CHAPTER 2

2.1 Experimental Methods

The experimental arrangement for the determination of dielectric permittivity ϵ', dielectric loss ϵ' at different microwave frequencies, static dielectric constant ϵ_0 refractive index n_D^2 and the viscosity (η) which are required for the determination of relaxation times and other thermodynamical parameters are described in the following sections.

2.2 Measurement of dielectric permittivity ϵ' and dielectric loss ϵ''

There are several methods for the determination of ϵ' and ϵ'' at different microwave frequencies. The choice of the method is generally governed by the nature of the liquids to be investigated. In the present investigations we have adopted Surber's[1] method for the determination of ϵ' and ϵ'' values at different microwave frequencies of wavelengths 8 mm, 1.25 cm, 1.62 cm, 3.17 cm and 3.49 cm, and at different temperatures. The essential features of the method are described briefly in the next section.

2.3 Surber's method

The technique of the measurement for the determination of dielectric properties are normally made upon a sample of material which completely enclosed within a hollow wave guide. The behaviour of the system must be analysed in terms of propagation characteristics of the electromagnetic energy through the dielectric medium.

This method of measurement of ϵ' and ϵ'' are based upon the variation of reflection co-efficient of uniform dielectric layer as the depth of the layer is varied.

2.3.1 Theory of the methods

If a beam of microwave power travelling through a wave guide is incident on a dielectric medium of suitable length terminating by a metallic shorting plate, the beam is reflected at the interface due to mismatch of the impedences and a system of stationary wave is formed. From the transmission line theory, in the case of rectangular wave guide. The propagation constant for the air filled guide is given by

$$\gamma_g = j\beta = \frac{2\pi j}{\lambda}\sqrt{1-(\lambda/\lambda_c)^2} \tag{2.1}$$

similarly the propagation constant for liquid filled guide is

$$\gamma_L = \alpha_L + j\beta_L = \alpha_L + \frac{2\pi j}{\lambda_d} \approx \frac{2\pi j}{\lambda}\left\{\epsilon' - (\lambda/\lambda_c)^2\right\}^{1/2} \tag{2.2}$$

where

λ = wavelength in the air filled guide

λ_c = cut off wavelength

λ_d = wavelength in the liquid filled guide

α_L = attenuation in the dielectric

β_L = phase constant in the dielectric and $Z_d = |Z_d| e^{j\phi_d} = \frac{\gamma_g}{\gamma_L}$; $|Z_d| = \left\{ \frac{1-(\lambda/\lambda_c)^2}{\epsilon' - (\lambda/\lambda_c)^2} \right\}^{1/2}$

$$\phi_d = \tfrac{1}{2} \tan^{-1} D \qquad (2.3)$$

where Z_d is the characteristic impedance of the dielectric filled guide relative to the air filled guide.

For a dielectric sample of length L, enclosed within a section of wave guide and terminated by a perfectly reflecting short-circuit plane, the magnitude of the voltage reflection co-efficient at the face of the dielectric will be given by the equation

$$|R| = \left| \frac{Z_d \tanh \gamma_d L - 1}{Z_d \tanh \gamma_d L + 1} \right| \qquad (2.4)$$

The output of a square law detector coupled to the reflected wave by a unidirectional coupler is proportional to $|R|^2$ for a constant incident power. In the case of dielectric with short-circuited termination and of length L, which are integral multiple of half wavelength in the dielectric ($L = n\lambda_d$; $n = \frac{1}{2}, 1, \frac{3}{2} \dots$ etc.), the values of $|R|^2$ alternates between maximum and minimum values and the magnitude of maximum decreases gradually, and for an effective infinite length of dielectric, it reaches a constant value $|R_\infty|^2$ The distances between two consecutive maxima or minima given by $\lambda_d/2$ determines the wavelength λ_d in the dielectric filled guide.

