CHAPTER II
EXPERIMENTAL

I. General outline of the optical method.

Most of the workers who worked on the determination of relaxation times of polar molecules used the dielectric constant method in which $\varepsilon'$ and $\varepsilon''$ are measured and the relaxation time are calculated by the method suggested by Smyth and other workers.

But many workers have used optical method as it gives clearer insight into the mechanism of absorption of radio-frequencies by polar molecules. This method gives us the value of absorption directly. In this method waves generated by an oscillator are made parallel by using suitable wave guide or reflector. The waves traverse the liquid under investigation, contained in a cell directly and are received by a detector which may be a galvanometer or a micro-ammeter. Suitable precautions are to be taken, however, so that the formation of stationary waves does not affect the result. Esau with his co-workers Baez and Kebbel has carried this method over into the ultra-high frequency range. But they could not avoid the standing waves set up between the transmitter and the receiver producing intensity fluctuations by interference; moreover serious boundary problem arose as the wavelength was of dimensions of the sample.

A suitable method for studying the absorption of microwaves in which these troubles have been minimised has been
CIRCUIT DIAGRAM OF THE POWER SUPPLY
described by Ghosh (1953, 1954).

Since a portion of the present work has been done by following Ghosh's modification a simple outline of the method is given below.

2. Experimental arrangement.

The investigation on the absorption of microwaves by polar organic liquids in the pure state and in solutions in different solvents required production of microwaves of suitable frequency and their detection after absorption. For this purpose a Klystron of the type 723 A/B was used as the source of microwaves. The power was derived from a stabilised power supply giving -150 volts and 300 volts with respect to the ground for the reflector and the resonator of the Klystron oscillator respectively. The circuit diagram of the power supply is shown in Fig. 2. The frequency of the oscillator was measured with the help of a reaction type cavity wave-meter and was found to be 9415 Mc/sec. The radio-waves used for the study of absorption came out through the open end of a wave guide of cross section 2.26 cm x 1 cm at a distance of 14 cm from the tuning plunger. The absorption was studied by optical method, a block diagram which is given in Fig. 3. For the detection of the transmitted waves another wave guide and matched crystal detector as shown in the block diagram were used.

In order to study the absorption the cell was placed between the transmitting and receiving wave guides and its
distances from the open end of the transmitting wave guide was adjusted till the maximum deflection in the detecting circuit was observed. The temperature of the liquid was measured just before starting this adjustment. This procedure was repeated with the cell at different high and low temperatures. The high temperature was provided by a suitable electrical heater while the low temperature was produced with ice and salt in mixture. Only when very low temperatures were required the cell containing the liquid was immersed in a bath of alcohol which was cooled to the required temperature by slowly adding liquid oxygen to it. Care was taken so that the sample did not absorb moisture during the process of cooling.

During the process of adjustment for maximum current in the detector care was taken so that the formation of stationary waves did not vitiate the results. It was first observed that even when a glass plate was placed between the transmitting and receiving wave guides after the position of the plunger had been adjusted for maximum current in the detecting micro-ammeter, reflection of waves at the glass plate occurred for certain distances of the plate from the open end of the transmitting wave guide, but for certain other distances full transmission of the waves through the glass plate was observed. It was also observed that the distances between the successive positions of the glass plate for which the transmission was maximum was about $\frac{\lambda}{2}$ where $\lambda$ is the wavelength of the microwaves in air. It was thus evident that when the distance
between the glass plate and tuning plunger was a multiple of \( \frac{\lambda}{2} \) stationary waves were formed and there was very little transmission through the plate in this case and for other distances equal to \( n \frac{\lambda}{2} + \frac{\lambda}{4} \) there was no reflection at the surface of the glass plate. When a glass cell with a distance of 1 cm between inner surfaces was placed between the two transmitting and receiving wave guides, the transmission through through the empty cell was not cent percent for any position of the cell owing to reflection at the air glass interface. When, however, the cell was filled with benzene full transmission was observed for certain distance of the cell from the end of the transmitting wave guide at which the stationary waves were not formed.

The value of attenuation coefficient \( \mu \) was calculated from the relation

\[
\mu = \frac{2 \cdot 3 \cdot 5}{\chi} \log_{10} \left( \frac{I_0}{I} \right) \quad \ldots \ldots (12)
\]

where \( \chi \) is the thickness of the liquid, \( I_0 \) is the current in the detector circuit with cell removed and \( I \) is the observed maximum current in the detecting crystal circuit with the liquid absorber in its position.

In this connection it may be clearly mentioned that the experimental technique mentioned above gives only the relative maximum values of the attenuation coefficient and not the absolute values.
In this method it was not necessary to take account of the boundary problems created by the cell as was done by previous workers (Whiffen and Thompson, 1946; Reberts and Von Hippel, 1946).

To calculate the relaxation times the temperature for maximum absorption in each case was obtained from the respective temperature-attenuation curves. The values of the relaxation times and the radii of the rotor were found out by applying Debye's theory.


The data for the coefficient of viscosity, static dielectric constant and the refractive indices of the liquids used in the present investigations were taken from the International Critical Tables. These data for the solutions and also in the case of some pure liquids were obtained from measurement made in the laboratory.

