_E values were determined for all the soil samples investigated in the experimental programme as follows:

- (1) The experimental values of C_w and K_w were computed from Eqs.8.2.3 & 4.
- (2) The experimental characteristic time $[\tau_w]$ was calculated from Eq.8.2.6.

(3) M_E was calculated from Eq.8.2.7.

(4) Values of M_E for all the soil samples investigated in this project are listed in Appendix-V.

8.2.2.2 Values of M_E were found to range between 1 and 10 in a consistent manner that indicates a suggested method for measuring the soil micro-structure using M.E.M. Variation of M_E with each of the investigated parameters follows the general trend:

M_E increases as electrolyte concentration decreases

cation valence decreases

c.e.c. increases

pH increases

water content decreases

consolidation pressure increases

rigid bonding increases

angle between current and the long axis of particles increases.

8.3. DISCUSSION

The preceding two sections show clearly an encouraging result of the application of the new model: A relationship between the electrical response and the soil micro-structure has been established and a quantitative description of the soil micro-structure was proved to be possible.

The general trend of M_E variation with different parameters indicates that M_E increases as the dispersed structure is promoted. This is consistent with the fact that a more dense and closely packed soil sample corresponds to a disperse structure.

Values of M_E for different soil samples can be used to investigate their micro-structures, while M_E for a given soil in different electric current directions would be useful for the study of the soil fabric variation in these directions. This result could be very useful for various investigations such as permeability and wave propagation in different directions through soil.

SUMMARY CONCLUSIONS AND RECOMMENDATIONS

9.1 SUMMARY AND CONCLUSIONS

9.1.1 The work of many investigators has led to a better understanding of the effect of the micro-structural and compositional factors on the engineering properties of soils. The direct methods used in the study of soil micro-structure, such as the optical and electron micro-scopy, and the x-ray diffraction are, except in special cases, difficult of quantitative expression, time consuming, and destructive in nature.

The review of several studies on the soil micro-structure (Chapter 1) suggested that

- (1) In principle, quantitative predictions of the engineering properties of a soil specimen should be possible if all micro-structural and compositional factors can be represented and evaluated numerically.
- (2) The inter-particle forces forming a component of the soil micro-structure are dominated by the adsorbed water phase. Any attempt to characterise soil-water systems and evaluate their engineering properties, to be successful, should represent the adsorbed water phase adequately.

This thesis is devoted to the development of the dielectric dispersion technique as an additional non-destructive method for the study of the engineering behaviour of soils in relation to their micro-structures.

9.1.2 The theoretical review presented in chapter 2 showed that in addition to the four well known mechanisms of polarization (electronic, atomic, orientation, and space-charge polarization), the adsorbed phase polarization suggested by Murphy and Lowry (1930) seems to be a very convincing explanation of the dielectric behaviour of systems in which adsorption phenomenon takes place.

In mixtures or heterogenous dielectrics, all types of polarization may take place and the electrical dispersion may be associated with orientation, space-charge, or adsorbed phase polarization.

The electrical network analogy often provides a convenient means of investigating the dielectric behaviour of materials. The electrical properties of matter may be represented by a parallel or a series combination of a capacitance C and a resistance R . The type of combination is not indicative of a mechanism, transformation from one to the other being readily effected by use of equations 2.4.8-12.

9.1.3 The review of previous studies presented in chapter 3 showed that the soil investigations by electrical network analogy were based on one and the same three-element model which was originally suggested by Wyllie and Southwick (1954). To apply the model to the complicated field of soil systems, several assumptions were inevitable resulting in possible inaccuracies which arose from such considerations as:

- (1) Assuming a "wet particle" phase which is in fact equivalent to the solid particles together with the adsorbed layer.
- (2) Assuming that the primary particles in the clay mass are arranged in clusters, packets or domains in order to

provide a solution layer in series combination with the solid phase.

- (3) Assuming a continuous current path through solid particles which were again considered as "wet particles".

9.1.4 In chapter 4 a new model was developed which, as far as the author believes, satisfies most of the concepts often suggested by earlier investigators interested in this field.

The adsorbed layer is represented in the model by a component normal to the particle surface which would therefore account for the maxwell-Wagner interfacial polarization, as well as a component parallel to the particle surface whose electrical response is frequency -dependent and would account for the adsorbed layer polarization.

9.1.5 In chapter 5 the experimental programme is described. The specifically designed cell and consolidation mould are shown to ensure the least disturbance to soil samples under test.

9.1.6 The experimental results analysed in Chapter 6 are essentially consistent with the results reported by earlier workers. However, the experimental results of the effects of the cation exchange capacity; pH values, and rigid bonding on the electrical properties of soil, are of especial interest.

The increase of c.e.c of the clay mineral or the pH value of the electrolyte produces an increase in the three components of the electrical response, i.e., ϵ , k , and Δk . This is consistent with the fact that at high pH values, the positive charges on the clay particle edges decreases and thus the surface density of negative charge increases resulting in an increase of c.e.c. Therefore, the increase in c.e.c. or pH value will have similar effects as indeed is confirmed by the present experimental observation.

As the rigid bonding strength increases, either by the type of cation (polymeric aluminium hydroxy cation) or by ageing, a corresponding decrease in the four components of the electrical response is observed.

In fact the increase in rigid bonding is associated with three other effects:

- (1) an increase in the tortuosity of electric current path.
- (2) a decrease in the effective surface area of the charged particles.
- (3) a decrease in the free pore water content as the amorphous growth and quasi-crystalline growth develop (Foster, et.al., 1975).

It has been shown in chapter 6 that these effects cause a decrease in the electrical response.

9.1.7 The results obtained by the application of the proposed model, show that the electrical network of the model provides theoretical responses which are consistent with the experimental observations. This lends support to the main concepts of the new model against the other model which has been frequently adopted by several investigators:

- (1) The representation of the adsorbed phase by discrete elements instead of the not very well defined "wet particle" element.
- (2) The recognition of the possibility of simultaneous polarization contributions of various mechanisms instead of a unique type of polarization.
- (3) The representation of a frequency-dependent component of admittance parallel to the particle surface.
- (4) The introduction of empirical numerical expressions to account for every factor that was expected to have an effect on the electrical properties of soil.

9.1.8 In chapter 8, a relationship between the electrical response and the soil micro-structure has been established and a quantitative description of the soil micro-structure was proved to be possible. The general trend of the "Micro-structural-Modulus" (M_E) variation with different parameters indicates that M_E increases as the dispersed structure is promoted. This is relevant with the fact that a more dense soil sample corresponds to a disperse structure.

Values of M_E for a given soil in different directions can be used to study the soil fabric variation in these directions. This result could be very useful for various investigations such as permeability and wave propagation in different directions through soil.

9.2 RECOMMENDATIONS FOR FURTHER STUDIES

The present investigation throws light on several important points, connected with the problem under consideration, the study of which could very well contribute to a better understanding of the soil micro-structure, the impact of which on geotechnical science has become increasingly appreciated:

9.2.1 Development of the "Micro-structure Electrical Modulus, M.E.M.

9.2.1.1 M_E may be resolved into two components corresponding to the two components of micro-structure, viz., the inter-particle geometry (M_{Eg}) and the inter-particle force (M_{Ef}). This can be studied by keeping the inter-particle geometry of the sample constant, after being consolidated, and changing the electrolyte properties (concentration, type, pH, rigid bonding effect) by leaching.