From the transmission line theory, the wavelength λ_d and the attenuation per wavelength ($\alpha_d \lambda_d$) in the dielectric is related to ϵ' and ϵ'' and the dissipation factor D, by the following relations

$$\lambda_d = \left[\frac{\lambda^2}{\epsilon' - (\lambda/\lambda_c)^2}\right]^{1/2} \left[1 - \tan^2(\tfrac{1}{2}\tan^{-1}D)\right]^{1/2} \tag{2.5}$$

$$\alpha_d = \frac{\pi \epsilon'' \lambda_d}{\lambda^2} \tag{2.6}$$

and

$$\alpha_d \lambda_d = 2\pi \tan(\tfrac{1}{2}\tan^{-1}D) \tag{2.7}$$

From eqn.(2.5) and (2.6) the expression for and are obtained as

$$\epsilon' = (\lambda/\lambda_c)^2 + (\lambda/\lambda_d)^2 \left[1 - \tan^2(\tfrac{1}{2}\tan^{-1}D)\right] \tag{2.8}$$

$$\epsilon' = (\lambda/\lambda_c)^2 + (\lambda/\lambda_d)^2 \left[1 - \left(\frac{\alpha_d\lambda_d}{2\pi}\right)^2\right] \tag{2.9}$$

and

$$\epsilon'' = \frac{1}{\pi}(\lambda/\lambda_d)^2 (\alpha_d \lambda_d) \tag{2.10}$$

Thus for the determination of ϵ' and ϵ'' of the liquid dielectrics, the attenuation per wavelength ($\alpha_d\lambda_d$) must be known. They are computed analytically by the method of successive approximations as follows.

Let M_n be the ratio of the nth maximum of the reflected signal for $L = n\lambda_d$ to that for an effectively infinite dielectric column, so that

$$M_n = \frac{|R_n|^2}{|R_\alpha|^2}, \text{ where } n = \tfrac{1}{2}, 1, \tfrac{3}{2} \ldots \text{ etc.} \tag{2.11}$$

Thus in order to simplify the final equation, define

$$x = \frac{\lambda_d}{\lambda_g} \qquad \text{and} \quad y = \frac{1-x}{1+x}$$

where $\lambda_g = \dfrac{\lambda}{\left[1-(\lambda/\lambda_c)^2\right]^{1/2}}$ the wavelength inside the guide. Physically x represent the characteristic impedence of the guide filled with an ideal dielectric having the same λ_d and y the corresponding reflection co-efficient for an infinite long column.

The eqn.(2.11) after substitution of the expression for $|R_n|^2$ and $|R_\alpha|^2$ for the particular case result in a quadratic equation for $\exp(-2\pi\alpha_d\lambda_d)$ which may be solved for attenuation per wavelength ($\alpha_d\lambda_d$) in nepers to give the expression

$$\alpha_d\lambda_d = \frac{1}{2\pi}\ln\left[K_1\left\{1+\left(1+K_2\right)^{1/2}\right\}\right] \qquad (2.12)$$

where

$$K_1 = \frac{C_1(1-M_nT)}{M_n-1} \qquad (2.13)$$

and

$$K_2 = \frac{C_2(M_n-1)(1-M_nT^2)}{(1-M_nT)^2} \qquad (2.14)$$

To a first approximation, K_1 and K_2 may be expressed as

$$K_1 = \frac{1-y^2M_n}{y(M_n-1)} \qquad (2.15)$$

and

$$K_2 = \frac{(M_n-1)(1-y^4M_n)}{(1-y^2M_n)^2} \qquad (2.16)$$

can be obtained from the known values of y and M_n The successive values of T, C_1 and C_2 are computed from the following expression.

$$T \simeq y^2 \left[1 + \frac{D^2 x}{(1-x^2)^2} - \cdots\right] \qquad (2.17)$$

$$C_1 \simeq \frac{1}{y}\left[1 - \frac{D^2 x(x+1)}{2(1-x^2)^2} + \cdots\right] \qquad (2.18)$$

