CHAPTER 1

INTRODUCTION
SECTION 1.1

A BRIEF REVIEW OF EXPERIMENTAL WORK ON
AND THEORIES IN DIELECTRIC STUDIES IN BINARY
LIQUID MIXTURES

The experimental work on measurement of dielectric constant ($\varepsilon$) has been carried out by several workers mostly with a view to:

1. determine polarizabilities
2. determine dipole moments
3. evaluate Kirkwood linear correlation factor 'g'
4. evaluate excess dielectric constants, dipolar excess Helmholtz energy, dipolar excess entropy of mixing or any other dipolar thermodynamic excess properties
5. evaluate relaxation times and
6. verify liquid state theories.

Dielectric studies have a long and one can definitely say distinguished history. Faraday, Maxwell, Drude, Debye\textsuperscript{1-3} and Kirkwood\textsuperscript{4} are among the several celebrated scientists of this field. The recent literature on dielectric studies contains a number of valuable reviews\textsuperscript{5-9} and excellent monographs\textsuperscript{10-13}. Some of the them relate to dipole moments, devoted to organic chemical applications. Numerous important contributions to dielectric literature on polymers are to be found from Russian sources\textsuperscript{11,14}. The annual digest of dielectric literature provides extensive coverage of work in this field.
Tabular\textsuperscript{15-17} works are also available which cover dielectric constants of pure liquids and dipole moments.

The progress of experimental work in this field got stimulus from various theories that were developed and modified from time to time. The Faraday's idea on dielectrics was treated mathematically by Mosotti\textsuperscript{18} and Clausius\textsuperscript{19}, and their conclusions are embodied in what is known as Clausius-Mosotti law. This law failed to explain the temperature dependance of specific polarization for some substances with high dielectric constant.

Debye\textsuperscript{1-3} was first among those who illuminated the molecular aspects. On the stimulus provided by Debye, the study of dielectric properties has been, over for the last 70 years, actively and widely pursued particularly by research schools all over the world and especially in Australia, France, Germany, India, Japan, The Netherlands, The United States, United Kingdom and USSR.

It must be mentioned, however, that the validity of Debye equation is restricted, particularly by the calculation of internal field where it was explicitly assumed the field of each molecule is homogeneous (Lorentz field). This is fulfilled in non-polar gases and may still be assumed to hold in dilute polar gases. But even in a solution of polar molecules in a non-polar solvent, the solute molecule produces near by induced dipoles which change as the molecule moves (Onsagar field).
Onsagar based on this concept, expresses the square of dipole moment as slightly more complex function of dielectric constant than Debye equation. From several other treatments of problem, the Kirkwood equation considers a large assembly of molecules from a statistical approach and takes into account the hindrance of molecular orientation. The progress achieved is, however, impaired by the appearance of an empirical parameter.

Several workers, by calculating dipole moment from measurement of dielectric constants on neat liquids and comparing these values with the 'True' values obtained in gas phase, have examined by Debye, Onsagar and Kirkwood equations.

The dipole moment value calculated from the dielectric constant value of pure liquid, on the basis of Onsagar equation is found to be close to gas phase or solution values in large number of normal liquids, but differed appreciably in associated liquids like water, alcohol etc.

The dipole moment values calculated from Kirkwood-Frohlich relation are found to be nearer to the gas phase value compared to the value obtained using the Onsagar equation not only in the case of associated liquids but for many non-associated liquids also.

There is a gradual improvement in the sequence given but none of the equations is quite satisfactory. In practice Debye equation is used throughout for polar or non-polar solutes in non-polar solvents as well, of course, as for gas measurements for the evaluation of dipole moment (μ) by solution method.
In solution method the general problem is that of separating the solution values into the contributions of the solute and solvent. This is based on the additivity rule for polarization. In order to obtain reliable results extrapolation to infinite dilution is carried out to obtain the value of molar polarization of the solute at infinite dilution \( P_{\infty} \) and finally \( \mu \) is computed from \( P_{\infty} \) using Debye's equation. There are variations of the extrapolation procedure. The plots of molar polarization of the solute \( P_2 \) against weight fraction \( (W_2) \) or mole fraction \( (X_2) \) are usually not linear and the extrapolation is likely to be inaccurate. These procedures are modified as well as simplified by Hedestrand, LeFevre, Halverstadt and Kumler, Higasi, Jai Prakash, Guggenheim, Smith and Palit. Of these procedures, the most common ones, those of Halverstadt and Kumler and Hedestrand are not substantially different. The Guggenheim-Smith method is less used although it is simpler and its lower degree of reliability is not proved with certainty. In fact, there are only a few comparisons of various methods for the same experimental material. Higasi's equation is generally considered to be merely approximate in spite of good results.