9.2.1.2 M_E may be determined in several directions through the soil sample in order to plot an integral M_E diagram covering the whole 180° spectrum. Probably such a diagram would help in a more comprehensive description of the soil micro-structure.

9.2.1.3 Construction of a soil micro-structure characterization chart based on M_E values may provide a useful and quick means of soil investigation which is critically needed in some cases.

9.2.2 Further Applications of the New Model

9.2.2.1 The new model may be developed to apply to the partially saturated soil systems by introducing an air capacitor in parallel with the model to account for the volume of the empty pores.

9.2.2.2 The experimental results of the effects of the development of rigid bonding on the magnitude of electrical dispersion suggest that the model may be used as an indicator of the growing of strength with time in soil cementation and soil stabilization processes.

9.2.2.3 A very important field of application of the new model is the "in situ" exploration of soil. This would require the development of the electrical measurement cell in a form suitable for such an application. In developing the cell, existing seismic methods and equipment could probably provide a useful guide.

9.2.3 Correlation with Other Techniques

The benefit of using a variety of methods of investigating soil micro-structure is self-evident. However, the concept of M.E.M. may provide an invaluable means of correlation between these methods.

In parallel with the M.E.M. by using the electrical dispersion technique, it is conceivable that an M.U.M. (M_u) by using ultrasonics technique, an M.M.M. (M_M) by using optical and electron microscopy, and an M.X.M. (M_X) by using x-ray diffraction, could be determined.

Such moduli may also be resolved into components thus permitting an even more thorough investigation of the soil micro-structure.

APPENDICES

APPENDIX I

UNITS

Three systems of units may be used for the purposes of dielectric application. Namely, the absolute electrostatic system (denoted by e.s.u.) which is based on three basic units (centimetre, gram and second for length, weight and time) and two practical systems, which have for electrical purposes four basic units, namely length, weight, time and an electrical unit. The difference between the two practical systems is that the practical c.g.s. system uses the centimetre and gram for length and weight, while the practical m.k.s. system (or international system of S.I. units) uses the metre = 100cm and the kilogram = 1000 grams. All three systems use the second as time units.

The dielectric constant is dimensionless in e.s.u. but has a physical dimension in the practical systems. One then writes in the practical systems

$$\epsilon \text{ (practical)} = \epsilon_v \epsilon \quad (\text{I.1})$$

where ϵ represents the dimensionless "relative" dielectric constant which is appropriate to the electrostatic system. The constant ϵ_v signifies the dielectric constant of empty space and has the dimension farad/length in either practical system but different numerical values in c.g.s. and m.k.s. units. Similar conversion factors apply to other entities relevant for dielectric application, as set out below (Table I.1). It may be noted that the factor 4π which enters into Eq. 2.1.2 is due to the different values of entities in the electrostatic system and the two practical systems.

TABLE I.1

Conversion Factors

Entity	Dimension in e.s.u.	Units in practical c.g.s. and m.k.s.	Multiply data in e.s.u. by conversion factor to get data in	
			practical c.g.s.	practical m.k.s.
Dielectric constant of free space (ϵ_v)	dimensionless	$\frac{\text{farad}}{\text{length}}$	$\frac{1}{4\pi \times 9 \times 10^{11}}$	8.85×10^{-12}
Capacitance (C)	cm	$\text{farad} = \frac{\text{Coulomb}}{\text{Volt}}$	$\frac{1}{9 \times 10^{11}}$	$\frac{1}{9 \times 10^{11}}$
charge (Q,q)	$\text{cm}^{\frac{3}{2}} \text{g}^{\frac{1}{2}} \text{sec}^{-1}$	Coulomb	$\frac{1}{3 \times 10^9}$	$\frac{1}{3 \times 10^9}$
current (I)	$\text{cm}^{\frac{3}{2}} \text{g}^{\frac{1}{2}} \text{sec}^{-2}$	$\text{Ampere} = \frac{\text{Coulomb}}{\text{sec}}$	$\frac{1}{3 \times 10^9}$	$\frac{1}{3 \times 10^9}$
Polarization (P)	$\text{cm}^{-\frac{1}{2}} \text{g}^{\frac{1}{2}} \text{sec}^{-1}$	$\frac{\text{Coulomb}}{\text{length}^2}$	$\frac{1}{3 \times 10^9}$	$\frac{1}{3 \times 10^5}$
Potential Difference (V)	$\text{cm}^{\frac{1}{2}} \text{g}^{\frac{1}{2}} \text{sec}^{-1}$	Volt	300	300
Field (E)	$\text{cm}^{-\frac{1}{2}} \text{g}^{\frac{1}{2}} \text{sec}^{-1}$	$\frac{\text{Volt}}{\text{length}}$	300	30000
Resistance (R)	$\text{cm}^{-1} \text{sec}$	$\text{Ohm} = \frac{\text{Volt}}{\text{length}}$	9×10^{11}	9×10^{11}
Resistivity	sec	Ohm.length	9×10^9	9×10^9
Conductance (K)	cm sec^{-1}	ohm^{-1}	$\frac{1}{9 \times 10^{11}}$	$\frac{1}{9 \times 10^{11}}$
Conductivity (k)	sec^{-1}	$\text{Ohm}^{-1} \text{length}^{-1}$	$\frac{1}{9 \times 10^{11}}$	$\frac{1}{9 \times 10^9}$

APPENDIX II

COMPLEX QUANTITIES

Complex quantities often provide good description and representation of periodic phenomena such as AC fields. For this purpose the x-axis corresponds to the axis of reals and the y-axis to the axis of imaginaries. The factor $i = \sqrt{-1}$ in front of a real quantity signifies an imaginary component orientated in the y-axis or i -axis direction. A complex quantity Z

$$Z = x + iy \quad (\text{II.1})$$

plotted in the complex plan corresponds in polar co-ordinates to a radius vector r

$$r = \sqrt{x^2 + y^2} \quad (\text{II.2})$$

inclined by an angle θ (radius)

$$\theta = \tan^{-1}(y/x) \quad (\text{II.3})$$

towards the axis of reals.