and

$$C_2 \simeq 1 + \frac{D^2 x^2}{(1-x^2)^2} \qquad (2.19)$$

and the dissipation factor D is then determined from the equation

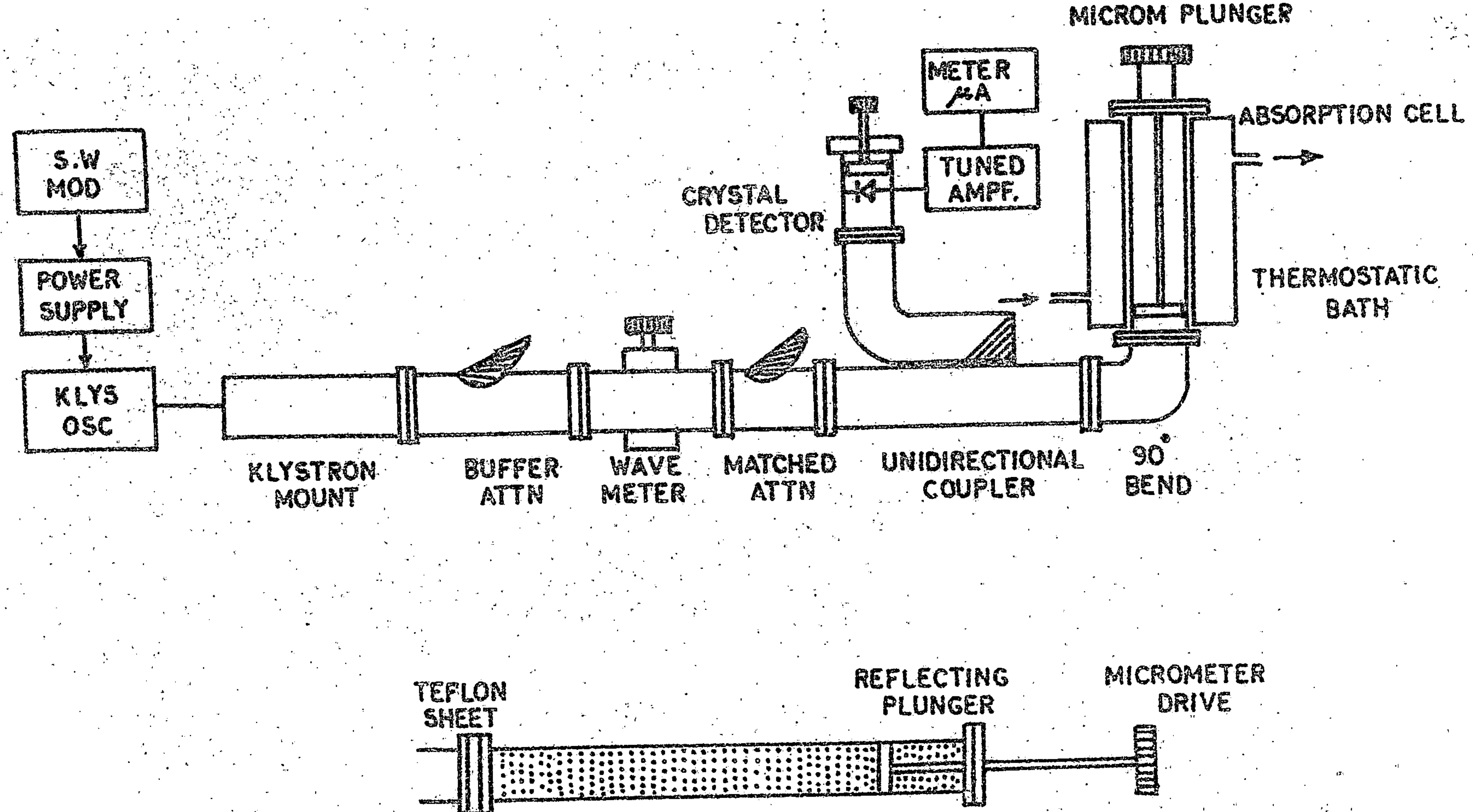
$$D = \tan\left[2\tan^{-1}\left(\frac{\alpha_d \lambda_d}{2\pi}\right)\right] \qquad (2.20)$$