(a) Measurement of refractive index.

The refractive indices of the liquids as well as of the solutions were measured by means of an Abbe's refractometer.

(b) Measurement of coefficient of viscosity.

The coefficients of viscosity of the liquids were measured by comparing the rate of flow of liquids investigated with those of carbon tetrachloride and benzene. The coefficients
of viscosity of the liquids at different temperatures were determined and their values at the required temperature were obtained from the corresponding temperature-viscosity curves.

(3) Measurement of dielectric constant.

To measure the dielectric constants of different liquids a metal cell was designed. The cell consisted of cylindrical glass vessel provided with a plunger made of brass. The two portions being connected with each other by means of a polystyrene cap to avoid any possible contact between the two metal portions. The inside of the brass vessel and the outside of the brass plunger was gold plated. The air gap between the two being 3 mm. The gap between the inner bottom of the cylindrical vessel and the tip of the plunger was about 1 cm. The liquid to be investigated could be introduced through a small inlet. To maintain a constant level of the liquid within the inner space an arrangement for a small outlet was made so that the liquid in excess could come out through the outlet. The whole thing could be immersed in an oil or water bath to get the readings at different temperatures. A skeleton sketch of the cell has been shown in Fig.4.

The dielectric constants of the liquids at different temperatures were measured by the resonance method. An alternating current of the order of kilocycles was set up in a primary circuit which was loosely coupled to a secondary circuit in which there was an inductance L, a variable standard condenser C and the cell X. The inductance L being inductively coupled to
Fig. 4. Skeleton sketch of the cell for the measurements of static dielectric constants.

I = Inlet for the liquid; Q = Polystyrene cap; B = Outer brass vessel; G₁ and G₂ = 3 mm. & 1 cm. gap
T₁ and T₂ = Electrical terminals;
Fig. 5. Diagram of the circuit used for the measurement of static dielectric constants.

C = Variable standard condenser; L = Inductance;
X = The cell; D = Detecting circuit with G as galvanometer
the oscillating circuit. A detector circuit is employed to detect the resonance. A diagram of the circuit is shown in Fig. 5.

The current in the secondary circuit is altered by changing the value of the total capacity C with the help of the standard variable condenser. When the resonance occur for a frequency a maximum current is read in the galvanometer. The first reading is taken without introducing the cell in the circuit. Then the cell without the liquid is introduced in the circuit. As the value of the total capacitance is changed the condition of resonance is altered. By adjusting the standard condenser C in the secondary circuit the condition of resonance is again reached. From the difference of the two condensers readings the capacitance of the cell in air is found out. Filling the cell with the experimental liquid, the capacitance of the cell with the liquid as dielectric is found. The ratio of the capacity of the cell with the liquid to the capacity of the cell without the liquid gives the value of the dielectric constant of the liquid at room temperature. To get the dielectric constant of the liquid at different temperatures the cell is kept in an electric heater the temperature of which can be controlled by the current flowing through the coil of the heater. Thus the dielectric constants of the investigating liquid at different temperatures, was measured and the dielectric constant of the liquid at the required temperature was found out from the temperature-dielectric constant curve. The dielectric constants of the liquid at a very low temperature was found out by the method of extrapolation as at such a low temperature abrupt variation of result is observed due to the absorption of moisture from the air because the condenser was not hermetically sealed.
4. Purification of liquids.

In order to study the absorption, the liquids under experiment have been carefully dehydrated with dehydrating agents like the anhydrous magnesium sulphate and calcium carbonates. The liquids thus dehydrated were subjected to fractional distillation, the first portion of the liquid being rejected. The liquids were also subjected to fractional distillation under reduced pressure. Special treatments like the filtration through charcoal column were also used in the case of o-nitroanisole.

In the case of ethylene chlorhydrin the sample was first dehydrated by mixing it with anhydrous \( \text{Na}_2\text{SO}_4 \) and then it was distilled in a triple-bulb distillation apparatus under reduced pressure. The first portion of the distillate was rejected and the middle portion boiling at 128.8°C at atmospheric pressure was used for the experiment. It was found in the preliminary investigation that the sample absorbed 3.18 cm microwaves highly at the room temperature (30°C) and also at higher temperatures. To be sure that the absorption was not due to the presence of water in the sample another sample of the pure substance was taken and mixed with requisite quantity of benzene and the mixture was subjected to fractional distillation. The portion boiling at 128.8°C at normal pressure was taken. It was expected to be pure. The liquid thus obtained was again mixed with anhydrous magnesium sulphate and distilled in a triple bulb under reduced pressure. The purity
of the distillate used for experiment was tested by the boiling point test.

The lower alcohols were made free from water by mixing them with anhydrous magnesium sulphate. They were kept in this condition for two days and was then filtered. After filtration they were treated with fresh quick lime and was then subjected to fractional distillation. The whole procedure was repeated until the purity of the liquid was ascertained by the boiling point test.

The higher alcohols are not expected to contain much water and they were distilled in vacuum after they had been properly dehydrated by quick lime.

References