The complex quantity Z can also be expressed by

$$Z = r\cos\theta + ir\sin\theta \quad (\text{II.4})$$

differentiation with respect to θ yields

$$\begin{aligned} dZ &= -r \sin\theta + r i \cos\theta \\ &= ir (\cos\theta + i \sin\theta) = iZ \end{aligned} \quad (\text{II.5})$$

Integration then yields $Z = Ae^{i\theta}$, where A is the constant of integration. In particular, when $\theta = 0$, $Z = 1$; this shows that $A = 1$, giving the result

$$r(\cos\theta + i\sin\theta) = r e^{i\theta} \quad (\text{II.6})$$

Therefore, a general complex number Z may be written in the form

$$Z = x + iy = r(\cos\theta + i\sin\theta) = r e^{i\theta}$$

The complex function

$$V = V_0 e^{i\omega t} = V_0(\cos \omega t + i \sin \omega t)$$

consequently can be plotted in the complex plane as a radius vector of length V_0 , the voltage amplitude, making an angle of ωt radians with the axis of reals. A capacitor, connected to a sinusoidal voltage source stores a charge

$$Q = CV$$

and draws a charging current I_c

$$I_c = \frac{dQ}{dt} = i\omega CV \quad (\text{II.7})$$

Simultaneously, the charging process is accompanied by some dissipation of part of the energy of the field in the form of heat, i.e., a loss current component I_p beside the charging current component. Such current is entirely due to the dielectric medium and is a property of it

$$I_p = KV \quad (\text{II.8})$$

in phase with the voltage, K represents the conductance of the dielectric. The total current traversing the condenser

$$I = I_c + I_p = (i\omega C + K)V \quad (\text{II.9})$$

It has therefore become customary to refer to the existence of a loss current in addition to a charging current by the introduction of a complex dielectric constant ϵ^* .

$$\epsilon^* = \epsilon' - i\epsilon''$$

where ϵ' and ϵ'' are the real part and the imaginary part of the dielectric constant respectively.

RELEVANT DATA AND CONSTANTSTABLE III.1 Physical Constants

Name	Symbol	Magnitude and Dimension
Charge of the electron	e	4.803×10^{-10} e.s.u.
Boltzmann constant	k	1.380×10^{-16} erg/ $^{\circ}$ C
Avogadro's number	N_A	6.022×10^{23}
Faraday constant = $e \cdot N_A$	F	96522 coulombs

TABLE III.2 Prefixes Commonly Used in Electrical Measurements
(Richart, et.al., 1970)

giga	$= 10^9$
mega	$= 10^6$
kilo	$= 10^3$
milli	$= 10^{-3}$
micro	$= 10^{-6}$
nano	$= 10^{-9}$
pico	$= 10^{-12}$

TABLE III.3

Ionic Mobilities at Infinite Dilution at 18°C
(Garside, et.al., 1962)

Cation	U_+ (mho)	Anion	U_- (mho)
H^+	315.2	OH^-	173.8
C_s^+	67.46	I^-	66.25
K^+	64.20	Br^-	67.31
NH_4^+	64.30	Cl^-	65.24
N_a^+	43.16	F^-	46.6
Li^+	33.02	NO_3^-	61.62
Ag^+	53.8	CH_3COO^-	35.0
$\frac{1}{2}Ba^{2+}$	55.0	$\frac{1}{2}SO_4^{2-}$	68.5
$\frac{1}{2}Pb^{2+}$	61.0	$\frac{1}{2}CO_3^{2-}$	60.0

TABLE III.4

Dielectric Dec rements for Various Ions

(Hasted, 1973)

Cation	δ	Anion	δ
H^+	-17	F^-	-5
Li^+	-11	Cl^-	-3
Na	- 8	I^-	-7
K^+	- 8	OH^-	-13
Rb^+	- 7	SO_4^{2-}	-7
Mg^{2+}	-24		
Ba^{2+}	-22		
La^{3+}	-35		

TABLE III.5 Contents of Dispersion for Various Dielectrics
(Cole and Cole, 1941)

Material	T°C	ϵ_0	ϵ_∞	a	b	α
<u>A. Liquids</u>						
Water	19	81	1.8	9.4	12	0.09
Methyl alcohol	19	31.8	2.0	6.4	11	0.13
Ethyl alcohol	20	25.8	1.85	9.4	11	0.15
Glycerine	-50	63	5.0	6.9	5	0.21
Rosin Oil No. 1	7	2.8	2.48	3.8	6	0.46
Transformer Oil	0	2.8	2.26	2.0	8	0.63
<u>B. Solids</u>						
Ice	-1	74	3.0	2.0	5	0.03
	-20	82	3.5	1.0	4	0.07
	-46	97	2.0	2.7	3	0.07
Glycol phthalate						
resin	30	17.2	5.8	5.7	7	0.44
Phenol formalde-						
byde resin	70	8.3	3.4	1.1	5	0.6
Vinsol	98	8.5	3.4	1.2	4	0.61
Rubber, 20%						
sulphur	75	4.85	2.7	1.1	5	0.64
Pyrex	21	--	--	--	-	0.885*
Mica	21	--	--	--	-	0.88*
Slate	21	(98)	8.0	2.7	4	0.53

$$\tau_0 = a \cdot 10^{-b} \text{ sec.}$$

- data do not permit even an approximate estimate.

* doubtful values or inconsistent data.

TORTUOSITY COEFFICIENT

From Fig. IV.1 it is seen that for particle axes a , b , and c if $a = b$, and axis ratio $a/c = R$, then

void ratio = volume of void/volume of solid

$$e = (\bar{a}p + c\bar{p} + \bar{p}^2)/ac$$

$$\bar{p}^2 + (a + c)\bar{p} - ace = 0$$

$$\bar{p} = \frac{1}{2} [-(a + c) + [(a + c)^2 + 4ace]^{\frac{1}{2}}]$$

Excess length = $(a + \bar{p})$ per $(c + \bar{p})$ along the c -axis, then the excess length δ per unit length along the c -axis is given by

$$\begin{aligned} \delta &= (a + \bar{p})/(c + \bar{p}) \\ &= \frac{[(a+c)^2 + 4ace]^{\frac{1}{2}} - (c-a)}{[(a+c)^2 + 4ace]^{\frac{1}{2}} + (c-a)} \\ &= \frac{[(R+1)^2 + 4eR]^{\frac{1}{2}} - (1-R)}{[(R+1)^2 + 4eR]^{\frac{1}{2}} + (1-R)} \end{aligned}$$

The tortuosity coefficient T_θ is the length of the tortuous path per unit length along the direction of the flow of current (at an angle θ with respect to the a -axis of the particle), therefore

$$T_0 = 1 \quad \text{along the } a\text{-axis.}$$

$$T_{90} = 1 + \delta \quad \text{along the } c\text{-axis (at } 90^\circ \text{ to } a\text{-axis)}$$

$$T_\theta = \cos^2 \theta T_0^2 + \sin^2 \theta T_{90}^2 \quad (\text{at } \theta^\circ \text{ to } a\text{-axis})$$

