ENCLOSURE – III

EXECUTIVE SUMMARY

Relaxation Studies on Molecular Interaction of Alcohols and Amines

The influence of association through hydrogen bonds on the structure of liquids and their relaxation behavior has been studied for a long time. The formation of hydrogen bonds leads to associate with restricted number of molecules, called multimers. The dynamic properties of such liquids are often interpreted in terms of the duration of life and the motion of the multimers. As pointed out earlier, at least three types of multimers can occur in the case of monohydric alcohols and mono substituted amines namely α - multimers, β - multimers, and γ - multimers. The relaxation times of such species are far and wide. Recently extensive dielectric relaxation studies of alcohols and amines have carried out.

In continuation of our studies on the static dielectric constants of amines we have taken measurements of dielectric constants at microwave frequencies, with a view to study the dynamic behavior of these liquids in dilute solutions. The study of Kirkwood's correlation factor generally gives evidence for the probable presence of n-mers open or cyclic, but not on the size of the multimers. Since the relaxation time is dependent on the size of the molecules and the viscosity of the medium, the results will be complementary. Both binary and ternary systems are taken for the investigation. Alcohol or amine in non polar solvents forms the binary whereas ternary contains alcohol and amine in non-polar solvents. The relaxation studies were carried out at the temperatures 303K, 313K and 323K.

EXPERIMENTAL SET UP

The schematic diagram of apparatus used to measure the dielectric constant and dielectric loss of liquids at X-band microwave frequency is given in Fig. The microwave X-band test bench arrangement is shown in Fig. K-27 Klystron, supplied by the Scientific instrument co. Ltd. Allahabad was used as the source for microwave power at 8.33 GHz. This was operated by a well regulated power supply of the same company. A variable attenuator and a slotted line wave guide with a slit in the broad face to accommodate a probe were connected with a liquid cell. The signal from the Klystron was fed to the attenuator through a ferrite isolator. This isolator allows free passage of power only in the forward direction and it attenuates the reverse wave strongly. The X-band liquid cell supplied by the same company was used. The sample length of liquids is adjustable by the micrometer plunger assembly. The microwave power was transmitted from the slotted line into the liquid through a teflon window, which has negligible dielectric loss. The probe is a crystal detector, which measures the microwave power. The microwave current is fed to a sensitive spot galvanometer. The temperature of the liquid inside the cell was kept constant by circulating water around it from a thermostat.