Some of these methods are widely followed in India especially by Raman, Soundarajan, Murthy, Rao et al., Baliah et al., Das and Roy, Ghosh et al., Subba Rao and Gopalakrishnan, Narasimhan, Rao and Ananthakrishnan.

All these methods are based on Debye equation and their
accuracy is given ultimately by its limited applicability to the solution. A more sophisticated approach is also possible: e.g., in the further development of the Onsagar\textsuperscript{20} theory, a formula for solutions has been derived by Scholte\textsuperscript{54} which, although complex, is ultimately based on measurements of dielectric constant of the solution ($\varepsilon_{12}$) and density of the solution ($\rho_{12}$). There are also further developments in this direction\textsuperscript{55,56}.

A different approach based on dielectric measurements is connected with the dielectric loss. By measuring the permittivity and its components ($\varepsilon'$ and $\varepsilon''$) in solutions at several concentrations and frequencies, it is possible to obtain dipole moment ($\mu$) and relaxation time ($\tau'$) simultaneously\textsuperscript{57,58}.

Though the results obtained in this way are comparable with those of classical methods, this approach has received less attention.

Dielectric data is also used to evaluate the Kirkwood-Frohlich linear correlation factor. It is a shape dependent correlation function that takes into account the short range interactions between the neighbouring molecules. This factor gives information regarding the relative alignments of the molecular dipoles. Evaluation of $g$ assumes importance in associated liquids. In non-associated liquids the value of $g$ is usually taken to be equal to unity whereby the Kirkwood-Frohlich equation\textsuperscript{59} reduces to the form of Onsagar equation. The studies on $g$ factor are carried out by Frohlich\textsuperscript{59}, Oster\textsuperscript{60}, Mecke\textsuperscript{61}, Huyskens\textsuperscript{62}.

Extensive review of the early work done in this field is given
by Bottcher. The static dielectric behaviour of mono alcohols and their solutions in non-polar solvents is studied with special reference to the variation of $g$ with concentration of the solute. Malecki studied the correlation factor ($g$) and the non-linear correlation factor due to the saturation effect in liquid complexes and from that he was able to decide whether the complex is of charge transfer type or proton transfer type or different from the two. Sabesan et al. have studied the linear correlation factor and dielectric polarization in fluid mixtures. A thorough investigation of the $g$ factor of 1-octanol with a variety of polar and non-polar solvents has been carried out by Ernest Gurnwald et al. They have studied a number of hydrogen bonded donors and acceptors and have proposed a chemical model which assumes that the dipole correlation between the solute and the solvent is considerable only in the case of molecular complex formation. Thiagarajan has studied the linear correlation factor in carboxylic acids with various solvents and pointed out that dioxane forms hydrogen bonded complexes. Many other investigators also studied solute-solvent interactions by evaluating correlation factor.

Excess dielectric constants, dipolar thermodynamic excess properties are evaluated in binary systems by several workers from dielectric data to understand the solute-solvent interactions. Rohdewald and Moldner have studied excess dielectric constants in a series of aqueous amide systems and discussed the effect of amides on hydrogen bonded water structure based on the sign of excess dielectric constant.
Sabesan et al.\textsuperscript{76} evaluated dipolar excess Helmholtz energy and dipolar excess entropy of mixing from dielectric data in solutions and felt that the information from these excess properties regarding the nature of solute-solvent interactions is more direct than that from the calorimetric methods.