$$= [1 + \delta \sin^2 \theta (2 + \delta)]^{1/2}$$

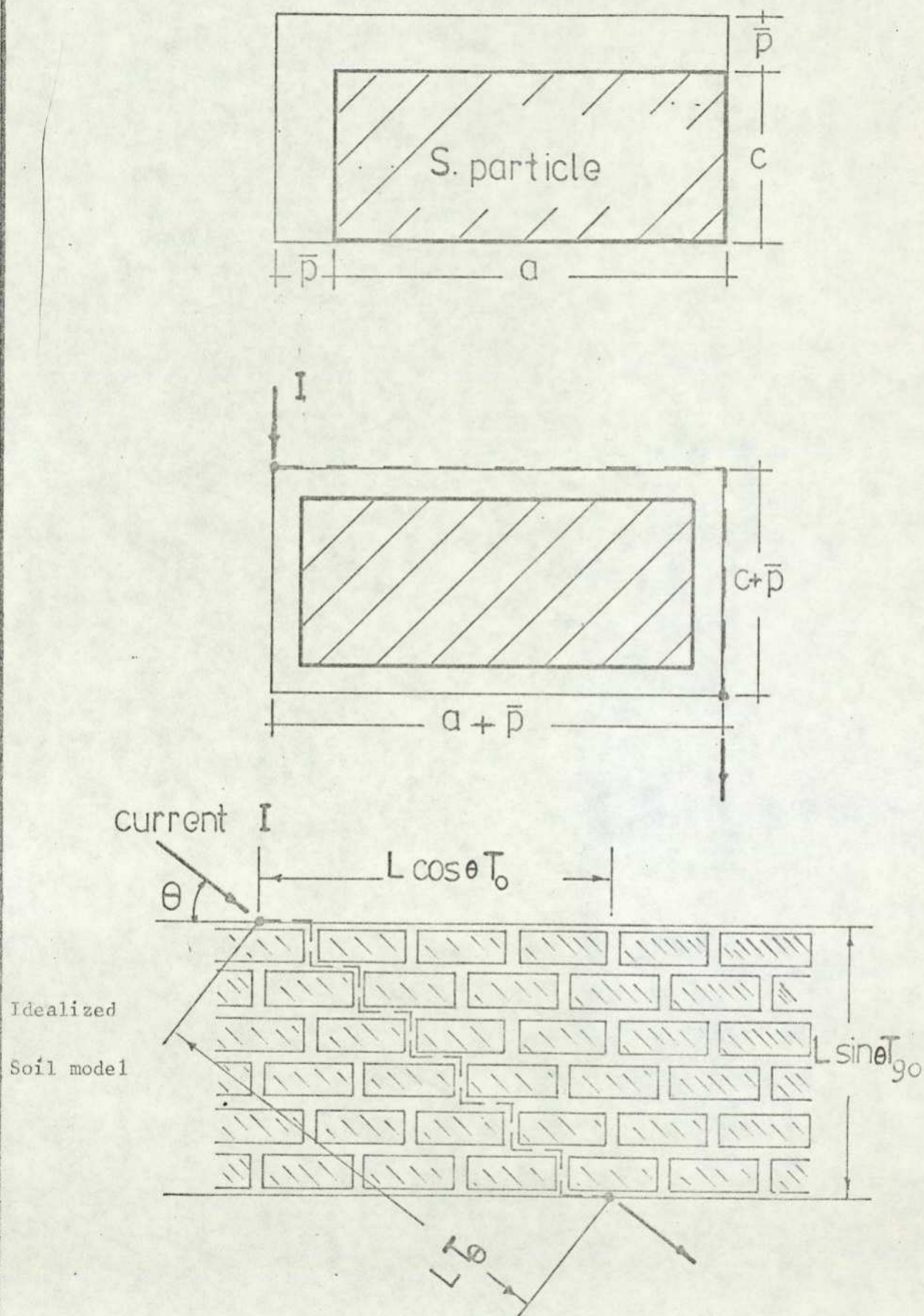


Fig. IV.1 Tortuosity Coefficient

APPENDIX V

EXPERIMENTAL AND THEORETICAL DATA

Table V. Stray Capacitance of the Cell (C_t)

$$C_t = C_p - C_o \text{ \& } C_o = \frac{A \epsilon_v}{L}$$

$A = x$ - sec. area of the electrode (2 cm^2)

L = distance between electrodes (cm)

frequency (MHz)	$L_1 = 4 \text{ (cm)}$		$L_2 = 3$		$L_3 = 2$		$L_4 = 1$	
	C_p	C_t	C_p	C_t	C_p	C_t	C_p	C_t
10	2.77	2.73	2.95	2.891	3.07	2.982	3.4	3.223
20	"	"	"	"	3.09	3.001	3.42	3.243
30	"	"	"	"	3.11	3.022	3.42	3.243
40	"	"	"	"	"	"	3.43	3.253
50	"	"	"	"	"	"	3.43	3.253
60	"	"	"	"	"	"	3.44	3.263
70	"	"	"	"	3.12	3.032	3.45	3.273
80	2.8	2.76	2.97	2.911	3.13	3.042	3.5	3.323
90	"	"	2.99	2.931	3.18	3.092	3.5	3.323
100	"	"	3.0	2.941	3.19	3.102	3.51	3.333
110	"	"	3.0	2.941	3.2	3.112	3.54	3.363
C_o (pf)	0.0445		0.059		0.0885		0.177	

TABLE V. 1.1

Experimental Results - Clay Mineral

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
Montmorillonite	ϵ'	89.9	82	79.5	76.5	74.5	73.5	73	71.3	69.7	69.2	68.9
	$k \times 10^{-5}$	621	625	638	646	662	671	686	701	720	741	747
Mica	ϵ'	68.5	61.7	57.1	54.5	53.4	53	52.6	52.4	52.3	52.2	52.1
	$k \times 10^{-5}$	68.5	72.5	77.5	80	81.5	82.8	83.5	85.5	86	86.1	86.5
Kaolinite	ϵ'	57.7	55.6	53.4	52.8	52.1	51.9	51.8	50.8	50.6	50.7	50.8
	$k \times 10^{-5}$	60.4	62	64.4	66.3	68	69.1	69.9	70.5	70.6	71.3	71.3
Slate Dust	ϵ'	35.9	34	32	32.4	31.8	30.8	30.5	31.1	30.6	30.3	30.3
	$k \times 10^{-5}$	16.9	20	20.8	23.5	22.5	25.7	26	25.2	25.4	25.6	27

TABLE V.1.2

Initial Theoretical Data - Clay Mineral

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	A _s	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
Montmorillonite	10.7	7	123	3.2	.762	495	5	4.39	.144	.62	.118	—	2.07	608	.549	*	4.62	4.62	1.28
Mica	5.7	7	80.7	2.3	.697	43	10	3.63	.33	.67	.095	.188	3.83	55.1	.593	*	2.5	5.04	.544
Kaolinite	4.37	7	85.4	2.26	.693	12.2	25	2.72	.33	.67	.067	.25	3.83	55.1	.593	*	0.69	3.56	.367
Slate Dust	9.15	7	30.4	0.85	.46	1.24	5	2.72	.186	.814	.001	.184	2.34	14.8	.288	*	.531	.531	.05

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

A_s - sq.m/gt_w - angstromsK_l - mhos x 10⁻⁵C_l - $\bar{C}_c$, C_{fd}, & C_{wd} - pfK_{wd} - mhos x 10⁻⁴