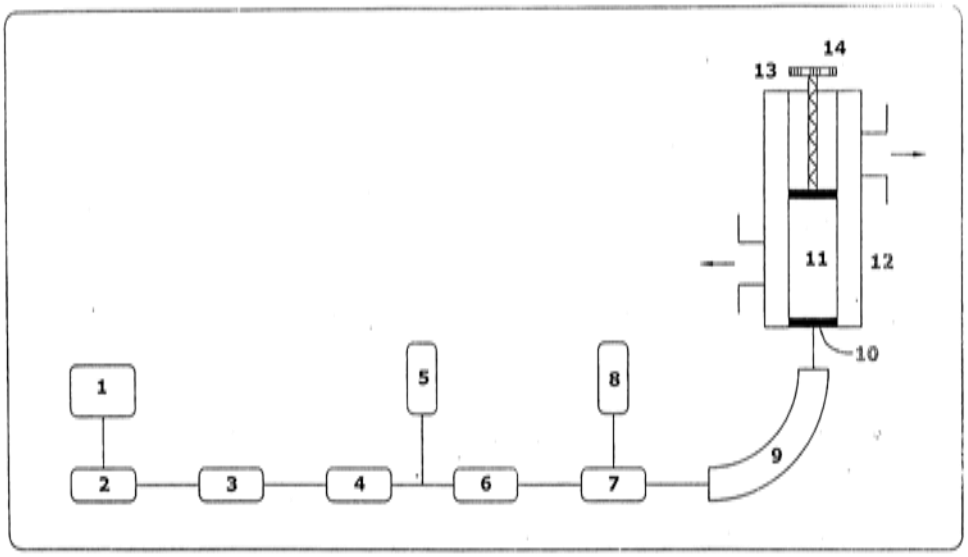

Fig.4(c). - Microwave X - Band Test Bench

1. Power supply
2. Reflux Klystron-K27
3. Tuner
4. Ferrite isolator
5. Frequency meter
6. Attenuator
7. Slotted line carriage
8. Crystal detector
9. H- Plane bend
10. Teflon window
11. Liquid cell
12. Constant temperature jacket
13. Micrometer head
14. Plunger

MATERIAL SCIENCE LAB,

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DEVAKOTTAI

Procedure

Smyth's method has been used for the evaluation of ε′ and ε″. The probe of the detector is fixed at a particular place and the plunger is moved in the liquid cell with air as the medium. As the detector is connected to a sensitive galvanometer, the detected output is in the form of deflections in the galvanometer. The distance between the successive minima is found out. This gives the value of $(\lambda_2^{\overline{g}})$.

The liquid cell is now filled with the given liquid. The plunger is moved up in the cell from the bottom of the cell. The distance between minima or maxima is found out. This gives the value of $(\lambda_2^{\overline{d}})$.

During the movement of plunger from the bottom of the cell, the position of plunger $(\ _1\ )$ corresponding to the first minimum deflection is noted. Then the plunger readings $'_1$ and $''_1$ corresponding to the double minimum above and below the first minimum position are noted. Let the difference between $'_1$ and $''_1$ be Δ . Then the inverse voltage standing wave ratio ρ_1 is given by

$$\rho_1 = \pi \frac{\Delta x}{\lambda_g}$$

The value of ρ is corrected for the approximation involved in the derivation of the above equation using a correction curve. Then the plunger is moved up and plunger readings corresponding to the second minimum ($_2$), double minimum above and below and second minimum $'_2$ and $''_2$ are noted. The value of ρ_2 is found out.

Similarly the values of ρ_3, ρ_4, etc., are obtained for third, fourth, etc., minimum positions respectively. A graph is plotted with n along the x-axis and ρ_n along the y-axis. A straight line is obtained and its slope ($\frac{d\rho}{dn}$) is found out using least square fitting technique.

The value of ε' and ε'' are calculated using Eqns. (39) and (38). The values of static dielectric constant ε_0 for solutions are measured at a fixed frequency 1 KHz using a VLCR-7 meter supplied by M/s. Vasavi Electronics, Secunderabad. Abbe's Refractrometer was used to measure the refractive indices for sodium D line.

DETERMINATION OF PARAMETERS FROM MEASURED DIELECTRIC CONSTANTS

Cole-Cole Plot

The measured values of ε', ε'', $\varepsilon 0$ and ε_∞ were fitted in a complex plane plot with a depressed circular arc. The angle made by the diameter drawn through the centre from the ε_∞ point and the x-axis is given by $(\frac{\alpha \pi}{2})$. From the Cole-Cole plot the relaxation time τ can be found out using the equation.

$$(\omega \tau)^{1-\alpha} = (\frac{v}{u}) -$$

where α is the distribution parameter, ω is the angular frequency, v is the distance between $\varepsilon 0$ and experiment point on the Cole-Cole plot, u is the distance between ε_∞ and that point on the Cole-Cole plot.

Higasi's method

For the study of solutions the method used by Smyth and Co-workers gives the best fit. This method provides multiple relaxation times, one for overall rotation and another for group rotation. Higasi assumed a linear variation of ε_0, ε' and ε'' and ε_∞ with weight fraction w_2 of the solute and hence one can write

$$\varepsilon_0 = \varepsilon_{01} + a_0 w_2$$
$$\varepsilon' = \varepsilon'_1 + a' w_2$$
$$\varepsilon'' = a'' w_2$$
$$\varepsilon_\infty = \varepsilon_{1\infty} + a_\infty w_2$$

where a_0, a', a'' and a_∞ are the constants known as Higasi's parameters.