The determination of D from the experimental data is then evidently, a process of successive approximations, which however converge very rapidly. For $D \leq 0.1$, K_1 and K_2 may be considered as a function solely of y and M_n and only one calculation need be made for obtaining the value of $\alpha_d \lambda_d$ from eqn.(2.12). For larger values of dielectric loss, the value of ($\alpha_d \lambda_d$) thus obtained from the eqn.(2.12) is used to calculate D from eqn.(2.20). For values of $D \leqslant 0.3$, this value of D is used to compute the values of C_1, C_2 and T from eqns.(2.17 to 2.19) which yield a second approximate value of $\alpha_d \lambda_d$ with the help of eqns. (2.12 to 2.14). For larger value of D lying within $0.3 \leqslant D \leqslant 1.0$ the D^2 term in the eqns.(2.17) and (2.18) are replaced by $4\sin^2(\frac{1}{2}\tan^{-1}D)$ while that in eqn. (2.19) by $\sin^2(\tan^{-1}D)$ and thus T, C_1 and C_2 are determined and with these value of T, C_1 and C_2 the value of $\alpha_d \lambda_d$ is again calculated. With this calculated value of $\alpha_d \lambda_d$ and measured values λ, λ_c and λ_d the constant ϵ' and ϵ'' of the dielectric medium are obtained from eqns. (2.9) and (2.10).

2.3.2 Experimental arrangement

A block diagram of the microwave benches in microwave regions of 8 mm, 1.25 cm, 1.62 cm, 3.17 cm and 3.49 cm wavelength used in the present investigations, are shown in Fig.2.1. The general set up of all these units are the same except 1.62 cm. and 8 mm. The 1.62 cm microwave power was generated from 3 cm Klystron oscillator by means of crystal harmonic generator and 8 mm microwave signal generator was imported from Poland Electronics Corporation, U.S.A. (Model no. G 3540-1).

Microwaves are generated by suitable Klystron oscillators and are modulated by square wave of 1000 c/s. Attenuators just after the oscillator were used to prevent the frequency pulling. The frequency of the microwave generator was measured by the absorption type frequency meter in each unit. The reflected power from the dielectric interface is coupled with the unidirectional coupler and finally the power was detected by a matched tunable crystal detector with 1N23B and 1N26 diodes for the X-band, k-band region respectively and with the crystal 1N53 in the 8 mm region signal from the detector was amplified by a tunable amplifier, rectified and read on a sensitive microammeter. The characteristic of the square law detector was tested and the linearity of the amplifier was also carefully checked before the actual experiment. At each wavelength of operation, the dielectric



BLOCK DIAGRAM OF EXPERIMENTAL ARRANGEMENT FOR SURBER'S METHOD

FIG. 2·1

cells used were of same general design. They are made of high quality silver waveguides of sufficient length to contain a liquid column of about five times the wavelength (λd) in the dielectric. One end of the cell was closed with thin teflon sheet, the other end of the cell was short circuited by a moveable plunger driven by a micrometer screw. The shorting plunger block was made of pure silver and the micrometer drive was a stainless steel to avoid chemical reaction with liquid used in the cell. The cell was maintained at the desired temperature within $\pm$ 1°C by means of a thermostat.