* - negligible

TABLE V.1.3

Theoretical Results - Clay Mineral

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	τ	M_E
Montmorillonite	ϵ'	89.8	82.9	80.5	78.7	77	75.2	73.4	71.6	69.7	67.9	66.1	5.11	1.42 $\times 10^{-4}$	3.6 $\times 10^{-8}$	3.682
	$k \times 10^{-5}$	621	628	636	647	659	673	689	705	722	739	756				
Mica	ϵ'	71.1	61.7	57.1	54.8	53.4	52.6	52	51.7	51.4	51.2	51	5.6	.604 $\times 10^{-4}$	9.26 $\times 10^{-8}$	3.617
	$k \times 10^{-5}$	67	74.7	79.1	81.6	83.1	84.2	84.9	85.5	86	86.3	86.6				
Kaolinite	ϵ'	57.9	55.6	54.2	53.2	52.4	51.9	51.6	51.3	51.1	50.9	50.8	3.95	.408 $\times 10^{-4}$	9.69 $\times 10^{-8}$	2.702
	$k \times 10^{-5}$	59.9	62.4	64.8	66.6	68	69	69.8	70.4	70.9	71.3	71.6				
Slate Dust	ϵ'	37.2	34.7	33.3	32.4	31.8	31.3	31.1	30.8	30.6	30.5	30.4	.546	.055 $\times 10^{-4}$	9.83 $\times 10^{-4}$	8.164
	$k \times 10^{-5}$	17.4	19.9	21.8	23.3	24.4	25.2	25.8	26.3	26.7	27	27.2				

k (mhos/cm) - K (mhos) - C_w (pF) - τ (sec.)

TABLE V.2.1

Experimental Results - Cation Valence

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
C.T.1	ϵ'	65.2	59.3	56.5	54.4	53.3	52.5	52	51.6	51.3	51	50.9
kaolin - 1.0.N Na Cl	$k \times 10^5$	2185	2190	2195	2198	2200	2202	2203	2203	2204	2204	2205
C.T.2	ϵ'	65.9	61.6	59	57.3	56	55	54.2	53.5	52.7	52.2	51.9
kaolin - 1.0.N Ca Cl ₂	$k \times 10^5$	2300	2305	2310	2313	2317	2321	2325	2329	2333	2336	2337
C.T.3	ϵ'	67.9	64.9	62.4	61	60	59.2	58.2	57.8	57.4	56.9	56.6
kaolin - 1.0.N Al Cl ₃	$k \times 10^5$	2450	2455	2459	2462	2465	2470	2475	2479	2482	2485	2490
	ϵ'											
	k											

TABLE V.2.2

Initial Theoretical Data - Cation Valence

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	As	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
C.T.1	4.6	7	60.8	1.61	.617	15.2	9	2.88	0.27	0.73	.026	0.23	3.73	2179	.646	*	.99	1.43	.65
C.T.2	3.65	7	64	1.7	.629	14.8	6.4	2.79	0.28	0.72	.018	.248	3.5	2296	.637	*	1.12	1.0	.81
C.T.3	3.25	7	68.3	1.81	.644	14.2	5.2	2.69	0.29	0.71	.015	.261	3.51	2447	.628	*	1.24	0.85	.97

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

A_s - sq.m/g

t - angstroms

K_l - mhos x 10⁻⁵C_l, $\bar{C}_c$, C_{fd} & C_{wd} - pfK_{wd} - mhos x 10⁻⁴

* - negligible

TABLE V.2.3

Theoretical Results - Cation Valence

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	τ	γ_{eff}
C.T.1	ϵ'	65	59.2	56.3	54.5	53.3	52.5	52	51.5	51.2	50.9	50.8	1.55	.711	2.18×10^{-8}	2.896
	$k \times 10^{-5}$	2185	2190	2194	2196	2199	2200	2201	2202	2203	2203	2204				
C.T.2.	ϵ'	66	61.6	59.2	57.6	56.2	55.1	54.2	53.4	52.6	52.1	51.5	1.11	.894	1.24×10^{-8}	2.767
	$k \times 10^{-5}$	2300	2305	2310	2314	2318	2322	2326	2330	2333	2336	2338				
C.T. 3	ϵ'	67.9	64.6	62.4	61	60	59.1	58.4	57.8	57.2	56.6	56.1	.876	1.0	0.876×10^{-8}	2.727
	$k \times 10^{-5}$	2450	2455	2459	2463	2467	2471	2475	2479	2483	2487	2492				
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pf) - τ (sec.)

TABLE V.3.1

Experimental Results - Cation Concentration

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
C.C.1	ϵ'	59.4	54.3	52	50.5	49	48.3	47.8	47.7	46.9	46.9	46.9
kaolin-0.01N Ca Cl ₂	$k \times 10^5$	66	70	73	77	78.5	80	81.5	82.5	83	83.5	83.5
C.C.2	ϵ'	63.8	59.1	57.1	55.7	54.6	53.3	52.5	52	51.1	50.8	50.8
kaolin - 0.1N Ca Cl ₂	$k \times 10^5$	221	224	228	232	235	239	243	246	247	248	248
C.C.3	ϵ'	65.9	61.6	59	57.3	56	55	54.2	53.5	52.7	52.2	51.9
kaolin - 1.0N Ca Cl ₂	$k \times 10^5$	2300	2305	2310	2313	2317	2321	2325	2329	2333	2336	2337
	ϵ'											
	k											

TABLE V. 3.2

Initial Theoretical Data - Cation Concentration

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	As	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
C.C.1	3.9	7	56.7	1.5	.6	15.9	21.6	2.92	0.26	0.74	.063	.183	3.38	58.5	.655	*	0.99	3.46	.681
C.C.2	4	7	63	1.67	.625	14.9	13.6	2.83	0.28	0.72	.039	.227	3.55	214	.637	*	1.0	2.14	.753
C.C.3	3.65	7	64	1.696	.629	14.8	6.4	2.79	0.28	0.72	.018	.248	3.5	2296	.637	*	1.12	1.0	.81

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

A_s - sq. m/gt_w - angstromsK_l - mhos x 10⁻⁵

* negligible

C_l, $\bar{C}_c$, C_{fd} & C_{wd} - pfK_{wd} - mhos x 10⁻⁴

TABLE V.3.3

Theoretical Results - Cation Concentration

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	γ	M_E
C.C.1	ϵ'	59	54.3	51.9	50.3	49.3	48.5	48	47.6	47.3	46.9	46.8	3.56	.7	5.08×10^{-8}	2.928
	$k \times 10^{-5}$	66.5	70.4	73.8	76.5	78.5	80	81.1	82	82.7	83.2	83.7				
C.C.2	ϵ'	64	59.1	57.1	55.6	54.5	53.5	52.7	52	51.3	50.9	50.4	2.13	.75	2.84×10^{-8}	2.826
	$k \times 10^{-5}$	221	225	229	232	236	239	242	245	247	249	250				
C.C.3	ϵ'	66	61.6	59.2	57.6	56.2	55.1	54.2	53.4	52.6	52.1	51.5	1.11	.894	1.24×10^{-8}	2.767
	$k \times 10^{-5}$	2300	2305	2310	2314	2318	2322	2326	2330	2333	2336	2338				
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pf) - γ (sec.)

