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DIELECTRIC RELAXATION OF TETRAHYDROFURAN IN BENZENE SOLUTION FROM MICROWAVE ABSORPTION STUDIES

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ABSTRACT

The dielectric constant (ε′) and dielectric loss (ε″) for dilute solutions of tetrahydrofuran (THF) have been measured at 9.90 GHz at different temperatures (25°C, 30°C, 35°C and 40°C). The dipole moment (μ) and relaxation time (τ) have been calculated at various temperatures at single frequency concentration variational method suggested by Gopala Krishna. It is observed that dielectric relaxation process can be treated as rate process like viscous flow. Based upon above studies, monomer structure for THF in benzene solution has been inferred. The solvent-solute molecular associations in benzene has been proposed and energy parameters for the dielectric relaxation process of THF in benzene solution at different temperatures have been calculated and compared with the corresponding energy parameters for viscous flow.

Key words: Dielectric relaxation, Microwave absorption studies, Tetrahydrofuran.

INTRODUCTION

Tetrahydrofuran (THF) is a non-aqueous dipolar aprotic solvent. It has low dielectric constant ε′ = 7.58 and low dipole moment μ = 1.75 D at 25^oC. THF has low boiling point 66^oC[1]. It is cyclic ether of moderate toxicity. It can be made either by catalytic hydrogenation of furan or by intermolecular removal of water from butane 1, 4-diol. THF is an important solvent, used in reduction with lithium aluminum hydride in the preparation of aryl magnesium chlorides and in hydroboration. It is used as a starting material for

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manufacture of nylon[2]. THF has also been used as the important constituent of binary mixture of the required characteristics. This molecular aspect of THF motivated the authors to study the molecular behaviour of THF in benzene. Recently, the study of dielectric relaxation of pure and binary mixtures of polar molecules from microwave absorption data has raised great interest to study solute-solvent and solute-solute type of associations in non-polar medium. Dielectric relaxation data obtained from microwave absorption studies is expected to throw light on solute-solvent type of molecular association present in the solution as microwave data is sensitive to detect weaker molecular interactions[3-7].

The present paper is concerned with the dielectric relaxation studies of THF in benzene at different temperature (25^oC, 30^oC, 35^oC, 40^oC,) for microwave absorption studies at *9.90 GHz*. It is found that THF occurs in monomer form in the benzene solution. The presence of solute-solvent association is predicated. Dielectric relaxation process of THF in benzene can be treated as rate process just like the viscous flow.

EXPERIMENTAL

Tetrahydrofuran (THF) (Merck, Merck Limited, Worli, Mumbai) was kept at 4Å molecular sieves for about 10-14 hrs with occasional shakings and then distilled through a long vertical column. The middle fraction was collected for use. Benzene (A. R. 99.7% pure, from Central Drug House Pvt. Ltd, New Delhi) was dried by refluxing over freshly cut sodium metal for 6-8 hrs and distilled through a long vertical fractionating column. The middle fraction of the distilled benzene was used. The *X*-band microwave bench was used to measure wavelength in the dielectric medium. The experimental technique of Arrawatia et al. used by Sharma and Sharma[8] for microwave measurement was used. A set of dilute solution of THF in benzene was prepared and all the measurements were made at 25^oC, 30^oC, 35^oC, C and 40^oC by circulating water around the dielectric cell through a thermostat (Lauda Dr. R.Wobser GMBH & Co. K. G. German Made). The dipole moment of purified acetone was measured to test the precession and working of the equipment. The density and viscosity of the solution were measured by the sealable type of pycnometer and Ubbelohde viscometer, respectively.

RESULTS AND DISCUSSION

Using standard standing wave microwave techniques[9], the dielectric constant (ε') and dielectric loss (ε'') of the dilute solutions of THF in benzene have been calculated and are shown in Table 1.