Evaluation of molar polarization, dipole moment, $g$ factor, dipolar excess properties require accurate measurement of dielectric constants. A brief review of the available experimental techniques for measurement of dielectric constants is given in Section 1.2.
A BRIEF REVIEW OF EXPERIMENTAL TECHNIQUES
FOR MEASUREMENT OF DIELECTRIC CONSTANT

The experimental methods of measuring dielectric constants mainly depend on the frequency range under investigation. They also depend on state of matter under investigation. Usually the experiments are performed using sinusoidal electric fields. However, experiments using other time dependent fields (such as step, ramp or square voltages) can also be used to find the dielectric constant in the low frequency region by transient methods.

Davidson and Wheeler used step up voltage to study the transient response in n-propanol. Williams and Reddish used step up and step down voltages to study polymers. Davidson, Auty and Cole studied glycerol by ramp voltage. Lakes and Harper designed a low frequency dielectric bridge using square waves.

In the frequency range $10^{-3}$ Hz to 10 MHz the condenser + sample may be treated as two- or three-terminal impedance (two-terminal impedance if one terminal is connected to a shield, three-terminal impedance if neither terminal is connected to a shield) and a suitable audio- and radio-frequency bridge be used to measure the impedance. The bridge design depends on the frequency. At very low frequencies a long time is required to complete a cycle and to reach the steady state so that bridges which permit relatively rapid measurements are desirable.
Scheiber\textsuperscript{82} designed a bridge which eliminates time consuming operations without sacrificing the accuracy in the frequency range 0.008 Hz to 200 Hz.

Harris\textsuperscript{83} designed an op-amp. bridge which allows the balance to be established very rapidly. It is intended to go down even up to $10^{-3}$ Hz. Roberts\textsuperscript{84} described a versatile op-amp. bridge which suited for very low frequencies.

Heterodyne beat measurement of capacitance can be used upto few MHz to compute the dielectric permittivity from the capacitance change required to restore resonance after introducing the sample. Dielectric loss also can be determined from the shape of the resonance curve. Apparatus of this type for liquids has been described and extensively used by many investigators\textsuperscript{85,86}.

The Wheatstone bridge principle is extended to complex impedances with improved design. A great many bridges, differing in choice of circuit elements, the nature of shielding\textsuperscript{87} and various grounding and guarding circuits have been described\textsuperscript{88}. Bridges may be divided roughly into two classes; those using inductors for the ratio arms and those using condensers and resistors. An example of the latter is the Schering bridge\textsuperscript{88}. The accuracy attainable with the Schering circuit is quoted as ($\pm 0.2\%$, 0.04 pf.) in the capacitance in the frequency range 20 Hz to 1 MHz. It can be used even beyond 1 MHz at the expense of increased error in the capacitance measurement. The effect of stray capacitance to ground on the bridge balance may be eliminated by using inductive ratio arms\textsuperscript{89,90}. 
The operation of bridges in MHz region becomes increasingly
difficult as the frequency is raised, since the admittances associated
with stray capacitances increase in proportion to frequency. These
difficulties can be reduced or eliminated by substitution measure­
ments in a circuit of simple design. Circuit theory concepts can be
used to about 200 MHz by employing resonant circuits. The difficulties
with distributed impedances resonant circuits may be reduced by using
the re-entrant cavity. The resonance method can be used even with
very lossy dielectrics by employing a double resonance technique.\textsuperscript{91}

When a sample extends over an appreciable part of wavelength,
the electric and magnetic fields vary over the sample dimensions and
it becomes necessary to confine them inside conductors and to analyse
the spacial distribution of fields using Maxwell's equations. The
dielectric constant is determined from transmission line measurements.
Microwave bridges\textsuperscript{92} are used in the microwave frequency regions,
employing entirely different circuit techniques.

A resonant system bounded by conductors which is analogous
to a resonant circuit is also being used for the determination of
dielectric constants in the microwave frequency region. The upper
limit on the frequency of transmission line apparatus is set by the
difficulty of fabricating components of precise geometry. The upper
limit is perhaps 75 GHz.

Electro magnetic waves interact with the sample in free space.
Free-spaced methods are unsuitable below 40 GHz since the optical
methods require that the sample be large when compared to wavelength
so that diffraction may be neglected.\textsuperscript{93}
Pressure dependent studies are most straightforward at those frequencies at which impedance bridges can be used.