TABLE V.4.1

Experimental Results - pH Value

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
pH.1 kaolin - 1.0 N NaOH pH (slurry) = 13.4	ϵ'	71	67.2	65.7	64.7	64.1	63.7	63.2	62.9	62.5	62.0	61.8
	$k \times 10^{-5}$	2935	2938	2940	2943	2947	2949	2954	2957	2960	2962	2965
pH.2 kaolin - 1.0 N NaCl pH (slurry)=4.6	ϵ'	65.2	59.2	56.5	54.4	53.3	52.5	52	51.6	51.3	51	50.9
	$k \times 10^{-5}$	2185	2190	2195	2198	2200	2202	2203	2203	2204	2204	2205
pH.3 kaolin-1.0 N HCl pH (slurry) = 1.1	ϵ'	59.1	52.9	50	47.8	46.8	45.7	45	44.7	44.4	44.1	44
	$k \times 10^{-5}$	1111	1116	1121	1124	1126	1127	1128	1129	1130	1130	1130
	ϵ'											
	k											

TABLE V.4.2

Initial Theoretical Data - pH Value

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	A _s	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
pH.1	13.4	7	78.3	2.07	.675	12.9	9	2.85	.31	.69	.024	.272	4.2	2931	.611	*	.99	1.32	.669
pH.2	4.6	7	60.8	1.61	.617	15.2	9	2.88	.27	.73	.026	.23	3.73	2179	.646	*	.99	1.43	.65
pH.3	1.1	7	52.8	1.4	.583	16.6	9	2.91	.25	.75	.026	.22	3.1	1104	.664	*	1.06	1.43	.696

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

A_s - sq. m/gt_w - angstromsK_l - mhos x 10⁻⁵C_l, $\bar{C}_c$, C_{fd} & C_{wd} - pfK_{wd} - mhos x 10⁻⁴

* negligible

TABLE V.4.3

Theoretical Results - pH Value

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	γ	M_E
pH.1	ϵ'	71.2	67.1	65.7	64.9	64.3	63.8	63.3	62.9	62.4	62	61.6	1.32	$.67_{-4}$ $\times 10$	1.97_{-8} $\times 10$	2.825
	$k \times 10^{-5}$	2936	2938	2941	2943	2946	2949	2953	2956	2959	2963	2967				
pH.2	ϵ'	65	59.2	56.3	54.5	53.3	52.5	52	51.5	51.2	50.9	50.9	1.55	$.711_{-4}$ $\times 10$	2.18_{-8} $\times 10$	2.896
	$k \times 10^{-5}$	2185	2190	2194	2196	2199	2200	2201	2202	2203	2203	2204				
pH.3	ϵ'	59.2	52.9	49.8	47.6	46.6	45.8	45.1	44.7	44.3	44	43.8	1.44	$.702_{-4}$ $\times 10$	2.05_{-8} $\times 10$	2.881
	$k \times 10^{-5}$	1110	1116	1120	1123	1125	1127	1128	1129	1130	1130	1131				
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pf) - γ (sec.)

TABLE V. 5.1

Experimental Results - Consolidation Pressure/Moisture Content

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
P ₁ /W ₁ P ₁ = 3.5 kg/sq.cm final m/C =	ε'	53.9	51.8	49.8	48.7	48.4	47.6	47.1	46.9	46.9	46.8	46.7
	k x 10 ⁻⁵	53.5	56	58.5	60.6	62.2	63.3	64.4	65	65.2	65.5	65.5
P ₂ /W ₁ P ₂ = 7.0 Kg/sq.cm final m/C =	ε'	53.5	51.4	50	48.9	47.8	47.3	47.1	46.8	46.7	46.6	46.5
	kx 10 ⁻⁵	53.3	56.2	58.7	60.4	62	63.1	64.1	64.5	64.8	65.3	65.5
P ₃ /W ₁ P ₂ = 14 kg/sq.cm. final m/C =	ε'	51.2	48.9	47.7	46.6	45.4	44.8	44.5	44	44	43.8	43.8
	kx 10 ⁻⁵	49.6	52.6	55.2	57.5	58.5	60.3	61.3	61.7	62.4	62.8	62.7
	ε'											
	k											

TABLE V.5.2

Initial Theoretical Data - Consolidation Pressure/Moisture Content

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	A _s	t _w	T _θ	$\bar{P}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
P ₁ /W ₁	4.75	3.5	65.7	1.74	.635	14.5	25	2.93	.285	.715	.071	.2	3.4	48.9	.633	*	.743	3.77	.332
P ₂ /W ₁	4.75	7	65.3	1.73	.634	14.6	25	2.94	.285	.715	.071	.2	3.4	48.9	.633	*	.743	3.77	.33
P ₃ /W ₁	4.75	14	56.3	1.49	.599	16	25	3.09	.26	.74	.073	.172	3.14	45.2	.655	*	.797	3.88	.305

pH - of the slurry

K_l - mhos x 10⁻⁵P - kg/cm²C_l, $\bar{C}_c$, C_{fd} & C_{wd} - pf

W - final m/c per cent.

K_{wd} - mhos x 10⁻⁴A_s - sq.m/gt_w - angstroms

TABLE V. 5.3

Theoretical Results - Consolidation Pressure/Moisture Content

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	τ	M_E
P_1/W_1	ϵ'	53.8	51.6	50	48.9	48.2	47.6	47.2	46.9	46.7	46.5	46.4	3.86	.34 $\times 10^{-4}$	11.36 $\times 10^{-8}$	2.925
	$k \times 10^{-5}$	53.5	56.1	58.7	60.6	62.1	63.2	64.1	64.7	65.2	65.7	66				
P_2/W_1	ϵ'	53.7	51.5	49.9	48.8	48.1	47.5	47.1	46.8	46.6	46.4	46.3	3.88	.34 $\times 10^{-4}$	11.42 $\times 10^{-8}$	2.933
	$k \times 10^{-5}$	53.4	56	58.5	60.5	62	63.1	64	64.5	65.1	65.6	65.9				
P_3/W_3	ϵ'	51.5	49.3	47.7	46.6	45.7	45.2	44.7	44.4	44.2	44	43.9	3.94	.31 $\times 10^{-4}$	12.71 $\times 10^{-8}$	3.094
	$k \times 10^{-5}$	49.7	52.5	55.2	57.3	58.9	60.1	61.0	61.7	62.3	62.7	63.1				
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pF) - τ (sec.)

TABLE V.5.4

Experimental Results - Consolidation Pressure/Moisture Content

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
P_1/W_2	ϵ'	56.4	54.4	53.1	51.5	50.5	50.1	49.6	49.5	49.2	49.2	49.2
	$k \times 10^5$	57.2	59.6	62.5	64.5	65.8	66.8	67.8	68.5	69.1	69.3	69.5
P_2/W_2	ϵ'	56.1	54.1	52.9	51.4	50	49.7	49.6	49.4	49.1	49.1	49.1
	$k \times 10^5$	56.3	59	62	63.5	65.3	66.5	67.3	67.7	68.4	68.6	68.9
P_2/W_2	ϵ'	53.2	51	49	48	47.1	46.6	46.4	46.2	46.1	46.1	46
	$k \times 10^5$	52.5	55	57.5	59.8	61.3	62.6	63.4	64	64.4	64.5	64.7
	ϵ'											
	k											