Following equations have been used:

$$\varepsilon' = \left(\frac{\lambda_o}{\lambda_c}\right)^2 + \left(\frac{\lambda_o}{\lambda_d}\right)^2 \qquad ...(1)$$

and

$$\varepsilon'' = \frac{2}{\pi}\left(\frac{\lambda_o}{\lambda_d}\right)^2 \frac{\lambda_g}{\lambda_d}\left(\frac{d\rho}{dn}\right) \qquad ...(2)$$

where λ_o, λ_c, λ_g and λ_d are the free space wavelength, the cut-off wavelength, the waveguide wavelength and the wavelength in the waveguide filled with solution, respectively. ρ is the inverse of voltage standing wave ratio (VSWR) and $d\rho/dn$ is the slope of the curve of ρ versus n, where n = (1, 2, 3, 4,……) is the integer such that ($n\lambda_d/2$) represents the length of the dielectric filled waveguide. The ε' and ε'' values were reproducible within ± 0.5% and ± 1.67%, respectively. Following the Gopala Krishna's single frequency concentration variational method[10], the dielectric relaxation time (τ) and the dipole moment (μ) have been calculated.

$$X = \frac{\varepsilon'^2 + \varepsilon' + \varepsilon''^2 - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad ...(3)$$

$$X = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad ...(4)$$

$$\tau = \frac{\lambda_o}{2\pi c}\left(\frac{dY}{dX}\right) \qquad ...(5)$$

$$\text{and } \mu^2 = \frac{9kTM}{4\pi N d_o}\left[1 + \left(\frac{dY}{dX}\right)^2\right]\frac{dY}{dW} \qquad ...(6)$$

The values of ε', ε'', τ and μ were determined and are given in Table 1. It is found that ε' and ε'' vary linearly with weight fraction of solute in benzene solution. This ensures that the rotating molecular entities retain their configuration in the concentration range studied. The essential condition for the application of the Gopala Krishna's method for the study of dielectric relaxation time and dipole moment using single frequency concentration variational method is the proper choice for the concentration range. This concentration range of dilute solutions of polar molecules in non-polar solvents should be such that the Debye theory is applicable and the participating molecular entities do not change their configuration in that concentration variation range. Thus, the linear variation of ε' and ε'' with the weight fraction of the solute ensures the applicability of Gopala Krishna's method for the determination of dielectric relaxation time and dipole moment of polar molecules in non-polar solvents.

Table 1: Dielectric constant (ε'), dielectric loss (ε''), relaxation time (τ) and dipole moment (μ) for THF in benzene solution at different temperatures

Temp. (^{o}C)	**Weight fraction of solute in benzene**	**ε' (± 0.5%)**	**ε'' (± 1.67%)**	**$\frac{\tau}{10^{-12}}$ sec**	**μ(D)**
25	0.00531	2.266	0.00532	1.29	1.85
	0.00873	2.283	0.00649		
	0.0120	2.303	0.00707		
	0.0196	2.341	0.01135		
	0.0266	2.374	0.01467		
30	0.00531	2.260	0.00507	1.23	1.76
	0.00873	2.280	0.00615		
	0.0120	2.290	0.00761		
	0.0196	2.323	0.01054		
	0.0266	2.355	0.01292		
35	0.00531	2.256	0.00468	1.17	1.71
	0.00873	2.272	0.00553		
	0.0120	2.286	0.00653		
	0.0196	2.313	0.00897		
	0.0266	2.344	0.01095		
40	0.00531	2.244	0.00435	1.12	1.66
	0.00873	2.260	0.00536		
	0.0120	2.273	0.00632		
	0.0196	2.296	0.00816		
	0.0266	2.323	0.01047		

The energy parameters ($\Delta H_{\varepsilon}, \Delta F_{\varepsilon}$, ΔS_{ε}) for the dielectric relaxation process of THF in benzene at 25^{o}C, 30^{o}C, 35^{o}C and 40^{o}C and the corresponding energy parameters (ΔH_{η},

ΔF_η, ΔS_η) for the viscous flow have been calculated by using Eyring *et al.*[11] relations for the rate process. Following relations were used:

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\varepsilon}{RT}\right) \qquad ...(7)$$

$$\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon \qquad ...(8)$$

$$\eta = \frac{hN}{V}\exp\left(\frac{\Delta F_\eta}{RT}\right) \qquad ...(9)$$

and

$$\Delta F_\eta = \Delta H_\eta - T\Delta S_\eta \qquad ...(10)$$

where V is the molar volume of the solvent and all other symbols have their usual significance. ΔH_ε, ΔF_ε and ΔS_ε are the enthalpy, free energy and entropy of activation, respectively for dielectric relaxation process and ΔH_η , ΔF_η and ΔS_η are corresponding parameters for the viscous flow. The plot of log (τT) versus 10^3/T and log η versus 10^3/T according to equations (7) and (9) were found to be linear, which shows that both relaxation and viscous processes can be considered as rate processes. The ΔH_ε and ΔH_η values were computed from the slope of the linear plot of log (τT) versus 10^3/T and log η versus 10^3/T, respectively using the relation : slope = ΔH/2.303R, where R is the gas constant. Both sets of energy parameters along with the dielectric relaxation time (τ) of THF in benzene solution at 25°C, 30°C, 35°C and 40°C have been summarized in table 2.

Table 2: Relaxation time (τ), free energy of activation (ΔF_ε, ΔF_η) in k cal mole^{-1}, entropies of activation (ΔS_ε, ΔS_η) in cal mole^{-1} deg^{-1}, enthalpies of activation (ΔH_ε, ΔH_η) in k cal mole^{-1}, for THF in benzene solution at different temperatures

Temp. (^{0}C)	$\frac{\tau}{10^{-12}}$ **sec**	ΔF_ε	ΔH_ε	ΔS_ε	ΔF_η	ΔH_η	ΔS_η
25	1.29	1.234	1.158	-0.255	2.917	2.608	-1.036
30	1.23	1.235	1.158	-0.253	2.924	2.608	-1.043
35	1.17	1.236	1.158	-0.253	2.930	2.608	-1.045
40	1.12	1.239	1.158	-0.259	2.945	2.608	-1.076

The calculated value of dipole moment of THF in benzene solution was found to be very close to the literature value of the unassociated THF molecule. Therefore, THF exists in monomer form in benzene solution. Dipole moment of the molecular entities is concerned with structure and charge separation in the molecular entities, whereas relaxation time is concerned with size and shape of molecular entities at the temperature of medium. With the rise of temperature, thermal energy of the system increases, this causes the decrease in relaxation time of the orienting molecular entities. In the present case, the variation in dipole moment value with rise in temperature may be attributed to the possible solute-solvent molecular associations. It is proposed that solute-solvent association arises because of the interaction of fractional positive charge at the site of carbon atom of the THF molecule and the π-delocalised electron cloud of the benzene ring of the benzene molecule as shown in Figure 1.

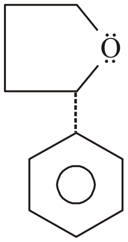

Fig. 1: Solute-solvent association of THF molecule in benzene solution

Energy parameters for the dielectric relaxation process of THF in benzene present an interesting behaviour. It is found that the free energy of activation (ΔF_ε) for the dielectric relaxation process is less than the free energy of activation (ΔF_η) for the viscous flow process. This may be explained on the basis that the dielectric relaxation process involves the rotation of molecular entities whereas in the viscous flow process, the rotational as well as the translational motion of the molecules is involved. Enthalpy of activation (ΔH_ε) for the dielectric relaxation process is less than the enthalpy of activation (ΔH_η) for the viscous flow process. The enthalpy of activation depends upon the local environment of the molecules. Different values for the enthalpy of activation indicate that the dielectric relaxation process and viscous flow process involve the breaking of bonds with the neighbouring molecules in a different way and to a different extent. The entropy of a system is the measure of the orderly nature of the system. If the environment of the system is cooperative for the activated process, then the change in entropy (ΔS_ε) becomes negative whereas the positive value of the change in the entropy (ΔS_ε) for activated process indicates the non-cooperative environment of the system and the activated state is unstable. In the present case, it has been observed that the change in entropy of the dielectric relaxation process is negative, indicating that the environment of the system is cooperative like that of the activated viscous flow state.

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