Practical considerations dealing mainly with construction, calibration and the use of cells are discussed elsewhere. A simple apparatus for the measurement of dipole moments was developed by Kurtz et al. using 555 timer with limited accuracy.

In the present work, a simple, low cost and novel dielectric-meter using IC's is developed. The technique is novel in the sense that while most of the existing techniques measure capacitance using bridge methods, the present technique utilizes time measurement for measurement of capacitance. Details of this technique are presented in Section 2.1.
SECTION 1.3

PURPOSE AND SCOPE OF THE PRESENT WORK

Several experimental techniques were developed for the measurement of capacitance and in turn the dielectric constant over a wide frequency range. In general, a bridge method or resonance technique is employed to determine the capacitance with or without the sample. Among them heterodyne beat method\textsuperscript{85,86} is popular at r.f. frequencies. All these methods suffer from some of the following drawbacks.

1. Manual control (human intervention) for adjusting a bridge or in attaining resonance is essential. Hence, some amount of time is required to reach the steady state and to sharply determine the capacitance. Scope for human error is not eliminated. Reproducibility of the results with higher precision is rather limited.

2. The apparatus usually consists of complex circuits and is a little bit expensive.

Hence, it is proposed to design an apparatus, using a slightly different principle, with IC version of monostable multivibrator. The time duration of the pulse produced with monostable multivibrator is directly proportional to the capacitance of timing capacitor, timing resistance in the circuit being kept constant. The duration of the pulse is determined with the frequency counter/timer with utmost precision. The apparatus is calibrated with some standard capacitors and is used to find the capacitance in terms of time duration of the
pulse. Since, the time duration is determined using a digital timer the scope for human error is very much reduced. The circuit is designed with a few components which are commonly available and inexpensive. The precise value of the capacitance measured, is used to determine dielectric constant accurately. The data obtained finds several applications.

Dielectric studies have a long and distinguished history. The dielectric data is used to determine the electric dipole moments, which is not only significant as a reflection of electronic structure of the molecule, but is also of prime importance in understanding of molecular interactions and it at least partly controls the transitions between the solid, liquid and gaseous states. A perusal of the existing literature will show a great variety of molecular behaviour remains to be adequately explored: for the liquid phase, in particular, it is clear that, whilst the principle features may be established, they are far from being fully understood in molecular terms. Hence, it is proposed to use the presently designed apparatus for evaluation of dipole moments of some standard liquids from solution measurements. The solution measurements are of great importance. Only in this way may one proceed to larger molecules and more complex problems. However, solution method of measurement of dipole moment has some serious problems. They are:

1. Problem of separating the solution values into contributions of solute and solvent. For this purpose various extrapolation procedures are found in literature.
2. Calculation of $\mu$ from $\mu_{200}$; the problem lies in the separation of orientation polarization from electric and atomic polarizations.

Several methods are in vogue for evaluation $\mu_{200}$. Among them Hedestrand, LeFevre and Vine method, Halverstadt and Kumler method, Guggenheim-Smith method are popular. In fact, there are only few comparisons of various methods for the same experimental material.

Hence, it is also proposed to apply all these methods to the same material data to find their relative suitability. These methods also require density and refractive index data in addition to dielectric data. Hence, density bottle method (single stem pycnometer) discussed in Section 2.2 is used to determine the densities and Pulfrich refractometer is used to determine refractive indices. Density and dielectric constant vary sensitively with change in temperature. They have to be determined at one constant temperature. Hence, a solid state temperature control is developed which can control the temperature with an accuracy of $\pm 0.01^\circ C$ using operational amplifiers and ON/OFF relays. All the measurements are made at $30 \pm 0.01^\circ C$.

According to some scientists, the mixed systems are exceedingly complex that our knowledge of them will surely remain incomplete. The Kirkwood linear correlation factor and excess dielectric constant ($\varepsilon^E$), data will throw some light on molecular interactions. So, the dielectric data is also used to evaluate both $g$ and $\varepsilon^E$. 
Benzene + nitrobenzene, carbon tetrachloride + nitrobenzene, Cyclohexane + nitrobenzene, Carbon tetrachloride + chlorobenzene and Cyclohexane + chlorobenzene systems are studied in the present investigation.
REFERENCES