TABLE V. 5.5

Initial Theoretical Data - Consolidation Pressure/Moisture Content

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	As	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
P ₁ /W ₂	4.78	3.5	78.7	2.08	.676	12.9	25	2.78	.31	.69	.068	.228	3.64	52.4	.611	*	.743	3.61	.35
P ₂ /W ₂	4.78	7	76.4	2.02	.669	13.2	25	2.81	.31	.69	.069	.227	3.64	52.4	.611	*	.743	3.66	.35
P ₃ /W ₂	4.78	14	63.8	1.69	.628	14.8	25	2.98	.28	.72	.072	.194	3.35	48.2	.637	*	.743	3.82	.32

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

A_s - sq. m/gt_w - angstromsK_l - mhos x 10⁻⁵C_l, $\bar{C}_c$, C_{fd} & C_{wd} - pfK_{wd} - mhos x 10⁻⁴

TABLE V. 5.6

Theoretical Results - Consolidation Pressure/Moisture Content

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	γ	M_E
P_1/W_2	ϵ'	56.4	54.1	52.6	51.5	50.7	50.2	49.7	49.5	49.2	49.1	48.9				
	$k \times 10^{-5}$	57.1	59.8	62.3	64.3	65.8	66.9	67.7	68.4	68.9	69.3	69.7	3.72	.36 $\times 10^{-4}$	10.32 $\times 10^{-8}$	2.788
P_2/W_2	ϵ'	56.3	54	52.5	51.4	50.6	50.1	49.6	49.4	49.1	49	48.8				
	$k \times 10^{-5}$	56.9	59.6	62.0	64.1	65.6	66.7	67.4	68.2	68.7	69.1	69.5	3.66	.35 $\times 10^{-4}$	10.47 $\times 10^{-8}$	2.808
P_3/W_2	ϵ'	53.2	51	49.5	48.4	47.7	47.1	46.7	46.4	46.2	46	45.9				
	$k \times 10^{-5}$	52.6	55.3	57.8	59.8	61.3	62.4	63.2	63.9	64.4	64.8	65.2	3.93	.33 $\times 10^{-4}$	11.91 $\times 10^{-8}$	2.995
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pf) - γ (sec.)

TABLE V. 5.7

Experimental Results - Consolidation Pressure/Moisture Content

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
P_1/W_3	ϵ'	59.1	56.3	54.7	53.6	53.4	52.8	52.4	52.2	51.8	51.7	52.1
	$k \times 10^{-5}$	61.4	63.5	65.7	68	69.6	70.6	71.2	72.2	72.1	72.5	72.7
P_1/W_3	ϵ'	57.7	55.6	53.4	52.8	52.1	51.9	51.8	50.8	50.6	50.7	50.8
	$k \times 10^{-5}$	60.4	62	64.4	66.3	68	69.1	69.9	70.5	70.6	71.3	71.3
P_3/W_3	ϵ'	55.6	53.2	51.2	50.5	49.1	48.5	48.3	48.5	48.2	47.5	48.3
	$k \times 10^{-5}$	55.7	57.7	60.3	63.1	63.7	65.4	65.8	66.2	67.2	67.7	68
	ϵ'											
	k											

TABLE V.5.8

Initial Theoretical Data - Consolidation Pressure/Moisture Content

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	A _s	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C ₁	K ₁	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
P ₁ /W ₃	4.37	3.5	93.5	2.48	.713	11.4	25	2.64	.34	.66	.066	.261	3.92	56.4	.584	*	0.69	3.51	.376
P ₂ /W ₃	4.37	7	85.4	2.26	.693	12.2	25	2.72	.33	.67	.067	.25	3.83	55.1	.593	*	0.69	3.56	.367
P ₃ /W ₃	4.37	14	73.3	1.94	.66	13.5	25	2.86	.3	.7	.07	.216	3.54	51	.62	*	0.74	3.72	.337

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

A_s - sq. m/gt_w - angstromsK₁ - mhos x 10⁻⁵C₁, $\bar{C}_c$, C_{fd} & C_{wd} - pfK_{wd} - mhos x 10⁻⁴

TABLE V.5.9

Theoretical Results - Consolidation Pressure/Moisture Content

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	τ	M_E
P1 / W3	ϵ'	58.9	56.6	55.1	54.1	53.4	52.9	52.5	52.2	52	51.9	51.7	3.5	.375 $\times 10^{-4}$	9.32 $\times 10^{-8}$	2.650
	$k \times 10^{-5}$	61.3	63.8	66.2	68.0	69.4	70.4	71.2	71.8	72.3	72.7	73.0				
P2 / W3	ϵ'	57.9	55.6	54.2	53.2	52.4	51.9	51.6	51.3	51.1	50.9	50.8	3.56	.367 $\times 10^{-4}$	9.69 $\times 10^{-8}$	2.702
	$k \times 10^{-5}$	59.9	62.4	64.8	66.6	68	69	69.8	70.4	70.9	71.3	71.6				
P3 / W3	ϵ'	55.3	53.1	51.6	50.5	49.7	49.2	48.8	48.5	48.2	48.1	47.9	3.75	.34 $\times 10^{-4}$	11.03 $\times 10^{-8}$	2.883
	$k \times 10^{-5}$	55.6	58.3	60.8	62.8	64.3	65.4	66.2	66.9	67.4	67.8	68.2				
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pf) - τ (sec.)

TABLE V.6.1

Experimental Results - Particle Orientation

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
O.X.H. Electric current parallel to consol.P.	ϵ'	47.3	42	41.1	40.7	40.4	40.1.	40	39.9	39.8	39.8	39.7
	$k \times 10^{-5}$	66.4	69.1	70	70.2	70.4	70.6	70.8	70.8	70.9	70.9	70.9
O.X.I Electric current at 45° to $P_{\frac{1}{2}}$	ϵ'	53.3	47	43.4	42	40.8	40.6	40.5	40.2	40	39.9	39.9
	$k \times 10^{-5}$	72.7	76.8	77.6	78.6	78.6	79.1	79	79	79.2	79.3	78.8
O.X.V. Electric current perpendicular to P.	ϵ'	69.6	58.9	50	46	43.5	42.4	41.6	41.3	41.2	40.8	40.9
	$k \times 10^{-5}$	75.1	86	92	94	95.1	96	96.7	96.7	96.9	97.1	97.1
	ϵ'											
	k											

TABLE V.6.2

Initial Theoretical Data - Particle Orientation

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	As	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
O.X.II	6.7	21	43	1.14	.533	18.6	25	3.174	.224	.776	.077	.132	2.82	58.11	.687	*	.934	4.16	.612
O.X.I	6.7	21	43	1.14	.533	18.6	25	2.062	.224	.776	.077	.132	2.82	58.11	.687	*	.934	4.16	1.45
O.X.V	6.7	21	43	1.14	.533	18.6	25	1.365	.224	.776	.077	.132	2.82	58.11	.687	*	.934	4.16	3.33

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

TABLE V.6.3

Theoretical Results - Particle Orientation

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70.	80	90	100	110	C_w	K_w	γ	M_E
O.X.H.	ϵ'	47.6	42.8	41.4	40.7	40.4	40.2	40.1	40	39.9	39.8	39.8	4.2	.618 $\times 10^{-4}$	6.796 $\times 10^{-8}$	3.205
	$k \times 10^{-5}$	66.6	68.8	69.7	70.1	70.4	70.6	70.7	70.8	70.9	71	71				
O.X.I	ϵ'	56.2	45.6	42.6	41.4	40.8	40.5	40.3	40.2	40.1	40	39.9	4.22	1.47 $\times 10^{-4}$	2.867 $\times 10^{-8}$	2.095
	$k \times 10^{-5}$	71.8	76.3	77.6	78.2	78.6	78.9	79.1	79.2	79.3	79.4	79.4				
O.X.V	ϵ'	74.3	56	48.5	45.2	43.4	42.5	41.8	41.4	41.1	40.9	40.8	4.16	3.33 $\times 10^{-4}$	1.26 $\times 10^{-8}$	1.386
	$k \times 10^{-5}$	73.5	86.3	91.6	94	95.2	96.1	96.4	96.7	97	97.2	97.4				
	ϵ'															
	k															

k (mhos/cm) - K - (mhos) - C_w (pf) - γ (sec.)