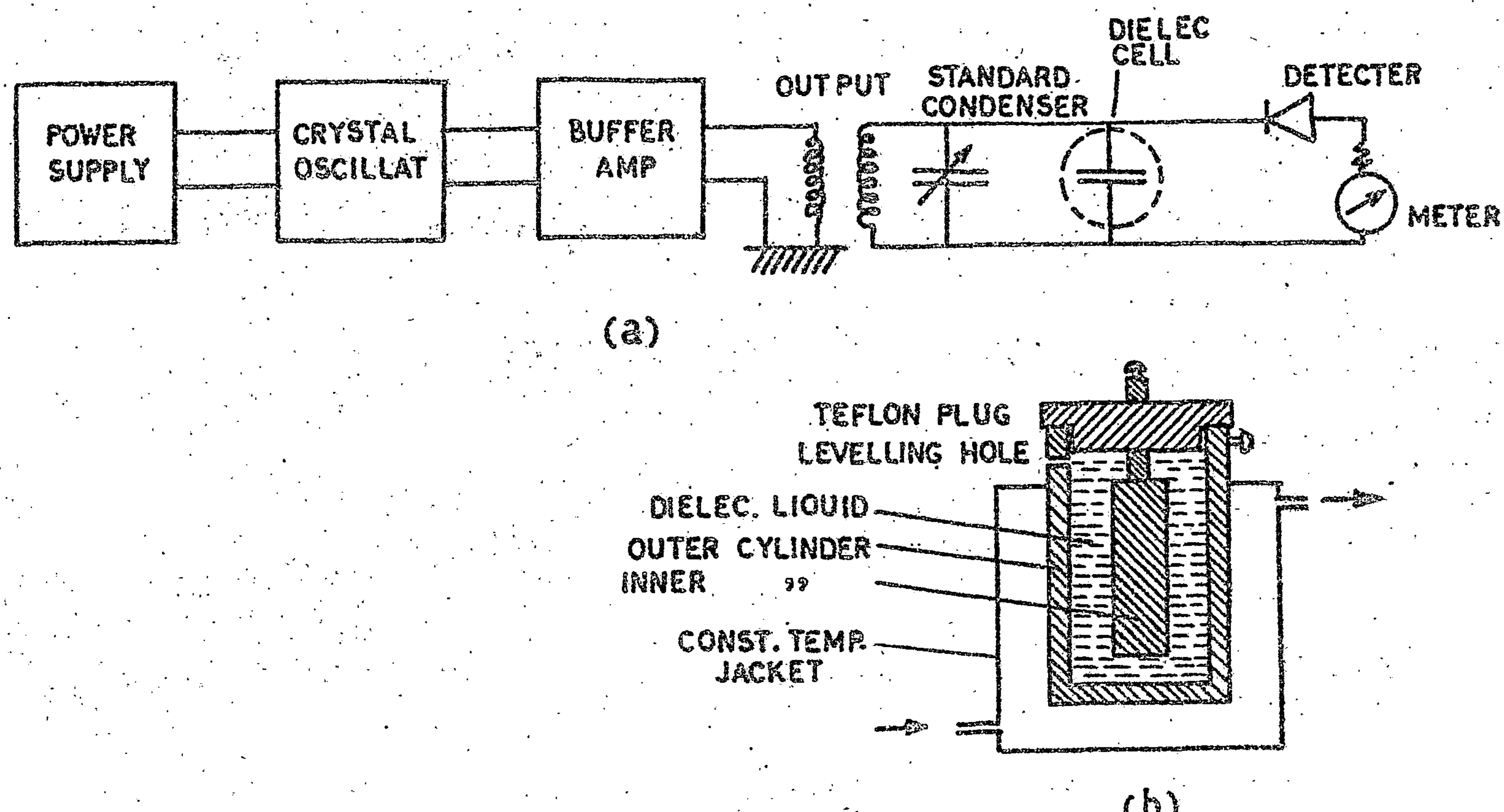
The absorption cell was filled with the liquid dielectric sample which was allowed to keep for sometime to reach thermal equilibrium. The reflecting plunger was slowly raised and the amplitude and the positions of the successive maxima were recorded accurately. The value of the reflected power which showed very little variation as the plunger was moved out, was taken to be the amplitude of the reflected power for an effective infinite dielectric length. Investigations for a given liquid at a particular temperature of a given wavelength was repeated two or three times. For a particular temperature the value of ϵ' and ϵ'' were calculated for each set of experimental data and the average values were used in the determination of relaxation time. The error in the measurement of ϵ' and ϵ'' in the present set up were about 2% and 4% respectively. Stadarisation was done with a liquid for which reliable data are available in literature.

2.4 Measurement of static dielectric constant

The value of the static dielectric constant (ϵ_0) at different temperature of the polar liquid investigated in the present study were measured by the resonance method. The experimental arrangement used for this purpose is shown in the diagram (Fig.2.2).

A constant frequency generator circuit which consists of a gold plated piezoelectric quartz crystal which has a natural frequency 1 Mc/sec was used as an electrical oscillator and amplified by a buffer amplifier. The detector circuit contained a calibrated standard variable condenser (Philips Type GM 4352) in parallel with the dielectric cell which could be tuned for resonance to show maximum current in the meter.