Higasi derived a relation connecting τ and α.

$$\tau = \frac{1}{\omega}\left(\frac{A^2+B^2}{C^2}\right)^{\frac{1}{2}}(1-\alpha)$$

$$\alpha = 1 - \left(\frac{2}{\pi}\right)\tan^{-1}\left(\frac{A}{B}\right)$$

where ω is the angular frequency, τ is the most probable relaxation time, α is the distribution parameter which can be calculated from the following equations.

$$A = a'(a_0 - a_\infty)$$
$$B = (a_0 - a')(a' - a_\infty) - a''^2$$
$$C = (a' - a_\infty)^2 + a''^2$$

From the above relations, the constants A, B and C can be calculated and using these values, the relaxation time τ can be determined.

The Debye equation in terms of a_0, a', a'' and a_∞ yields two independent Eqs.

$$\tau(1) = \frac{a''}{\omega (a' - a_\infty)}$$

$$\tau(2) = \frac{(a_0 - a')}{\omega a''}$$

τ(1) is the molecular relaxation time of the complex as a whole and τ(2) indicates the relaxation time of the base molecule of alcohols or amines.

The mean relaxation time τ is given as

$$\tau = \sqrt{\tau(1)\tau(2)}$$

Dipole moment is given by Higasi's relation

$$\mu = \left(\frac{27 M_2 k T}{\pi N_A d_1} \right)^{\frac{1}{2}} \left(\frac{1}{2 \varepsilon_1 + 2} \right)$$

τ(1) given by the Eq. may be described as the relaxation time for overall rotation of the molecules and τ(2) given by the Eq. may be described as a sort of average dielectric relaxation time.

In the present investigation, both Cole-Cole and Higasi's methods have been used to calculate α and τ. This will enable us to study quantitatively the relaxation mechanism involved in the case of alcohols, amines and their mixtures.

The values of the dielectric constant at high frequency (ε′), the dielectric loss (ε″), the distribution parameter (α), the most probable relaxation time (τ), the relaxation time for overall rotation of the molecule τ(1), the relaxation for group rotation τ(2) and the excess dipole moment for various systems are reported in Tables. Higasi's parameters were obtained. Relaxation time (τ) was determined by Cole-Cole method. The variation of the average relaxation time (τ), the excess dipole moment (Δμ) and the activation free energy due to relaxation (ΔF_τ) with the concentration (w2) are reported.

The values of dielectric constants, Higasi's parameters, relaxation times, distribution parameter, activation free energies and change in dipole moment for the ternary mixtures of equimolar concentrations of dibutyl phthalate + octanol, dibutyl phthalate + isobutanol, dibutyl phthalate + benzyl alcohol, dibutyl phthalate + benzonitrile, dimethyl phthalate + octanol, dimethyl phthalate + isobutanol, dimethyl phthalate + benzyl alcohol, dimethyl phthalate + benzonitrile, dioctyl phthalate + dodecanol, dioctyl phthalate + benzyl amine, diethyl phthalate + dodecanol, diethyl phthalate + heptanol, dibutyl phthalate + isopropyl alcohol, dibutyl phthalate + triethanol amine and dioctyl phthalate + triethyl amine in benzene at temperatures 303K, 313K and 323K are reported. The non linear variation of these parameters with change in concentration indicates the hetero interaction between the components of the mixture. The results are interpreted accordingly.

By this Project, the following outputs are obtained.

- Project Fellow is pursuing Ph.D. at Alagappa University
- A Research Lab is set up in the Department of Physics by the funding from the UGC which helps many scholars to do Ph.D.
- The systems studied under investigation are of Industrial use. The results are useful for the R&D people.