TABLE V. 7.1

Experimental Results - Rigid Bonding

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
S.C Small Polymeric Al. Hydroxy cation	ϵ'	58.7	52.5	50.1	49.7	49.3	49	49	48.9	48.9	48.9	48.9
	$k \times 10^5$	135	137	140	141	142	142	141	141	140	139	138
M.C Medium Polymeric Al. Hydroxy cation.	ϵ'	62.8	58.3	56	54.7	54	53.4	52.7	52.6	52.5	52.5	52.6
	$k \times 10^5$	157	160	164	167	168	169	169	169	169	169	167
L.C Large Polymeric Al. Hydroxy cation	ϵ'	70.8	66	63	61.5	60.4	60	59.3	58.8	58.3	58.1	58.4
	$k \times 10^5$	250	253	257	261	264	265	267	267	268	268	269
	ϵ'											
	k											

TABLE V.7.2

Initial Theoretical Data - Rigid Bonding

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	As	τ_w	T_θ	$\bar{p}$	d_r	d_w	d_{la}	C_1	K_1	$\bar{C}_c$	$\bar{K}_c$	C_{fd}	C_{wd}	K_{wd}
S.C	4.8	7	76.9	2	.67	13.1	23	2.59	.329	.69	.06	.244	3.7	127	.61	*	.78	3.02	.816
M.C	4.8	7	89.6	2.4	.71	11.8	28	2.54	.296	.67	.07	.245	3.9	144	.59	*	.78	4.04	1.23
L.C	4.7	7	114	3	.75	9.94	40	2.43	.25	.63	.1	.258	4.3	236	.56	*	.71	5.34	1.7

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

TABLE V. 7.3

Theoretical Results - Rigid Bonding

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	C_w	K_w	γ	M_E
S.C. Small polym. Al. Hydroxy cation	ϵ'	58.7	5.25	50.7	50	49.6	49.4	49.3	49.2	49.1	49	49	3.7	.801 $\times 10^{-4}$	4.62 $\times 10^{-8}$	2.595
	$k \times 10^{-5}$	137	139	140	141	141	141	141	141	141	141	141				
M.C. Medium Polym. Al. Hydroxy cation	ϵ'	63.5	58.4	56.3	54.9	54	53.4	53	52.6	52.4	52.2	52	4.1	1.22 $\times 10^{-4}$	3.36 $\times 10^{-8}$	2.586
	$k \times 10^{-5}$	157	160	163	165	167	168	169	169	169	170	171				
L.C. Large Polym. Al. Hydroxy cation	ϵ'	74.7	65.5	63	61.7	60.7	60	59.3	58.8	58.3	57.9	57.6	5.4	1.72 $\times 10^{-4}$	3.14 $\times 10^{-8}$	2.423
	$k \times 10^{-5}$	250	254	257	260	262	265	267	269	271	273	275				
	ϵ'															
	k															

k (mhos/cm) - K (mhos) - C_w (pf) - γ (sec.)

TABLE V.7.4

Experimental Results - Rigid Bonding

Sample Code	Electrical Property	Frequency - (MHz)										
		10	20	30	40	50	60	70	80	90	100	110
L.C/T.1 15 days	ϵ'	70.8	66	63	61.5	60.4	60	59.3	58.8	58.3	58.1	58.4
	$k \times 10^{-5}$	250	253	257	261	264	265	267	267	268	268	269
L.C./T.2 35 days	ϵ'	66.5	62	59.7	58.5	57.6	57	56.4	56.3	55.5	55.2	55.3
	$k \times 10^{-5}$	238	240	242	248	250	251	254	256	257	257	257
L.C/T.3 160 days	ϵ'	60.8	56	54	53	52.4	52.3	52	50.8	50.9	50.5	50.4
	$k \times 10^{-5}$	222	224	226	230	232	234	236	237	237	237	237
	ϵ'											
	k											

TABLE V. 7.5

Initial Theoretical Data - Rigid Bonding

Sample Code	Experimental			Calculated (Sample)					Calculated (model)										
	pH	P	W	e	p	As	t _w	T _θ	$\bar{p}$	d _r	d _w	d _{la}	C _l	K _l	$\bar{C}_c$	$\bar{K}_c$	C _{fd}	C _{wd}	K _{wd}
L.C./T.1	4.7	7	114	3	.75	9.94	40	2.43	.25	.63	.1	.258	4.3	236	.56	*	.71	5.34	1.7
L.C./T.2	"	"	92.7	2.46	.711	11.5	"	2.62	.29	.61	.105	.221	3.99	224	.59	*	.73	5.61	1.5
L.C./T.3	"	"	68.3	1.8	.644	14.2	"	3.06	.36	.71	.112	.164	3.51	210	.63	*	.75	5.99	1.2

pH - of the slurry

P - kg/cm²

W - final m/c per cent.

TABLE V. 7.6

Theoretical Results - Rigid Bonding

Sample Code	Electrical Property	Frequency (MHz)											M.E.M.			
		10	20	30	40	50	60	70	80	90	100	110	G_w	K_w	γ	M_E
L.C./T.1	ϵ'	74.7	65.5	63	61.7	60.7	60	59.3	58.8	58.3	57.9	57.6	5.4	1.72×10^{-4}	3.14×10^{-8}	2.423
	$k \times 10^{-5}$	250	254	257	260	262	265	267	269	271	273	275				
L.C./T.2	ϵ'	69.4	61.7	59.7	58.5	57.6	56.9	56.3	55.8	55.3	54.9	54.6	5.64	1.54×10^{-4}	3.66×10^{-8}	2.618
	$k \times 10^{-5}$	238	241	243	246	249	251	254	256	258	259	261				
L.C./T.3	ϵ'	60.8	55.8	54.3	53.3	52.6	51.9	51.4	50.9	50.4	50	49.7	6	1.2×10^{-4}	5.0×10^{-8}	3.06
	$k \times 10^{-5}$	221	224	226	229	231	234	236	238	240	242	244				
	ϵ'															
	k															

k (mhos/cm) - K (mhos) - C_w (pf) - γ (sec.)

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وما أوتيتم من العلم إلا قليلا

قرآن كريم