A sketch of the dielectric cell used in this investigation is shown in Figure 2.2(b). The inner and outer cylinders were made up of metal brass having a narrow space between them. The inner cell was held in concentric position with a tight fitting teflon cap. The surface of the cylinders coming in contact with the liquids were well silvered in order to avoid any possible chemical reactions. Holes were kept on the wall of the outer cylinder which served as inlet for injecting liquids and also maintained constant level of liquid inside. The dielectric cell was provided with a jacket for circulation of water whose temperature was maintained at the desired value within $\pm$ 1°C by a thermostat.



BLOCK DIAGRAM OF EXPERIMENTAL ARANGEMENT FOR MEASUREMENT OF STATIC DIELECTRIC CONSTANT

FIG. 2·2

The capacity of the empty dielectric cell and the stray capacitance of the associated lids were determined carefully and care was taken to keep the stray capacity value as small as possible. The overall air capacitance of the cells used were in the range 8-20 pf and the accuracy in the determination of values were checked with measurement using specpure benzene and carbon tetrachloride. The accuracy in the measured ϵ_0 -values was about 1%.

2.5 Determination of viscosity η

The viscosity of liquids were measured with the help of a Ostwald Viscometer.

The liquids were taken in a viscometer kept immersed in water taken in a flask provided with water jacket. The temperature was maintained constant by means of a thermostat.

The time of fall 't' seconds of the liquid between two fixed marks in the viscometer at any temperature was noted. The density of liquid d at that temperature was determined by a picnometer. The viscosity η of the liquid at that temperature was given by the relation

$$\eta = d\,(at - b/t) \tag{2.21}$$

where a and b are the two constants of the viscometer determined by the time of fall of water at two different temperature. Knowing the density and viscosity of water at that two particular temperature from critical table, the values of a and b were determined. In this way viscosity of liquids at different temperatures were determined.

2.6 Refractive index n_D

The refractive index of the liquids at different temperatures were found out with Abbe's refractometer. The temperature was maintained constant with a thermostat.

2.7 Purifications of samples

Pure samples were procured from Schuchardt (Germany), Fluka (Switzerland) and E. Merck (Germany). All these chemicals were dried by dehydrating agents and then were distilled by fractional distillation. The proper fractions were distilled again under reduced pressure before use in the investigations.

2.8 Standardisation of the dielectric data obtained in the investigations

The values of ϵ', ϵ'' and n_D determined in the present investigation in the case of chlorobenzene, bromobenzene and anisole were found to be in good agreement with respective values reported in literatures[2].

2.9 Activation energy of dielectric relaxation

The dielectric relaxation has been treated as a rate process[3] in which polar molecules rotate from one equilibrium position to another. The process of this molecular rotation requires an activation energy sufficient to overcome the energy barrier separating the two equilibrium positions. The number of time such rotations occur per second is given by the rate expression

$$K_0 = \frac{1}{\tau_0} = \frac{kT}{h} e^{-\Delta F/RT} \qquad (2.22)$$

where τ_0 = Most probable relaxation time

ΔF = Free energy of activation

$= \Delta H - T\Delta S$

or $$\tau_0 = \frac{h}{kT} e^{E_\tau/RT} \qquad (2.23)$$

where ΔH is the heat of activation of the dipole relaxation

and ΔS is the entropy of activation.

From the slope of the straight line plot of $\log T\tau$ vs $\frac{1}{T}$ the heat of activation E_τ for dipole relaxation can be obtained.

2.10 Activation energy for viscous flow

The viscosity of liquids may be approached in an analogue manner.

Viscous flow is pictured as the movement of one layer of molecule with respect to another layer, involving translational as well as rotational motion of the molecules with an activation energy required to pass over a hindering potential barrier. The equation for viscosity in terms of this mechanism

$$\eta = \frac{hN}{v} e^{\Delta F_v/RT} \qquad (2.24)$$

where

ΔF_v = Free energy of activation for viscous flow

v = Molar volume

$\Delta F_v = \Delta H_v - T\Delta S_v$

$$\eta = \frac{hN}{v} e^{\Delta H/RT} \qquad (2.25)$$

From the slope of the straight line plot of $\log \eta$ vs $\frac{1}{T}$ the heat of activation for viscous flow can be obtained.

References

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